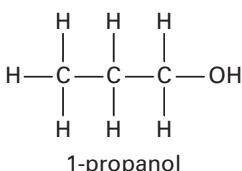
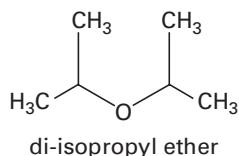


**EXAMPLE 11-4****DATA REDUCTION USING THE 1- AND 2-PARAMETER MARGULES EQUATION**

Perform a reduction of the data in Table 11-1 for the di-isopropyl ether (1) + 1-propanol (2) system at 303.15 K using both the 1-parameter and 2-parameter Margules equations.

**TABLE 11-1** Experimental  $P_{xy}$  data for the di-isopropyl ether (1) + 1-propanol (2) system at 303.15 K.

$P$ (kPa)	$x_1$	$y_1$	$P$ (kPa)	$x_1$	$y_1$
3.77	0	0	19.51	0.5296	0.8774
5.05	0.0199	0.2671	20.23	0.5902	0.8890
6.15	0.0399	0.4090	20.71	0.6505	0.8974
7.22	0.0601	0.5061	21.35	0.7101	0.9093
8.29	0.0799	0.5783	21.92	0.7685	0.9209
10.60	0.1192	0.6847	22.62	0.8300	0.9372
12.16	0.1694	0.7346	23.20	0.8803	0.9521
14.07	0.2294	0.7822	23.59	0.9179	0.9637
15.62	0.2891	0.8133	23.80	0.9397	0.9709
16.81	0.3495	0.8343	23.99	0.9581	0.9785
17.91	0.4090	0.8524	24.19	0.9804	0.9885
18.77	0.4708	0.8659	24.36	1	1

Based on data from I. Hwang et al., J. Chem. Eng. Data, 52, 2503 (2007).

**SOLUTION:**

**Step 1** Obtain the experimental activity coefficients and the experimental excess molar Gibbs free energy

We can obtain the experimental activity coefficients and the excess molar Gibbs free energy in a manner similar to the Example 11-2 by using the data in Table 11-1 and

$$\gamma_1 = \frac{y_1 P}{x_1 P_{1\text{sat}}^{\text{Temp Constant}}} \quad (11.86)$$

$$\gamma_2 = \frac{(1 - y_1)P}{(1 - x_1)P_2^{\text{sat}}} \quad (11.87)$$

$$\frac{G^E}{RT} = x_1 \ln[\gamma_1] + x_2 \ln[\gamma_2] \quad (11.74)$$

The resulting data is given in Table 11-2. At this point it is important to note a few things. First, the activity coefficient for component 1 when  $x_1 = 0$  does not exist (since component 1 is not present at this point). Likewise, the activity coefficient for component 2 when  $x_1 = 0$  also does not exist. Thus, those entries are not included in Table 11-2.

Second, by definition, the excess molar Gibbs free energy when  $x_1 = 1$  or  $x_2 = 1$  is zero. Thus, we can put those endpoint entries into the table by hand.

Third, when a substance becomes very dilute in a mixture, its activity coefficient approaches a limiting value called the **infinite dilution activity coefficient** and is

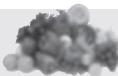
**TABLE 11-2** Experimental activity coefficient data for the di-isopropyl (1) + 1-propanol (2) system at 303.15 K.

<b>P (Kpa)</b>	<b>x<sub>1</sub></b>	<b>y<sub>1</sub></b>	<b>γ<sub>1</sub></b>	<b>γ<sub>2</sub></b>	<b>G<sup>E</sup>/RT</b>
3.77	0	0	—	1	0
5.05	0.0199	0.2671	2.782	1.001	0.0213
6.15	0.0399	0.4090	2.587	1.003	0.0408
7.22	0.0601	0.5061	2.499	1.005	0.0597
8.29	0.0799	0.5783	2.464	1.006	0.0776
10.60	0.1192	0.6847	2.498	1.005	0.1135
12.16	0.1694	0.7346	2.165	1.030	0.1554
14.07	0.2294	0.7822	1.970	1.053	0.1953
15.62	0.2891	0.8133	1.804	1.087	0.2299
16.81	0.3495	0.8343	1.648	1.134	0.2564
17.91	0.4090	0.8524	1.533	1.185	0.2751
18.77	0.4708	0.8659	1.417	1.260	0.2864
19.51	0.5296	0.8774	1.327	1.346	0.2896
20.23	0.5902	0.8890	1.251	1.452	0.2850
20.71	0.6505	0.8974	1.173	1.611	0.2705
21.35	0.7101	0.9093	1.123	1.770	0.2479
21.92	0.7685	0.9209	1.078	1.984	0.2163
22.62	0.8300	0.9372	1.049	2.214	0.1748
23.20	0.8803	0.9521	1.030	2.460	0.1338
23.59	0.9179	0.9637	1.017	2.764	0.0989
23.80	0.9397	0.9709	1.009	3.047	0.0756
23.99	0.9581	0.9785	1.006	3.259	0.0552
24.19	0.9804	0.9885	1.001	3.750	0.0269
24.36	1	1	1	—	0

denoted as  $\gamma_i^\infty$ . We introduced this earlier in the chapter when working with Henry’s Law. Recall that  $\gamma_i^\infty$  changes depending on which component is dilute and which component is concentrated. For example, in this problem, when 1-propanol is dilute in di-isopropyl ether, its infinite dilution activity coefficient would seem to be a little above 3.75, according to Table 11-2. On the other hand, when di-isopropyl ether is dilute in 1-propanol, its infinite dilution activity coefficient is likely a little above 2.78. Just by looking at the data, we can tell that the 1-parameter Margules equation will have trouble modeling this system, since it predicts a symmetric system (and the same infinite dilution activity coefficient for each compound). At any rate, we have the experimental data we need for modeling and the next step is to find the model parameters.

### FOOD FOR THOUGHT

#### 11-2



If there is no value for the activity coefficients of 1 when  $x_1 = 0$  or of 2 when  $x_2 = 0$ , how is this different than the infinite dilution activity coefficient discussed previously?

The infinite dilution activity coefficients for both components in a binary mixture, according to the 1-parameter Margules equation, are the same and are easily calculated by taking the limit as the composition of the component of interest goes to zero (or, equivalently, while the other goes to 1).

$$\begin{aligned}\ln \gamma_1^\infty &= \lim_{x_1 \rightarrow 1} [\ln \gamma_1] \\ &= \lim_{x_1 \rightarrow 1} [Ax_2^2] = A\end{aligned}$$

$$\begin{aligned}\ln \gamma_2^\infty &= \lim_{x_2 \rightarrow 1} [\ln \gamma_2] \\ &= \lim_{x_2 \rightarrow 1} [Ax_1^2] = A\end{aligned}$$

In Section 11.4, we discussed the Henry's Law constants and how they are different for the different components in the same mixture. The same discussion applies here for the activity coefficients at infinite dilution.

Another objective function you could use is to minimize the difference between the experimental pressure and the model-predicted pressure. Both approaches are used in practice.

We use only 22 points for the modeling, since the endpoints would provide a denominator of 11.93 that is divided by zero.

Notice how the value  $A_{12}$  and  $A_{21}$  bracket the value of  $A$ .

### Step 2 Defining the objective function

In Example 11-2 we had a single data point. Thus, we used that one data point to solve for the  $A$  parameter of the 1-parameter Margules equation. Here, we have 24 data points and we need to find the best value for  $A$  (1-parameter Margules equation) and the best value for  $A_{12}$  and  $A_{21}$  (2-parameter Margules equation) across all of the data. Therefore, we need to define an objective function that, once minimized, will provide us with the best values for the parameters.

One approach is to try to minimize the deviation between the predicted value of  $\underline{G^E}/RT$  from the model and the experimental value for the 24 points. There are a few procedural issues that one must be aware of when performing minimizations of this kind. First, if you have a program that does minimization (such as Solver in MS Excel), it will try to minimize your objective function—all the way to negative infinity, if possible! That's certainly not what you want. Therefore, you need to define your objective function such that only positive terms exist. Second, it is important to make the terms in your objective function have the same order of magnitude (which is just good practice). This way, if fitting data whose values change across orders of magnitude, the minimization process isn't biased toward the larger values (whose actual deviations from the model will be a much smaller percentage than the smaller values).

A reasonable objective function, therefore, looks like

$$\text{OBJ} = \frac{1}{22} \sum_{i=1}^{22} \left[ \frac{\left( \frac{\underline{G^E}}{RT} \right)_i^{\text{Model}} - \left( \frac{\underline{G^E}}{RT} \right)_i^{\text{Expt.}}}{\left( \frac{\underline{G^E}}{RT} \right)_i^{\text{Expt.}}} \right]^2 \quad (11.93)$$

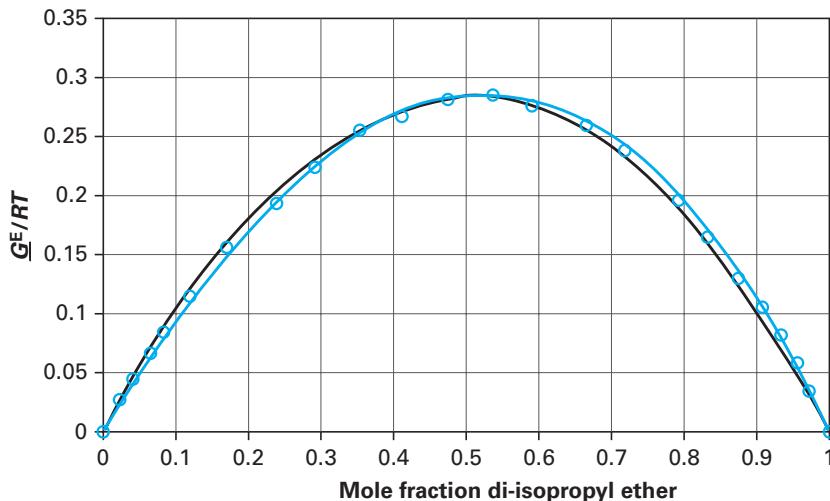
Here, OBJ will always be positive, and the terms are scaled so that they are the same order of magnitude. Note that the endpoints ( $x_1 = 0$  and  $x_1 = 1$ ) have been removed since the denominator of the objective function for both of those points will be zero and, thus, the objective function will become undefined.

If we minimize the objective function (OBJ) to find the best values for both models, we arrive at the following result, presented in Table 11-3.

**TABLE 11-3** Model parameters for the di-isopropyl (1) + 1-propanol (2) system at 303.15 K.

Model	$A$	$A_{12}$	$A_{21}$	OBJ
1-parameter Margules	1.165			0.0653
2-parameter Margules		1.041	1.317	0.0065

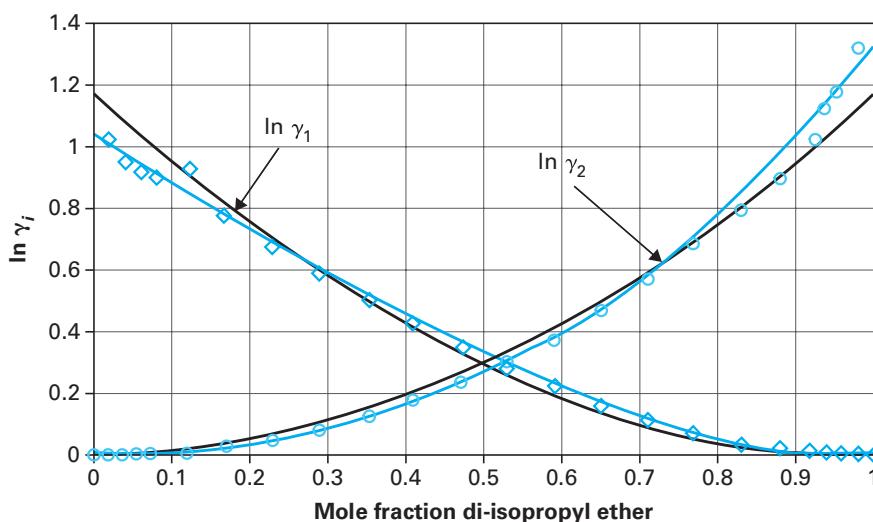
Note that the 2-parameter Margules equation fits the data better than the 1-parameter Margules equation, as evidenced by its smaller OBJ value (an order of magnitude smaller). You might have anticipated this result since the model contains a second parameter and, thus, more flexibility to fit the experimental data.



**FIGURE 11-5** The excess molar Gibbs free energy for the di-isopropyl ether (1) + 1-propanol (2) system at 303.15 K. The experimental data is given by empty circles while the models are given by the solid lines: black for the 1-parameter Margules equation and blue for the 2-parameter Margules equation.

We can plot the results as well to compare the two models relative to the experimental data in Figure 11-5.

Likewise, we can plot the activity coefficients as well for both models relative to the experimental data in Figure 11-6.



**FIGURE 11-6** The natural logarithm of the activity coefficients for the di-isopropyl ether (1) + 1-propanol (2) system at 303.15 K. The experimental data is given by empty circles while the models are given by the solid lines: black for the 1-parameter Margules equation and blue for the 2-parameter Margules equation.

Note that while the black curves (1-parameter Margules equation) predict the same infinite dilution activity coefficient for both substances, the blue curves (2-parameter Margules equation) do not and better reflect what is observed experimentally.

The infinite dilution activity coefficients for both components in a binary mixture, according to the 2-parameter Margules equation, are *different*.

$$\ln \gamma_1^\infty = \lim_{x_2 \rightarrow 1} [\ln \gamma_1] = A_{12}$$

$$\ln \gamma_2^\infty = \lim_{x_1 \rightarrow 1} [\ln \gamma_2] = A_{21}$$

These are obtained through observation of Equations 11.91 and 11.92.