

and the equilibrium constant at $T^\circ = 298$ K is

$$K_{298} = 0.04092.$$

To calculate the equilibrium constant at 120°C (393.15 K) we will use the shortcut equation (14.36), which assumes the standard heat of reaction to be independent of temperature and equal to ΔH_{298}° . We find

$$K = (0.04092) \exp \left[-\frac{7790}{(8.314 \text{ J/mol K})} \left(\frac{1}{393.15 \text{ K}} - \frac{1}{298} \right) \right] = 3.6929.$$

Liquid-phase fugacities. To proceed we need a method to calculate the activity coefficients in ethanol/water solutions. We will use UNIFAC for this purpose. We also need the saturation pressures of ethanol and water at 120°C . We use the following values calculated from the Antoine equation:

$$P_1^{\text{sat}} = 4.325 \text{ bar}, \quad P_2^{\text{sat}} = 1.917 \text{ bar}.$$

Numerical procedure. The activity coefficients depend on the unknown mole fractions in the liquid, which complicates the direct solution of the above equations. We adopt a trial-and-error approach. For the first pass we assume the activity coefficients to be 1. Equations [A]–[E] are then solved and the following values are obtained:

$$y_1 = 0.2093, y_2 = 0.6097, y_3 = 0.1811, x_1 = 0.3387, x_2 = 0, x_3 = 0.6613.$$

With the mol fractions in the liquid known, we calculate the activity coefficients in the liquid using UNIFAC:

$$x_1 = 0.3387, x_3 = 0.6613 \quad \Rightarrow \quad \gamma_1 = 1.554, \gamma_2 = 1.259.$$

Using the activity coefficients calculated above we solve eqs. [A]–[E] again and use the new liquid compositions to refine the estimate of the activity coefficients. The procedure is repeated until the solution converges and the mol fractions do not change any more. A sample of the iterations are shown in the table below:

iteration	liquid				vapor		
	γ_1	γ_3	x_1	x_3	y_1	y_2	y_3
1	1.0000	1.0000	0.3387	0.6613	0.2093	0.6097	0.1811
2	1.5544	1.2593	0.2535	0.7465	0.2435	0.4991	0.2574
3	1.8787	1.1635	0.2084	0.7916	0.2419	0.5060	0.2522
\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots	\vdots
20	2.7281	1.0629	0.1429	0.8571	0.2409	0.5096	0.2494
21	2.7282	1.0629	0.1429	0.8571	0.2409	0.5096	0.2494

Notice that the gas-phase compositions converge quickly but the liquid phase compositions require more iterations to converge.