Introductory Chemical Engineering Thermodynamics

SOLUTIONS FOR HOMEWORK PROBLEMS: Chapter 11

(11.01) The volume change on mixing for the methyl formate(1) + ethanol(2)…

a)

$V_{mixture} = x_1V_1 + x_2V_2 + \Delta V_{mix}$

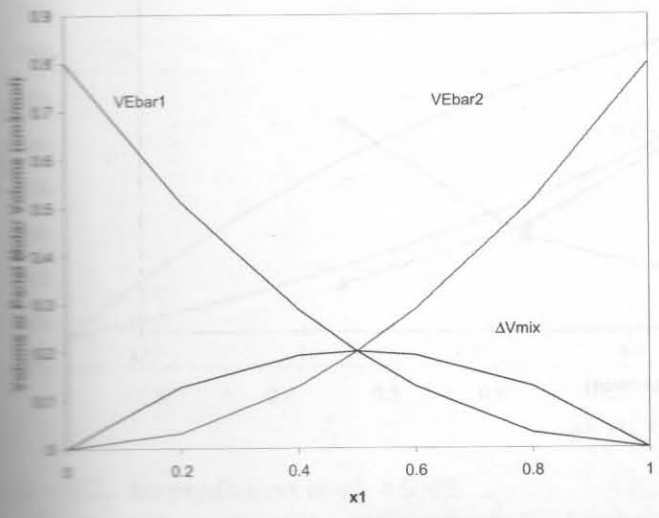
Across the composition range:

V1= 67.28 V2= 58.68

x1	x2	ΔVmix	V	VEbar1	VEbar2
0	1	0	58.68	0.8	0
0.2	0.8	0.128	60.528	0.512	0.032
0.4	0.6	0.192	62.312	0.288	0.128
0.5	0.5	0.2	63.18	0.2	0.2
0.6	0.4	0.192	64.032	0.128	0.288
0.8	0.2	0.128	65.688	0.032	0.512
1	0	0	67.28	0	0.8

Plot shown below

b) $\Delta V_{mix} = V^E$, $\underline{V} = 0.8\ n_1n_2/n_T$, $(\partial\underline{V}/\partial n_1)_{T,P,n2} = 0.8(n_1/n_T - n_1n_2/n_T^2) = 0.8(x_1 - x_1x_2) = 0.8x_1(1-x_2) = 0.8x_1^2$. Likewise, $(\partial\underline{V}/\partial n_2)_{T,P,n1} = 0.8\ x_2^2$.



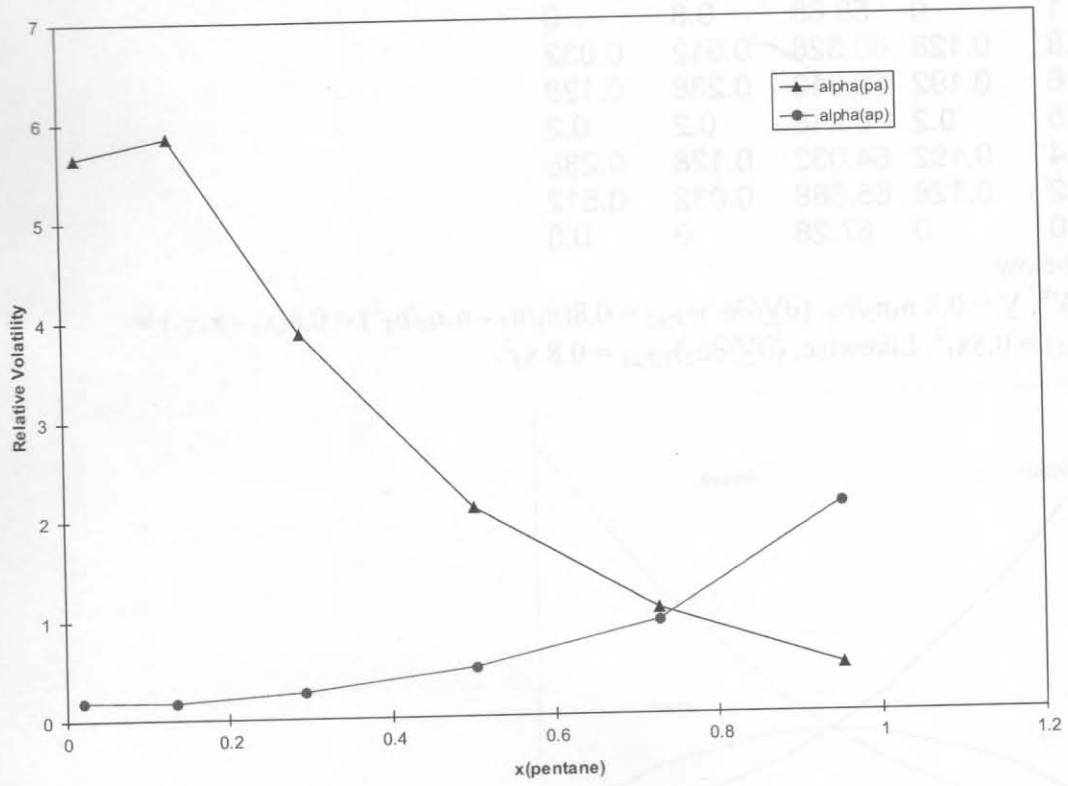
(11.02) In vapor-liquid equilibria the relative volatility is defined to be the ratio....

(a) Raoult's Law $y_iP = x_iP_i^{sat} \rightarrow K_i = y_i/x_i = P_i^{sat}/P$, therefore $\alpha_{ij} = K_i/K_j = P_i^{sat}/P_j^{sat}$, independent of composition.

(b)

x_p	y_p	K_p	K_a	α_{pa}	α_{ap}
0.021	0.108	5.14286	0.9111	5.6453	0.17716
0.134	0.475	3.544776	0.606236	5.847193	0.171022
0.292	0.614	2.10274	0.545198	3.856839	0.25928
0.503	0.678	1.347913	0.647887	2.080474	0.48066
0.728	0.739	1.01511	0.959559	1.057892	0.945276
0.953	0.906	0.950682	2	0.475341	2.103753

The relative volatility is a strong function of composition. It has a value of one for both components of a binary system at the azeotrope, and it is greater than one on one side and less than one on the other side.



(11.03) After fitting the two-parameter Margules equation to the data below…

The Margules equations reduce to $\ln \gamma_1^{\infty} = A_{12}$, and $\ln \gamma_2^{\infty} = A_{21}$. Therefore:
A12 = ln (1.6934) = 0.527, A21 = ln (1.9523) = 0.669. The plot can quickly be generated by just putting the parameters in GAMMAFIT, or by modifying the sheet MARGULES in the workbook ACTCOEFF. We show the use of GAMMAFIT.

System Components	Parameters to adjust		
(1) ethanol	A_{12}	A_{21}	T(C)
(2) water	0.527	0.669	78.15
		<---optional----->	

	A	B	C	P^{sat}(mm Hg)	P^{sat}(mm Hg)	P^{sat}(mm Hg)
1				1	764.5	764.5
2				1	333.6	333.6

x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	P_{expt}	P_{calc}	$(P_{error})^2$
0	1	1.693843	1			0	1		333.6	111288.96
0.05	0.95	1.62976	1.000998			0.164142	0.835858		379.534	144046.08
0.1	0.9	1.568115	1.004143			0.284509	0.715491		421.3661	177549.41
0.15	0.85	1.509134	1.009667			0.37674	0.62326		459.3612	211012.75
0.2	0.8	1.453002	1.017829			0.449905	0.550095		493.8023	243840.69
0.25	0.75	1.399864	1.02891			0.509634	0.490366		524.9823	275606.38
0.3	0.7	1.349829	1.043226			0.559625	0.440375		553.1975	306027.45
0.35	0.65	1.30298	1.061135			0.602419	0.397581		578.7414	334941.59
0.4	0.6	1.259376	1.083044			0.639836	0.360164		601.8992	362282.67
0.45	0.55	1.219056	1.109425			0.673233	0.326767		622.9432	388058.18
0.5	0.5	1.18205	1.140823			0.703658	0.296342		642.1278	412328.12
0.55	0.45	1.148375	1.177876			0.731959	0.268041		659.6858	435185.36
0.6	0.4	1.118048	1.221334			0.75885	0.24115		675.8233	456737.16
0.65	0.35	1.091083	1.272083			0.784964	0.215036		690.715	477087.2
0.7	0.3	1.067503	1.331175			0.810895	0.189105		704.4981	496317.52
0.75	0.25	1.047336	1.399864			0.837231	0.162769		717.265	514469.15
0.8	0.2	1.030628	1.479654			0.864588	0.135412		729.0544	531520.27
0.85	0.15	1.017439	1.572354			0.893652	0.106348		739.8381	547360.43
0.9	0.1	1.007857	1.680155			0.925217	0.074783		749.5058	561758.9
0.95	0.05	1.001994	1.805716			0.960256	0.039744		757.8425	574325.28
1	0	1	1.952284			1	0		764.5	584460.25

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0

Objective
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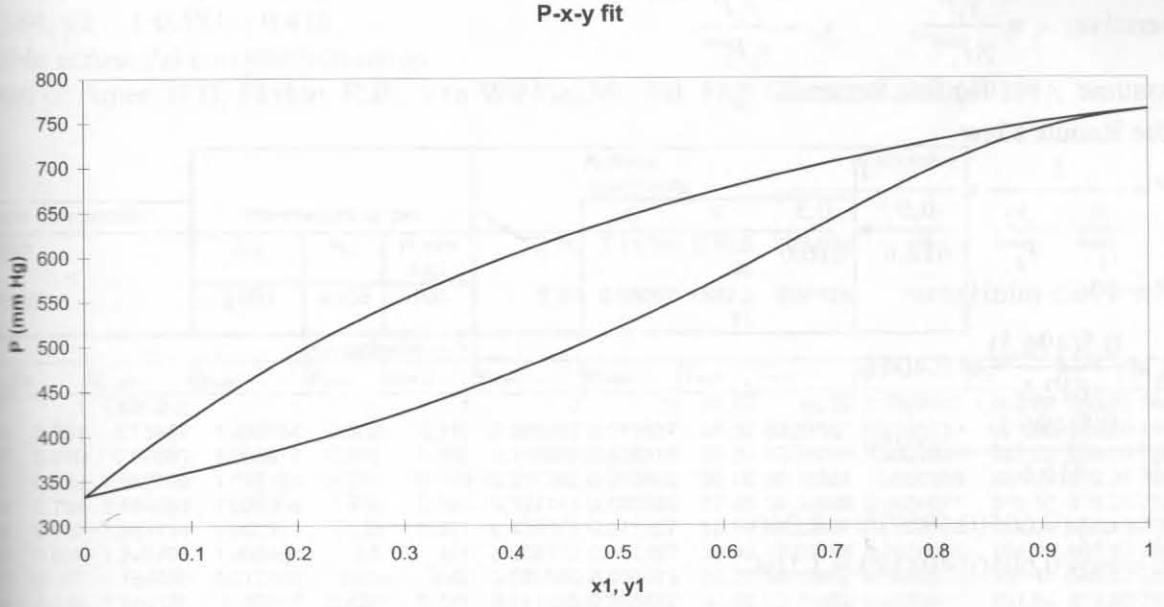


At x1 = 0.2, the prediction is y1 = 0.45.
This fit does not represent the azeotrope that is known to exist in this system, so for accurate calculations, more data should be fit.

(11.04) A stream with equimolar methanol + benzene at 350 K and 1500 mmHg...

(a) List all the unknown variables that need to be determined to solve for the outlet.
(b) List all the equations that apply to determine the unknown variables.

Solution: (a) Known: P^{in}, P^{out}, z_1,z_2,z_3, T^{in}.
Unknown: T, x_1,x_2,x_3, y_1,y_2,y_3, K_1,K_2,K_3, V/F.
(b) Equations: $y_i/x_i=K_i$, $K_i=\gamma_i P_i^{sat}/P$, $x_i=z_i/[1+(V/F)(K_i-1)]$, $\Sigma(x_i-y_i)=0$, $\ln\gamma_i = (1-x_i)^2 A_{12}$.
$H^V=\sum_i y_i(H_{f,i}^{ig}+{}_{298}\int^{Ts} Cp_i^{ig}dT)$; $H^L=\sum_i x_i(H_{f,i}^{ig}+{}_{298}\int^{Ts} Cp_i^{ig}dT - H_i^{vap})$; $H^{in}=H^{out}=(V/F)H^V+(1-V/F)H^L$

(11.05) In the system A + B, activity coefficients can be expressed ...

at $x_A = 0.01$, P = 900*1.63*.01+600*1*.99=608.7; $y_A = 0.024 > x_A$
at $x_A = 0.99$, P = 900.8; $y_A = .989 < x_A \Rightarrow$ azeotrope exists.
(Note also that 900.8>900 $\Rightarrow$ azeotrope)
Exact value by trial and error $\Rightarrow$ $x_A = 0.905$; P = 904.1

(11.06) The system acetone (1) + methanol(2) ...

a) gammas are calculated with Eqn. 11.6, and bubble pressure with $P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$.

vapor pressure from spreadsheet Antoine in ACTCOEFF.xls

$\gamma_1 = \exp(0.605(0.5)^2) = 1.163$, $\gamma_2 = \exp(0.605(0.5)^2) = 1.163$

P = 0.5(1.163)612.6+ 0.5(1.163)416.6 = 598.5 mmHg, y1 = 0.596

(11.06 (b)) Use Raoult's Law for first guess

Iterative: $x_1 = \dfrac{y_1 P}{\gamma_1 P_1^{sat}}$, $\quad x_2 = \dfrac{y_2 P}{\gamma_2 P_2^{sat}}$

Assume $\gamma_i = 1$ for first iteration.

Use Raoult's law

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} = \frac{1}{\dfrac{0.5}{612.6} + \dfrac{0.5}{416.6}}$$

$P = 496.5$ mmHg

$$x_1 = \frac{0.5(496.5)}{612.6} = 0.4041$$

$$x_2 = \frac{0.5(496.5)}{416.6} = 0.5959$$

$\gamma_1 = \exp(0.605(0.5959)^2) = 1.240$
$\gamma_2 = \exp(0.605(0.4041)^2) = 1.104$

$$P = \frac{1}{\dfrac{0.5}{1.240(612.6)} + \dfrac{0.5}{1.104(416.6)}}; \quad P = 573.4$$

$$x_1 = \frac{0.5(573.4)}{1.240(612.6)} = 0.376; \qquad x_2 = (1-x_1) = 0.624$$

calculate new gammas, iterate. Summary of iterations:

x_1	x_2	γ_1	γ_2	P
		1	1	496.5
0.404	0.596	1.240	1.104	573.4
0.376	0.624	1.265	1.090	573.1
0.369	0.631	1.273	1.086	573.1
0.366	0.634	1.275	1.085	573.1

(11.06 (c))

$\ln\gamma_1 = Ax_2^2 = 0.605\ (0.5)^2 \Rightarrow\ \gamma_1 = 1.163$

$\ln\gamma_2 = Ax_1^2 = 0.605\ (0.5^2 \Rightarrow\ \gamma_2 = 1.163$

P_1^{sat} = 10^(7.11714-1210.595/(T+229.664))

P_2^{sat} = 10^(8.08097-1582.271/(T+239.726))

$P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat} = y_1P + y_2P = (y_1 + y_2)P =$

0.5(1.163) 10^(7.11714-1210.595/(T+229.664)) +

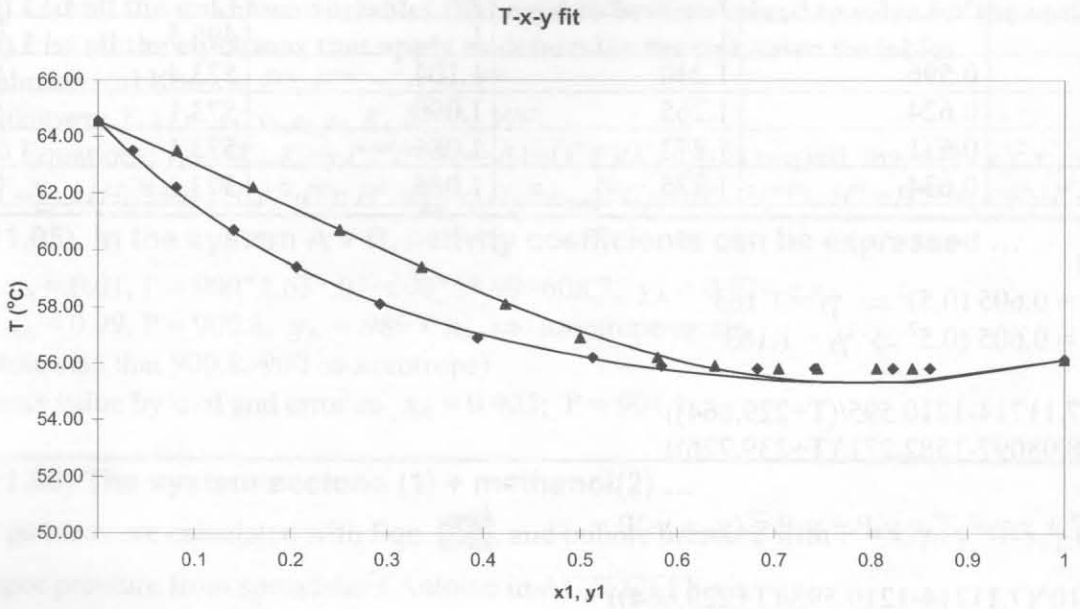
0.5(1.163) 10^(8.08097-1582.271/(T+239.726)) = 760 mm Hg

Program into Excel, guess T until equal to 760. Answer, 56.2°C,
where P1sat = 763.6 mmHg and P2sat = 543.0 mmHg, y1 = $x_1\gamma_1 P_1^{sat}$ = 0.5(1.163)763.6/760 = 0.584, y2 = 1-0.584 = 0.416
Table across the composition range
Data of Amer, H.H, Paxton, R.R., Van Winkle, M., Ind. Eng. Chem., 48:142(1956)

System Components	Parameters to use				Antoine Coefficents			Calculated
					A	B	C	T^{sat}(C)
Acetone	A_{12}	A_{21}	P(mm Hg)	1.00	7.11714	1210.595	229.664	56.10
Methanol	0.605	0.605	760	2.00	8.08097	1582.271	239.726	64.55

				<---optional----->									
	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	T_{calc}	1/T	P_1^{sat}	P_2^{sat}	P_{calc}
	1	1.831252	1		1	0	1	64.55	64.55	0.0029612	1,005.69	760.07	760.07
	0.964	1.75457	1.000784	0.082	0.918	0.080363	0.919637	63.50	63.33857	0.0029719	967.06	724.55	760.09
	0.919	1.66689	1.003977	0.161	0.839	0.164685	0.835315	62.20	62.04254	0.0029834	927.03	688.09	760.03
	0.859	1.562705	1.012101	0.251	0.749	0.256505	0.743495	60.70	60.62354	0.002996	884.73	649.94	759.99
	0.794	1.464353	1.026006	0.336	0.664	0.337141	0.662859	59.40	59.39589	0.0030071	849.37	618.37	759.98
	0.707	1.353114	1.053311	0.423	0.577	0.424673	0.575327	58.10	58.12807	0.0030186	814.04	587.13	759.97
	0.606	1.248793	1.098469	0.5	0.5	0.508133	0.491867	56.90	57.04708	0.0030285	784.85	561.55	759.97
	0.487	1.154292	1.172593	0.58	0.42	0.593325	0.406675	56.20	56.15862	0.0030367	761.49	541.22	759.98
	0.416	1.110376	1.22917	0.639	0.361	0.641488	0.358512	55.90	55.78462	0.0030401	751.82	532.85	759.99
	0.317	1.062682	1.326078	0.705	0.295	0.709514	0.290486	55.80	55.4377	0.0030433	742.94	525.19	760.01
	0.258	1.041093	1.395275	0.745	0.255	0.75236	0.24764	55.80	55.33041	0.0030443	740.21	522.84	760.02
	0.177	1.019135	1.506492	0.806	0.194	0.816634	0.183366	55.80	55.32206	0.0030444	740.00	522.65	760.04
	0.139	1.011758	1.56596	0.843	0.157	0.849933	0.150067	55.80	55.38357	0.0030438	741.56	524.00	760.05
	0	1	1.831252	1		1	0	56.10	56.1	0.0030372	759.97	539.90	759.97

Plot comparing with literature data:



(11.06 (d)) Use Raoult's Law for first guess

Iterative: $x_1 = \dfrac{y_1 P}{\gamma_1 P_1^{sat}}, \qquad x_2 = \dfrac{y_2 P}{\gamma_2 P_2^{sat}}$

Assume $\gamma_i = 1$ for first iteration.

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} = \frac{1}{\dfrac{0.5}{P_1^{sat}} + \dfrac{0.5}{P_2^{sat}}}$$

Put in spreadsheet, adjust T until P = 760 $\Rightarrow$ find T = 61.0 C

$x_1 = 0.424$

$x_2 = 0.576$

$\gamma_1 = \exp(0.605(0.576)^2) = 1.222$

$\gamma_2 = \exp(0.605(0.424)^2) = 1.115$

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} = \frac{0.5(760)}{1.222(895.8)} = 0.347, \qquad x_2 = \frac{y_2 P}{\gamma_2 P_2^{sat}} = \frac{0.5(760)}{1.115(659.9)} = 0.516$$

$x_T = 0.8635$

Normalize x and make next T_{guess} lower, when the temperature is bracketed, then interpolate.
Summary of calculations

x_1	x_2	T_{guess}	γ_1	γ_2	x_1	x_2	x_T
0.424	0.576	61.0	1.222	1.115	0.347	0.516	0.8635
0.402	0.598	55.0	1.242	1.103	0.418	0.668	1.08
0.385	0.615	57.2*	1.257	1.094	0.384	0.616	0.997

* found by interpolating previous T_{guess}'s with x_T.

Solution using Matlab

```
function p11_06
% problem 11.06
addpath(genpath('../gammaModels')); %add path to gamma models
addpath(genpath('../Psat')); % add path to Antoine constants
x1 = 0.5; x2 = 1-x1; Am = 0.605;
% let 1 = acetone (row 37 of Antoine Table)
% let 2 = methanol (row 2 of Antoine Table)
% get Antoine constants
[names A B C] = AntoineGet([37 2]);
% because Psat is needed several places,
% I have created function PsatCalc below.
% Part (a), BP
T = 50; %in C
Psat = PsatCalc(T); %
[gamma1 gamma2] = Marg1P(Am,x1,x2); % gamma = [1.1633 1.1633]
% Answer to (a) ----------------------------------------------------
Pbub = (x1*gamma1*Psat(1)) + (x2*gamma2*Psat(2)); % 261.2 mmHg
y1 = x1*gamma1*Psat(1)/Pbub; y2 = 1 - y1; %y1 = 0.6349
fprintf('(a) Pbub = %g mmHg, gamma = [%g %g], y1 = %g\n    Psat(mmHg) = [%g %g]\n', ...
    Pbub, gamma1, gamma2, y1, Psat)
% ------------------------------------------------------------------------
% Part (b), DP
y1 = 0.5; y2 = 1 - y1;
%RL first guess;
Pdew = (1/(y1/Psat(1) + y2/Psat(2))); x1 = y1*Pdew/Psat(1); x2 = y2*Pdew/Psat(2);
[gamma1 gamma2] = Marg1P(Am,x1,x2);
xdiff = 1; %force at least one loop
while xdiff > 0.001
    x1last = x1;
    Pdew = (1/(y1/gamma1/Psat(1) + y2/gamma2/Psat(2)));
    x1 = y1*Pdew/gamma1/Psat(1); x2 = y2*Pdew/gamma2/Psat(2);
    if abs(x1/x1last - 1) < 0.001; break; end
    xdiff = abs(x1 - x1last);
    [gamma1 gamma2] = Marg1P(Am,x1,x2);
end
%answer to (b) ----------------------------------------------
fprintf('(b) Pdew = %g mmHg, x1 = %g, gamma = [%g %g], \n    Psat(mmHg) = [%g %g]\n'...
    ,Pdew,x1,gamma1,gamma2, Psat)
% ----------------------------------------------------------
%part (c), BT
Tguess = 30;
x1 = 0.5; x2 = 1 - x1;
[Tbub fval exitflag] = fzero(@BP, Tguess);
    function obj = BP(T)
        %adjust T till match P = 760
        Psat = PsatCalc(T);
        % since gamma is not f(T) this does not need to be in loop.
        [gamma1 gamma2] = Marg1P(Am,x1,x2);
        Pbub = (x1.*gamma1*Psat(1)) + (x2.*gamma2*Psat(2));
        obj = Pbub - 760;
    end
% answers to (c) ---------------------------------------------------
fprintf('(c) Tbub = %g C, gamma = [%g %g], \n    Psat(mmHg) = [%g %g], y1 = %g\n', ...
    Tbub, gamma1, gamma2, Psat, x1*gamma1*Psat(1)/Pbub)
% ------------------------------------------------------------------------
% part (d) DT
Tguess = 50; %C
x1 = 0.5; y2 = 1 - y1; [Tdew fval exitflag] = fzero(@DTRL,Tguess);
    function obj = DTRL(T)
        Psat = PsatCalc(T);
        obj = y1*760/Psat(1) + y2*760/Psat(2) - 1;
    end
x1 = y1*760/Psat(1); x2 = 1 - x1; [gamma1 gamma2] = Marg1P(Am,x1,x2);
xdiff = 1; %force at least one iteration
while xdiff > 0.001
    x1last = x1;
    [Tdew fval exitflag] = fzero(@DT,Tdew);
    x1 = y1*760/gamma1/Psat(1); x2 = 1 - x1;
```

```
    x1last = x1; xdiff = abs(x1last - x1);
end
% answers  to (d) ---------------------------------------------------------------
fprintf('(d) Tdew = %g C, gamma = [%g %g], \n    Psat(mmHg) = [%g %g], x1 = %g\n', ...
    Tdew, gamma1, gamma2, Psat, y1*760/gamma1/Psat(1))
% ------------------------------------------------------------------------------
    function obj = DT(T)
        [gamma1 gamma2] = Marg1P(Am,x1,x2); %does not need to be in loop.
        Psat = PsatCalc(T);
        obj = y1*760/gamma1/Psat(1) + y2*760/gamma2/Psat(2) - 1;
    end
    function Psat = PsatCalc(T)
        Psat = 10.^(A - B./(T + C));
    end
end
```

Output from Matlab

(a) Pbub = 599.617 mmHg, gamma = [1.16329 1.16329], y1 = 0.595902
Psat(mmHg) = [614.316 416.585]

(b) Pdew = 573.061 mmHg, x1 = 0.365871, gamma = [1.27543 1.08436],
Psat(mmHg) = [614.316 416.585]

(c) Tbub = 56.2396 C, gamma = [1.16329 1.16329],
Psat(mmHg) = [763.594 543.048], y1 = 0.584394

(d) Tdew = 57.127 C, gamma = [1.22214 1.115],
Psat(mmHg) = [786.982 563.403], x1 = 0.395093

(11.07) The Gibbs energy for a liquid mixture…

a) gammas are calculated with Eqn. 11.6, and bubble pressure with $P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$.

$A = 1089/8.314/303.15 = 0.432$

vapor pressure from spreadsheet Antoine in ACTCOEFF.xls

$\gamma_1 = \exp(0.432(0.5)^2) = 1.114$, $\gamma_2 = \exp(0.432(0.5)^2) = 1.114$

$P = 0.5(1.114)187.3 + 0.5(1.114)119.3 = 171$ mmHg

(11.07 (b)) Use Raoult's Law for first guess

Iterative: $x_1 = \dfrac{y_1 P}{\gamma_1 P_1^{sat}}$, $\quad x_2 = \dfrac{y_2 P}{\gamma_2 P_2^{sat}}$

Assume $\gamma_i = 1$ for first iteration.

Use Raoult's law

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} = \frac{1}{\dfrac{0.5}{187.3} + \dfrac{0.5}{119.3}}$$

$P = 145.77$ mmHg

$$x_1 = \frac{0.5(145.77)}{187.3} = 0.389$$

$$x_2 = \frac{0.5(145.77)}{119.3} = 0.611$$

$\gamma_1 = \exp(0.432(0.611)^2) = 1.175$

$\gamma_2 = \exp(0.432(0.389)^2) = 1.068$

$$P = \frac{1}{\frac{0.5}{1.175(187.3)} + \frac{0.5}{1.068(119.3)}} = 161.4$$

$$x_1 = \frac{0.5(161.4)}{1.175(187.3)} = 0.367; \qquad x_2 = (1\text{-}x_1) = 0.633$$

calculate new gammas, iterate. Summary of iterations:

x_1	x_2	γ_1	γ_2	P
		1	1	145.77
0.389	0.611	1.175	1.068	161.4
0.367	0.633	1.189	1.060	161.3
0.362	0.638	1.192	1.058	161.3
0.361	0.639			

(11.07 (c))

$G^E = 1089\ x_1x_2$ J/mol = ART x_1x_2 at 30 C. Therefore A = 1089/RT = 0.432. Therefore,

$\ln\gamma_1 = Ax_2^2 = 0.432\ (0.5)^2 \Rightarrow\ \gamma_1 = 1.114$

$\ln\gamma_2 = Ax_1^2 = 0.432\ (0.5^2 \Rightarrow\ \gamma_2 = 1.114$

$P_1^{sat} = 10\text{^}(6.91058\text{-}1189.64/(T+226.28))$

$P_2^{sat} = 10\text{^}(6.87987\text{-}1196.76/(T+219.161))$

$P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} = y_1P + y_2P = (y_1 + y_2)P =$

$0.5(1.114)10\text{^}(6.91058\text{-}1189.64/(T+226.28)) +$

$0.5(1.114)10\text{^}(6.87987\text{-}1196.76/(T+219.161)) = 760$ mm Hg

Program into Excel, guess T until equal to 760. Answer, 70.7°C,

where P1sat = 802.7 mmHg and P2sat = 563.5 mmHg, y1 = $x_1\gamma_1P_1^{sat}$ = 0.5(1.114)802.7/760 = 0.588, y2 = 1-0.587 = 0.412

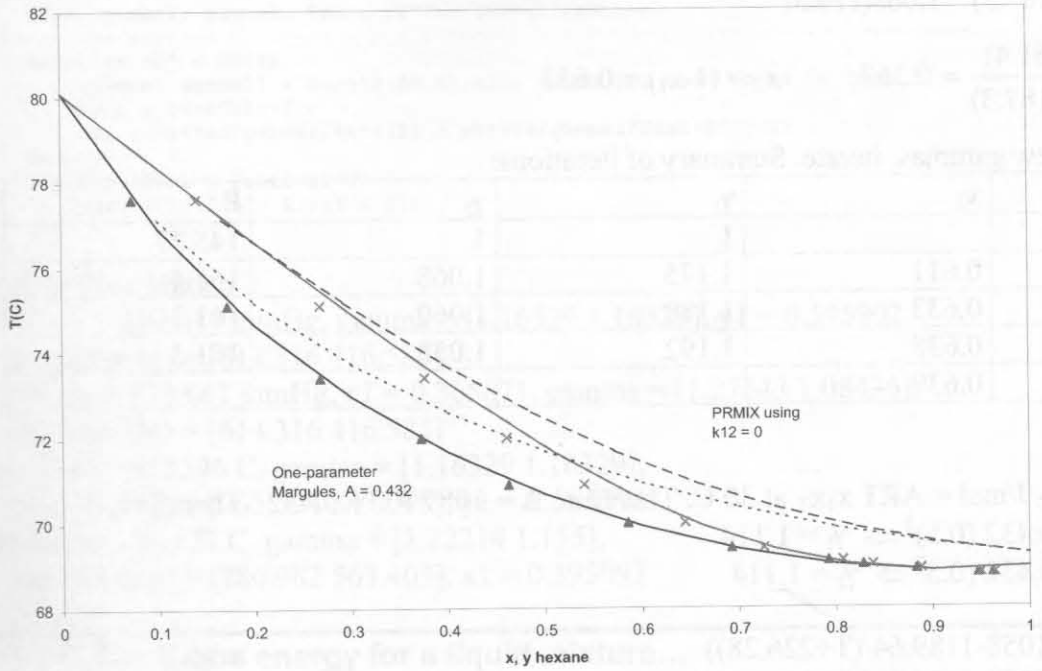
Table across the composition range:

A= 1089/8.314/(273.15+30) = 0.432

	A	B	C
Hexane(1)	6.91058	1189.64	226.28
Benzene(2)	6.87987	1196.76	219.161

x1	x2	y1	y2	T	P1sat	P2sat	gamma1	gamma2	P
0		0		80.0996	1065.82	760			760
0.1	0.9	0.18118	0.81882	76.9466	971.202	689.019	1.41895	1.00433	760.611
0.2	0.8	0.31431	0.68569	74.6662	906.945	641.008	1.31848	1.01743	760.903
0.3	0.7	0.41956	0.58044	72.9669	861.26	606.976	1.23575	1.03965	761.019
0.4	0.6	0.50826	0.49174	71.6746	827.735	582.06	1.16827	1.07156	761.035
0.5	0.5	0.58755	0.41245	70.6822	802.69	563.48	1.11405	1.11405	760.989
0.6	0.4	0.66245	0.33755	69.9252	783.988	549.625	1.07156	1.16827	760.9
0.7	0.3	0.73704	0.26296	69.3695	770.479	539.627	1.03965	1.23575	760.771
0.8	0.2	0.81516	0.18484	69.0055	761.729	533.155	1.01743	1.31848	760.596
0.9	0.1	0.90103	0.09897	68.8467	757.937	530.352	1.00433	1.41895	760.351
1		1		68.9331	760				760

Plot compared with literature data: Data of Prabhu., P.S., Van Winkle, M., J. Chem. Eng. Data. 8(2), 210(1963).



(11.07 (d)) Use Raoult's Law for first guess

Iterative: $x_1 = \dfrac{y_1 P}{\gamma_1 P_1^{sat}}, \qquad x_2 = \dfrac{y_2 P}{\gamma_2 P_2^{sat}}$

Assume $\gamma_i = 1$ for first iteration.

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} = \frac{1}{\dfrac{0.5}{P_1^{sat}} + \dfrac{0.5}{P_2^{sat}}}$$

Put in spreadsheet, adjust T until P = 760 $\Rightarrow$ find T = 74.97 C

$x_1 = 0.413; x_2 = 0.587$

$\gamma_1 = \exp(0.432(0.587)^2) = 1.161$

$\gamma_2 = \exp(0.432(0.413)^2) = 1.076$

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} = \frac{0.5(760)}{1.161(920.4)} = 0.356, \qquad x_2 = \frac{y_2 P}{\gamma_2 P_2^{sat}} = \frac{0.5(760)}{1.076(647.3)} = 0.545$$

$x_T = 0.901$

Normalize x and make next T_{guess} lower, when the temperature is bracketed, then interpolate.

Summary of calculations

x_1	x_2	T_{guess}	γ_1	γ_2	x_1	x_2	x_T
0.413	0.587	74.97	1.161	1.076	0.356	0.545	0.901
0.395	0.605	70	1.171	1.070	0.410	0.645	1.055
0.389	0.611	71.78*	1.175	1.068	0.387	0.609	0.996
0.388	0.612						

* found by interpolating previous T_{guess}'s with x_T.

(11.08) The liquid phase activity coefficients of the ethanol(1) + toluene(2)…

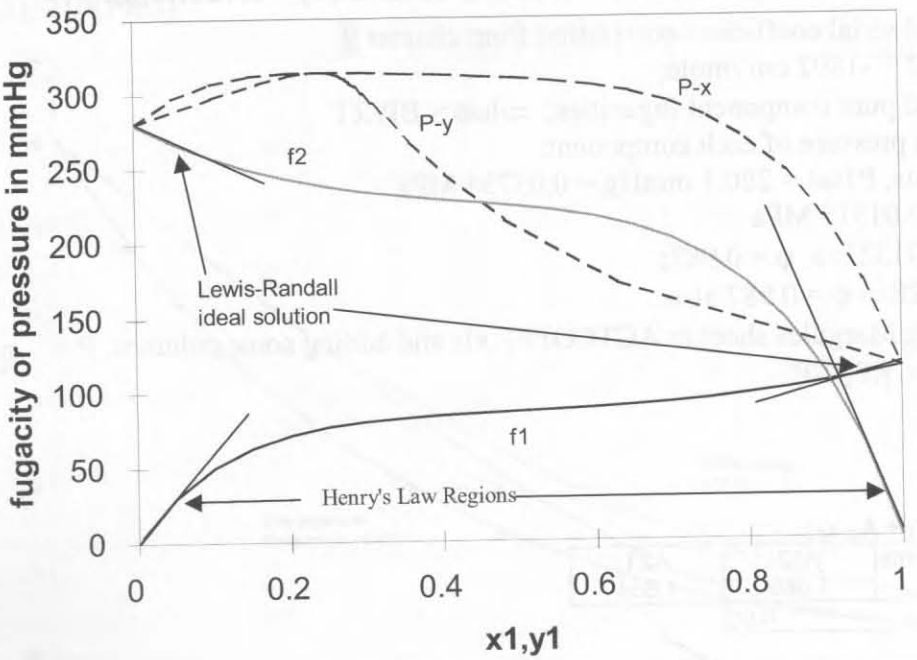
(a) Using the generalized virial coefficient correlation from chapter 7
B1 = -966 cm^3/mole; B2 = -1802 cm^3/mole;
for part (a), we only need pure component fugacities; $\Rightarrow \ln\varphi = BP/RT$
where P is the saturation pressure of each component.
From Antoine coefficients, P1sat = 280.1 mmHg = 0.03734 MPa
P2sat = 113.6 mmHg = 0.01515 MPa
$\Rightarrow$ for ethanol $\ln\varphi = -0.01321 \Rightarrow \varphi = 0.987$;
for toluene $\ln\varphi = -0.01328 \Rightarrow \varphi = 0.987$ also.
(b),(c) $f_i = x_i\gamma_i P_i^{sat}$, using Margules sheet in ACTCOEFF.xls and adding some columns, $P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$, $y_1 = x_1\gamma_1 P_1^{sat}/P$

Margules Equation

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

Interaction Coefficients	A12	A21
	1.869	1.654
Table x1 increment	0.05	

x1	x2	gamma1	gamma2	f1	f2	y1	P	
0	1	6.4818113	1	0	280.1	0	280.1	
0.05	0.95	5.2982085	1.0051696	30.093824	267.4706	0.1011338	297.56442	
0.1	0.9	4.3888183	1.0206197	49.856975	257.28802	0.1623239	307.145	
0.15	0.85	3.683087	1.0464869	62.759802	249.15283	0.2012096	311.91264	
0.2	0.8	3.1302723	1.0832004	71.119787	242.72355	0.2266092	313.84333	
0.25	0.75	2.6935062	1.1314854	76.495575	237.69679	0.2434673	314.19236	
0.3	0.7	2.3457378	1.1923784	79.942746	233.78964	0.2548119	313.73239	
0.35	0.65	2.0669338	1.2672558	82.181288	230.72292	0.2626404	312.90421	
0.4	0.6	1.8421254	1.3578737	83.706177	228.20425	0.2683661	311.91043	
0.45	0.55	1.6600351	1.4664232	84.860995	225.90983	0.2730662	310.77082	
0.5	0.5	1.5121009	1.5956003	85.88733	223.46382	0.277637	309.35115	
0.55	0.45	1.3917769	1.7486932	86.958218	220.41403	0.2829085	307.37225	
0.6	0.4	1.2940282	1.9296912	88.200963	216.2026	0.2897501	304.40357	
0.65	0.35	1.2149632	2.1434169	89.712879	210.12988	0.2991998	299.84276	
0.7	0.3	1.1515628	2.3956869	91.572276	201.30957	0.3126594	292.88185	
0.75	0.25	1.1014817	2.6935062	93.846239	188.61277	0.3322473	282.45901	
0.8	0.2	1.0628989	3.0453018	96.596253	170.59781	0.361521	267.19406	
0.85	0.15	1.0344074	3.4612031	99.882383	145.42245	0.4071766	245.30483	
0.9	0.1	1.0149304	3.9533764	103.76648	110.73407	0.4837586	214.50055	
0.95	0.05	1.0036579	4.5364227	108.31476	63.5326	0.6302963	171.84736	
1	0	1	5.2278495	113.6	0	1	113.6	



Lewis-Randall and Henry's law valid at some compositions near purity, but for opposite components.

(d) The ideal gas assumption will be fine since φ is about 1 for all components.

(11.09) The acetone(1) + chloroform(2) system can be represented by…

There appears to be a systematic error in the P measurement, but the x-y data are well represented.

Margules Equation

This solution obtained by modifying Margules spreadsheet in ACTCOEFF.xls

Acetone(1) + Chloroform(2) T(C)= 35.17

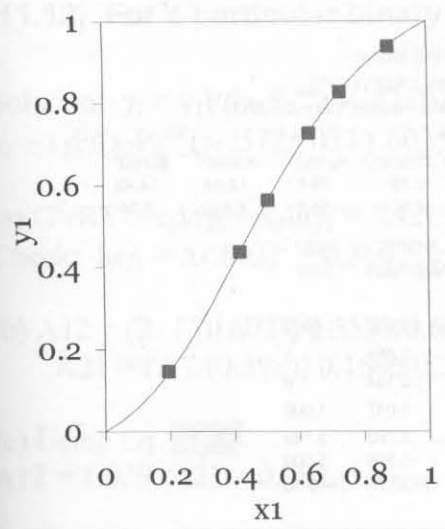
$G^E/RT = x_1 x_2 (A_{21} x_1 + A_{12} x_2)$

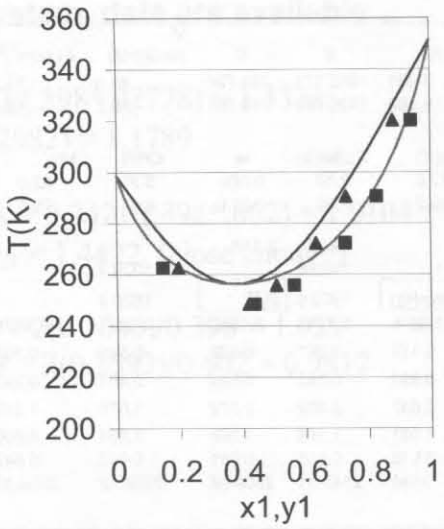
Interaction Coefficients	A12	A21
	-1.0105	-0.756
Table x1 increment	0.05	

Vapor Pressures from Antoine Coeff in Appendix

	A	B	C	Psat(mm Hg
1	7.11714	1210.595	229.664	351.55522
2	6.95465	1170.966	226.232	298.59999

x1	x2	gamma1	gamma2	activity1	activity2	G(mix) /RT	y1	y2	P(mm Hg)
0	1	0.3640369	1	0	1	0	0	1	298.59999
0.05	0.95	0.4110635	0.9969059	0.0205532	0.9470606	-0.24591	0.0249142	0.9750858	290.01786
0.1	0.9	0.4596564	0.9879324	0.0459656	0.8891392	-0.413737	0.057373	0.942627	281.6564
0.15	0.85	0.5091954	0.9736098	0.0763793	0.8275684	-0.546681	0.0980114	0.9019886	273.96345
0.2	0.8	0.5590211	0.9545378	0.1118042	0.7636303	-0.653938	0.1470319	0.8529681	267.32535
0.25	0.75	0.6084576	0.93136	0.1521144	0.69852	-0.739874	0.2040666	0.7959334	262.05467
0.3	0.7	0.6568353	0.9047406	0.1970506	0.6333184	-0.807036	0.2681065	0.7318935	258.38303
0.35	0.65	0.7035137	0.8753433	0.2462298	0.5689731	-0.857071	0.3375333	0.6624667	256.45875
0.4	0.6	0.7479015	0.8438133	0.2991606	0.506288	-0.8911	0.4102667	0.5897333	256.34905
0.45	0.55	0.7894738	0.8107627	0.3552632	0.4459195	-0.909893	0.4840011	0.5159989	258.04619
0.5	0.5	0.8277865	0.7767591	0.4138933	0.3883796	-0.91396	0.5564797	0.4435203	261.47646
0.55	0.45	0.862486	0.7423179	0.4743673	0.3340431	-0.903594	0.6257376	0.3742624	266.51155
0.6	0.4	0.893315	0.7078975	0.535989	0.283159	-0.878884	0.6902668	0.3097332	272.981
0.65	0.35	0.9201145	0.6738967	0.5980744	0.2358639	-0.839701	0.749082	0.250918	280.68514
0.7	0.3	0.9428218	0.6406558	0.6599753	0.1921967	-0.785658	0.8016986	0.1983014	289.40768
0.75	0.25	0.9614652	0.6084576	0.7210989	0.1521144	-0.716015	0.8480522	0.1519478	298.92744
0.8	0.2	0.9761568	0.5775317	0.7809255	0.1155063	-0.629506	0.8883916	0.1116084	309.02862
0.85	0.15	0.9870825	0.5480587	0.8390202	0.0822088	-0.523966	0.9231711	0.0768289	319.50946
0.9	0.1	0.9944912	0.5201755	0.8950421	0.0520176	-0.395413	0.952959	0.047041	330.18916
0.95	0.05	0.9986835	0.4939808	0.9487493	0.024699	-0.23503	0.9783665	0.0216335	340.9129
1	0	1	0.4695408	1	0	0	1	0	351.55522





(11.10) Fit the Margules two-parameter equation to the methanol(1)+benzene(2) ...

(a) using Psat.m

```
names =  'methanol' 'benzene'; A = 8.0810 6.8799; B = 1582.3 1196.8;
C =  239.7260  219.1610;  T(C) 90; Psat(mmHg) 1915.25 Psat(mmHg) 1020.65
```

$\gamma_1 = y_1P/(x_1P_1^{sat}) = 0.65(2273)/ (0.549(1915.25)) = 1.405$

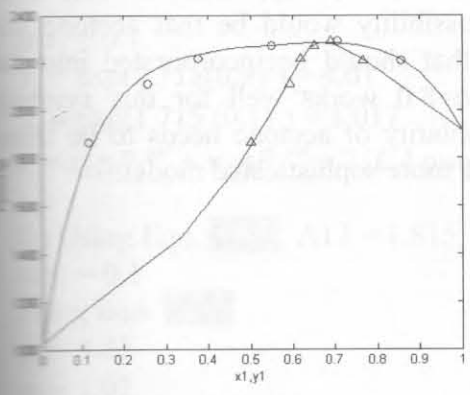
$\gamma_2 = y_2P/(x_2P_2^{sat}) = 0.35(2273)/ (0.451(1020.65)) = 1.728$, using 'g1' and 'g2' to write matlab

A12 = (2-1/x2)*log(g1)/x2 + 2*log(g2)/x1 = 1.8288

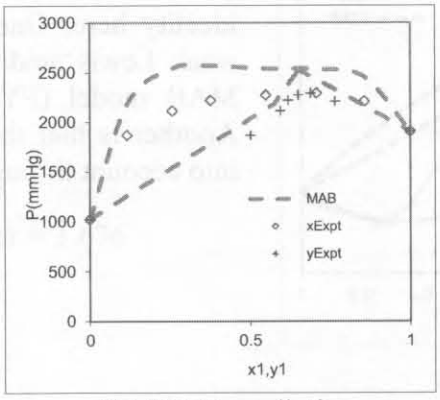
A21 = (2-1/x1)*log(g2)/x1 + 2*log(g1)/x2 = 1.6858

now write code to generate Pxy diagram

```
x1 = 0:0.05:1; x1 = x1'; x2 = 1-x1; Psat = [1915.25 1020.65];
addpath(genpath('../computer/Matlab/gammaModels'));
A12 = 1.8288; A21 = 1.6858;
[gamma1, gamma2] = Marg2P(A12,A21, x1, x2);
P = x1.*gamma1*Psat(1) + x2.*gamma2*Psat(2);
y1 = x1.*gamma1*Psat(1)./P;
data = [ 0.117  0.502   1865; 0.257 0.594 2113; 0.376 0.618 2218;
1.549 0.65 2273; 0.707 0.689 2292; 0.856 0.765 2208];
plot(x1,P); hold on; plot(y1,P);plot(data(:,1),data(:,3),'o');
plot(data(:,2),data(:,3),'^'); xlabel('x1,y1'); ylabel('P(mmHg)');
```



(a) M2 model fit to x_1=0.549



(b) MAB prediction

(b) MAB model

Antoine Coeff		A	B	C	V^L (cm3/mol)	δ (J/cm^3)$^{1/2}$	MAB Model
1	methanol	8.081	1582.271	239.726	40.5	19.3	$\ln\gamma_i = A12*(1-x_i)^2$
2	benzene	6.880	1196.760	219.161	89.7	18.6	$A12 \sim \Delta\alpha*\Delta\beta*(V1+V2)/(4RT)$

Mixture data to be used in all sets:

		Tc(K)	Pc(MPa)	w	CP/R	MW	ρ^L298g/cm3	δ(J/cc)$^{0.5}$	α(J/cc)$^{0.5}$	β(J/cc)$^{0.5}$
LightKey	methanol	512.6	8.10	0.566	5.3	32.0	0.79	29.6	17.43	14.49
HeavyKey	benzene	562.2	4.90	0.211	9.8	78.0	0.87	18.7	0.63	2.24

MAB model with binary interaction coefficient: A12= 2.218 A12*RT= 6697

Pxy Table		Pred =	1903.6		1020.7		MabPred=	6697	
T=	363.2	P_1^{sat}(mmHg)	1903.6	P_2^{sat}	1020.7				
wFrac1	0.0000	0.0516	0.1243	0.1982	0.3331	0.4975	0.7092	1.0000	
x_1	0	0.117	0.257	0.376	0.549	0.707	0.856	1	
x_2	1	0.883	0.743	0.624	0.451	0.293	0.144	0	
γ_1	9.189	5.637	3.402	2.372	1.570	1.210	1.047	1.000	
γ_2	1.000	1.031	1.158	1.368	1.951	3.030	5.080	9.189	
y1	0.000	0.575	0.655	0.661	0.646	0.642	0.696	1.000	
P	1020.65	2185	2542.51	2569.08	2539.12	2534.37	2452.74	1903.58	

(11.11) Fit the specified model to the n-pentane (1) + acetone (2) system T-x-y…

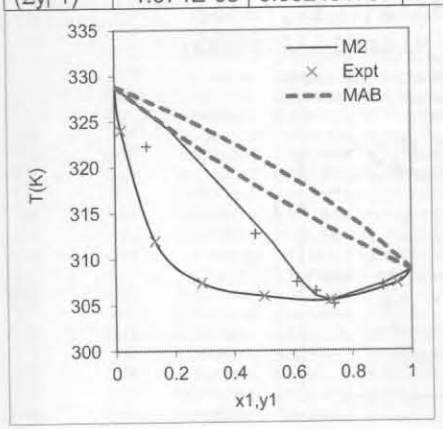
(a) Fit the Margules two-parameter equation to x_1=0.503.
Plot the resultant fit together with the original data for both phases.
(b) Compare the data with the predictions of the MAB model.

Solution(a):	x1	y1	P	γ1	γ2	A12Pred	A21pred
$\gamma_i = y_i P/(x_i P_i^{sat})$	0.503	0.678	1.0	1.493	1.539	1.704	1.622

Computing Pisat's by Antoine coeffs because Txy requires comparing T's.

P = 750 mm Hg

x1	0	0.021	0.134	0.292	0.503	0.728	0.953	1	
γ_1	5.387	5.004	3.470	2.263	1.481	1.121	1.003	1.000	
γ_2	1.000	1.001	1.032	1.158	1.531	2.387	4.273	4.906	
P_1^{sat}	1421.7	1170.0	859.5	720.0	677.3	660.0	715.5	749.9	
P_2^{sat}	749.9	602.3	413.3	339.8	315.8	307.5	333.8	358.3	
$y_{1\,calc}$	0	0.163934673	0.532845966	0.634383	0.67267	0.71836	0.912191	0.99982	
$y_{2\,calc}$	0.9999	0.7868	0.4924	0.3715	0.3203	0.2662	0.0894	0.0000	
y1expt		0.108	0.475	0.614	0.678	0.739	0.906		
Texpt(C)		49.15	39.58	34.35	33.35	31.93	33.89		
T(K)	328.9	322.3	312.7	307.5	306.5	305.1	307.0	308.8	OBJ
$(\Sigma y_i - 1)^2$	1.674E-08	0.002431787	0.000638407	3.43E-05	4.9E-05	0.00024	2.45E-06	3.4E-08	0.003396



The MAB model predicts A12=0 because n-pentane is inert and acetone has α=0. Clearly, there is some non-ideality here. One possibility would be that acetone has weak Lewis acidity that should be incorporated into the MAB model (FYI: α=8.0 works well for this system). Another is that the polarity of acetone needs to be taken into account through a more sophisticated model.

(11.12) For a particular binary system, data are available…

Solution: $\gamma_1 = y_1P/(x_1P_1^{sat}) = .428*.037/(.398*.02778) = 1.4323$;
$\gamma_2 = y_2P/(x_2P_2^{sat}) = .572*.037/(.602*.02982) = 1.1789$

(a) $G^E/RT = x_1\ln\gamma_1 + x_2\ln\gamma_2 = .2421$; $A = 0.2421/(.398*.602) = 1.0104$
Check: $\ln\gamma_1 = A(.602)^2 = 0.3662 \Rightarrow \gamma_1 = 1.4422$ (close enough)

(b) $A12 = (2- 1/(0.602))\ 0.3593/0.602 + 2(0.1646)/0.398 = 1.029$
$A21 = (2-1/(0.398))\ 0.1646/0.398 + 2(0.3593)/0.602 = 0.9817$

(c) Using Eq. 11.38
A12 = 1.029, A21 = 0.982

(11.13) The compositions of coexisting phases of ethanol(1) + toluene(2) …

All three methods will use activity coefficients calculated from vapor pressures using Antoine constants in Appendix

$P_1^{sat} = 280.1$ mmHg

$P_2^{sat} = 113.6$ mmHg

$$\gamma_1 = \frac{y_1P}{x_1P_1^{sat}} = \frac{(0.7431)(307.81)}{(0.7186)(280.1)} = 1.136$$

$$\gamma_2 = \frac{y_2P}{x_2P_2^{sat}} = \frac{(0.2569)(307.81)}{(0.2814)(113.6)} = 2.474$$

(a) $$\frac{G^E}{RT} = x_1\ln\gamma_1 + x_2\ln\gamma_2 = Ax_1x_2;$$
$$= 0.7186\ln\gamma_1 + 0.2814\ln\gamma_2$$
$$= 0.7186(0.1275)+0.2814(0.9057)$$
$$=0.3467$$

$$A_{12} = \frac{0.3467}{(0.7186)(0.2814)} = 1.715$$

at $x_1 = 0.1$
$\gamma_1 = \exp(1.715(0.9)^2) = 4.01$
$\gamma_2 = \exp(1.715\ (0.1)^2) = 1.017$
$P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} = 216.4$ mmHg

(b) Using Eqn. 11.38, A12 = 1.815, A21 = 1.676
at $x_1 = 0.1$
Using Eqn. 11.37
$\gamma_1 = 4.25$
$\gamma_2 = 1.02$
$P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} = 223.3$ mmHg

(c) $A_{12} = 1.821 \qquad A_{21} = 1.676$

at $x_1 = 0.1, \quad \gamma_1 = 4.26 \qquad \gamma_2 = 1.02$

$y_1 P = x_1 \gamma_1 P_1^{sat} = (0.1)(4.26)(280.1) = 119.3$ mmHg

$y_2 P = x_2 \gamma_2 P_2^{sat} = (0.9)(1.02)(113.6) = 104.3$ mmHg

$P = y_1 P + y_2 P = 223.6$ mmHg

$$y_1 = \frac{y_1 P}{P} = \frac{119.3}{223.6} = 0.53$$

$y_2 = 1 - y_1 = 0.47$

(11.14) A vapor/liquid experiment for the carbon disulfide(1) + chloroform(2)...

For all parts:

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

$\gamma_1 = 1.355 \qquad \gamma_2 = 1.020$

These values will be used to determine activity coefficient parameters for the second and subsequent iterations.

at 298K

Iterative: $x_1 = \dfrac{y_1 P}{\gamma_1 P_1^{sat}}, \qquad x_2 = \dfrac{y_2 P}{\gamma_2 P_2^{sat}}$

Assume $\gamma_i = 1$ for first iteration.

Use Raoult's law

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} = \frac{1}{\dfrac{0.6}{46.85} + \dfrac{0.4}{27.3}}$$

$P = 36.418$ mmHg

$$x_1 = \frac{0.6(36.418)}{46.85} = 0.4664$$

$$x_2 = \frac{0.4(36.418)}{27.3} = 0.5336$$

(a) iterations – One-parameter Margules

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

$$= 0.2 \ln \gamma_1 + 0.8 \ln \gamma_2$$

$$= 0.07682$$

$$A = \frac{0.07681}{(0.2)(0.8)} = 0.4801$$

$\gamma_1 = \exp(0.4801(0.5336)^2) = 1.1465$
$\gamma_2 = \exp(0.4801(0.4664)^2) = 1.1101$

$$P = \frac{1}{\frac{0.6}{1.1465(46.85)} + \frac{0.4}{1.1101(27.3)}}$$
$P = 41.035$

$$x_1 = \frac{0.6(41.035)}{1.1465(46.85)} = 0.4584$$
$$x_2 = \frac{0.4(41.035)}{1.1101(27.3)} = 0.5416$$

calculate new gammas, iterate. Summary of iterations:

x_1	x_2	γ_1	γ_2	P
		1	1	36.418
0.4664	0.5336	1.1465	1.1101	41.035
0.4584	0.5416	1.151	1.106	41.034
0.4565	0.5435	1.152	1.105	41.033
0.156	0.544			

(b) iterations – Two parameter Margules
$A_{12} = 0.4854$
$A_{21} = 0.4591$

$\gamma_1 = 1.140$
$\gamma_2 = 1.112$

$$P = \frac{1}{\frac{y_1}{\gamma_1 P_1^{sat}} + \frac{y_2}{\gamma_2 P_2^{sat}}}$$
$P = 40.965$

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^{sat}} = 0.460$$
$x_2 = 0.540$

calculate new gammas, iterate. Summary of iterations:

x_1	x_2	γ_1	γ_2	P
		1	1	36.418
0.4664	0.5336	1.140	1.112	40.965
0.460	0.540	1.144	1.109	40.965
0.459	0.541	1.145	1.108	40.965
0.458	0.542			

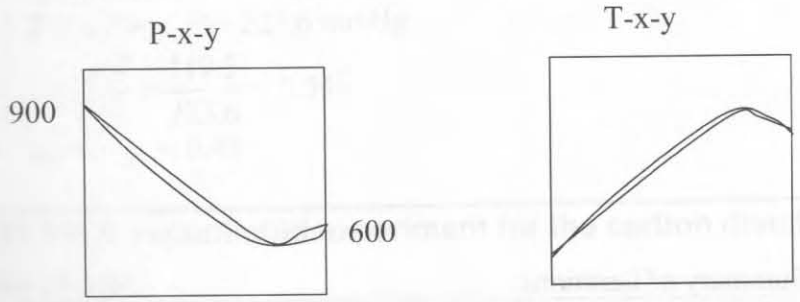
(11.15) The (1) + (2) system forms an azeotrope at $x_1 = 0.75$...

$x_1\gamma_1 P_1^{sat} = y_1 P$, $\gamma_1 = P/P_1^{sat}$, $\gamma_2 = P/P_2^{sat}$

$1 = \alpha_{12} = (y_1/x_1)/(y_2/x_2) = (\gamma_1 P_1^{sat})/(\gamma_2 P_2^{sat}) = [\exp(Ax_2^2)P_1^{sat}]/[\exp(Ax_1^2)P_2^{sat}] \Rightarrow$

$P_2^{sat}/P_1^{sat} = \exp(A(x_2^2 - x_1^2)) \Rightarrow A = [\ln(P_2^{sat}/P_1^{sat})]/(x_2^2 - x_1^2) = \ln(900/600)/(0.25^2 - 0.75^2) = -0.811$

$\therefore \ln \gamma_1 = -0.811(x_2^2) \Rightarrow \gamma_1 = 0.9506 \Rightarrow$ at azeotrope, $P = 0.9506 * P_1^{sat} = 570.3$ mmHg



(11.16) Ethanol(1) + benzene(2) form an azeotropic mixture...

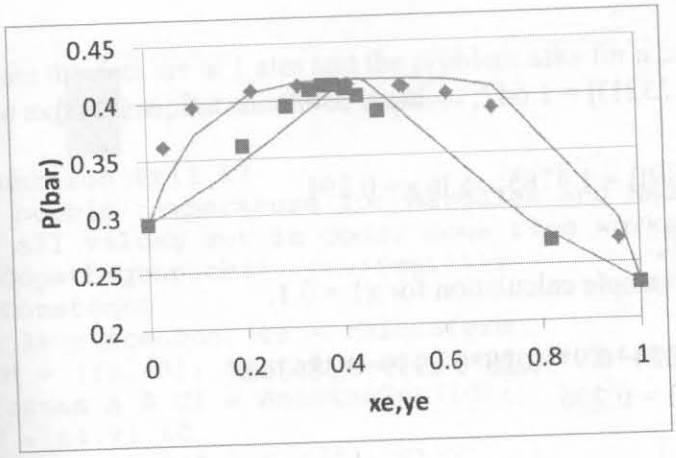
Solution :

(a) MAB model

	ρ(g/ml)	MW	α	β	V(cm3/mol)
ethanol	0.79	46	12.58	13.29	46/0.79= 58.23
benzene	0.87	78	0.63	2.24	78/0.87= 89.66

A12 = (12.58-0.63)(13.29-2.24)(58.23+89.66)/(4(8.314)318.15)=1.846

xe	ye	P	ge	gb	P(calc)	ye(calc)
0	0	0.2939	6.332691	1	0.2939	0
0.0374	0.1965	0.3613	5.530326	1.002585	0.331646	0.144752
0.0972	0.2895	0.3953	4.501247	1.017591	0.371549	0.273312
0.2183	0.337	0.4088	3.088975	1.091942	0.407375	0.384193
0.3141	0.3625	0.4124	2.382946	1.199731	0.415572	0.418034
0.415	0.3842	0.4128	1.880717	1.374211	0.417424	0.43398
0.5199	0.4065	0.41	1.530252	1.646896	0.417033	0.44278
0.5284	0.4101	0.4093	1.507573	1.674205	0.416942	0.443447
0.6155	0.4343	0.4028	1.313733	2.012213	0.415066	0.452161
0.7087	0.4751	0.3891	1.169551	2.526983	0.408721	0.470684
0.9591	0.8201	0.2711	1.003092	5.462095	0.288953	0.772775
1	1	0.2321	1	6.332691	0.2321	1



(b) 1-parameter Margules

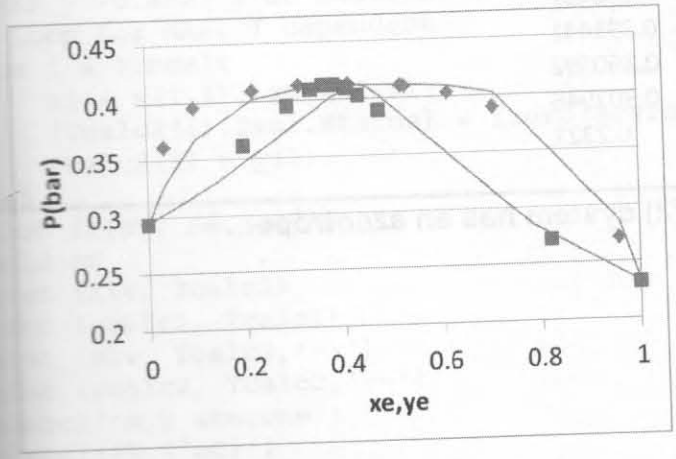
γ_E = 0.3842*0.4128/0.415/0.2321 = 1.647

γ_B = (1-0.3842)*0.4128/(1-0.415)/0.2939 = 1.479

G^E/RT = 0.415ln(1.647) + (1-0.45)ln(1.479) = 0.4357

A_{12} = 0.4357/0.415/(1-0.415) = 1.795

x_E	y_E	P(bar)	γ_E	γ_B	P(calc)	y_E (calc)
0	0	0.2939	6.018	1.000	0.294	0.000
0.0374	0.1965	0.3613	5.275	1.003	0.329	0.139
0.0972	0.2895	0.3953	4.318	1.017	0.367	0.265
0.2183	0.337	0.4088	2.994	1.089	0.402	0.377
0.3141	0.3625	0.4124	2.326	1.194	0.410	0.413
0.415	0.3842	0.4128	1.848	1.362	0.412	0.432
0.5199	0.4065	0.41	1.512	1.624	0.412	0.443
0.5284	0.4101	0.4093	1.491	1.651	0.412	0.444
0.6155	0.4343	0.4028	1.304	1.974	0.409	0.455
0.7087	0.4751	0.3891	1.164	2.463	0.402	0.476
0.9591	0.8201	0.2711	1.003	5.212	0.286	0.781
1	1	0.2321	1.000	6.018	0.232	1.000



(c) 2-parameter Margules

$\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}}$ =0.3842(0.4128)/[0.4150(0.2321)] = 1.647; $\Rightarrow \ln\gamma_1$= 0.499 Eqn. (11.3)

$\gamma_2 = \frac{y_2 P}{x_2 P_2^{sat}}$ = 0.6158(0.4128)/[0.5850(0.2939)] = 1.4785; $\Rightarrow \ln\gamma_2$= 0.391.

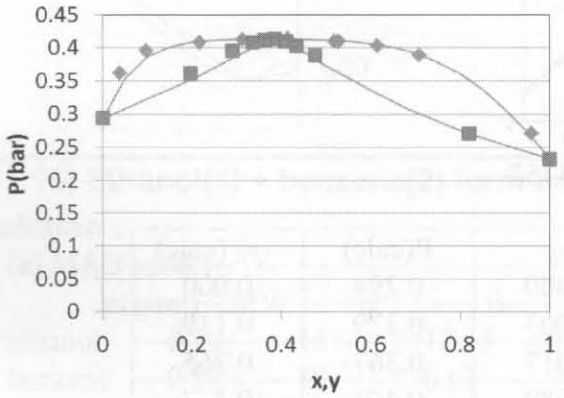
Using Eqn. 11.38, A_{12} = 1.279; A_{21} = 1.320,

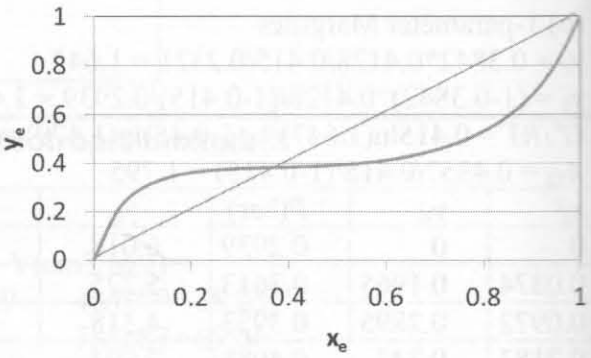
Performing bubble pressure calculations. Example calculation for x1 = 0.1,

Using Eq 11.37,

$P = x_1*\gamma_1*P_1^{sat} + x_2*\gamma_2*P_2^{sat}$ = 0.1*4.93*0.2321+0.9*1.028*0.2939=0.3863bar

$y_1 = x_1*\gamma_1*P_1^{sat}/P$ = 0.1*4.93*0.2321/0.3863 = 0.296





selected values

x1	x2	gamma1	gamma2	y	P(bar)
0	1	8.431713	1	0	0.2939
0.1	0.9	4.930182	1.028206	0.296142	0.3864
0.2	0.8	3.179131	1.110453	0.361116	0.408665
0.3	0.7	2.238827	1.247463	0.377886	0.41253
0.4	0.6	1.705169	1.443548	0.383439	0.412863
0.5	0.5	1.390968	1.704037	0.391962	0.41183
0.6	0.4	1.203478	2.032072	0.412305	0.406487
0.7	0.3	1.093702	2.424264	0.453948	0.391441
0.8	0.2	1.033873	2.865297	0.532669	0.360392
0.9	0.1	1.006727	3.322588	0.682896	0.307946
1	0	1	3.743421	1	0.2321

(11.17) The acetone(1) + chloroform(2) system has an azeotrope…

$P_{acetone}^{sat}$ = 351.56 mmHg

$P_{CCl_4}^{sat}$ = 298.60 mmHg

$\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}} = \frac{248}{351.56} = 0.7054$

$\gamma_2 = \frac{y_2 P}{x_2 P_2^{sat}} = \frac{248}{298.6} = 0.8305$

x_1 = 0.38 x_2 = 0.62

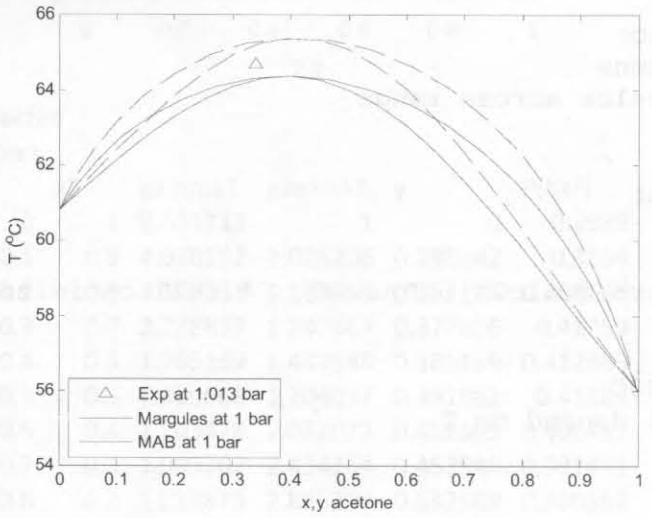
Note the data are at 1 atm and the problem asks for a plot at 1 bar. The calculations won't match the expt points, but should be close.

```
function Pr11_17
% bubble temperature for Margules and MAB
% all values set in code, none from workspace.
addpath(genpath('../../Psat'));
%Constants
% 36 - acetone, 49 - chloroform
id = [36 49]; %Antoine coeff id in database
[names A B C] = AntoineGet(id);
T = 64.7; %C
Psat = 10.^(A - B./(T + C));
% Find 1 parameter Margules,
g1 = 760/Psat(1); g2 = 760/Psat(2);
x1ex = 0.2/58/(0.2/58 + 0.8/119.2);
x2ex = 1 - x1ex;
Am = (x1ex*log(g1) + x2ex*log(g2))/x1ex/x2ex

Punits = 'mmHg';
Tunits = 'C';
P = 750; %mmHg, 1 bar
x1v = 0:0.05:1; %composition vector
x = [x1v' (1-x1v)']; %set up columns
ncalc = length(x1v); %number of calcs across range
Tguess = 50; %temperature guess

% Loop for Margules, T independent
for i = 1:ncalc
    x1 = x(i,1); x2 = 1-x1;
    [Tcalc1(i),fval,status] = fzero(@calcObj1,Tguess);  % Call optimizer
    ycalc1(i) = y(1);
end
% MAB, eq 11.10 gives -0.888 at 60C
AMAB = -0.888; % at 333.15K, will depend on T
% Loop for MAB, T dependent
for i = 1:ncalc
    x1 = x(i,1); x2 = 1-x1;
    [Tcalc2(i),fval,status] = fzero(@calcObj2,Tguess);  % Call optimizer
    ycalc2(i) = y(1);
end
plot (x1ex, 64.7,'^')
hold on
plot (x1v, Tcalc1)
plot (ycalc1, Tcalc1)
plot (x1v, Tcalc2,'--')
plot (ycalc2, Tcalc2,'--')
xlabel('x,y acetone')
ylabel('T (^oC)')
legend('Exp at 1.013 bar', 'Margules at 1 bar','MAB at 1
bar','location','southwest')
    function [obj]= calcObj1(T)
```

```
    Psat = 10.^(A - B./(T + C));
    g1 = exp(Am*x2^2); g2 = exp(Am*x1^2);
    y = [x1*g1*Psat(1)/P x2*g2*Psat(2)/P];
    obj = 1 - sum(y);
    end
    function [obj]= calcObj2(T)
    Psat = 10.^(A - B./(T + C));
    TK = T + 273.15;
    g1 = exp(AMAB*333.15/TK*x2^2); g2 = exp(AMAB*333.15/TK*x1^2);
    y = [x1*g1*Psat(1)/P x2*g2*Psat(2)/P];
    obj = 1 - sum(y);
    end
end
```

Note the azeotrope composition is missed, even with the fitted 1 parameter Margules. The phase diagram is shifted downwards from the experimental azeotrope because the pressure (750 mmHg) s lower than the azeotrope measurement (760 mmHg). The MAB does pretty well for a prediction. Because the T range is so small, it doesn't really matter much if the MAB is temperature dependent or not.

From the above code, the one-parameter Margules constant is Am = -0.7397



	Margules		MAB	
X1	Y1	T(C)	Y1	T(C)
0	0	60.80	0	60.80
.2	0.1580	63.29	0.1473	63.85
.4	0.4021	64.35	0.3956	65.37
.6	0.6705	63.03	0.6764	64.00
.8	0.8796	59.76	0.8886	60.26
1	1.0000	55.98	1.0000	55.98

(11.18) Use the γ_i^∞ data to estimate A_{12} and A_{21} and get pxy for E+W...

Solution : from given data, $P_e^{sat} = 1.006$; $P_w^{sat} = 0.439$ bars

Margules 2-Parameter Model

$\ln \gamma_1 = x_2^2(A_{12} + 2(A_{21} - A_{12})x_1)$; $\ln \gamma_2 = x_1^2(A_{21} + 2(A_{12} - A_{21})x_2)$ (11.37)

=> using eq. 11.38, $A_{12} = \ln\gamma_1^\infty = \ln(1.6931) = 0.5266$ & $A_{21} = \ln\gamma_2^\infty = \ln(1.9523) = 0.6690$

plug into Eq. 11.37 at $x_1 = 0.2$, $\gamma_1 = 1.453$, $\gamma_2 = 1.018$,

$P = y_1P + y_2P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} = 0.2(1.453)1.006+0.8(1.018)0.439 = 0.650$ bar

$y1 = x_1\gamma_1P_1^{sat}/P = 0.2(1.453)1.006/0.650 = 0.450$.

Note: a more detailed analysis in problem 11.19 shows that fitting the infinite dilution activity coefficients does not reproduce the azeotrope.

(11.19) Using the data from problem 11.18, fit the two-parameter Margules...

Solution : from given data, $P_e^{sat} = 1.006$; $P_w^{sat} = 0.439$ bars

Margules 2-Parameter Model

$\ln \gamma_1 = x_2^2(A_{12} + 2(A_{21} - A_{12})x_1)$; $\ln \gamma_2 = x_1^2(A_{21} + 2(A_{12} - A_{21})x_2)$ (11.37)

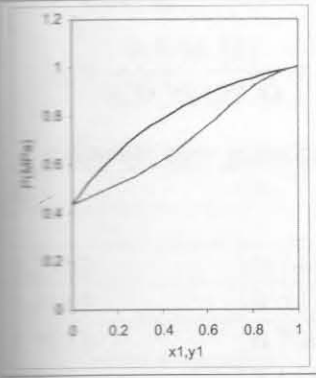
=> using eq. 11.38 $A_{12} = \ln\gamma_1^\infty = \ln(1.6931) = 0.5266$ & $A_{21} = \ln\gamma_2^\infty = \ln(1.9523) = 0.6690$

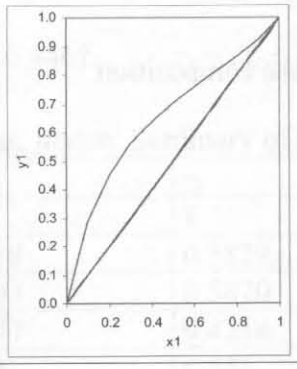
example calculation: plug into Eq. 11.37 at $x_1 = 0.2$, $\gamma_1 = 1.453$, $\gamma_2 = 1.018$,

$P = y_1P + y_2P = x_1\gamma_1P_1^{sat} + x_2\gamma_2P_2^{sat} = 0.2(1.453)1.006+0.8(1.018)0.439 = 0.650$ bar

$y1 = x_1\gamma_1P_1^{sat}/P = 0.2(1.453)1.006/0.650 = 0.450$.

x1	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
x2	0	0.145	0.276	0.395	0.504	0.604	0.696	0.781	0.859	0.890	1.000
γ_1	1.693	1.568	1.453	1.350	1.259	1.182	1.118	1.068	1.031	1.008	1.000
γ_2	1	1.004	1.018	1.043	1.083	1.141	1.221	1.331	1.479	1.680	1.952
y1	0.000	0.284	0.450	0.560	0.640	0.704	0.759	0.811	0.865	0.925	1.000
P(bar)	0.439	0.554	0.650	0.728	0.792	0.845	0.889	0.927	0.959	0.986	1.006





FYI: The plots show that this approach to fitting the Aij's to infinite dilution fails to predict the azeotrope in this system.

(11.20) A liquid mixture of 50 mol% chlorform(1) and 50 mol% 1,4-dioxane at 0.1013 MPa…

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^{sat}} = \frac{(0.62)(24.95)}{(0.36)(69.4)} = 0.619$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^{sat}} = \frac{(0.38)(24.95)}{(0.64)(15.8)} = 0.938$$

(a) Using one-parameter Margules

$$G^E = RT\left(x_1 \ln \gamma_1 + x_2 \ln \gamma_2\right)$$

$$\frac{G^E}{RT} = 0.36\ln(0.619) + 0.62\ln(0.938) = -0.214$$

$$\frac{G^E}{RT} = Ax_1x_2 = -0.214$$

$$A = \frac{-0.214}{(0.36)(0.62)} = -0.928$$

perform a bubble pressure at the exiting liquid composition desired at $x_1 = 0.4$

$$\ln \gamma_1 = -0.928x_2^2 \quad \Rightarrow \quad \gamma_1 = \exp\left(-0.928(0.6)^2\right) = 0.716$$

$$\ln \gamma_2 = -0.928x_1^2 \quad \Rightarrow \quad \gamma_2 = \exp\left(-0.928(0.4)^2\right) = 0.862$$

P = (0.4)(0.716)(69.4) + (0.6)(0.862)(15.8)
= 19.88 + 8.17
= 28.05 kPa
y_1 = 19.88/28.05 = 0.709

(b) using the two-parameter Margules

A_{12} = -0.686
A_{21} = -1.359

leading to at x_1 = 0.4, inserting the new liquid-phase composition

γ_1 = 0.644
γ_2 = 0.916

P = (0.4)(0.644)(69.4) + (0.6)(0.916)(15.8)
= 17.88 + 8.68
= 26.6kPa
y_1 = 17.88/26.6= 0.67

(11.21) an equimolar mixture of chlorform(1) and triethylamine(2)...

Easiest if check bubble pressure first.

$$x_1\gamma_1 P_1^S + x_2\gamma_2 P_2^S = P_{bp}$$

$$0.5e^{-1.74(.25)}(193.4) + 0.5e^{-1.74(.25)}(67.3) = 62.56 + 21.78 = 84.37 \text{ mmHg}$$

$90 > 84.37$ mmHg all liquid

Dew pressure calculation

Use Raoult's Law for first guess

Iterative: $x_1 = \dfrac{y_1 P}{\gamma_1 P_1^{sat}}, \qquad x_2 = \dfrac{y_2 P}{\gamma_2 P_2^{sat}}$

Assume $\gamma_i = 1$ for first iteration.

Use Raoult's law

$$P = \frac{1}{\dfrac{y_1}{P_1^{sat}} + \dfrac{y_2}{P_2^{sat}}} = \frac{1}{\dfrac{0.5}{193.4} + \dfrac{0.5}{67.3}}$$

$P = 99.85$ mmHg

$$x_1 = \frac{0.5(99.85)}{193.4} = 0.2582$$

$$x_2 = \frac{0.5(99.85)}{67.3} = 0.7418$$

$\gamma_1 = \exp(-1.74(0.7418)^2) = 0.3839$

$\gamma_2 = \exp(-1.74(0.2582)^2) = 0.8905$

$$P = \frac{1}{\dfrac{0.5}{0.3839(193.4)} + \dfrac{0.5}{0.8905(67.3)}}$$

$P = 66.32$

$$x_1 = \frac{0.5(66.32)}{0.3839(193.4)} = 0.4467; \qquad x_2 = (1\text{-}x_1) = 0.5533$$

calculate new gammas, iterate. Summary of iterations (converges slowly):

x_1	x_2	γ_1	γ_2	P
		1	1	99.85
0.2582	0.7418	0.3839	0.8905	66.32
0.4467	0.5533	0.5870	0.7067	67.04
0.2953	0.7047	0.4214	0.8592	67.65
0.415	0.585	0.551	0.741	67.95
skipping a few...				
0.3608	0.6392	0.491	0.797	68.58
0.3608	0.6392			

Can't be all vapor since above dew pressure.

(b) Assume $V^E = 0$, (good assumption for liquids)

$V = x_1V_1 + x_2V_2 = 0.5(80.19)+0.5(139) = 109.6$ cm^3/mol

(11.22) Ethanol(1) + Benzene(2) form azeotropic mixtures…

a) This can be solved by fitting G^E as in Example 11.1. We can average the value of A.

x1	y1	P(bar)	gamma1	gamma2	G^E/RT	A
0.3141	0.3625	0.4124	2.050612	1.304183	0.407726	1.892518
0.5199	0.4065	0.41	1.381177	1.72454	0.42953	1.720846
					Average	1.806682

b) gamma's are calculated with Eqn. 11.6, and $P = x_1\gamma_1 P_1^{sat} + x_2\gamma_2 P_2^{sat}$.

$\gamma_1 = \exp(1.807(0.2)^2) = 1.075$, $\gamma_2 = \exp(1.807(0.8)^2) = 3.179$

$P = 0.8(1.075)0.2321 + 0.2(3.179)0.2939 = 0.387$ bar

(11.23) An equimolar mixture of acetone, n-butane, and ammonia at 1 MPa…

Erratum: after the US 4th printing includes the following before the hint:
The multicomponent MAB expression is: $G^E = \sum\sum x_i\, x_j\, A_{ij}$

(a) Bubble temperature
(b) Dew temperature
(c) Flash temperature at 25 mol% vapor.
(d) Raised to midway between the bubble and dew temperature, then adiabatically flashed

Solution: For all of a-d, $A_{ij} = \Delta\alpha\Delta\beta/(4RT)$.

(a) Known: P, x_1,x_2,x_3. Unknown: $T, y_1,y_2,y_3, K_1,K_2,K_3$. Eqns: $y_i/x_i=K_i$, $\Sigma y_i=1$, $K_i=\gamma_i P_i^{sat}/P$,
Since this is multicomponent, $\underline{G^E} = (\sum\sum n_i\, n_j\, A_{ij})/n$.
$RT\ln\gamma_k = \partial\underline{G^E}/\partial n_k = -(\sum\sum n_i\, n_j\, A_{ij})/n^2+(1/n)\partial(n_1^2A_{11}+2n_1n_2A_{12}+n_2^2A_{22}+n_3^2A_{33}+2n_1n_3A_{13}+...)/\partial n_k$
For example, if k=1, then the derivative becomes $2n_1A_{11}+2n_2A_{12}+2n_3A_{13}+... = 2\sum x_j A_{kj}$
$\Rightarrow RT\ln\gamma_k = 2\sum x_j A_{kj} - G^E$. All the A_{ij}'s can be computed from MAB in the usual way.

(b) Known: P, y_1,y_2,y_3. Unknown: $T, x_1,x_2,x_3, K_1,K_2,K_3$. Eqns: $y_i/x_i=K_i$, $\Sigma x_i=1$, $K_i=\gamma_i P_i^{sat}/P$,
$RT\ln\gamma_k = 2\sum x_j A_{kj} - G^E$.

(c) Known: $P, z_1,z_2,z_3, V/F$. Unknown: $T, x_1,x_2,x_3, y_1,y_2,y_3, K_1,K_2,K_3$.
Equations: $y_i/x_i=K_i$, $x_i=z_i/[1+(V/F)(K_i-1)]$, $\Sigma(x_i-y_i)=0$, $K_i=\gamma_i P_i^{sat}/P$, $RT\ln\gamma_k = 2\sum x_j A_{kj} - G^E$.

(d) Known: P, z_1,z_2,z_3, T^{in}. Unknown: $T, x_1,x_2,x_3, y_1,y_2,y_3, K_1,K_2,K_3, V/F$.
Equations: $y_i/x_i=K_i$, $x_i=z_i/[1+(V/F)(K_i-1)]$, $\Sigma(x_i-y_i)=0$, $K_i=\gamma_i P_i^{sat}/P$, $RT\ln\gamma_k = 2\sum x_j A_{kj} - G^E$.
$H^V = \sum_i y_i(H_{f,i}^{ig} + {}_{298}\int^{Ts} Cp_i^{ig} dT)$; $H^L = \sum_i x_i(H_{f,i}^{ig} + {}_{298}\int^{Ts} Cp_i^{ig} dT - H_i^{vap})$;
$H^{in} = H^{out} = (V/F)H^V + (1-V/F)H^L$.

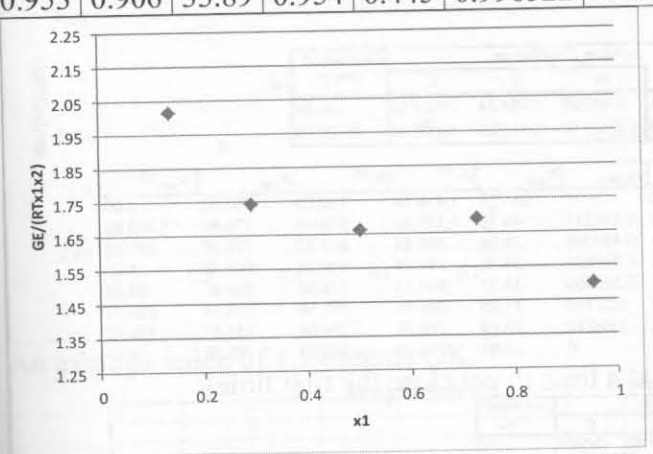
Note: In the solution to HW10.7, we wrote equations for K_i separately to prepare for non-ideal solutions. Thus the only change is the expression for K_i. This makes this HW problem a very simple extension as long as the students have understood HW10.7 properly.

(11.24) Fit the data of problem 11.11 to the following,

(a)

x1	y1	T (°C)	P1sat	P2sat	g1	g2	GE/RT	GE/(RTx1x2)
0.021	0.108	49.15	1.56	0.803	3.296703	1.134662	0.148733	7.234467
0.134	0.475	39.58	1.146	0.551	3.093173	1.100246	0.234045	2.016862
0.292	0.614	34.35	0.96	0.453	2.190354	1.203527	0.360108	1.741874
0.503	0.678	33.35	0.903	0.421	1.492705	1.538925	0.415745	1.663042

0.728	0.739	31.93	0.88	0.41	1.153534	2.340387	0.335266	1.693128
0.953	0.906	33.89	0.954	0.445	0.996522	4.494382	0.067313	1.502817

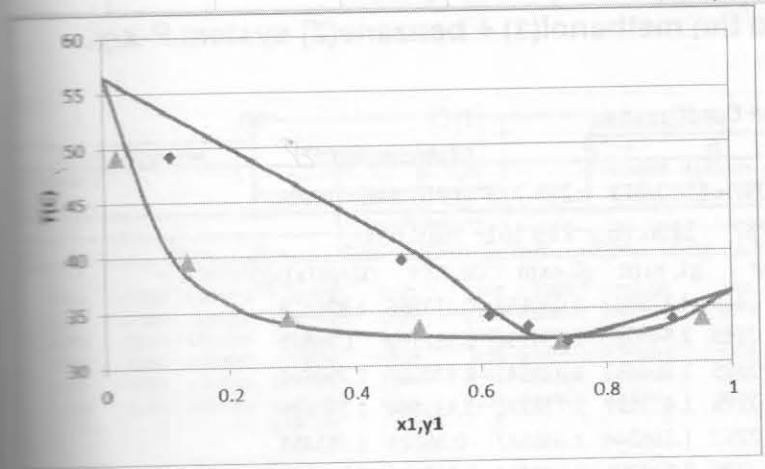


The plot shows that the two parameter is going to do a much better job. The average value of 1.75 may be reasonable. Different students will have different values and thus scatter is expected.

using Antoine equation to generate T-x-y

	A	B	C		Margules A
n-pentane	6.87632	1075.78	233.205		1.75
acetone	7.11714	1210.595	229.664		

x1	T (°C)	P1sat	P2sat	g1	g2	Ptot	(err^2)	y1
0	56.48738	1.8891413	0.999999	5.754603	1	0.999999	1.78E-12	0
0.1	40.84566	1.15960787	0.569341	4.126791	1.017654	0.999998	2.41E-12	0.478546
0.2	35.75691	0.97733014	0.467274	3.064854	1.072508	0.999999	1.68E-12	0.599075
0.3	33.79482	0.91337366	0.432119	2.35726	1.170581	0.999999	1.37E-12	0.645918
0.4	33.01402	0.88885591	0.41874	1.877611	1.32313	0.999999	1.41E-12	0.66757
0.5	32.6726	0.87829874	0.412997	1.54883	1.54883	0.999999	1.16E-12	0.680168
0.6	32.47084	0.87210655	0.409633	1.32313	1.877611	0.999999	1.75E-12	0.692346
0.7	32.35404	0.86853758	0.407696	1.170581	2.35726	0.999999	1.03E-12	0.711685
0.8	32.4882	0.87263794	0.409922	1.072508	3.064854	0.999999	8.83E-13	0.748729
0.9	33.38181	0.90033972	0.425	1.017654	4.126791	0.999999	3.53E-13	0.824611
1	36.42823	0.99999938	0.47982	1	5.754603	0.999999	3.8E-13	0.999999
						sum(err^2):	1.42E-11	



(b) from T-x-y fit P

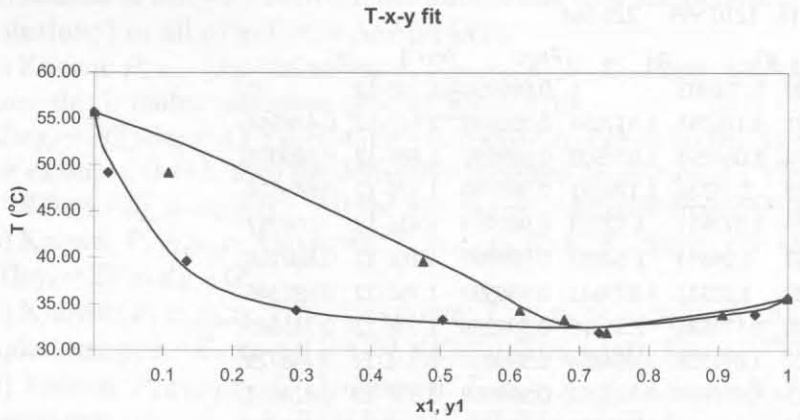
System Components	Parameters to adjust			Antoine Coefficents				Calculated
					A	B	C	T^{sat}(C)
(1) n-pentane	A_{12}	A_{21}	P(mm Hg)	1	6.85296	1064.84	232.012	35.68
(2) acetone	1.706305	1.537118	750	2	7.11714	1210.595	229.664	55.71
		<---optional----->						

x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	P_1^{sat}	P_2^{sat}	P_{calc}	$(P_{error})^2$
0	1	5.508569	1	0	1	0	1	55.715	1,419.35	750.03	750.03	0.00
0.021	0.979	5.096642	1.000824	0.108	0.892	0.175753	0.824247	49.15	1,163.26	595.93	708.40	1,730.60
0.134	0.866	3.475189	1.033408	0.475	0.525	0.515914	0.484086	39.58	855.51	417.70	772.20	493.03
0.292	0.708	2.238445	1.163564	0.614	0.386	0.625595	0.374405	34.35	716.54	340.25	748.65	1.82
0.503	0.497	1.461453	1.539494	0.678	0.322	0.670444	0.329556	33.35	692.11	326.86	758.87	78.68
0.728	0.272	1.114064	2.371272	0.739	0.261	0.72852	0.27148	31.93	658.55	308.59	733.14	284.14
0.953	0.047	1.003062	4.097872	0.906	0.094	0.91288	0.08712	33.89	705.22	334.04	738.47	132.92
1	0	1	4.651165	1	0	1	0	35.68	750.08	358.74	750.08	0.01

from T-x-y calc T (had to converge points one at a time to get close the first time).

System Components			Parameters to use			Antoine Coefficents			Calculated
						A	B	C	T^{sat}(C)
(1) n-penta			A_{12}	A_{21}	P(mm Hg)	1.00	6.85296	1064.84	232.012	35.68
(2) acetone			1.706305	1.537118	750	2.00	7.11714	1210.595	229.664	55.71
				<---optional----->						

x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	T_{calc}	1/T	P_1^{sat}	P_2^{sat}	P_{calc}	log(P_{calc})	[log(P_{calc}/P
	1	5.508569	1		1	0	1	55.72	55.71918	0.0030407	1,419.53	750.14	750.14	2.875142	6.46E-09
0.021	0.979	5.096642	1.000824	0.108	0.892	0.174613	0.825387	49.15	50.78974	0.003087	1,223.59	631.80	750.01	2.875064	8.71E-12
0.134	0.866	3.475189	1.033408	0.475	0.525	0.516971	0.483029	39.58	38.77022	0.0032059	832.72	404.86	750.10	2.875118	3.23E-09
0.292	0.708	2.238445	1.163564	0.614	0.386	0.625526	0.374474	34.35	34.40429	0.0032515	717.89	340.99	750.14	2.875141	6.34E-09
0.503	0.497	1.461453	1.539494	0.678	0.322	0.670828	0.329172	33.35	33.03302	0.003266	684.51	322.71	750.10	2.87512	3.43E-09
0.728	0.272	1.114064	2.371272	0.739	0.261	0.727838	0.272162	31.93	32.55352	0.0032711	673.13	316.51	750.07	2.875104	1.8E-09
0.953	0.047	1.003062	4.097872	0.906	0.094	0.91269	0.08731	33.89	34.33052	0.0032522	716.06	339.98	749.98	2.875048	1.85E-10
1	0	1	4.651165	1		1	0	35.68	35.68184	0.003238	750.12	358.77	750.12	2.875132	5.04E-09

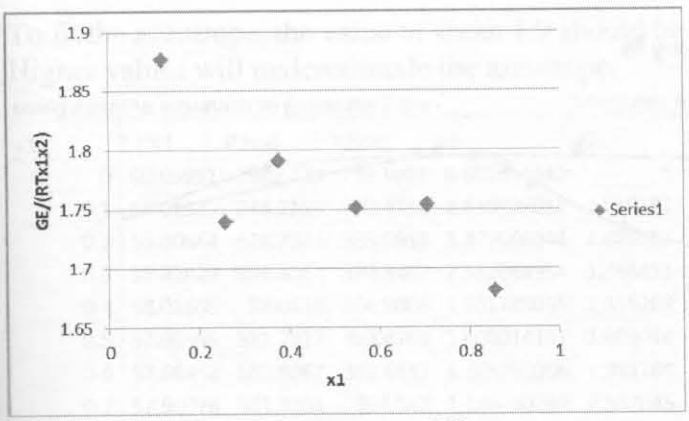


(11.25) Fit the specified model to the methanol(1) + benzene(2) system P-x-y...

(a)

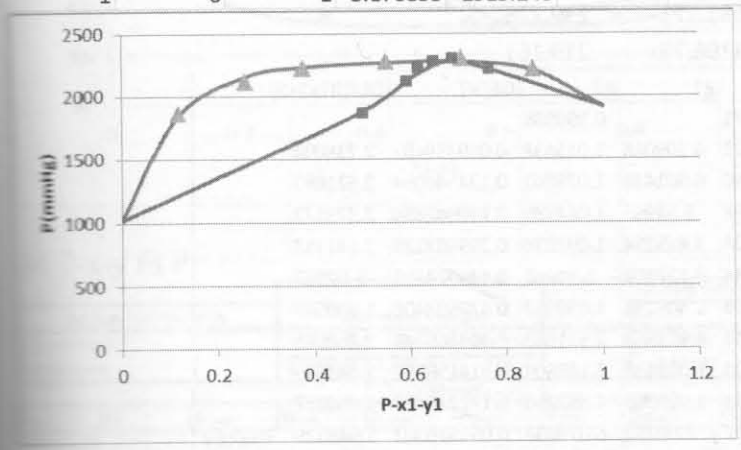
		Antoine Coefficents			T(C)	90
		A	B	C	Psat(mmHg)	
(1) methanol	1	8.08097	1582.271	239.726	1915.248	
(2) benzene	2	6.87987	1196.76	219.161	1020.651	

x1	x2	y1,expt	y2,expt	Pexpt	g1, expt	g2,expt	GE/RT	GE/(RTx1x2)
0.117	0.883	0.502	0.498	1865	4.178032	1.030553	0.193866	1.876524
0.257	0.743	0.594	0.406	2113	2.549928	1.131252	0.332199	1.73971
0.376	0.624	0.618	0.382	2218	1.903431	1.330341	0.420127	1.790641
0.549	0.451	0.65	0.35	2273	1.405127	1.728278	0.433484	1.750749
0.707	0.293	0.689	0.311	2292	1.166244	2.383582	0.36323	1.753453
0.856	0.144	0.765	0.235	2208	1.030295	3.530427	0.207192	1.680881



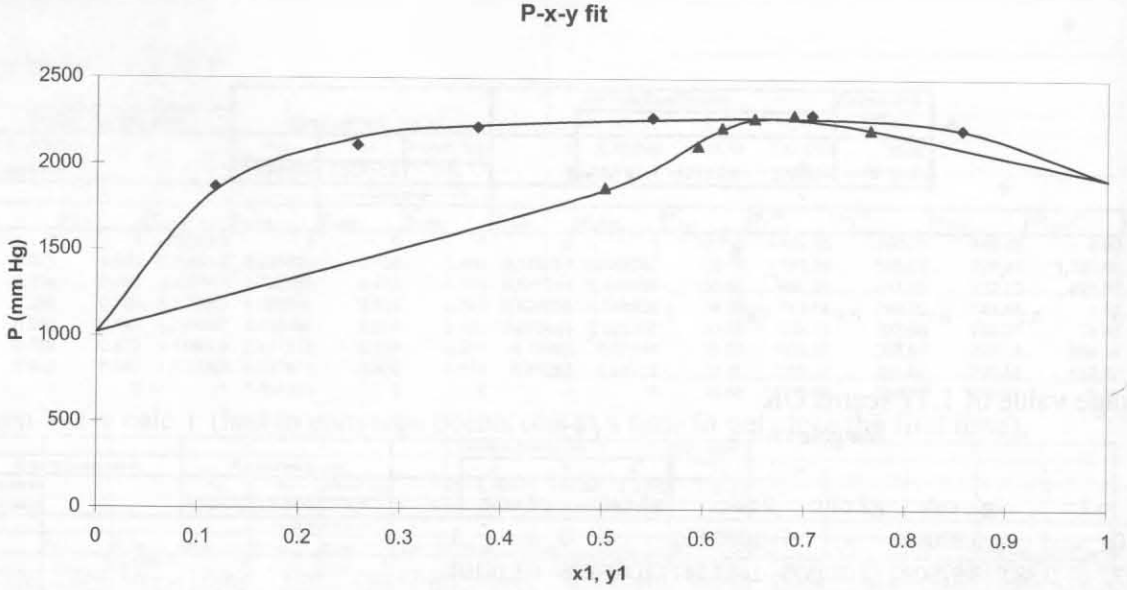
An average value of 1.77 seems OK.

			Margules A =		1.77	
x1	x2	g1, calc	g2,calc	Pcalc	y1,calc	y2,calc
0	1	5.870853	1	1020.651	0	1
0.117	0.883	3.975099	1.024525	1841.142	0.483806	0.516194
0.257	0.743	2.656812	1.124015	2152.548	0.607527	0.392473
0.376	0.624	1.992112	1.284328	2226.772	0.644245	0.355755
0.549	0.451	1.433358	1.704855	2261.908	0.666311	0.333689
0.707	0.293	1.164105	2.422337	2270.251	0.694325	0.305675
0.856	0.144	1.037385	3.658096	2202.725	0.772108	0.227892
1	0	1	5.870853	1915.248	1	0



System Components		Parameters to adjust				Antoine Coefficents			Calculated	Expt	Selected
						A	B	C	P^{sat}(mm Hg)	P^{sat}(mm Hg)	P^{sat}(mm Hg)
		A_{12}	A_{21}	T(C)	1	8.08097	1582.271	239.726	1915.2478		1915.2478
		1.853575	1.641753	90	2	6.87987	1196.76	219.161	1020.6509		1020.6509

				<---optional----->							Enter 1 to use Calculated P^{sat}
	y_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	P_{expt}	P_{calc}	$(P_{error})^2$	Enter 0 to use Expt P^{sat}
	1	6.382596	1	0	1	0	1		1020.651		1
	0.883	4.081913	1.027979	0.502	0.498	0.496807	0.503193	1865	1841.142	569.22164	
	0.743	2.61996	1.137948	0.594	0.406	0.599101	0.400899	2113	2152.548	1564.0809	
	0.624	1.934239	1.309281	0.618	0.382	0.625529	0.374471	2218	2226.772	76.949933	
	0.451	1.390567	1.73744	0.65	0.35	0.646419	0.353581	2273	2261.908	123.02159	Objective Function
	0.293	1.142723	2.417354	0.689	0.311	0.681572	0.318428	2292	2270.251	473.03332	2834.133876
	0.144	1.031399	3.482226	0.765	0.235	0.767653	0.232347	2208	2202.725	27.826486	
	0	1	5.164214	1	0	1	0		1915.248		Named cell ranges. See

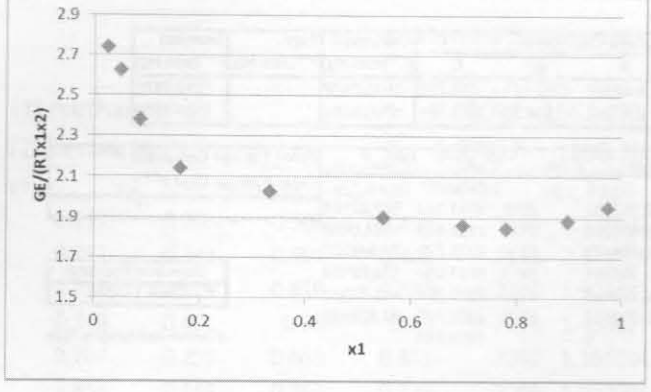


(11.26) Fit the specified model to the methanol(1) + benzene(2) system T-x-y…

(a)

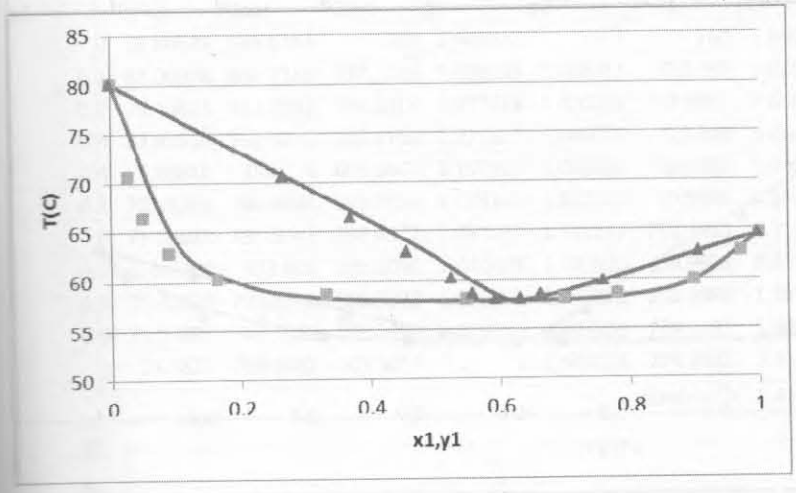
		A	B	C
(1) methanol	1	8.08097	1582.271	239.726
(2) benzene	2	6.87987	1196.76	219.161

x1	y1	T (°C)	P1sat	P2sat	g1	g2	GE/RT	GE/(RTx1x2)
0	0	80.1	1360.451	760.009471		0.999988		
0.026	0.267	70.67	962.4579	563.2550223	8.109046	1.015438	0.069339492	2.738094
0.05	0.371	66.4	817.1053	488.6091298	6.901436	1.029862	0.124540094	2.621897
0.088	0.457	62.87	711.1832	433.0187298	5.54965	1.044989	0.190942854	2.379172
0.164	0.526	60.2	638.8987	394.4124604	3.815254	1.092534	0.293583125	2.141317
0.333	0.559	58.64	599.5826	373.1591944	2.127807	1.34658	0.449923491	2.02567
0.549	0.595	58.02	584.5293	364.9707353	1.409133	1.869967	0.470583405	1.900587
0.699	0.633	58.1	586.4537	366.0191704	1.173563	2.531683	0.391465248	1.860585
0.782	0.665	58.47	595.4232	370.8995204	1.085432	3.148804	0.314158057	1.842829
0.898	0.76	59.9	631.1752	390.2521181	1.019063	4.582256	0.172220792	1.880222
0.973	0.907	62.71	706.6676	430.6237692	1.00252	6.079037	0.051179302	1.948129
1	1	64.55	760.0678	458.8110165	0.999911			



To fit the azeotrope, the value of about 1.9 should be used since the azeotrope is near 60 mol%. Higher values will underestimate the azeotrope.

using Antoine equation to generate T-x-y					Margules A =		1.9	
x1	T (°C)	P1sat	P2sat	g1	g2	Ptot	(err^2)	y1
0	80.09951	1360.428	759.9981	6.685894442	1	759.9981	3.507E-06	0
0.1	64.01533	744.2153	450.4735	4.659928012	1.019182	760.0019	3.62612E-06	0.456313
0.2	59.80644	628.7824	388.9618	3.373666044	1.078963	760.0005	2.78111E-07	0.558237
0.3	58.42829	594.4062	370.3467	2.537044954	1.186491	759.9997	9.37497E-08	0.595277
0.4	58.01508	584.411	364.9063	1.981789055	1.355269	759.9994	3.07923E-07	0.609569
0.5	57.90565	581.7877	363.4763	1.608014197	1.608014	759.999	1.07067E-06	0.615476
0.6	57.86462	580.8067	362.9413	1.355269056	1.981789	759.9988	1.44784E-06	0.621435
0.7	57.91076	581.9101	363.543	1.186490749	2.537045	759.9991	7.41756E-07	0.635924
0.8	58.32935	592	369.0382	1.078962574	3.373666	759.999	9.88102E-07	0.672365
0.9	59.87297	630.4832	389.8791	1.019181649	4.659928	760.0001	6.25267E-09	0.760946
1	64.54768	759.9986	458.7747	1	6.685894	759.9986	2.03722E-06	1
						sum(err^2):	1.41047E-05	



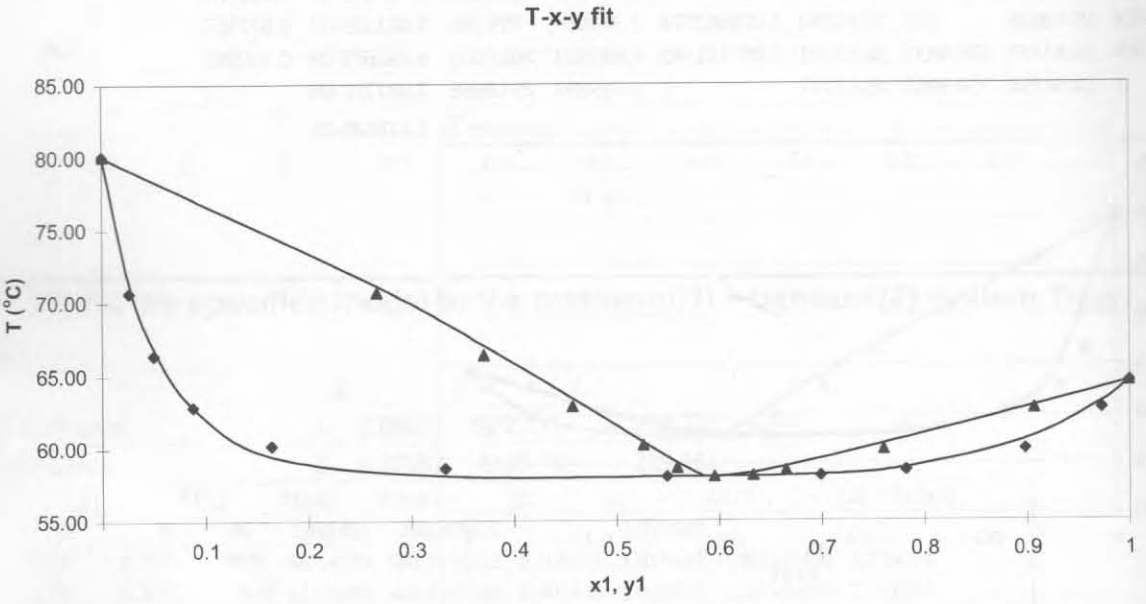
(b) T-x-y fit P:

System Components	Parameters to adjust				Antoine Coefficents			Calculated
					A	B	C	T^{sat}(C)
(1) methanol	A_{12}	A_{21}	P(mm Hg)	1	8.08097	1582.271	239.726	64.55
(2) benzene	2.182683	1.677053	760	2	6.87987	1196.76	219.161	80.10
		<---optional----->						

x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	P_1^{sat}	P_2^{sat}	P_{calc}	$(P_{error})^2$
0	1	8.870077	1	0	1	0	1	80.1	1,360.45	760.01	760.01	0.00
0.026	0.974	7.734695	1.001801	0.267	0.733	0.260448	0.739552	70.67	962.46	563.26	743.15	283.90
0.05	0.95	6.849931	1.006616	0.371	0.629	0.374587	0.625413	66.4	817.11	488.61	747.11	166.27
0.088	0.912	5.705417	1.020333	0.457	0.543	0.46982	0.53018	62.87	711.18	433.02	760.01	0.00
0.164	0.836	4.094149	1.070199	0.526	0.474	0.548671	0.451329	60.2	638.90	394.41	781.86	477.76
0.333	0.667	2.273307	1.297919	0.559	0.441	0.584204	0.415796	58.64	599.58	373.16	776.94	286.94
0.549	0.451	1.392409	1.902042	0.595	0.405	0.588006	0.411994	58.02	584.53	364.97	759.91	0.01
0.699	0.301	1.143061	2.633029	0.633	0.367	0.617635	0.382365	58.1	586.45	366.02	758.66	1.79
0.782	0.218	1.068384	3.191118	0.665	0.335	0.658469	0.341531	58.47	595.42	370.90	755.48	20.40
0.898	0.102	1.013349	4.202004	0.76	0.24	0.774463	0.225537	59.9	631.18	390.25	741.63	337.63
0.973	0.027	1.000874	5.020673	0.907	0.093	0.921809	0.078191	62.71	706.67	430.62	746.56	180.55
1	0	1	5.349765	1	0	1	0	64.55	760.07	458.81	760.07	0.00

Resulting T-x-y calc T:

System Components			Parameters to use				Antoine Coefficents			Calculated					
							A	B	C	T^{sat}(C)					
(1) methan			A_{12}	A_{21}	P(mm Hg)	1.00	8.08097	1582.271	239.726	64.55					
(2) benzen			2.182683	1.677053	760	2.00	6.87987	1196.76	219.161	80.10					
			<---optional----->												
x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	T_{calc}	1/T	P_1^{sat}	P_2^{sat}	P_{calc}	$\log(P_{calc})$	[log(P_calc
	1	8.870077	1		1	0	1	80.10	80.1	0.0028309	1,360.45	760.01	760.01	2.880819	
0.026	0.974	7.734695	1.001801	0.267	0.733	0.261084	0.738916	70.67	71.32886	0.0029029	986.69	575.53	760.00	2.880816	4.39E-12
0.05	0.95	6.849931	1.006616	0.371	0.629	0.375158	0.624842	66.40	66.87997	0.0029409	832.47	496.59	760.00	2.880811	5.79E-12
0.088	0.912	5.705417	1.020333	0.457	0.543	0.469826	0.530174	62.87	62.87494	0.002976	711.32	433.09	760.15	2.8809	7.4E-09
0.164	0.836	4.094149	1.070199	0.526	0.474	0.547716	0.452284	60.20	59.45865	0.0030065	619.95	384.20	760.00	2.880812	3.75E-12
0.333	0.667	2.273307	1.297919	0.559	0.441	0.583482	0.416518	58.64	58.07172	0.0030191	585.77	365.65	759.98	2.880804	9.76E-11
0.549	0.451	1.392409	1.902042	0.595	0.405	0.588009	0.411991	58.02	58.02272	0.0030196	584.59	365.01	759.99	2.88081	1.45E-11
0.699	0.301	1.143061	2.633029	0.633	0.367	0.617693	0.382307	58.10	58.14682	0.0030184	587.58	366.63	760.05	2.880843	8.48E-10
0.782	0.218	1.068384	3.191118	0.665	0.335	0.658653	0.341347	58.47	58.62738	0.0030141	599.27	372.99	760.15	2.880902	7.84E-09
0.898	0.102	1.013349	4.202004	0.76	0.24	0.775027	0.224973	59.90	60.52222	0.002997	647.28	398.92	760.00	2.880812	1.78E-12
0.973	0.027	1.000874	5.020673	0.907	0.093	0.921977	0.078023	62.71	63.16322	0.0029734	719.52	437.44	760.00	2.880816	5.14E-12
1	0	1	5.349765	1		1	0	64.55	64.55	0.0029612	760.07	458.81	760.07	2.880852	

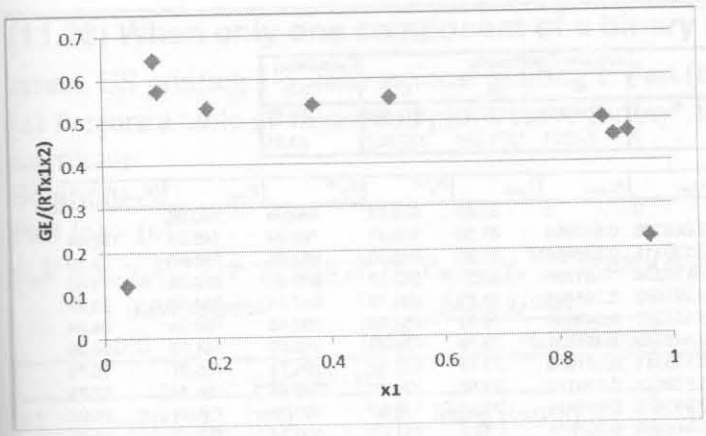


(11.27) VLE data for the system carbon tetrachloride and 1,2 dichloroethane(2)...

(a)

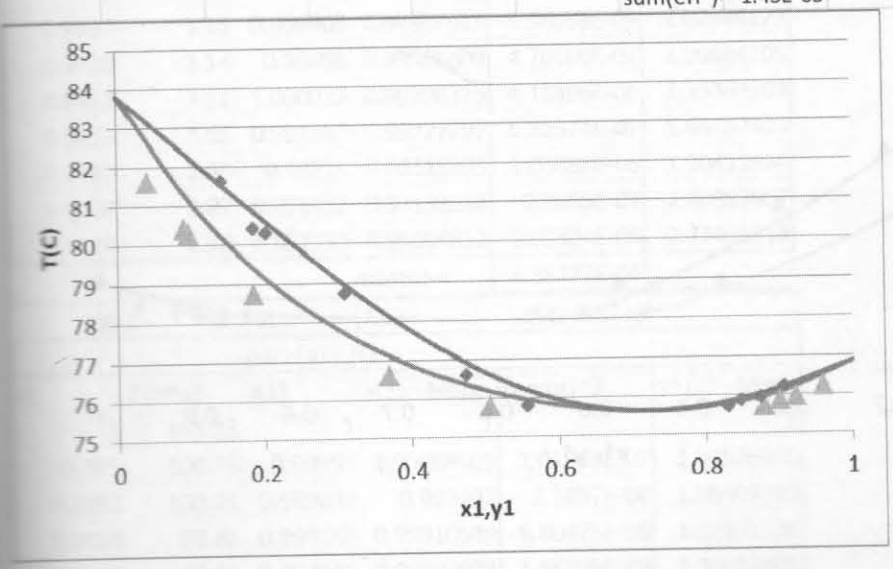
	A	B	C
(1) carbon tetrachloride	6.84093	1177.91	220.576
(2) 1,2-dichloroethane	7.0253	1271.254	222.927

x1	x2	y1,expt	y2,expt	T_{expt}	P1sat	P2sat	g1	g2	GE/RT	GE/(RTx1x2)
0.04	0.96	0.141	0.859	81.59	876.4124	708.9949	3.05678	0.959163	0.004668	0.121563905
0.091	0.909	0.185	0.815	80.39	845.6013	682.5384	1.827167	0.998344	0.053345	0.644897784
0.097	0.903	0.202	0.798	80.27	842.5672	679.9364	1.878403	0.987781	0.050049	0.571391413
0.185	0.815	0.31	0.69	78.73	804.3763	647.2369	1.583231	0.994127	0.080201	0.531923306
0.37	0.63	0.473	0.527	76.62	754.2558	604.475	1.288114	1.051733	0.125453	0.538193068
0.506	0.494	0.557	0.443	75.78	734.9954	588.0902	1.138239	1.158901	0.13837	0.553558163
0.88	0.12	0.831	0.169	75.71	733.4079	586.7409	0.978557	1.824201	0.053062	0.502484831
0.9	0.1	0.848	0.152	75.86	736.813	589.6352	0.971873	1.959177	0.041576	0.461951173
0.923	0.077	0.875	0.125	75.95	738.862	591.3773	0.975117	2.086259	0.033366	0.469472318
0.96	0.04	0.907	0.093	76.2	744.577	596.2378	0.964362	2.963583	0.008619	0.224449973



A value of approximate A = 0.5 should be reasonable.

using Antoine equation to generate T-x-y					Margules A =		0.5	
x1	T (°C)	P1sat	P2sat	g1	g2	Ptot	(err^2)	y1
0	83.80678	935.6184	760	1.648721	1	760	1.56E-09	0
0.1	81.06078	862.7185	697.2289	1.499303	1.005013	759.999	1.02E-06	0.170194
0.2	79.15824	814.8581	656.2018	1.377128	1.020201	759.9991	7.63E-07	0.295307
0.3	77.81538	782.3416	628.4156	1.277621	1.046028	759.999	9.82E-07	0.394554
0.4	76.86616	759.974	609.3447	1.197217	1.083287	759.9988	1.44E-06	0.478871
0.5	76.21363	744.8894	596.5036	1.133148	1.133148	759.9988	1.55E-06	0.55531
0.6	75.80681	735.6042	588.6077	1.083287	1.197217	759.9989	1.31E-06	0.629109
0.7	75.6304	731.606	585.2096	1.046028	1.277621	759.9991	8.41E-07	0.704864
0.8	75.70228	733.2331	586.5923	1.020201	1.377128	759.9988	1.35E-06	0.787417
0.9	76.07839	741.7926	593.8694	1.005013	1.499303	759.9987	1.64E-06	0.882843
1	76.8672	759.9982	609.3653	1	1.648721	759.9982	3.41E-06	1
						sum(err^2):	1.43E-05	



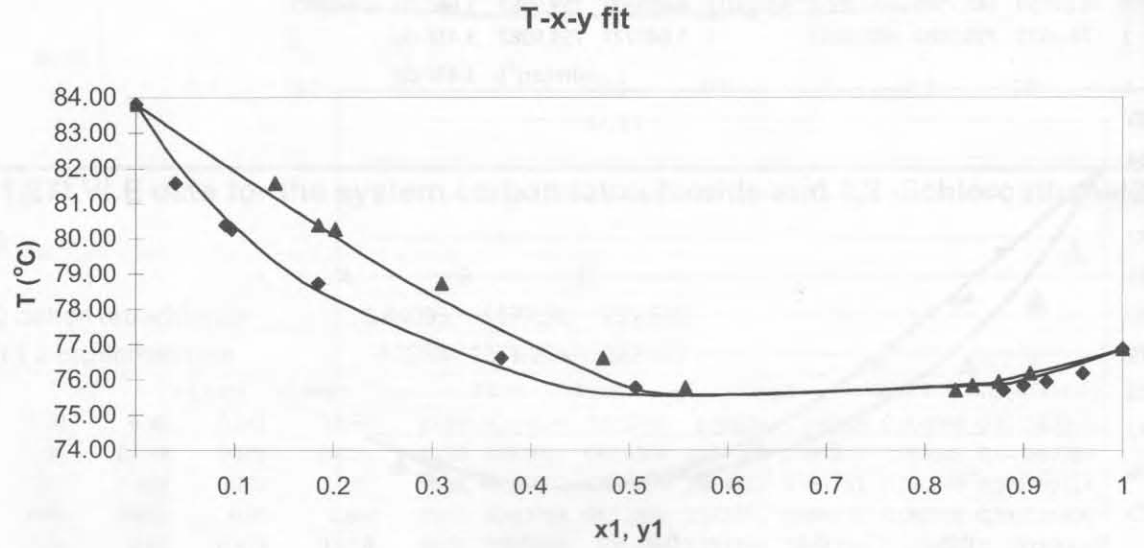
(b)

System Components	Parameters to adjust				Antoine Coefficents			Calculated
					A	B	C	T^{sat}(C)
(1) carbon tetrachloride	A_{12}	A_{21}	P(mm Hg)	1	6.84093	1177.91	220.576	76.87
(2) 1,2 - dichloromethane	0.673397	0.499725	760	2	7.0253	1271.254	222.927	83.81

				<---optional----->								
x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	P_1^{sat}	P_2^{sat}	P_{calc}	$(P_{error})^2$
0	1	1.960887	1	0	1	0	1	83.81	935.71	760.08	760.08	
0.04	0.96	1.836383	1.001334	0.141	0.859	0.086306	0.913694	81.59	876.41	708.99	745.92	198.24
0.091	0.909	1.699438	1.006776	0.185	0.815	0.173115	0.826885	80.39	845.60	682.54	755.40	21.14
0.097	0.903	1.684756	1.007682	0.202	0.798	0.18204	0.81796	80.27	842.57	679.94	756.39	13.01
0.185	0.815	1.49871	1.027154	0.31	0.69	0.291592	0.708408	78.73	804.38	647.24	764.84	23.47
0.37	0.63	1.241429	1.103371	0.473	0.527	0.451911	0.548089	76.62	754.26	604.48	766.64	44.04
0.506	0.494	1.129124	1.187536	0.557	0.443	0.548979	0.451021	75.78	735.00	588.09	764.93	24.29
0.88	0.12	1.005309	1.520843	0.831	0.169	0.858341	0.141659	75.71	733.41	586.74	755.91	16.76
0.9	0.1	1.003614	1.541741	0.848	0.152	0.879822	0.120178	75.86	736.81	589.64	756.44	12.71
0.923	0.077	1.002094	1.565986	0.875	0.125	0.905515	0.094485	75.95	738.86	591.38	754.71	28.02
0.96	0.04	1.000544	1.605365	0.907	0.093	0.949186	0.050814	76.2	744.58	596.24	753.47	42.64
1	0	1	1.648268	1	0	1	0	76.87	760.06	609.42	760.06	

Resulting T-x-y fit T

System Components			Parameters to use				Antoine Coefficents			Calculated					
							A	B	C	T^{sat}(C)					
(1) carbon			A_{12}	A_{21}	P(mm Hg)	1.00	6.84093	1177.91	220.576	76.87					
(2) 1,2 - di			0.673397	0.499725	760	2.00	7.0253	1271.254	222.927	83.81					
				<---optional----->											
x_1	x_2	$\gamma_{1,calc}$	$\gamma_{2,calc}$	$y_{1,expt}$	$y_{2,expt}$	$y_{1,calc}$	$y_{2,calc}$	T_{expt}	T_{calc}	1/T	P_1^{sat}	P_2^{sat}	P_{calc}	$\log(P_{calc})$	$[\log(P_{calc}/P$
	1	1.960887	1		1	0	1	83.81	83.81	0.0028014	935.71	760.08	760.08	2.880857	
0.04	0.96	1.836383	1.001334	0.141	0.859	0.086219	0.913781	81.59	82.183	0.0028143	891.96	722.37	759.91	2.880765	2.38E-09
0.091	0.909	1.699438	1.006776	0.185	0.815	0.173063	0.826937	80.39	80.58202	0.002827	850.47	686.72	759.98	2.880803	1.12E-10
0.097	0.903	1.684756	1.007682	0.202	0.798	0.181998	0.818002	80.27	80.42047	0.0028283	846.37	683.20	759.98	2.880805	7.5E-11
0.185	0.815	1.49871	1.027154	0.31	0.69	0.29167	0.70833	78.73	78.52965	0.0028435	799.51	643.08	760.01	2.88082	4.28E-11
0.37	0.63	1.241429	1.103371	0.473	0.527	0.45204	0.54796	76.62	76.34852	0.0028612	747.99	599.14	760.05	2.880842	7.81E-10
0.506	0.494	1.129124	1.187536	0.557	0.443	0.549075	0.450925	75.78	75.57951	0.0028676	730.46	584.23	760.07	2.880855	1.68E-09
0.88	0.12	1.005309	1.520843	0.831	0.169	0.8583	0.1417	75.71	75.8865	0.002865	737.42	590.15	760.07	2.880856	1.79E-09
0.9	0.1	1.003614	1.541741	0.848	0.152	0.879791	0.120209	75.86	76.01423	0.002864	740.33	592.62	760.07	2.880853	1.59E-09
0.923	0.077	1.002094	1.565986	0.875	0.125	0.905477	0.094523	75.95	76.17824	0.0028626	744.08	595.81	760.07	2.880851	1.42E-09
0.96	0.04	1.000544	1.605365	0.907	0.093	0.949159	0.050841	76.20	76.48256	0.0028601	751.08	601.77	760.07	2.880853	1.57E-09
1	0	1	1.648268	1		1	0	76.87	76.87	0.002857	760.06	609.42	760.06	2.88085	



(11.28) When only one component of a binary mixture is volatile…

errata, US printing 1-3, International printing 1. Part (c) is more clear with a separate plot.

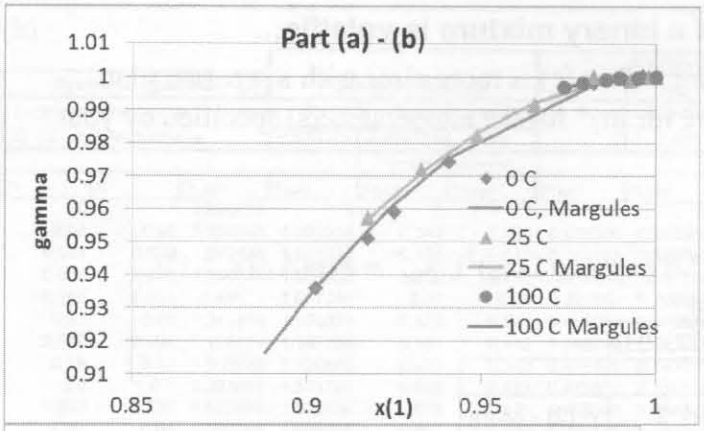
(c) Prepare a table of values and plot a curve for lnγ^* for the temperature(s) specified by your instructor.

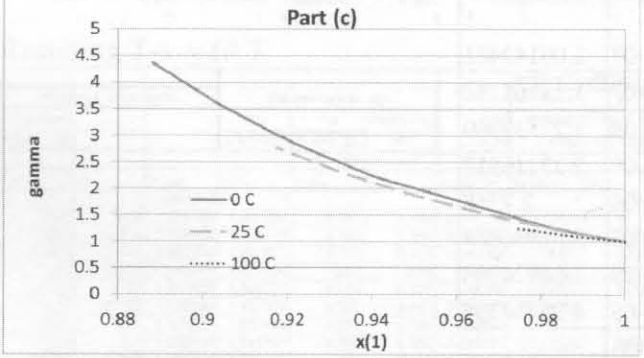
Solution:

Part (a) – (c)

$y_wP = x_w\gamma_wP_w^{sat} \rightarrow \gamma_w = y_wP/x_wP_w^{sat}$, $\gamma_w^{Marg} = \exp(A_{12}(1-x_w)^2)$, $\gamma_{suc}^* = \exp(A_{12}(x_w^2-1))$

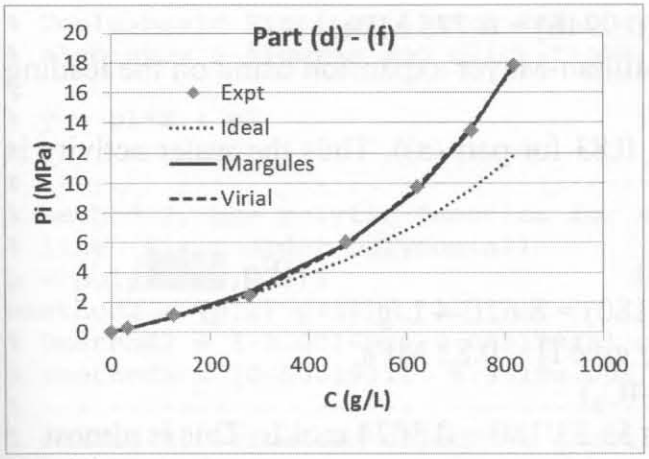
	MW sucrose		342.3 g/mol		
0	C		A12 =	-6.97731033	
		part (a) - (c)			
x1	P(kPa)	γ(1)	γ(1) - Marg	(error)^2	γ*(2) - Marg
1	0.611	1	1		1
0.9964	0.609	1.000328	0.99990958	1.74958E-07	1.05142481
0.9911	0.605	0.999072	0.99944748	1.41157E-07	1.13161232
0.9823	0.599	0.998025	0.99781647	4.35324E-08	1.27737969
0.9407	0.56	0.974307	0.97576291	2.12065E-06	2.23216812
0.9251	0.542	0.958891	0.9616134	7.40962E-06	2.7348
0.9174	0.533	0.950883	0.95351081	6.90333E-06	3.01936684
0.9025	0.516	0.935753	0.93582381	4.99813E-09	3.64824948
0.8881	0.499	0.919597	0.91634059	1.06031E-05	4.36734334
			sumsq =	2.74013E-05	
25	C		A12 =	-6.44223925	
		part (a) - (c)			
x1	P(kPa)	γ(1)	γ(1) - Marg	(error)^2	γ*(2) - Marg
1	3.166	1	1		1
0.9982	3.16	0.999905	0.99997913	5.54053E-09	1.02344173
0.9928	3.14	0.99898	0.99966609	4.70166E-07	1.09684105
0.9823	3.11	1.000012	0.99798375	4.11496E-06	1.25362202
0.9653	3.03	0.991447	0.99227297	6.82574E-07	1.55167403
0.9487	2.95	0.98216	0.98318893	1.05888E-06	1.90411964
0.9328	2.87	0.971812	0.97132698	2.3566E-07	2.30883907
0.9174	2.78	0.957139	0.95699812	1.99324E-08	2.77403814
			sumsq =	6.58772E-06	
100	C		A12 =	-4.43818333	
		part (a) - (c)			
x1	P(kPa)	γ(1)	γ(1) - Marg	(error)^2	γ*(2) - Marg
1	101.33	1	1		1
0.995	100.78	0.99957	0.99988905	1.01768E-07	1.04526546
0.9893	100.21	0.999643	0.999492	2.2857E-08	1.09907509
0.9858	99.81	0.999188	0.99910549	6.80473E-09	1.13331786
0.9789	99.01	0.998166	0.99802603	1.95388E-08	1.20359801
0.9737	98.35	0.996807	0.99693486	1.63057E-08	1.2590766
			sumsq =	1.67275E-07	





part (d)-(f) at 25 C

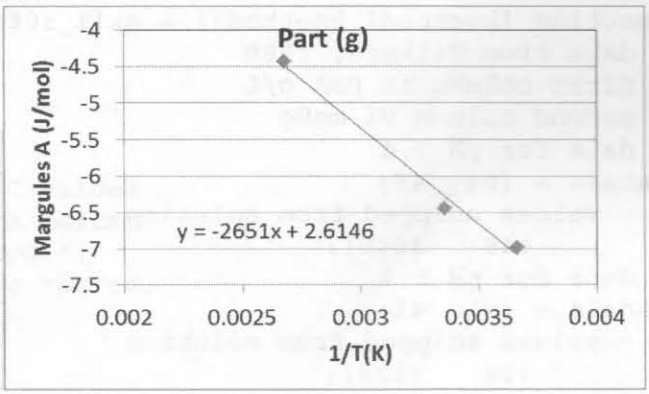
					virial coeff	c2(L/g) c3(L/g)^2	0.07456 2.85617	E-3 E-6
		part (d)				part (e)	part (f)	
x1	wt frac (2)	density (g/mL)	C(2)(g/L)	Pi(MPa) data	Pi(MPa) ideal	Pi(MPa) Marg	Pi(MPa) Osmotic	error
1	0	0.99721	0	0	0	0	0	0
0.9982	0.033119	1.009729	33.4414413	0.260212923	0.24713846	0.250002	0.243549	0.000278
0.9928	0.12108	1.044751	126.49845	1.131171645	0.99123662	1.037049	0.966566	0.027095
0.9823	0.254999	1.103016	281.267746	2.448066924	2.44975186	2.726612	2.539797	0.008414
0.9653	0.405767	1.175752	477.080904	6.022876077	4.84453864	5.908614	5.82369	0.039675
0.9487	0.5067	1.228673	622.569273	9.693343562	7.2240277	9.549699	9.708681	0.000235
0.9328	0.577785	1.267979	732.619155	13.46472991	9.54254269	13.53327	13.72829	0.069465
0.9174	0.631038	1.298526	819.418635	17.83529373	11.8261359	17.85553	17.67642	0.025241
							sumsq=	0.170404



Part (g)

$$\left(\frac{\partial G^E/T}{\partial(1/T)}\right) = Rx_1x_2\left(\frac{\partial A_{12}}{\partial(1/T)}\right) = H^E$$

$H^E = -8.314(2651)x_1x_2$ J/mol based on fit below.



part (g)

Values from above

T(C)	T(K)	1/T(K)	A
0	273.15	0.003661	-6.9773103
25	298.15	0.003354	-6.4422392
100	373.15	0.00268	-4.4381833

Note the 'x' on the plot fit equation is '(1/T)'.

(11.29) Red blood cells have…

For hemoglobin (Mw = 68000) at 0.3M and 37°C, Π = 0.83MPa.
(a) Determine B2 (L/g) and aW. (b)Calculate Π^{is}. (c) Glucose(Mw=180) has Π=2MPa at 0.7M and 37°C. Compute Cg such that Π(glucose) = 0.83 and compare B2(glucose) to B2(hg).

Solution: 0.83 = 0.008314*310*(0.3)*(1+B2*0.3*68000) (Eq. 11.73)
=> B2 = (-1+0.83/(0.008314*310*0.3))/(0.3*68000) = 3.6E-6 L/g
Vw=0.018L/mol=>aW = exp(-0.018*0.83/(0.008314*310)) = 0.9942 (Eq.11.71)

(b) $\Pi^{is} = RT/V_w \ln a_w$. Determine the ideal activity of water for a 0.3M solution. Let us assume that the molar density of the solution does not change with the small addition of hemoglobin. Water molar density is (1000 g/L)/(18.02 g/mol) = 55.5 mol/L. Thus is the molar density of the solution is the same, then the mole fraction of water is $x_w = 1 - 0.3/55.5 = 0.9946$.

Π = -8.314 * 310 / (1/0.0555 mol/cm^3) ln(0.9946) = 0.775 MPa
Note this can also be calculate by the McMillian-Mayer expansion using on the leading term, combining eq (11.71) and eq (11.72),
Π = 0.008314*310*0.3 = 0.773 MPa. (vs. 0.83 for part (a)). Thus the water activity is higher than the ideal activity.
(c) Glucose has MW = 180 g/mol.
2 = 0.008314*310*(0.7) * (1+B2*0.7*180) (Eq. 11.73)
=> B2 = (-1+2/(0.008314*310*0.7))/(0.7*180) = 8.62E-4 L/g
Now calculate the glucose concentration to give Π = 0.83 MPa.
180*0.83/(0.008314*310) = C_g*(1+8.62E-4C_g)
Trial and Error. Cg = 55.33 g/L => [Cg] = 55.33/180 = 0.3074 mol/L, This is almost the same as the molar concentration of hemoglobin, thus glucose and hemoglobin have similar effects on activity of water at the same molar concentration. The molar glucose concentration is slightly higher to give the same osmotic pressure, so it is slightly more ideal. (The molarity and the molality are assumed to be the same for the comparison.)

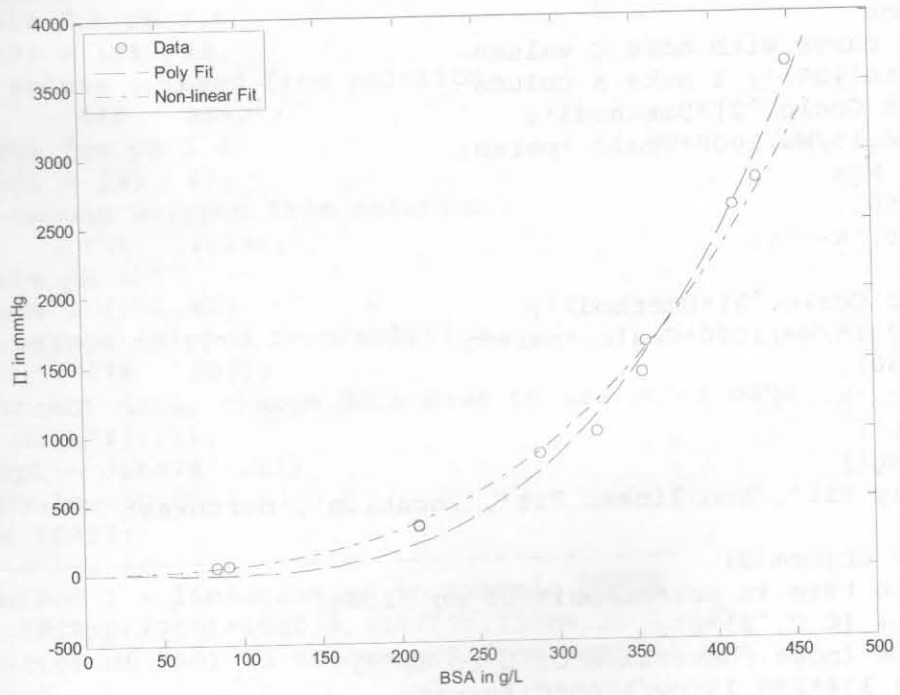
(11.30) Osmotic pressure of bovine serum albumin (BSA) has been measured...

```
function [Bmethod2 Bmethod3] = ex11_30fitOsmoticCoeff
% data from Vilkers, 1980
% first column is BSA g/L
% second column Pi mmHg
% data for pH 7.4
data74 = [84   48;
----values snipped from solution
        448    3640];
% data for pH 5.4
data54 = [91   41;
----values snipped from solution
        454    1529];
% data pH 4.5
data45 = [126 47;
----values snipped from solution
        475    889];
% extract data, change data name to use other data
C = data74(:,1);
PiExpt = data74(:,2);
ndata=length(C);
Mw = 66399;
% ---------------------------------------
% method 1 - linearize as in example 11.11
y = (PiExpt/7501*1000/8.314/298.15*Mw./C-1)./C;
% factor of 7501 is to convert from mmHg to MPa.
% Plot
plot(C,y,'o')
disp('See m-file at pause stmt to see how to fit interactively using
graph tools.')
disp('Press any key to resume from pause')
pause();
```

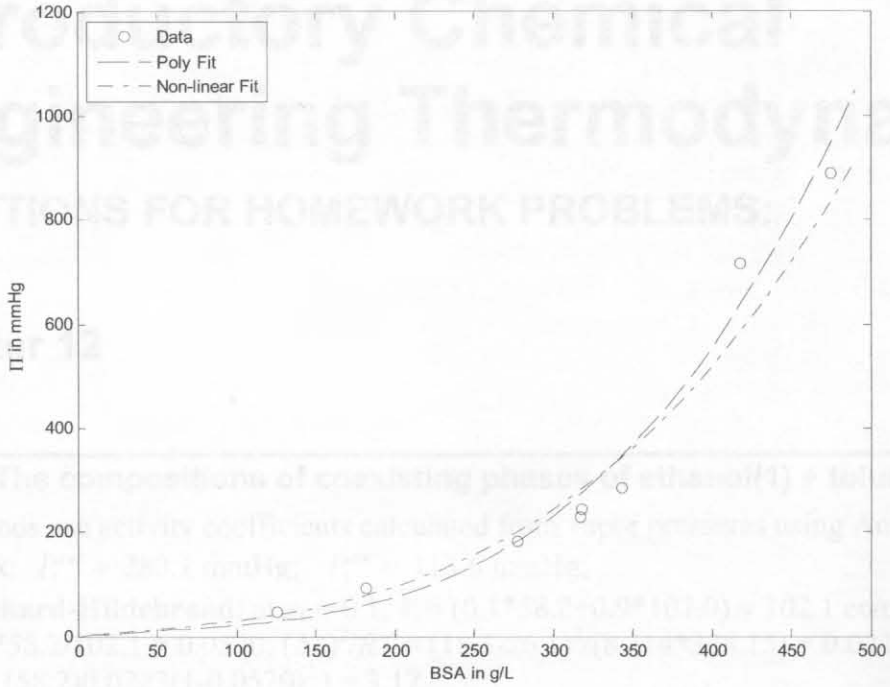
```
% Tools>Basic Fitting>(linear and show equations)
% also show 5 figures and click right arrow to show results:
%
% y = p1*x + p2
%
% ----------------------------------------
% method 2, use polyfit function for a
% line (first order polynomial)
p = polyfit(C,y,1);
Bmethod2 = [p(2) p(1)]
% Bmethod2 = [-0.0016969 0.00012249] pH 7.4
% Bmethod2 = [0.00019311  5.3519e-005] pH 5.4
% ----------------------------------------
% method 3, write own objective function
Bmethod3 = [0 0];
Bmethod3 = lsqnonlin(@objOsm,Bmethod3);
[Bmethod3,resnorm,residual,exitflag,output,lambda,jacobian] =
lsqnonlin(@objOsm,Bmethod3);
Bmethod3
Bmethod3ci = nlparci(Bmethod3,residual,jacobian);
uncertainty = [(Bmethod3ci(1,2)- Bmethod3ci(1,1))/2 (Bmethod3ci(2,2)-
Bmethod3ci(2,1))/2]
% plot results ------------
% plot data
plot(C, PiExpt,'ko')
hold on
% plot calculations
% create a smooth curve with more C values
Ccalc=(0:10:C(ndata)+20)'; % make a column
paren = 1 + [Ccalc Ccalc.^2]*Bmethod3';
PiCalc = 8.314*298.15/Mw/1000*Ccalc.*paren;
% convert back to MPa
PiCalc = PiCalc*7501;
plot(Ccalc, PiCalc,'k--');
% now linear fit
paren = 1 + [Ccalc Ccalc.^2]*Bmethod2';
PiCalc = 8.314*298.15/Mw/1000*Ccalc.*paren;
PiCalc = PiCalc*7501;
plot(Ccalc, PiCalc,'k-.');
xlabel('BSA in g/L')
ylabel('\Pi in mmHg')
legend('Data','Poly Fit','Non-linear Fit','location','northwest')
hold off
    function obj = objOsm(B)
        % calculate term in parenthesis of eq 11.64
        paren = 1 + [C C.^2]*B';
        % Pi in MPa (note conversion of L to cm^3)
        PiCalc = 8.314*298.15/Mw/1000*C.*paren;
        % convert to mmHg; (10 bar/MPa)(750.1 mmHg/bar)
        PiCalc = PiCalc*7501;
        % use percent as error
        obj = (PiCalc - PiExpt);
        obj = obj.^2;
```

```
        % commment for lsqnonlin
%        obj = sum(obj);
    end %objOsm
end
See m-file at pause stmt to see how to fit interactively using graph
tools.
Press any key to resume from pause
Bmethod2 =       -0.00169693369090047       0.000122487772639615
Local minimum possible.
lsqnonlin stopped because the size of the current step is less than
the default value of the step size tolerance.

Local minimum possible.
lsqnonlin stopped because the size of the current step is less than
the default value of the step size tolerance.
Bmethod3 =        -0.0310458686936842       0.000202307275421787
uncertainty =      0.00909675771614017      2.21387418290774e-005
Bmethod2 =       -0.00169693369090047       0.000122487772639615
Bmethod3 =        -0.0310458686936842       0.000202307275421787
```

(a) Result for pH 7.4
poly fit, B2 = -0.001697, B3 = 0.0001225
non-lin fit, B2 = -0.0310+/-0.0091, B3 = 0.000202+/-2.2E-5
The uncertainty in B2 is larger than the value.



(b) Result for pH 4.5
poly fit, B2 = -0.001853, B3 = 2.732E-5
non-lin fit, B2 = -0.00630+/-0.00581, B3 = 4.04E-5+/-1.36E-5
The uncertainty in B2 is about the size of B2.



(11.31) Osmotic pressure of boric acid

a. Isotonic => 0.308 mol/L *61.83 g/mol /(0.308*61.83+55.2*18) = 1.88w%

b. MW =22*12+23+35.4+28+32 = 382.4 => 0.00025g/100g => 0.000025g/1000g

0.000025g/382.4 g/mol = 6.5E-8 mol/L => the Claritin is negligible. Make 1.88%