Problem 1. (3 points) chapter 9

A phase diagram for a mixture of diethyl carbonate ("DEC") and propylene glycol ("PG") is shown at right. The diagram was published by Chi-Chuh Hu, et al., in the Journal of Chemical & Engineering Data, 2015, 60, 1487-1494.

DEC: \((\text{CH}_3\text{CH}_2\text{CO}_3)\), component “1.”
PG: \(\text{CH}_3\text{CHOHCH}_2\text{OH}\), component “2.”

The total pressure is fixed at standard pressure, 101.3 kPa.

Suppose that 0.945 grams DEC and 0.913 grams PG are mixed at room temperature, where vapor pressure is negligible. The total mass of the system is then 1.858 grams; that is constant. Vapor is not allowed to escape from the system.

a) Calculate \(z_1\), the bulk mole fraction of DEC.

b) The mixture is slowly heated until vapor appears. At what temperature does vapor first appear, and what is the mole fraction DEC, \(y_1\), in that vapor?

c) The temperature is raised to 430.0 K. Based on the graph, what are the mole fractions of DEC (component 1) in liquid and vapor phases?

d) How many moles (DEC plus PG) are in the liquid phase? Use the lever rule.

e) How many moles of DEC are in the liquid phase?

f) Chi-Chih Hu, et al., gave this equation for the activity coefficient of DEC. (An equivalent expression is given by Engel and Reid.)

\[
\gamma_{\text{DEC}} = \frac{P_y}{x} \frac{y_{\text{DEC}}}{P_{\text{DEC}}^S},
\]

where \(P\) is the total pressure, \(x\) and \(y\) are liquid and vapor mole fractions, and \(P_{\text{DEC}}^S\) is the vapor pressure of pure DEC, 226 kPa at 430.0 K. Calculate \(\gamma_{\text{DEC}}\) at 430 K, using the conditions of parts c-e above.

Problem 2 is on the next page.
Problem 2. (2 points) Probability problem.

At high temperature and pressure a mixture of liquid quartz and water contains five forms of the silicate anion, SiO$_4^{4-}$. Each silicate tetrahedron is labeled "Q$^n$", 0 $\leq$ n $\leq$ 4, where n is the number of other silicates to which it is bonded. For example, Q$^0$ refers to an isolated silicate, and Q$^4$ refers to a tetrahedron that is bonded to four others. The average value of n is the "degree of polymerization," and may range from 0 (no polymerization) to 4 (a complete tetrahedral network of SiO$_4$ tetrahedra). Georg Spiekermann, et al. (Chemical Geology, 426, 85-94, 2016) calculated the mole fractions of Q$^n$ at T=3000 K and P=5.6 GPa. Mole fractions may be interpreted as probabilities ($x_n$=p$_n$), as they are in this problem.

Here are the mole fractions:

<table>
<thead>
<tr>
<th>n</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_n$</td>
<td>0.05</td>
<td>0.10</td>
<td>0.26</td>
<td>0.46</td>
<td>0.13</td>
</tr>
</tbody>
</table>

- Show that the probability distribution is normalized.
- Calculate the degree of polymerization.
- Calculate the standard deviation of the degree of polymerization.