

Table 12-1: P_{xy} data for the system ethanol(1)/acetonitrile(2) at 40 °C (from Sugi H., Katayama T., *J. Chem. Eng. Jpn.*, **11**, 167, (1978).)

P (bar)	x_1	y_1	P (bar)	x_1	y_1
0.2290	0	0	0.2810	0.4813	0.4376
0.2402	0.0281	0.0663	0.2766	0.5623	0.4753
0.2558	0.0831	0.1596	0.2681	0.6965	0.5344
0.2661	0.1415	0.2435	0.2580	0.7885	0.5987
0.2742	0.2314	0.3117	0.2418	0.8681	0.6687
0.2784	0.2884	0.3442	0.2189	0.9252	0.7708
0.2801	0.3330	0.3684	0.2012	0.9659	0.8664
0.2809	0.4040	0.4115	0.1799	1	1
0.2812	0.4140	0.414			

Azeotropes form when deviations from ideality are strong enough, whether these are positive or negative.

Example 12.6: Experimental Activity Coefficients

Table 12-1 shows P_{xy} data for the system ethanol (1)/acetonitrile (2) at 40 °C. Determine the activity coefficients and excess Gibbs energy of the solution at 40 °C.

Solution The saturation pressures of the pure components correspond to $x_1 = 1$ (ethanol) and $x_1 = 0$ (acetonitrile):

$$P_1^{\text{sat}} = 0.1799 \text{ bar}, \quad P_2^{\text{sat}} = 0.2290 \text{ bar}.$$

The activity coefficients are obtained from eq. (12.24), which we solve for γ_i :

$$\gamma_i = \frac{y_i P}{x_i P_i^{\text{sat}}}$$

denominator should read $x_1 P_i^{\text{sat}}$

For example, at $x_1 = 0.1415$ we obtain

$$\gamma_1 = \frac{(0.2435)(0.2661 \text{ bar})}{(0.1415)(0.1799 \text{ bar})} = 2.54619,$$

$$\gamma_2 = \frac{(1 - 0.2435)(0.2661 \text{ bar})}{(1 - 0.1415)(0.2290 \text{ bar})} = 1.02378.$$

The excess Gibbs free energy of the solution at this composition is

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 = (0.1415) \ln(2.54619) + (1 - 0.1415) \ln(1.02378) = 0.1524,$$

from which we obtain

$$G^E = (8.314 \text{ J/mol K})(313.15 \text{ K})(0.1524) = 396.78 \text{ J/mol K}.$$

Since temperature is constant, it is more convenient to work with the dimensionless ratio G^E/RT rather than G^E itself.

Repeating these calculations we obtain the results shown below.

x_1	γ_1	γ_2	G^E/RT	x_1	γ_1	γ_2	G^E/RT
0	—	1	0	0.4813	1.4208	1.3304	0.3171
0.0281	3.1517	1.0077	0.0397	0.5623	1.3002	1.4479	0.3096
0.0831	2.7321	1.0238	0.1051	0.6965	1.1438	1.7957	0.2712
0.1415	2.5462	1.0238	0.1524	0.7885	1.0891	2.1371	0.2279
0.2314	2.0540	1.0722	0.2202	0.8681	1.0358	2.6521	0.1592
0.2884	1.8473	1.1201	0.2577	0.9252	1.0141	2.9286	0.0933
0.3330	1.7230	1.1580	0.2790	0.9659	1.0034	3.4413	0.0454
0.4040	1.5909	1.2110	0.3017	1.0000	1	—	0
0.4140	1.5634	1.2276	0.3052				

Notice that the activity coefficients at infinite dilution ($x_1 = 0$, $x_1 = 1$) cannot be determined by direct calculation because the ratios y_1/x_1 and $(1 - y_1)/(1 - x_1)$ are indeterminate in this limit. As a consequence, the values of G^E/RT cannot be obtained by direct calculation either. However, these values are known to be zero and for this reason they are shown in the table. The results of these calculations are shown in Figure 12-8.

Comments The excess Gibbs free energy is zero at both ends ($x_1 = 0$, $x_1 = 1$), as is true for all excess properties. The activity coefficients have the expected general behavior: at the pure limit the activity coefficient approaches 1; at the infinite dilution limit it reaches the corresponding infinite dilution value. In this system the activity coefficients are larger than 1, that is, the system exhibits *positive* deviations from Raoult's law.

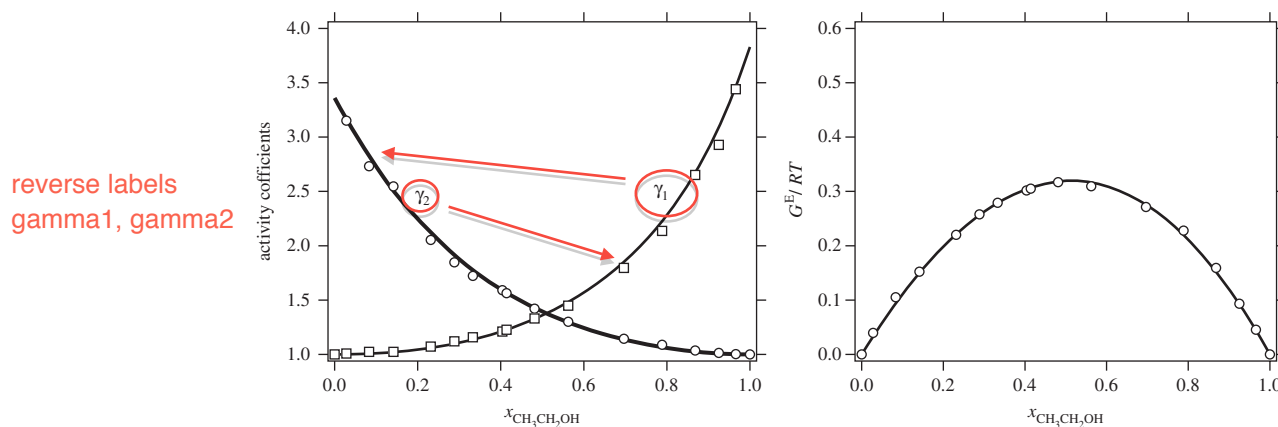


Figure 12-8: Activity coefficients and excess Gibbs energy of ethanol (1)/acetonitrile (2) solutions at 40 °C.