Title : Name of Topic: **Margules Equations and VanLaar Equations**

Date: 23-03-2020

Name of Faculty: Krunal J. Suthar

Lecture No : 01 (09:30 to 10:30 a.m.)

Source of information : Smith J.M, Van Ness H.C., Abbott M. M, "Introduction to Chemical Engineering Thermodynamics"

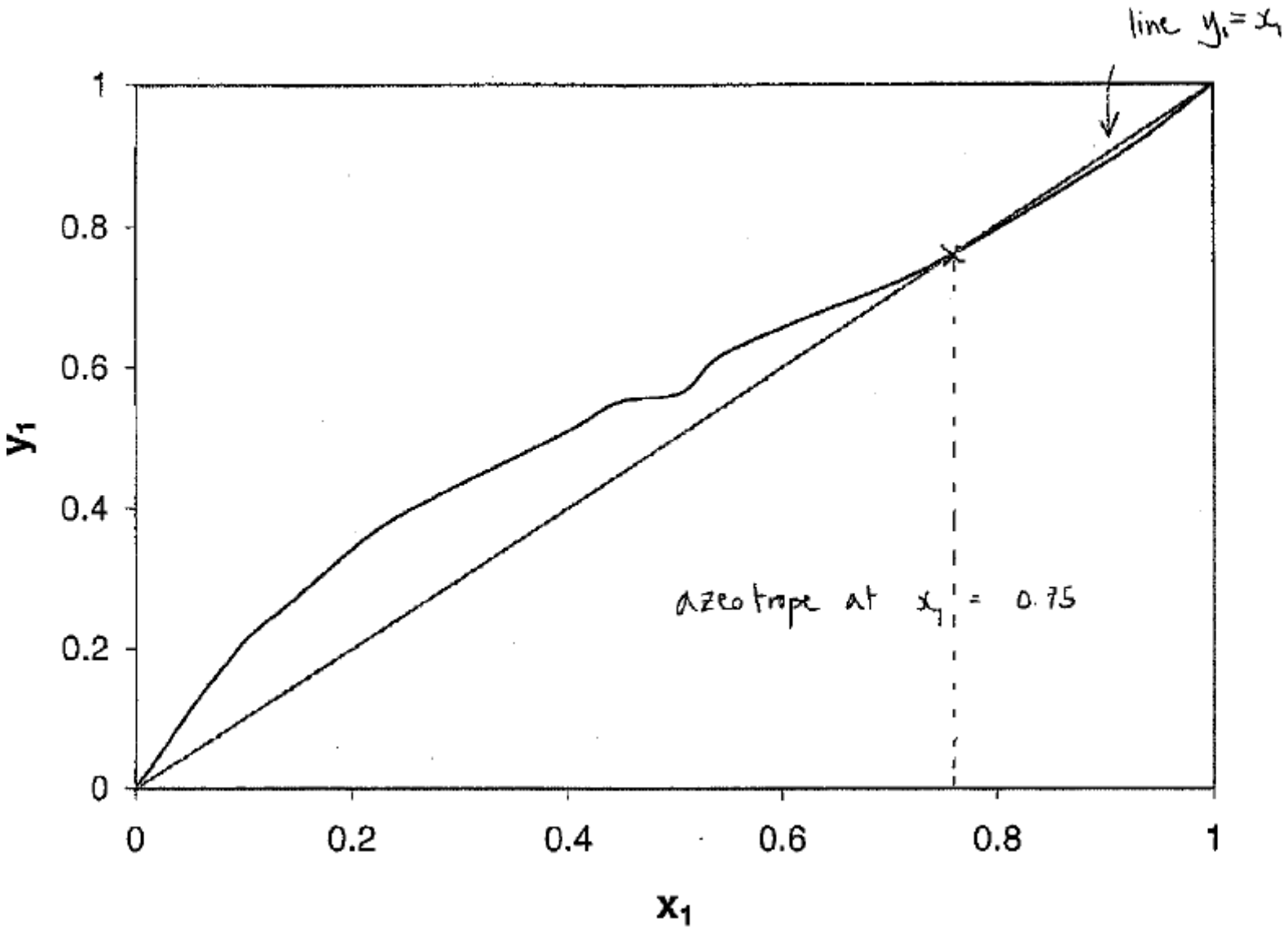
The following VLE data were collected for acetone(1)/methanol(2) at 55 °C:

P (kPa)	x_1	y_1	P (kPa)	x_1	y_1	P (kPa)	x_1	y_1
68.728	0.0000	0.0000	93.206	0.3579	0.4779	100.467	0.7327	0.7383
72.278	0.0287	0.0647	95.017	0.4050	0.5135	100.999	0.7752	0.7729
75.279	0.0570	0.1295	96.365	0.4480	0.5512	101.059	0.7922	0.7876
77.254	0.0858	0.1848	97.646	0.5052	0.5644	99.877	0.9080	0.8959
78.951	0.1046	0.2190	98.462	0.5432	0.6174	99.799	0.9448	0.9336
82.528	0.1452	0.2694	99.811	0.6332	0.6772	96.885	1.0000	1.0000
86.762	0.2173	0.3633	99.950	0.6605	0.6926			
90.088	0.2787	0.4184	100.278	0.6945	0.7124			

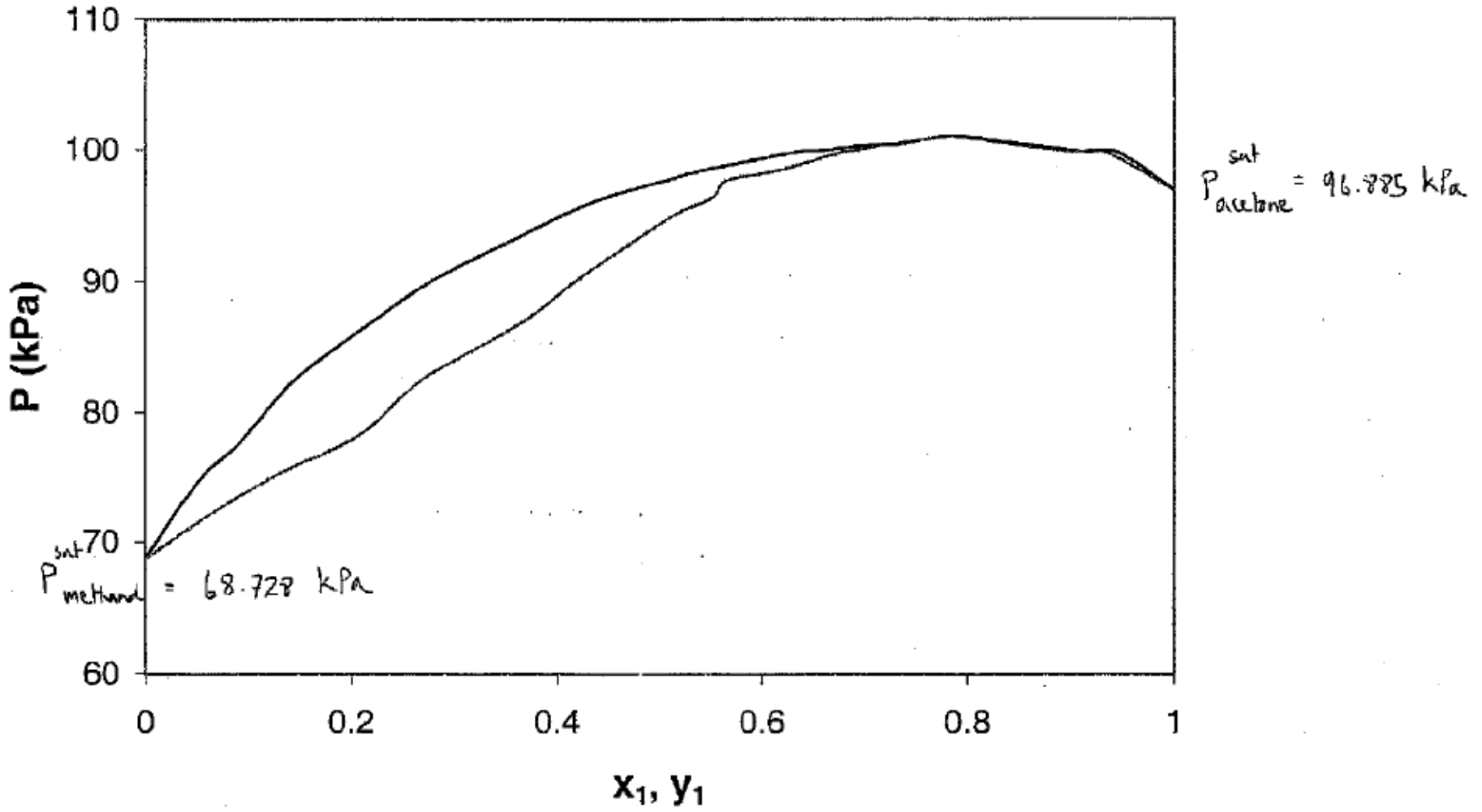
a) Plot y_1 vs x_1 identifying the location of the azeotrope.
b) Generate a P-xy diagram, noting the values of the saturation pressures for acetone and methanol at 55 °C.
c) Determine values of γ_1, γ_2, and G^E/RT, and plot ln γ_1, ln γ_2, and G^E/RT vs. x_1 on one graph.
d) Determine the parameters that best fit the data by the Margules equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.
e) Determine the parameters that best fit the data by the van Laar equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.
f) Determine the composition of the azeotrope using the parameters obtained for the Margules and van Laar equations.

Solution

Azeotrope is formed when, the liquid phase acetone composition is 0.75



b) Generate a P-xy diagram, noting the values of the saturation pressures for acetone and methanol at 55 °C.



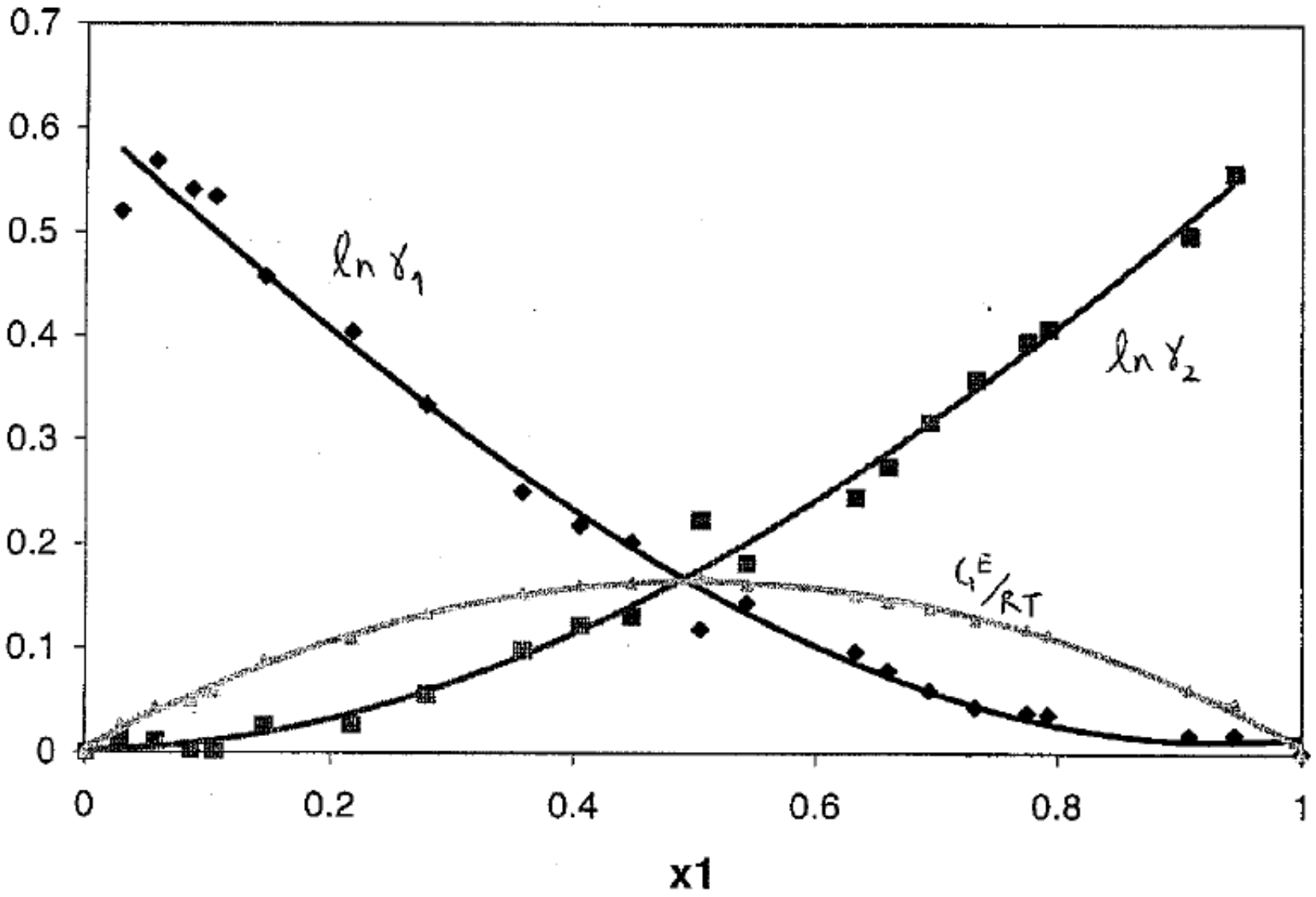
c) Determine values of γ_1, γ_2, and G^E/RT, and plot ln γ_1, ln γ_2, and G^E/RT vs. x_1 on one graph.

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

$$\frac{G^E}{RT} = x_1 ln\gamma_1 + x_2 ln\gamma_2$$

P (kPa)	x_1	y_1	γ_1	γ_2	$ln\gamma_1$	$ln\gamma_2$	G^E/RT
68.728	0	0	#DIV/0!	1	#DIV/0!	0	0
72.278	0.0287	0.0647	1.681791	1.012675	0.519859	0.012595	0.027154
75.279	0.057	0.1295	1.765274	1.011107	0.568306	0.011046	0.04281
77.254	0.0858	0.1848	1.71743	1.002329	0.540829	0.002326	0.04853
78.951	0.1046	0.219	1.706136	1.001977	0.534231	0.001975	0.057649
82.528	0.1452	0.2694	1.580432	1.02632	0.457698	0.02598	0.088665
86.762	0.2173	0.3633	1.497196	1.026917	0.403594	0.026561	0.10849
90.088	0.2787	0.4184	1.395935	1.056919	0.333564	0.055358	0.132894
93.206	0.3579	0.4779	1.284584	1.10271	0.250435	0.09777	0.152409
95.017	0.405	0.5135	1.243455	1.130403	0.217894	0.122575	0.161179
96.365	0.448	0.5512	1.223754	1.139986	0.201923	0.131016	0.162782
97.646	0.5052	0.5644	1.125956	1.250774	0.118633	0.223763	0.170651
98.462	0.5432	0.6174	1.155098	1.199924	0.144186	0.182258	0.161577
99.811	0.6332	0.6772	1.101788	1.278053	0.096934	0.245338	0.151369
99.95	0.6605	0.6926	1.081772	1.31678	0.078601	0.275189	0.145343
100.278	0.6945	0.7124	1.061697	1.373566	0.059869	0.31741	0.138548
100.467	0.7327	0.7383	1.044897	1.431181	0.043919	0.3585	0.128006
100.999	0.7752	0.7729	1.03937	1.484582	0.038615	0.395133	0.11876
101.059	0.7922	0.7876	1.037025	1.50297	0.036356	0.407443	0.113468
99.877	0.908	0.8959	1.017144	1.644352	0.016999	0.497346	0.061191
99.799	0.9448	0.9336	1.017866	1.746713	0.017708	0.557736	0.047518
96.885	1	1	1	#DIV/0!	0	#DIV/0!	0

c) Determine values of γ_1, γ_2, and G^E/RT, and plot ln γ_1, ln γ_2, and G^E/RT vs. x_1 on one graph.



d) Determine the parameters that best fit the data by the Margules equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2$$

$$\frac{G^E}{x_1x_2RT} = A_{21}x_1 + A_{12}x_2$$

$$\ln\gamma_1 = x_2^2\left[A_{12} + 2\left(A_{21} - A_{12}\right)x_1\right]$$

$$\ln\gamma_2 = x_1^2\left[A_{21} + 2\left(A_{12} - A_{21}\right)x_2\right]$$

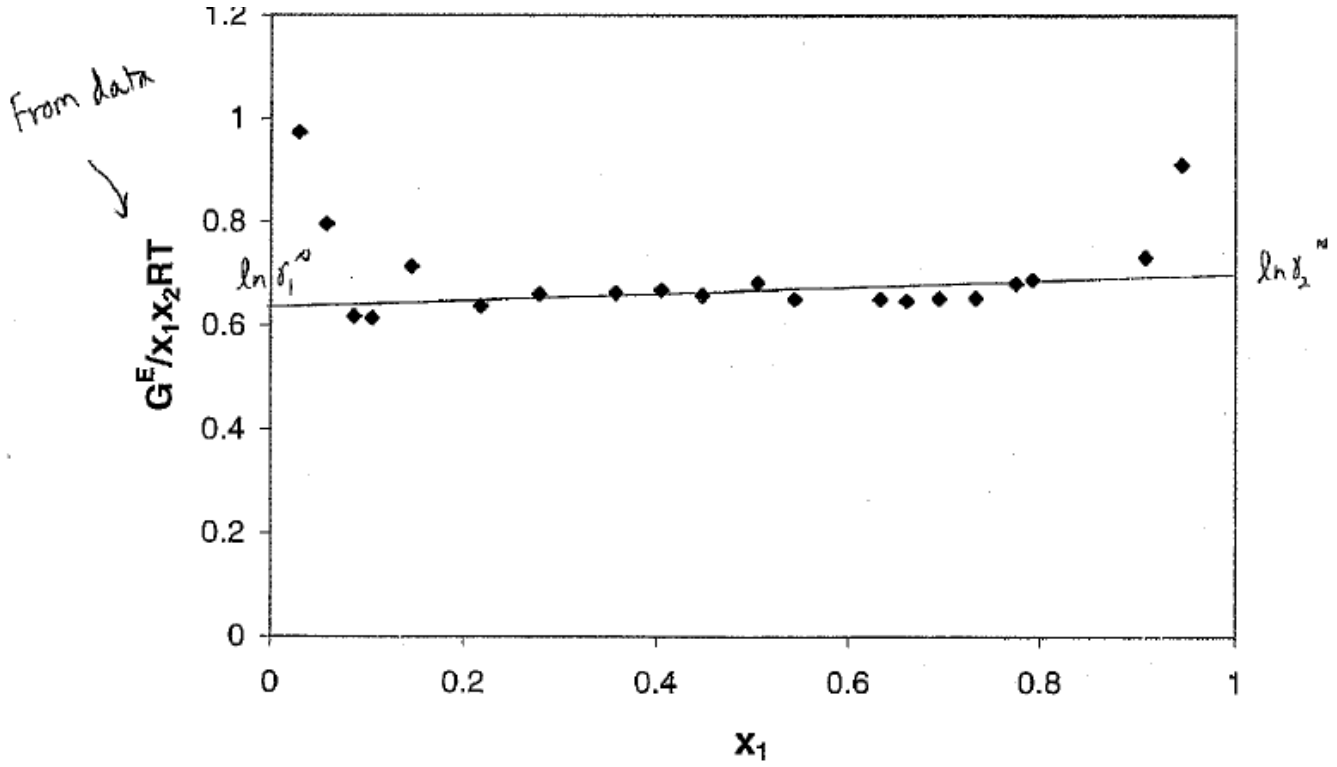
Plot $\frac{G^E}{x_1x_2RT}$ vs. x_1 and get $\ln\gamma_2^\infty$ as $x_1 = 1$ intercept

$\ln\gamma_1^\infty$ as $x_1 = 0$ intercept

d) Determine the parameters that best fit the data by the Margules equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.

Plot $\frac{G^E}{x_1 x_2 RT}$ vs. x_1 and get $\ln \gamma_2^\infty$ as $x_1 = 1$ intercept

$\ln \gamma_1^\infty$ as $x_1 = 0$ intercept



$\ln \gamma_1^\infty \approx 0.63$ $\ln \gamma_2^\infty \approx 0.71$

$\frac{G^E}{RT} = (0.71 x_1 + 0.63 x_2) x_1 x_2$

d) Determine the parameters that best fit the data by the Margules equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.

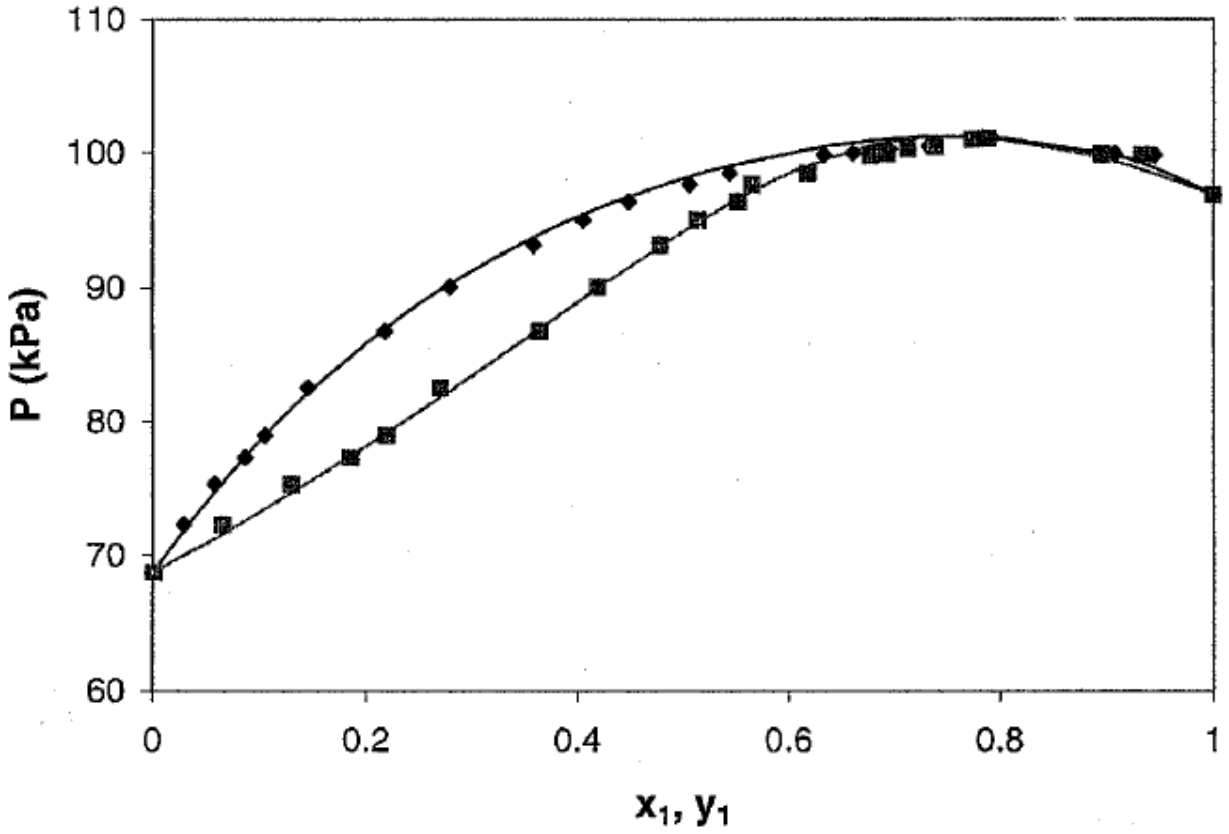
From Margules

$$\ln\gamma_1 = x_2^2\left[A_{12} + 2(A_{21} - A_{12})\,x_1\right]$$
$$\ln\gamma_2 = x_1^2\left[A_{21} + 2(A_{12} - A_{21})\,x_2\right]$$

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

then $$y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P}$$

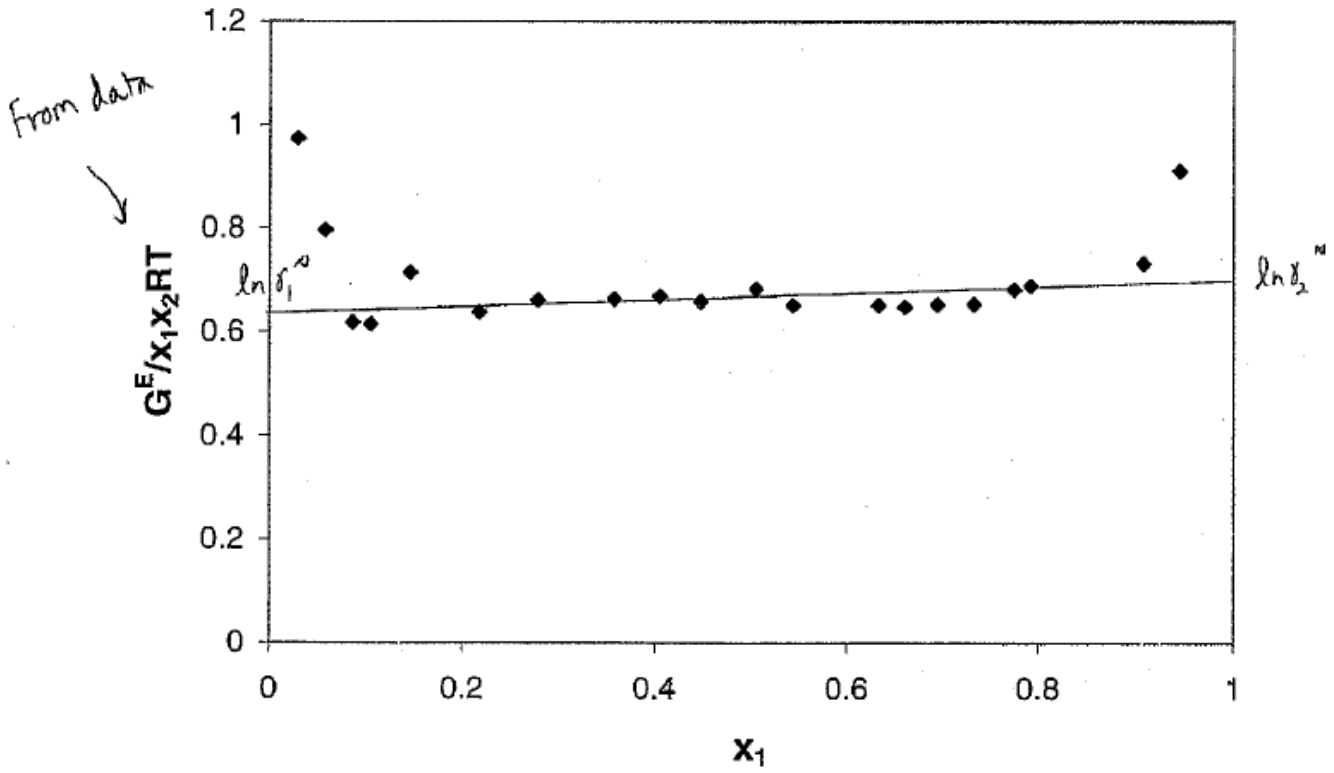
x_1	G^E/RT	$\ln\gamma_1$	$\ln\gamma_2$	$P_{Margules}$	y_1
0	0	0.63	0	68.728	0
0.0287	0.017626	0.598689	0.000457	71.84595	0.070428
0.057	0.034108	0.568337	0.001817	74.67727	0.130547
0.0858	0.049955	0.538003	0.00415	77.32868	0.184101
0.1046	0.059789	0.518515	0.006201	78.94248	0.215608
0.1452	0.079635	0.477306	0.012085	82.13629	0.276045
0.2173	0.110108	0.40725	0.027612	86.93554	0.363903
0.2787	0.131129	0.350972	0.046184	90.27144	0.424882
0.3579	0.151359	0.283354	0.077786	93.73384	0.491112
0.405	0.159622	0.245977	0.100843	95.41286	0.525934
0.448	0.16466	0.213805	0.124774	96.73077	0.555679
0.5052	0.167586	0.174031	0.161005	98.19789	0.593196
0.5432	0.167107	0.149595	0.187931	99.00607	0.617338
0.6332	0.158088	0.098392	0.261138	100.4228	0.674057
0.6605	0.15312	0.084795	0.286047	100.7155	0.691606
0.6945	0.145455	0.069169	0.318878	100.9878	0.714002
0.7327	0.134866	0.053389	0.358203	101.165	0.740183
0.7752	0.120594	0.038105	0.405049	101.1878	0.771065
0.7922	0.114143	0.032677	0.424717	101.1407	0.784074
0.908	0.058696	0.006562	0.573233	99.76766	0.88757
0.9448	0.036798	0.00238	0.625896	98.84916	0.928233
1	0	0	0.71	96.885	1



d) Determine the parameters that best fit the data by the Margules equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.

Plot $\frac{G^E}{x_1 x_2 RT}$ vs. x_1 and get $\ln \gamma_2^\infty$ as $x_1 = 1$ intercept

$\ln \gamma_1^\infty$ as $x_1 = 0$ intercept



$\ln \gamma_1^\infty \approx 0.63$ $\ln \gamma_2^\infty = 0.71$

$\frac{G^E}{RT} = (0.71 x_1 + 0.63 x_2) x_1 x_2$

d) Determine the parameters that best fit the data by the Margules equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.

From Margules

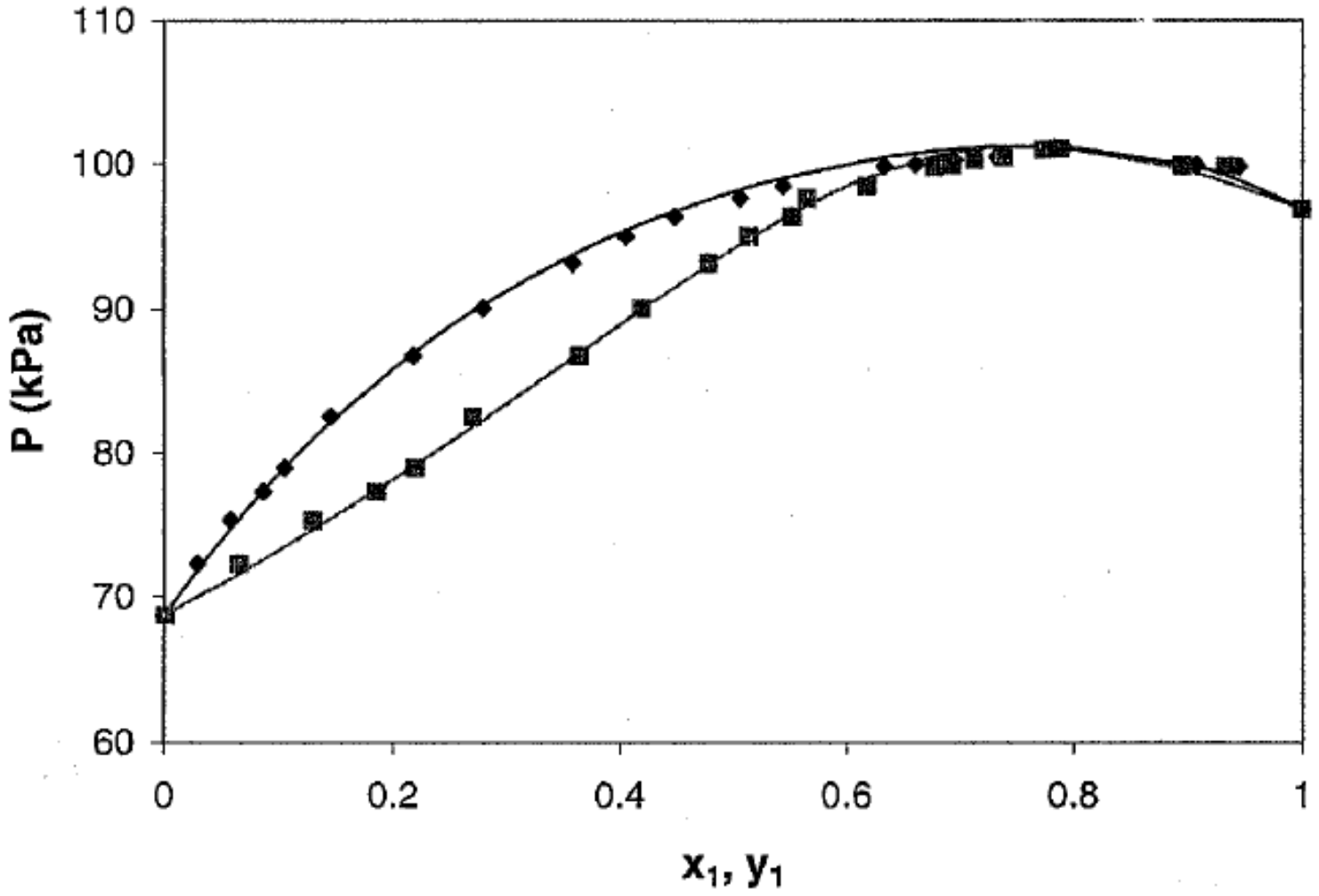
x_1	G^E/RT	$\ln\gamma_1$	$\ln\gamma_2$	$P_{Margules}$	y_1
0	0	0.63	0	68.728	0
0.0287	0.017626	0.598689	0.000457	71.84595	0.070428
0.057	0.034108	0.568337	0.001817	74.67727	0.130547
0.0858	0.049955	0.538003	0.00415	77.32868	0.184101
0.1046	0.059789	0.518515	0.006201	78.94248	0.215608
0.1452	0.079635	0.477306	0.012085	82.13629	0.276045
0.2173	0.110108	0.40725	0.027612	86.93554	0.363903
0.2787	0.131129	0.350972	0.046184	90.27144	0.424882
0.3579	0.151359	0.283354	0.077786	93.73384	0.491112
0.405	0.159622	0.245977	0.100843	95.41286	0.525934
0.448	0.16466	0.213805	0.124774	96.73077	0.555679
0.5052	0.167586	0.174031	0.161005	98.19789	0.593196
0.5432	0.167107	0.149595	0.187931	99.00607	0.617338
0.6332	0.158088	0.098392	0.261138	100.4228	0.674057
0.6605	0.15312	0.084795	0.286047	100.7155	0.691606
0.6945	0.145455	0.069169	0.318878	100.9878	0.714002
0.7327	0.134866	0.053389	0.358203	101.165	0.740183
0.7752	0.120594	0.038105	0.405049	101.1878	0.771065
0.7922	0.114143	0.032677	0.424717	101.1407	0.784074
0.908	0.058696	0.006562	0.573233	99.76766	0.88757
0.9448	0.036798	0.00238	0.625896	98.84916	0.928233
1	0	0	0.71	96.885	1

$$\ln\gamma_1 = x_2^2\left[A_{12} + 2\left(A_{21} - A_{12}\right)x_1\right]$$
$$\ln\gamma_2 = x_1^2\left[A_{21} + 2\left(A_{12} - A_{21}\right)x_2\right]$$

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

then $$y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P}$$

d) Determine the parameters that best fit the data by the Margules equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.



e) Determine the parameters that best fit the data by the van Laar equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.

x_1	G^E/RT	x_1x_2RT/G^E
0	0	#DIV/0!
0.0287	0.027154	1.026618
0.057	0.04281	1.255576
0.0858	0.04853	1.616297
0.1046	0.057649	1.624632
0.1452	0.088665	1.399841
0.2173	0.10849	1.567703
0.2787	0.132894	1.51268
0.3579	0.152409	1.507833
0.405	0.161179	1.495077
0.448	0.162782	1.519184
0.5052	0.170651	1.464819
0.5432	0.161577	1.535698
0.6332	0.151369	1.534386
0.6605	0.145343	1.542835
0.6945	0.138548	1.531382
0.7327	0.128006	1.530011
0.7752	0.11876	1.467372
0.7922	0.113468	1.450797
0.908	0.061191	1.365167
0.9448	0.047518	1.097546
1	0	#DIV/0!

van Laar eqn.

$$\ln \gamma_1 = A_{12}' \left(1 + \frac{A_{12}' x_1}{A_{21}' x_2} \right)^{-2}$$

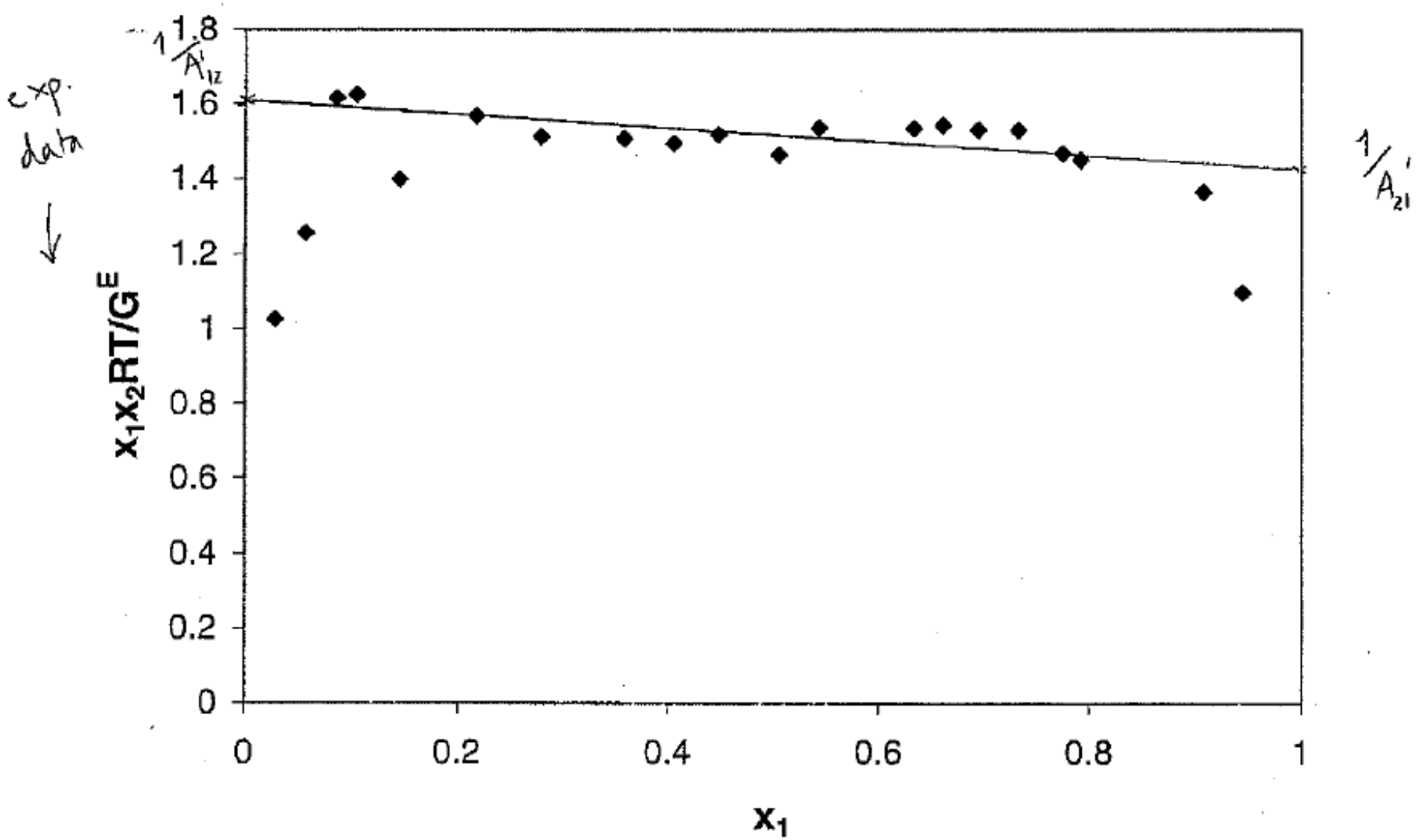
$$\ln \gamma_2 = A_{21}' \left(1 + \frac{A_{21}' x_2}{A_{12}' x_1} \right)^{-2}$$

$$\frac{x_1 x_2}{G^E/RT} = \frac{x_1}{A_{21}'} + \frac{x_2}{A_{12}'} \quad \therefore \text{ Plot } \frac{x_1 x_2}{G^E/RT} \text{ vs. } x_1$$

intercept at $x_1 = 1$ gives $1/A_{21}'$

$x_1 = 0$ gives $1/A_{12}'$

e) Determine the parameters that best fit the data by the van Laar equation. Prepare a P-xy diagram that compares the experimental points with the curves determined by this correlation.



$\therefore \quad A_{12} \approx \frac{1}{1.6} = 0.625 \qquad A'_{21} \approx \frac{1}{1.4} = 0.714$

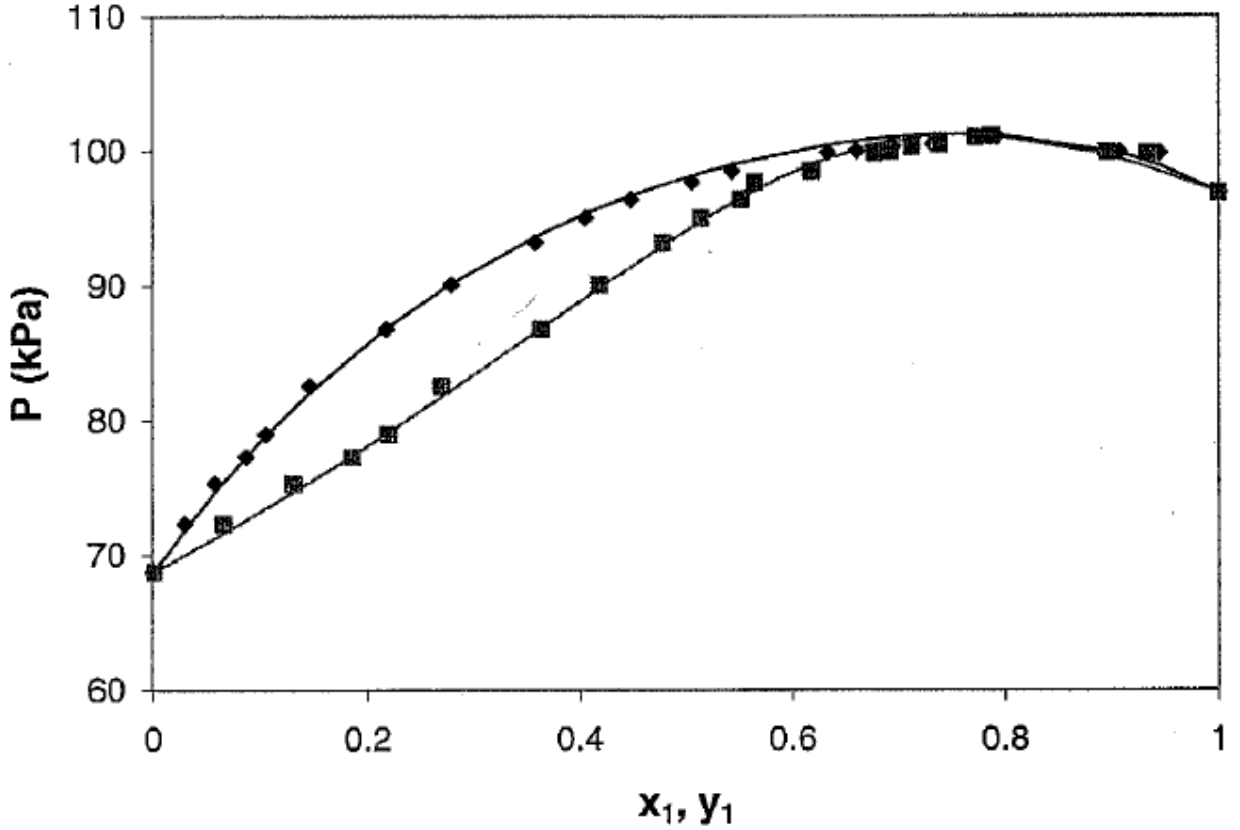
From van Laar

x_1	$\ln\gamma_1$	$\ln\gamma_2$	$P_{van\ Laar}$	y_1
0	0.625	0	68.728	0
0.0287	0.593881	0.000454	71.82149	0.070114
0.057	0.563763	0.001803	74.63191	0.130031
0.0858	0.533706	0.004115	77.26543	0.183461
0.1046	0.514415	0.006145	78.8694	0.214925
0.1452	0.473668	0.011964	82.0467	0.275343
0.2173	0.404503	0.027292	86.83105	0.363341
0.2787	0.348998	0.045609	90.16592	0.42454
0.3579	0.28231	0.076776	93.63766	0.491104
0.405	0.245419	0.099533	95.3257	0.526121
0.448	0.213634	0.123177	96.65301	0.556031
0.5052	0.174275	0.159032	98.13336	0.593731
0.5432	0.150048	0.185729	98.95038	0.617965
0.6332	0.099118	0.258557	100.3875	0.674783
0.6605	0.085544	0.283423	100.6863	0.692325
0.6945	0.069912	0.316268	100.9661	0.714686
0.7327	0.054084	0.355715	101.1517	0.740794
0.7752	0.038703	0.402862	101.1838	0.771556
0.7922	0.033226	0.422706	101.1404	0.784507
0.908	0.006726	0.573541	99.78569	0.887555
0.9448	0.002447	0.627447	98.86628	0.928134
1	0	0.714	96.885	1

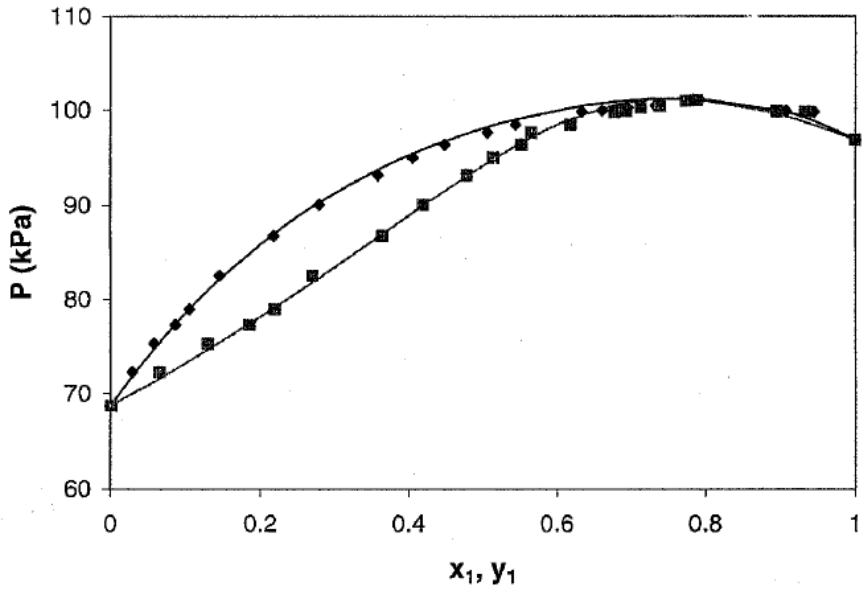
$$\ln\gamma_1 = A z_2^2 = \frac{A x_2^2}{\left[\left(\frac{A}{B}\right)x_1 + x_2\right]^2} \qquad \ln\gamma_2 = B z_1^2 = \frac{B x_1^2}{\left[x_1 + \left(\frac{B}{A}\right)x_2\right]^2}$$

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

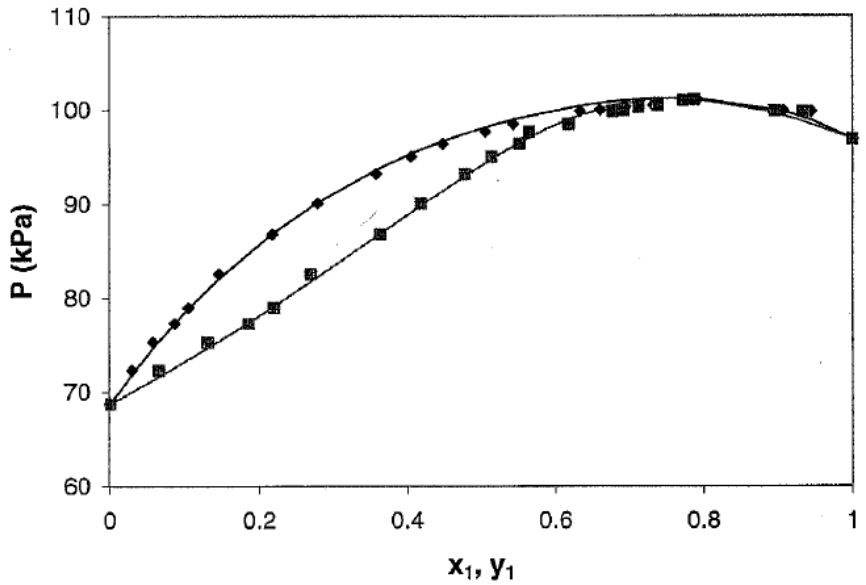
$$y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P}$$



Margules



Van Laar



Margules $x_1 = 0.759$

Van Laar $x_1 = 0.761$

- Solve the same problem using MS Excel and submit the assignment by 25th March 2020
- The Hard copy can be submitted on 31/3/2020.
- Krunal J. Suthar (9974090049)

NEXT LECTURE: Thermodynamic Consistency of VLE