# Homework 10: Problem 9.15

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Find the equilibrium composition of the isomerization reaction between propylene oxide (p.o.) and acetone (a) at 298 K and 1 bar, given a two-suffix Margules parameter of $A = -650$ J/mol.

Start be finding the Gibbs free energy of formation for the two species from Table A.3.1:

$$
\begin{aligned}
\Delta g^{\circ}_{f,298,a} &= -155.50 \text{ [kJ/mol]} \\
\Delta g^{\circ}_{f,298,p.o.} &= -26.75 \text{ [kJ/mol]}
\end{aligned}
$$

For consistency, assume that we are going from p.o. to a. The equilibrium constant is:

$$
\begin{aligned}
K &= \exp\left[-\Delta g^{\circ}_{rxn}/RT\right] \\
&= \exp\left[-\left(\Delta g^{\circ}_{f,298,a} - \Delta g^{\circ}_{f,298,p.o}\right)/RT\right] \\
&= 3.69 \times 10^{22}
\end{aligned}
$$

Since this number is very large (to say the least), we expect the equilibrium composition of p.o. will be close to zero. Next, we assume that the pressure is low enough such that the pressure dependence of the fugacities is not significant. Thus, we can relate the equilibrium constant to the mole fractions via:

$$
\begin{aligned}
K &= \prod \left(\frac{x_i \gamma_i f_i}{f_i^{\circ}}\right)^{\nu_i} \\
&= \frac{x_a \gamma_a}{x_{p.o.} \gamma_{p.o.}}
\end{aligned}
$$

Since we're given the two-suffix Margules parameter, we know that: $RT \ln \gamma_1 = Ax_2^2$. Plugging this in to the previous equation, we get:

$$\begin{aligned} K &= \frac{x_a \gamma_a}{x_{p.o.} \gamma_{p.o.}} \\ &= \frac{(1 - x_{p.o.})}{x_{p.o.}} \frac{\exp\left[A/RT x_{p.o.}^2\right]}{\exp\left[A/RT x_a^2\right]} \\ &= \frac{(1 - x_{p.o.})}{x_{p.o.}} \exp\left[A/RT\left(2x_{p.o.} - 1\right)\right] \end{aligned}$$

Equating the two equations for $K$, we get:

$$\exp\left[-\left(\Delta g^{\circ}_{f,298,a} - \Delta g^{\circ}_{f,298,p.o}\right)/RT\right] = \frac{(1 - x_{p.o.})}{x_{p.o.}} \exp\left[A/RT\left(2x_{p.o.} - 1\right)\right]$$

The solution to this problem is numerically unstable. Depending upon your initial guess, you will get values of: $1.9 \times 10^{-35} < x_{p.o} < 2.5 \times 10^{-23}$. Essentially, it is beyond the precision available to most machines. The left-hand side is essentially zero, so we would expect the extent to be close to unity. In any case, we can assume the amount is small. Thus

$$x_a \approx 1.0$$