Problem Set 23 Solution

◇ Suggested model: (no superscript = derived or model properties)

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2 - Cx_1x_2)x_1x_2 \quad \text{— (1)}$$

$$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21}-A_{12}-C)x_1 + 3Cx_1^2] \quad \text{— (2)}$$

$$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12}-A_{21}-C)x_2 + 3Cx_2^2] \quad \text{— (3)}$$

◇ Modified Raoult's Law: (superscript * = experimental properties)

S+VN, (11.1)

$$\gamma_1^* = \frac{y_1P}{x_1P_1^{sat}}, \quad P_1^{sat} = P(x_1=1) = 49.624\,kPa \quad \text{— (4)}$$

$$\gamma_2^* = \frac{(1-y_1)P}{(1-x_1)P_2^{sat}}, \quad P_2^{sat} = P(x_1=0) = 85.265\,kPa \quad \text{— (5)}$$

◇ Also,

S+VN, (11.5)

$$\left(\frac{G^E}{RT}\right)^* = x_1\ln\gamma_1 + x_2\ln\gamma_2 \quad \text{— (6)}$$

Part a)

◇ Rewriting the model, ①, as:

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}(1-x_1) - Cx_1(1-x_1)$$

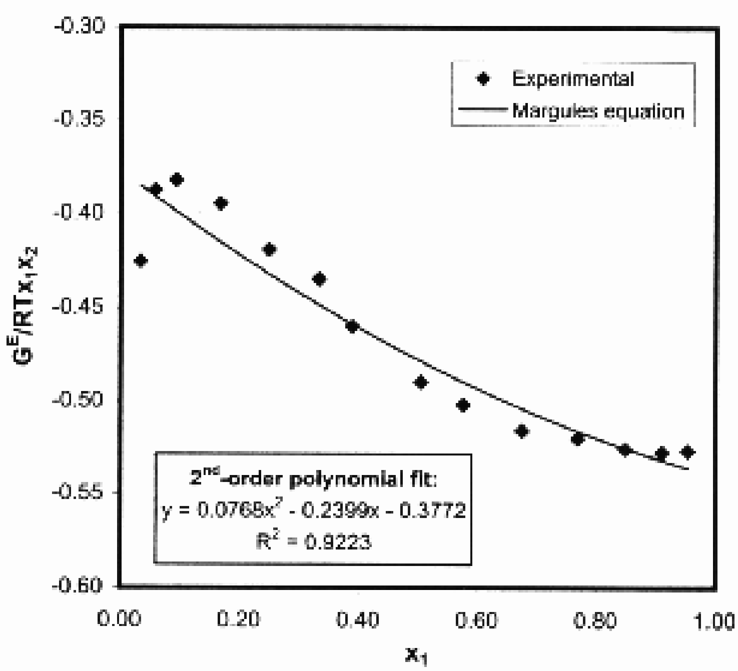
$$\frac{G^E}{RTx_1x_2} = [C]x_1^2 + [A_{21} - A_{12} - C]x_1 + [A_{12}]$$

— This is a 2nd-order polynomial in x_1, of the form:

$$y = \alpha x_1^2 + \beta x_1 + \gamma$$

◇ Using the data we have, we can calculate γ_1^* & γ_2^* from eq. ④ & ⑤, and then use eq. ⑥ to calculate $(G^E/RT)^*$ for each x_1. We can then calculate the property $(G^E/RTx_1x_2)^*$ for each x_1 and plot it.

◇ Excel can fit a 2nd-order polynomial to the data easily:



◇ From the fit,

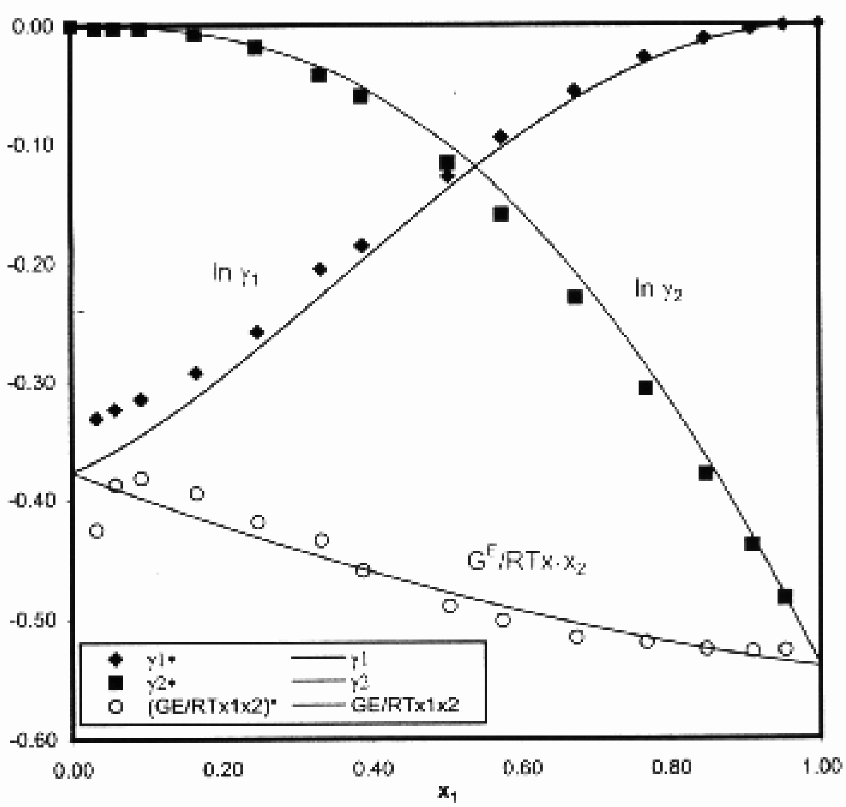
$$\left.\begin{aligned} \alpha &= 0.0768 = C \\ \beta &= -0.2399 = A_{21} - A_{12} - C \\ \gamma &= -0.3772 = A_{12} \end{aligned}\right\}$$

◇ Thus,

$$\left.\begin{aligned} A_{21} &= -0.5403 \\ A_{12} &= -0.3722 \\ C &= 0.0768 \end{aligned}\right\} \rightarrow$$

Part b)

◇ $\ln\gamma_1$ and $\ln\gamma_2$ can now be calculated from eq'n (2) & (3) and compared w/ experimental data.



Part c)

◇ The total pressure, P, is just the sum of the partial pressures P_1 & P_2:

$$P = P_1 + P_2$$

◇ Thus,

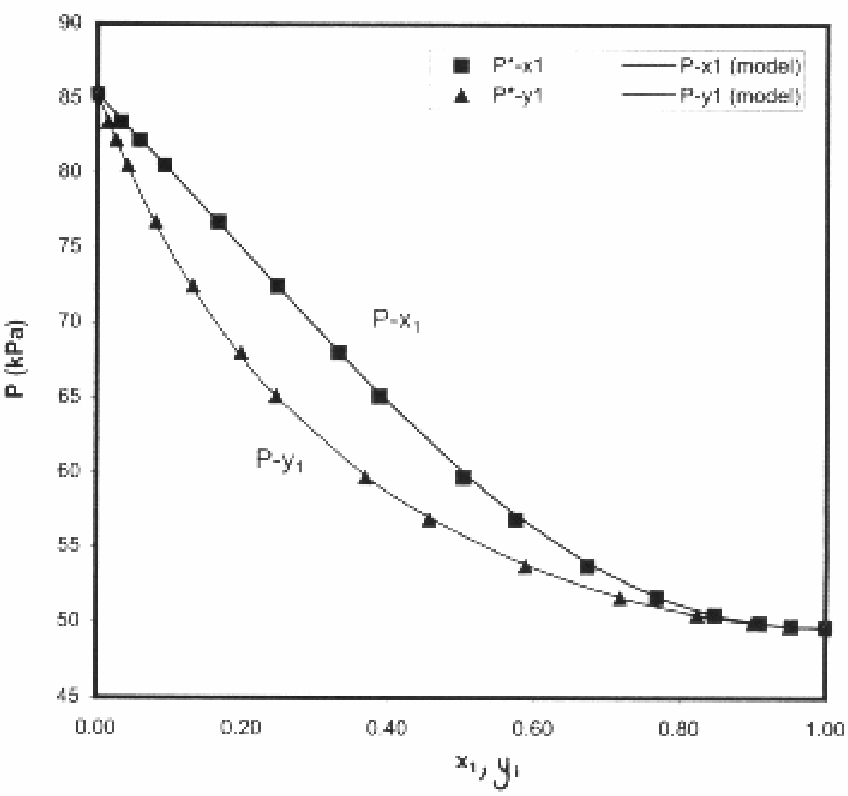
$$P = y_1 P + y_2 P$$
$$= \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat}$$

$$\boxed{P = \left[\gamma_1 P_1^{sat} - \gamma_2 P_2^{sat}\right] x_1 + \gamma_2 P_2^{sat}} \quad \text{— (7)}$$

◇ For each x_1, we thus know P and the corresponding y_1 from the model can be calculated using:

$$\boxed{y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P}} \quad \text{— (8)}$$

◇ The Pxy diagram is as shown:



Part d)

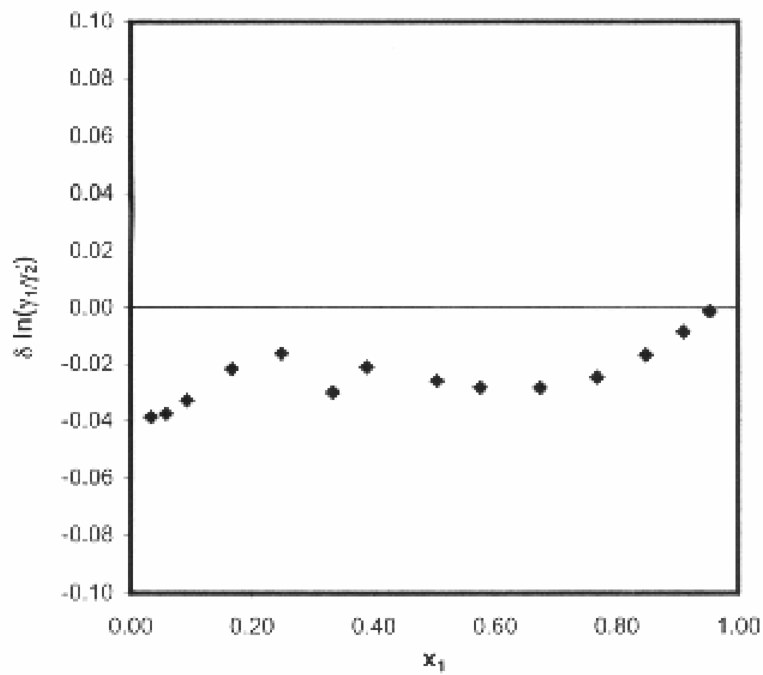
◇ As discussed by SVN (p. 382), the system is consistent if:

$$\boxed{\delta\left(\ln \frac{\gamma_1}{\gamma_2}\right) = 0} \qquad (11.11) \qquad \text{——— (9)}$$

where

$$\delta\left(\ln \frac{\gamma_1}{\gamma_2}\right) = \ln \frac{\gamma_1}{\gamma_2} - \ln \frac{\gamma_1^*}{\gamma_2^*}$$

◇ This plot is shown below:



◇ Hence the data are consistent at higher x_1's and reasonably consistent at lower x_1's.

Spreadsheet calculations

◇ Spreadsheet calcs are shown below for reference :

PROBLEM SET 23

Model parameters
A_{12} = -0.3772
A_{21} = -0.5403
C = 0.0768

	EXPERIMENTAL								MODEL							
x_1	y_1^*	P^* [kPa]	γ_1^*	γ_2^*	$(G^E/RT)^*$	$(G^E/RTx_1x_2)^*$	$\ln(\gamma_1^*)$	$\ln(\gamma_2^*)$	G^E/RTx_1x_2	$\ln(\gamma_1)$	$\ln(\gamma_2)$	γ_1	γ_2	y_1	P [kPa]	$\delta\ \ln(\gamma_1/\gamma_2)$
0.0000	0.0000	85.265		1.0000				0.0000	-0.37720	-0.3772	0.0000	0.686	1.000	0.0000	85.265	
0.0330	0.0141	83.402	0.7181	0.9973	-0.0136	-0.4253	-0.3311	-0.0027	-0.38503	-0.3673	-0.0002	0.693	1.000	0.0136	83.571	-0.039
0.0579	0.0253	82.202	0.7238	0.9974	-0.0211	-0.3874	-0.3232	-0.0026	-0.39083	-0.3588	-0.0006	0.699	0.999	0.0244	82.289	-0.038
0.0924	0.0416	80.481	0.7302	0.9967	-0.0320	-0.3820	-0.3145	-0.0033	-0.39871	-0.3456	-0.0017	0.708	0.998	0.0403	80.504	-0.033
0.1665	0.0804	76.719	0.7465	0.9927	-0.0548	-0.3946	-0.2923	-0.0073	-0.41501	-0.3131	-0.0066	0.731	0.993	0.0788	76.645	-0.022
0.2482	0.1314	72.422	0.7726	0.9813	-0.0782	-0.4190	-0.2580	-0.0188	-0.43201	-0.2725	-0.0173	0.761	0.983	0.1296	72.384	-0.018
0.3322	0.1975	68.005	0.8147	0.9584	-0.0964	-0.4346	-0.2049	-0.0424	-0.44842	-0.2280	-0.0356	0.796	0.965	0.1928	68.075	-0.030
0.3880	0.2457	65.096	0.8307	0.9410	-0.1092	-0.4599	-0.1855	-0.0608	-0.45872	-0.1980	-0.0524	0.820	0.949	0.2418	65.311	-0.021
0.5036	0.3686	59.651	0.8798	0.8899	-0.1224	-0.4896	-0.1280	-0.1167	-0.47854	-0.1381	-0.1009	0.871	0.904	0.3626	60.031	-0.026
0.5749	0.4564	56.833	0.9092	0.8524	-0.1226	-0.5018	-0.0952	-0.1598	-0.48974	-0.1042	-0.1406	0.901	0.869	0.4494	57.198	-0.028
0.6735	0.5882	53.689	0.9447	0.7944	-0.1134	-0.5158	-0.0568	-0.2301	-0.50395	-0.0635	-0.2085	0.938	0.812	0.5813	53.965	-0.028
0.7676	0.7176	51.620	0.9725	0.7357	-0.0928	-0.5201	-0.0279	-0.3070	-0.51610	-0.0329	-0.2874	0.968	0.750	0.7126	51.724	-0.025
0.8476	0.8238	50.455	0.9882	0.6842	-0.0679	-0.5257	-0.0119	-0.3796	-0.52536	-0.0144	-0.3654	0.986	0.694	0.8214	50.476	-0.017
0.9093	0.9002	49.926	0.9960	0.6443	-0.0435	-0.5275	-0.0040	-0.4396	-0.53184	-0.0051	-0.4322	0.995	0.649	0.8994	49.912	-0.009
0.9529	0.9502	49.720	0.9991	0.6166	-0.0236	-0.5267	-0.0009	-0.4836	-0.53606	-0.0014	-0.4828	0.999	0.617	0.9501	49.699	-0.001
1.0000	1.0000	49.624	1.0000				0.0000		-0.54030	0.0000	-0.5403	1.000	0.583	1.0000	49.624	