(P12.1)

Short-cut VP eqn

	Tc(K)	Pc(MPa)	w	MW
(1)				
acrolein	506	5.16	0.33	56.06
(2)water	647.3	22.12	0.344	18.02
Antoine	A	B	C	
(2)water	8.07131	1730.63	233.426	

T =	325.55	K
T =	52.4	C

vapor pressures		Psat (mmHg)	Psat (MPa)	
	(1)		0.098287	shortcut
	(2)		0.017595	shortcut
	(2)	103.8657691	0.013848	

Calc gamma using azeotrope data, Antoine for water

gamma(1) = P/Psat(1)		w	x
gamma(1)	1.017432	0.974	0.923323
gamma(2)	7.221452	0.026	0.076677

	x	gamma	ln(gamma)	Aij
1	0.923323	1.017432065	0.017282	1.905464
2	0.076677	7.221452158	1.977056	2.415166

x1	x2	g1	g2	Psat.1	Psat.2	P(MPa)
0.1	0.9	5.006280904	1.015812	0.098287	0.017595	0.065291
0.3	0.7	2.898407803	1.166734	0.098287	0.017595	0.099833
0.5	0.5	1.813735923	1.599573	0.098287	0.017595	0.103205

Repeat using shortcut Psat for water also:

Calc gamma using azeotrope data, shortcut Psat for water

gamma(1) = P/Psat(1)		w	x
gamma(1)	1.017432	0.974	0.923323
gamma(2)	5.68342	0.026	0.076677

	x	gamma	ln(gamma)	Aij
1	0.923323	1.017432	0.017282	1.51066
2	0.076677	5.68342	1.737553	2.178683

x1	x2	g1	g2	Psat.1	Psat.2	P(MPa)
0.1	0.9	3.677636	1.01121	0.098287	0.017595	0.052159
0.3	0.7	2.454185	1.121133	0.098287	0.017595	0.086173
0.5	0.5	1.693527	1.440922	0.098287	0.017595	0.095902

Practice Problem P12.4

(12.7) $$U^E = x_1 \frac{a_{11}}{V_1} + x_2 \frac{a_{22}}{V_2} - \left(\frac{x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22}}{x_1 V_1 + x_2 V_2} \right)$$

(12.21) $$\delta_i = \frac{\sqrt{a_{ii}}}{V_i} \Rightarrow \delta_i^2 = \frac{a_{ii}}{V_i^2} \Rightarrow V_i \delta_i^2 = \frac{a_{ii}}{V_i} \Rightarrow a_{ii} = V_i^2 \delta_i^2$$

for $a_{ij} = \sqrt{a_{ii} a_{jj}}$ $\quad a_{ij} = \sqrt{V_i^2 \delta_i^2 V_j^2 \delta_j^2} = V_i \delta_i V_j \delta_j$

Then (12.7) becomes

$$U^E = x_1 V_1 \delta_1^2 + x_2 V_2 \delta_2^2 - \left(\frac{x_1^2 V_1^2 \delta_1^2 + 2 x_1 x_2 V_1 \delta_1 V_2 \delta_2 + x_2^2 V_2^2 \delta_2^2}{x_1 V_1 + x_2 V_2} \right)$$

Multicomponent form of a is eqn (12.3). Generalizing

$$U^E = \sum_i x_i V_i \delta_i^2 - \frac{\sum\sum (x_i V_i \delta_i)(x_j V_j \delta_j)}{\sum x_i V_i} \qquad (12.64)$$

$$U^E = \sum_i x_i V_i \delta_i^2 - \frac{\left(\sum_i x_i V_i \delta_i\right)^2}{\sum_i x_i V_i}$$

Second term, defining $\langle\delta\rangle = \sum_i x_i V_i \delta_i / V$, becomes

$$\frac{V^2 \langle\delta\rangle^2}{V} = V \langle\delta\rangle^2$$

$$U^E = \sum x_i V_i \delta_i^2 - V\langle\delta\rangle^2 \qquad (12.65)$$

subtract and add $V\langle\delta\rangle^2$

$$U^E = \sum x_i V_i \delta_i^2 - 2V\langle\delta\rangle^2 + V\langle\delta\rangle^2$$

$$= \sum_i x_i V_i \delta_i^2 - 2V\langle\delta\rangle \frac{\sum x_i V_i \delta_i}{V} + \langle\delta\rangle^2 \sum x_i V_i$$

factoring $\sum x_i V_i$

$$u^E = \sum x_i V_i (\delta_i^2 - 2 \delta_i \langle\delta\rangle + \langle\delta\rangle^2)$$

$$u^E = \sum x_i V_i (\delta_i - \langle\delta\rangle)^2 \qquad 12.67$$

To get activity coefficients, start with 12.65

$$G^E = u^E = \sum x_i V_i \delta_i^2 - V\langle\delta\rangle^2$$

$$nG^E = \sum n_i V_i \delta_i^2 - (\sum n_i V_i)\langle\delta\rangle^2$$

$$\left(\frac{\partial nG^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} = V_i \delta_i^2 - V_i \langle\delta\rangle^2 - (\sum n_i V_i)\left(\frac{\partial \langle\delta\rangle^2}{\partial n_i}\right)_{T,P,n_{j=i}} \qquad (A)$$

$$\langle\delta\rangle = \sum \Phi_i \delta_i$$

Derivatives of Φ_i are in Eqn 12.27, 12.28

$$\frac{\partial \langle\delta\rangle}{\partial n_i} = \frac{1}{n}\left(\frac{V_i}{V}(1-\Phi_i)\delta_i - \frac{V_i}{V}\sum_{j\neq i}\Phi_j \delta_j\right)$$

$$= \frac{1}{n}\left(\frac{V_i}{V}\left(\delta_i - \sum_i \Phi_i \delta_i\right)\right) = \frac{V_i}{Vn}(\delta_i - \langle\delta\rangle)$$

Then $\dfrac{\partial\langle\delta\rangle^2}{\partial n_i} = 2\langle\delta\rangle \dfrac{\partial\langle\delta\rangle}{\partial n_i} = 2\langle\delta\rangle \dfrac{V_i}{nV}(\delta_i - \langle\delta\rangle)$

insert into Eqn (A), note $nV = \sum n_i V_i$

$$\left(\frac{\partial nG^E}{\partial n_i}\right)_{T,P,n_{j\neq i}} = V_i \delta_i^2 - V_i\langle\delta\rangle^2 - 2\langle\delta\rangle V_i(\delta_i - \langle\delta\rangle)$$

$$\left(\frac{\partial nG^E}{\partial n_i}\right) = V_i \delta_i^2 - 2 V_i \delta_i \langle\delta\rangle + V_i \langle\delta\rangle^2$$

$$= V_i \left(\delta_i^2 - 2\delta\langle\delta\rangle + \langle\delta\rangle^2\right)$$

$$= V_i \left(\delta_i - \langle\delta\rangle\right)^2$$

$$\ln \gamma_i = \frac{V_i}{RT}\left(\delta_i - \langle\delta\rangle\right)^2 \qquad (12.54)$$

Practice problem can be repeated including k_{ij}