

Example 11.9

Estimate $\hat{\phi}_1$ and $\hat{\phi}_2$ by Eqs. (11.59) and (11.60) for an equimolar mixture of methyl ethyl ketone(1)/toluene(2) at 323.15 K (50°C) and 25 kPa. Set all $k_{ij} = 0$.

From table B.1 in Appendix B

$$w_{11} = 0.323 \quad T_{c11} = 535.5 \text{ K} \quad P_{c11} = 41.5 \text{ bar} \quad V_{c11} = 267 \times 10^{-3} \frac{\text{cm}^3}{\text{mol}} \quad z_{c11} = 0.249$$

$$w_{22} = 0.262 \quad T_{c22} = 591.8 \quad P_{c22} = 41.1 \quad V_{c22} = 316 \times 10^{-3} \quad z_{c22} = 0.262$$

$$T_{c12} = (535.5 * 591.8)^{1/2} = 563.0 \text{ K} \quad w_{12} = \frac{0.323 + 0.262}{2} = 0.293$$

$$z_{c12} = \frac{0.249 + 0.262}{2} = 0.256$$

$$V_{c12} = \left[\frac{(267 \times 10^{-3})^{1/3} + (316 \times 10^{-3})^{1/3}}{2} \right]^3 = 291 \times 10^{-3} \text{ cm}^3/\text{mol}$$

$$P_{c12} = \frac{0.256 * 83.14 * 563}{291 \times 10^{-3}} = 41.3 \text{ bar}$$

ij	T_{cij}/K	P_{cij}/bar	$V_{cij}/\text{cm}^3 \text{ mol}^{-1}$	Z_{cij}	w_{ij}
11	535.5	41.5	267	0.249	0.323
22	591.8	41.1	316	0.264	0.262
12	563.0	41.3	291	0.256	0.293

$$B_{11}^{\circ} = 0.083 - \frac{0.422}{\left(\frac{50 + 273.15}{535.5}\right)^{1.6}} = -0.865$$

$$B_{22}^{\circ} = -1.028$$

$$B_{12}^{\circ} = 0.083 - \frac{0.422}{\left(\frac{50 + 273.15}{563.0}\right)^{1.6}} = -0.943$$

$$B_{11}' = 0.139 - \frac{0.172}{\left(\frac{50 + 273.15}{535.5}\right)^{4.2}} = -1.300$$

similarly,

$$B_{22}' = -2.045 \quad B_{12}' = -1.632$$

$$B_{11} = \frac{83.14 * 535.5}{41.5} \left(-0.865 + 0.323 (-1.300) \right)$$

$$= -1387 \text{ cm}^3/\text{mol}$$

similarly,

$$B_{22} = -1860, \quad B_{12} = -1611 \text{ cm}^3/\text{mol}$$

ij	T_{rij}	B^0	B^1	$B_{ij}/\text{cm}^3 \text{ mol}^{-1}$
11	0.603	-0.865	-1.300	-1387
22	0.546	-1.028	-2.045	-1860
12	0.574	-0.943	-1.632	-1611

$$S_{12} = 2 B_{12} - B_{11} - B_{22} = 25 \text{ cm}^3/\text{mol}$$

$$\ln(\hat{\phi}_1) = \frac{25 * 10^{-2}}{(83.14)(50 + 273.15)} \left[-1387 + (6.5)^2 (25) \right]$$

$$= -0.0128$$

$$\Rightarrow \hat{\phi}_1 = 0.987 \quad \text{similarly,} \quad \hat{\phi}_2 = 0.983$$