Problem Set K

Problem 36

a)

$$\underset{\text{(A)}}{\boxed{\begin{array}{c}1 \text{ mol HCl}\\ 3 \text{ mol } H_2O\end{array}}} \xrightarrow{\Delta H^{process}} \underset{\text{(B)}}{\boxed{\begin{array}{c}2 \text{ mol HCl}\\ 3 \text{ mol } H_2O\end{array}}}$$

Condition A:

$\tilde{n}_A = 3$

$\Delta\tilde{H}_A = -56$ kJ / mol solute

$\Delta H_A^{total} = -56 \times 1$

$= -56$ kJ

Condition B:

$\tilde{n}_B = \frac{3}{2}$

$\Delta\tilde{H}_B = -41$ kJ/ mol solute

$\Delta H_B^{total} = -41 \times 2$

$= -82$ kJ

$\Delta H^{process} = (-82) - (-56)$

$$\boxed{\Delta H^{process} = -26 \text{ kJ}}$$

b)

(A) 400 lb_m 30 wt% H_2SO_4

(B) 175 lb_m H_2SO_4

$\longrightarrow$ 120 °F Final mixture (C)

(A): $0.3 \times 400 = 120$ lb_m H_2SO_4

$0.7 \times 400 = 280$ lb_m H_2O

ie 30 wt% H_2SO_4

$\therefore$ $H_A = -24$ Btu/lb_m solution

$H_A^{total} = -24 \times 400 = -9600$ Btu

(B): $H_{H_2SO_4} = 8$ Btu / lb_m

$\therefore$ $H_B^{total} = 8 \times 175 = 1400$ Btu

(c) : $120 + 175 = 295 \ lb_m \ H_2SO_4$

$280 \ lb_m \ H_2O$

$\therefore$ we have $\left(\frac{295}{295+280}\right) \times 100 = 51.3$ wt% H_2SO_4

$H_B = -82$ Btu/lb$_m$ solution

$\therefore H_B^{total} = -82 \times (295+280) = -47150$ Btu

$\therefore \Delta H^{process} = -47150 - (-9600 + 1400)$

$$\boxed{\Delta H^{process} = -38950 \text{ Btu}}$$

c) $H^E = H - H^{id}$

from chart, 60 wt% H_2SO_4 at 100°F

$H = -110$ Btu/lb$_m$ solution

also from chart $H_{H_2SO_4} = 8$ Btu/lb$_m$ (at 100 wt% H_2SO_4)

$H_{H_2O} = 68$ Btu/lb$_m$ (at 0 wt% H_2SO_4)

$$\therefore H^{id} = \sum_i x_i H_i = x_{H_2SO_4} H_{H_2SO_4} + x_{H_2O} H_{H_2O}$$

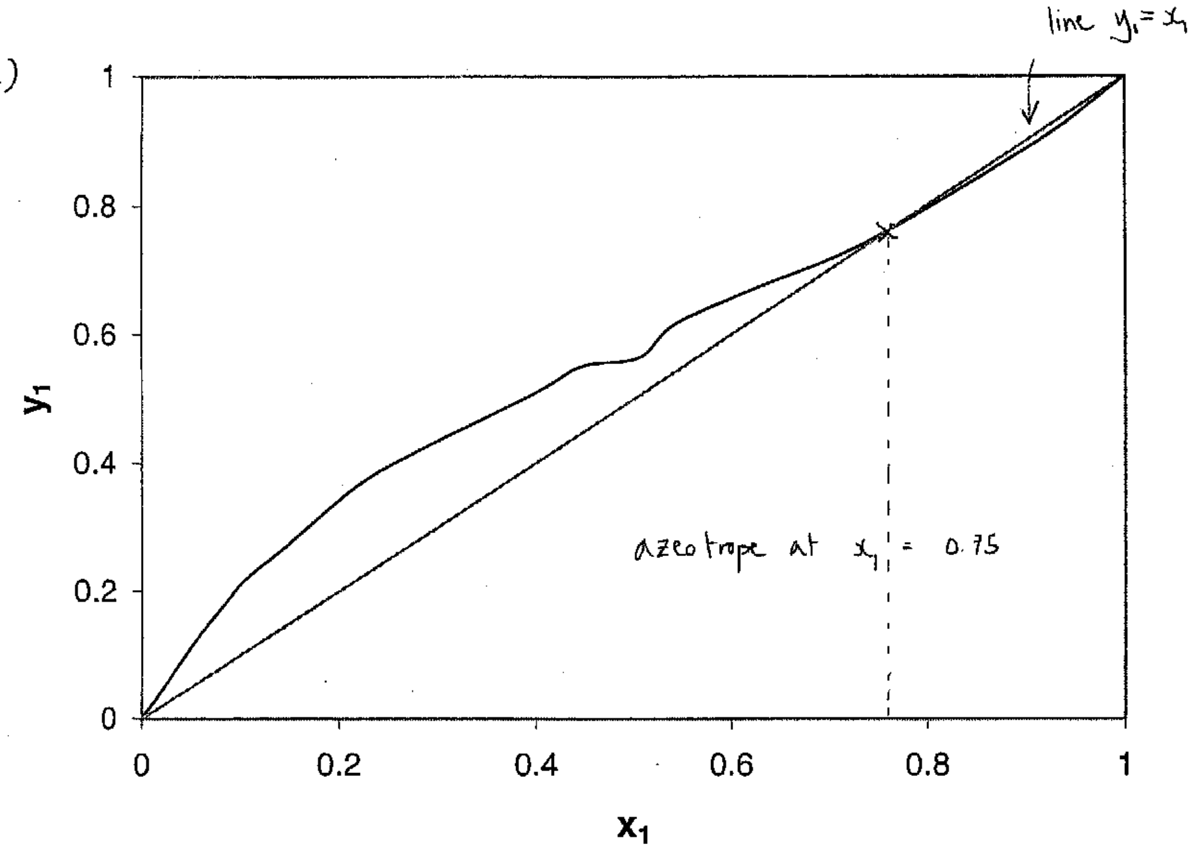
$$= (0.6 \times 8) + (0.4 \times 68)$$

$$= 32 \text{ Btu/lb}_m$$

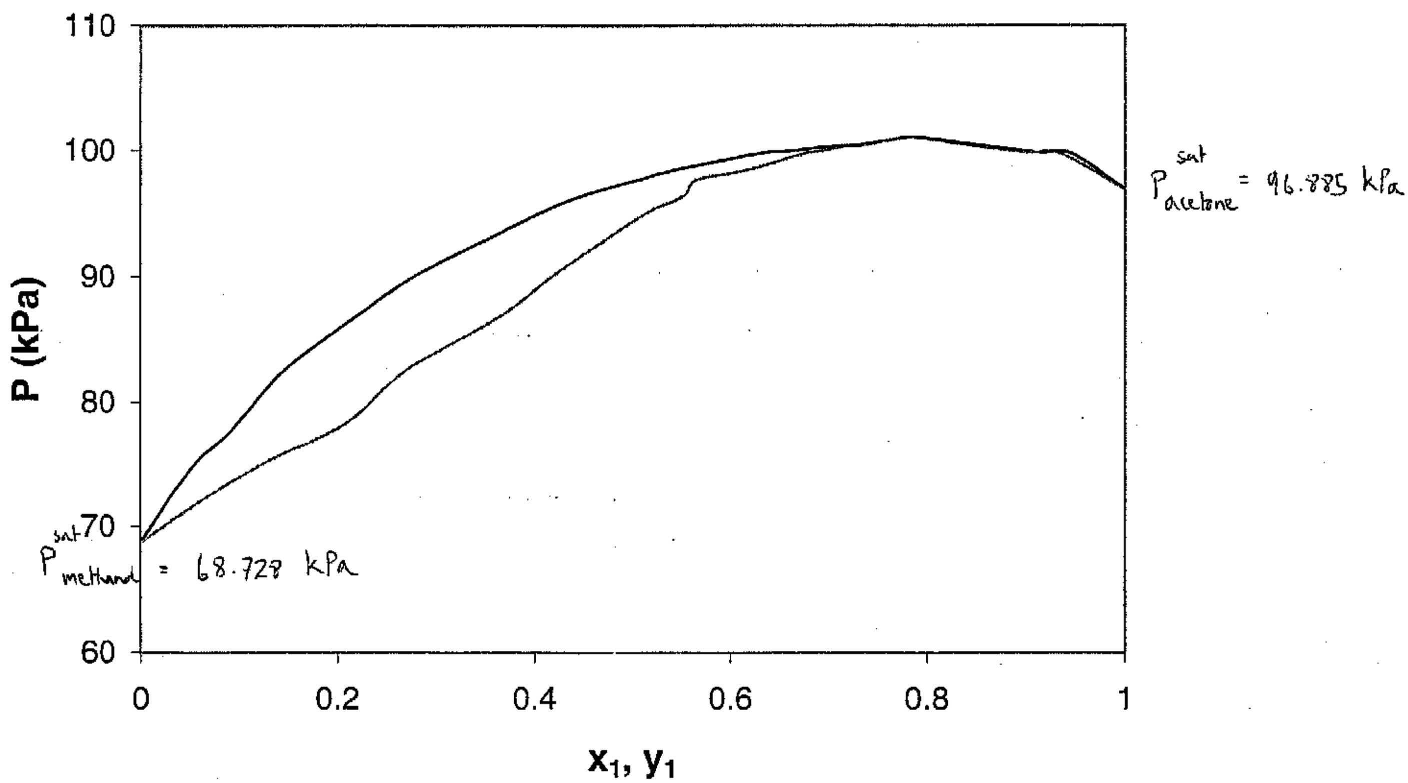
$\therefore H^E = -110 - 32 = -142$ Btu/lb$_m$ $\boxed{H^E = -142 \text{ Btu/lb}_m}$

Problem 37

a)

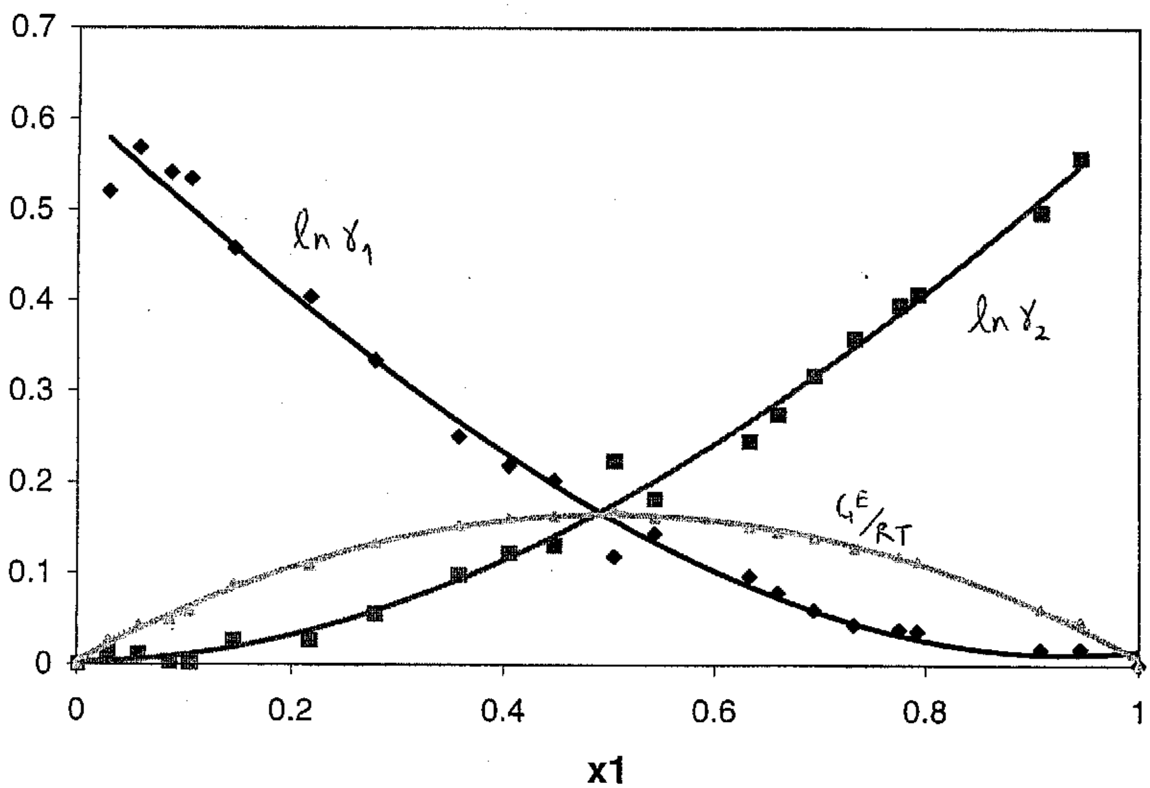


b)



c)

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



d) Margules eqn. $\ln \gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$, $\ln \gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$

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

$$= \ln \gamma_2^\infty x_1 + \ln \gamma_1^\infty x_2$$

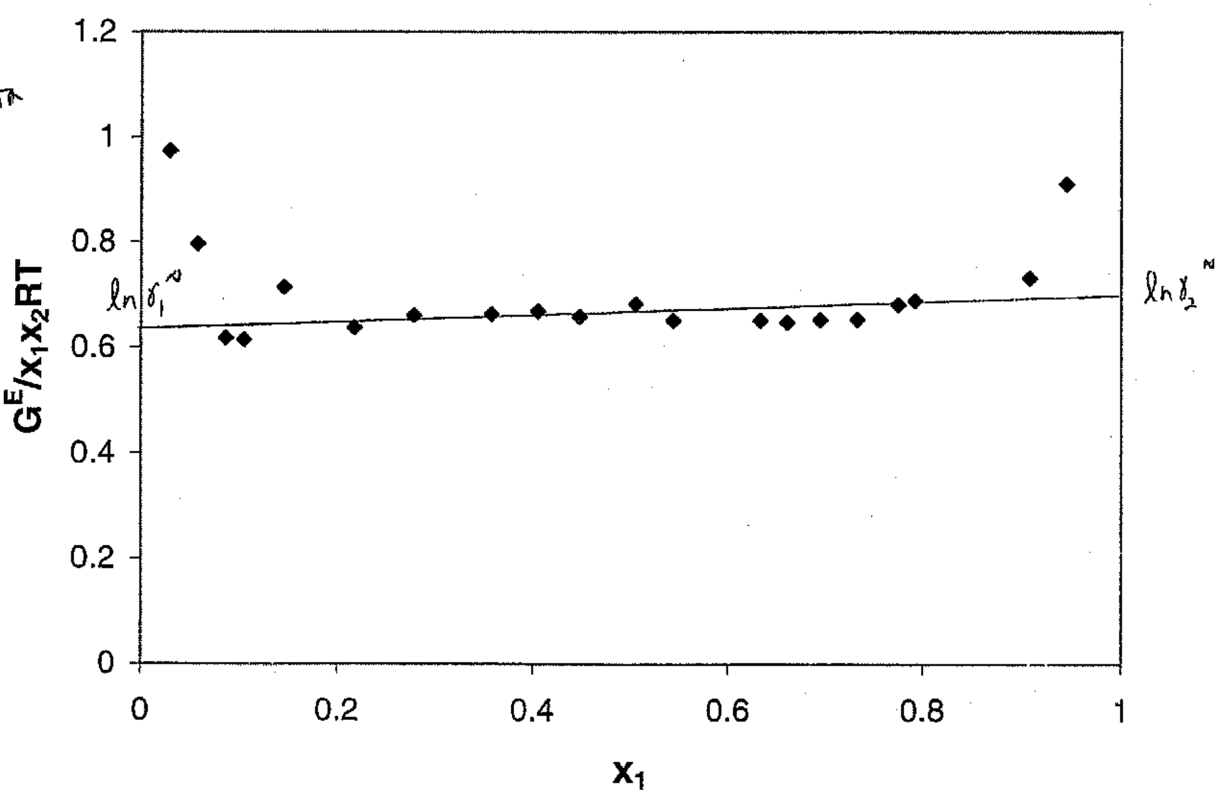
$\therefore$ Plot $\frac{G^E}{x_1 x_2 RT}$ vs. x_1 and get $\ln \gamma_2^\infty$ as $x_1 = 1$ intercept
$\ln \gamma_1^\infty$ as $x_1 = 0$ intercept

From best fit line

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

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

From data

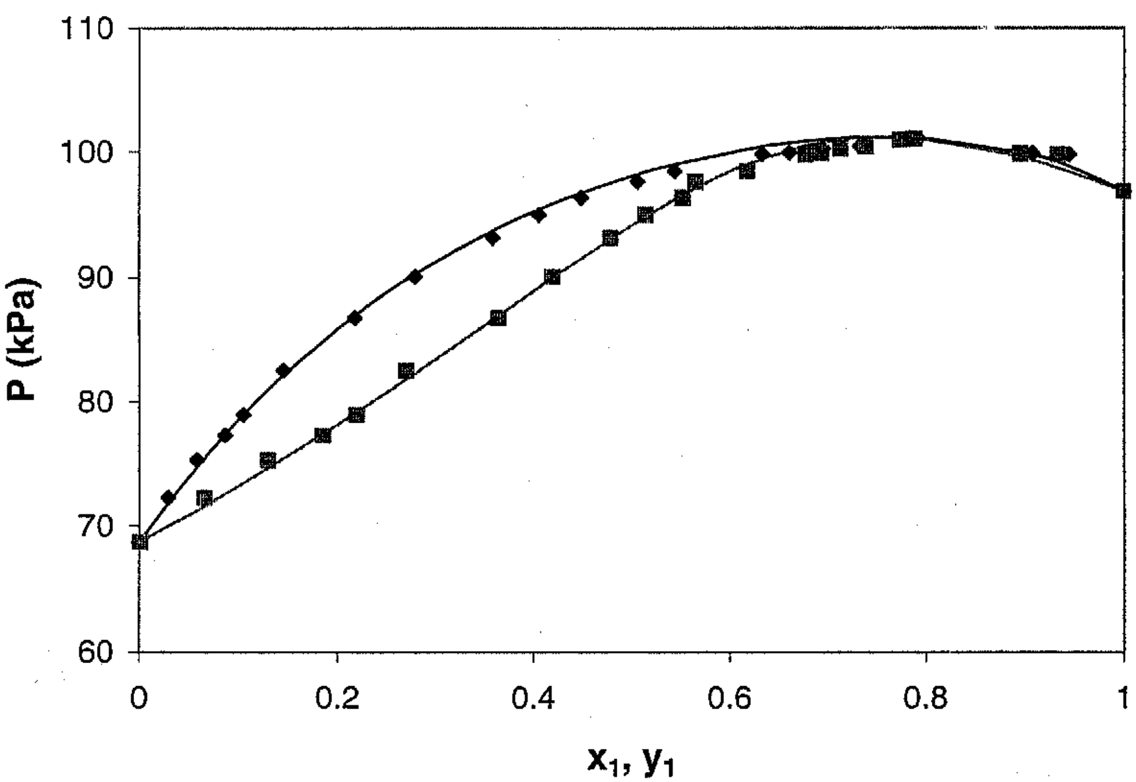


From Margules

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

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

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



e)

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.

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

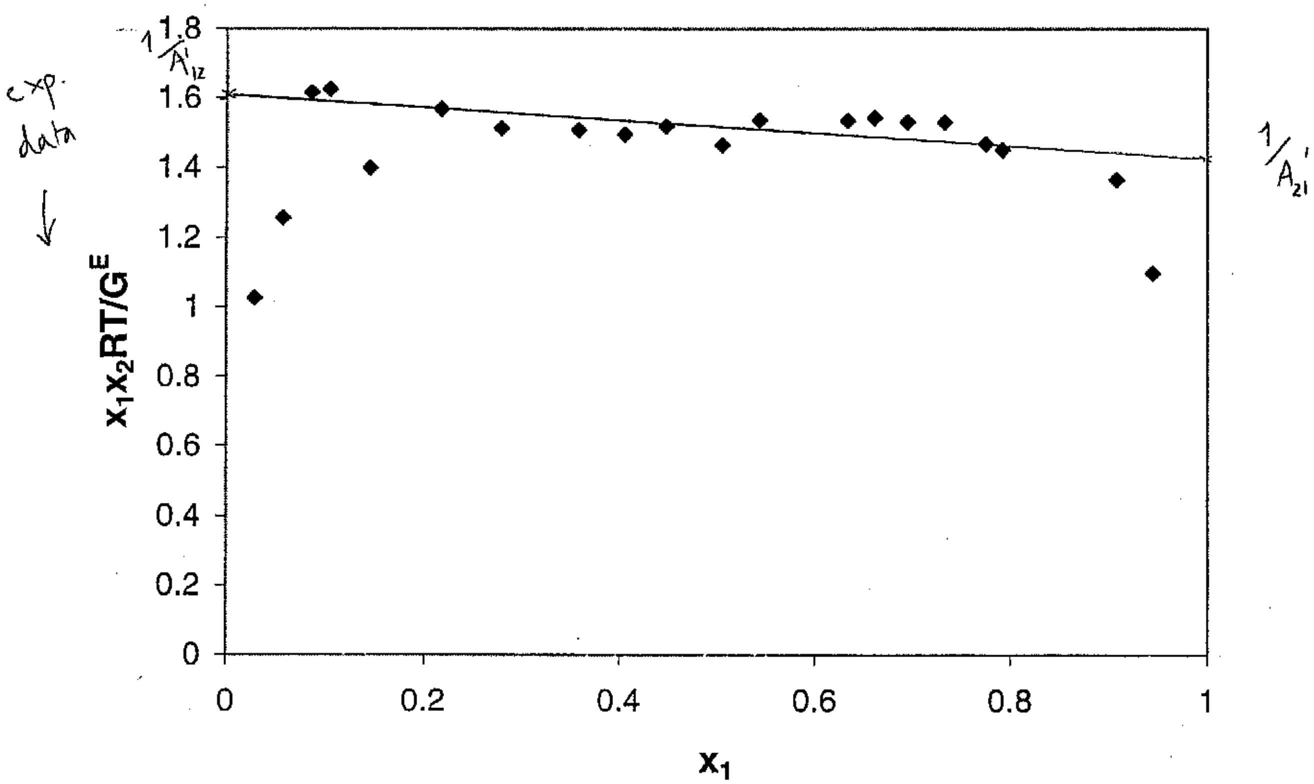
$$\ln \gamma_2 = A'_{21}\left(1 + \frac{A'_{21}x_2}{A'_{12}x_1}\right)^{-2}$$

$$\frac{x_1x_2}{G^E/RT} = \frac{x_1}{A'_{21}} + \frac{x_2}{A'_{12}} \quad \therefore \text{ Plot } \frac{x_1x_2}{G^E/RT} \text{ vs. } x_1$$

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

$x_1 = 0$ gives $1/A'_{12}$

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

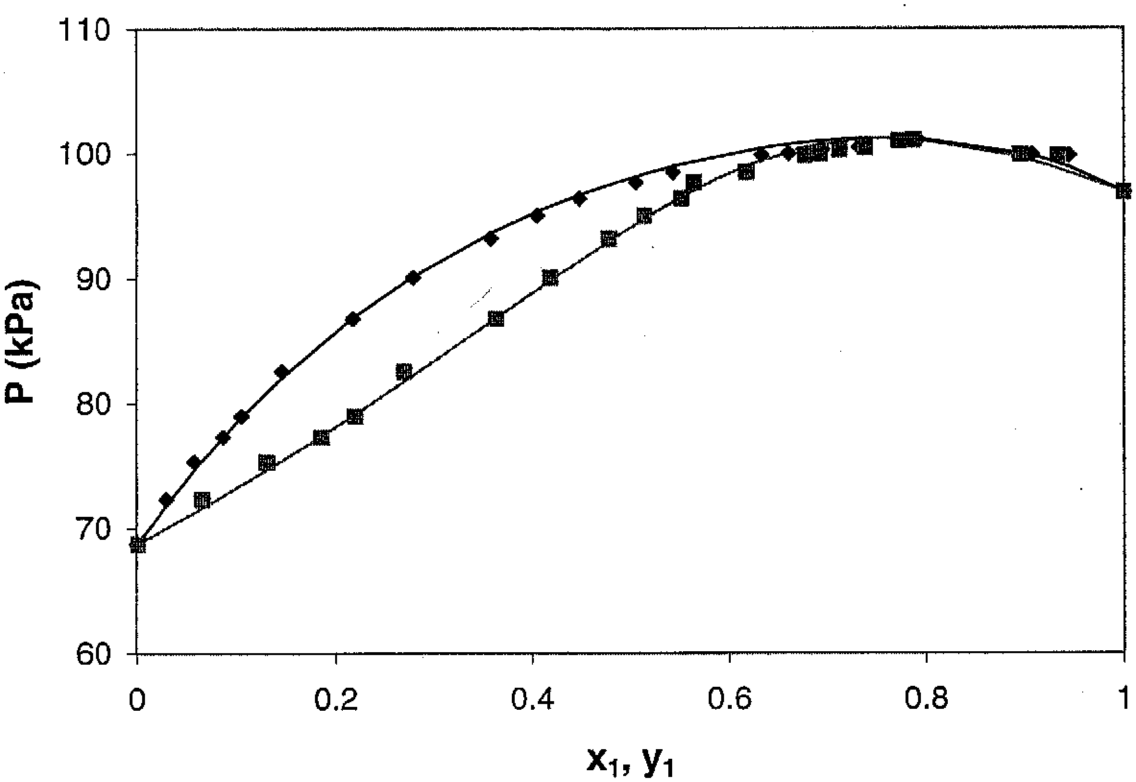


from van Laar

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

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

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



f) you can read this of the P-x-y diagram or calculate them using

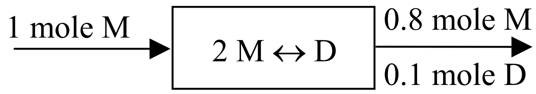
$$y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P} = \frac{\gamma_1 x_1 P_1^{sat}}{\gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat}}$$

and using either Margules or van Laar to get γ_1 and γ_2 as a function of x_1 and x_2

Margules	$x_1 = 0.759$
van Laar	$x_1 = 0.761$

38)

Using 1 mole of M feed as a basis:



We know the final composition because we are told 20% of M is converted to D, i.e. 0.2 mole of M is consumed and 0.1 mole of D is produced (by stoichiometry).

Reaction equilibrium equation:

$$\exp\left(-\frac{\Delta G^{o}_{rxn}(T)}{RT}\right) = K = \prod_i \left(\frac{\hat{f}_i}{f_i^{o}}\right)^{\nu_i}$$

$$\exp\left(-\frac{\Delta G^{o}_{rxn}(T)}{RT}\right) = \prod_i (\gamma_i x_i)^{\nu_i} \qquad \text{(for liquids at low to moderate P)}$$

$$\exp\left(-\frac{\Delta G^{o}_{rxn}(T)}{RT}\right) = (\gamma_M x_{Mi})^{\nu_M} (\gamma_D x_{Di})^{\nu_D} = \frac{(\gamma_D x_{Di})^1}{(\gamma_M x_{Mi})^2}$$

According to the reaction, the stoichiometric coef.: $\nu_M = -2$ (reactant) and $\nu_D = 1$ (product).

We are given ΔG^{o}_{rxn} at temperature of interest (298 K). What about the other side of the eqn?

$x_M = n_M/n_{total} = 0.8 \text{ mol}/(0.8 \text{ mol}+0.1\text{mol}) = 0.889.$ $\qquad x_D = 1 - x_M = 0.111.$

$G^E/RT = Ax_Mx_D$

→ $\ln \gamma_M = Ax_D^2$ and $\ln \gamma_D = Ax_M^2$ (see pset J if you don't know why this is so)

→ $\gamma_M = \exp(Ax_D^2)$ $\qquad \gamma_D = \exp(Ax_M^2)$

Putting everything together:

$$\exp\left(-\frac{\Delta G^{o}_{rxn}(T)}{RT}\right) = \frac{(\gamma_D x_{Di})}{(\gamma_M x_{Mi})^2} = \frac{\exp(Ax_M^2)x_D}{(\exp(Ax_D^2)x_M)^2}$$

$$\exp\left(-\frac{-1000 \text{ J/mol}}{(8.314 \text{ J/mol K})(298 \text{ K})}\right) = \frac{\exp(A \cdot 0.889^2)0.111}{(\exp(A \cdot 0.111^2)0.889)^2}$$

The only unknown in the equation above is A. We can re-arrange the equation to solve it

A = **3.09 (ans)**

39)

Here it is… The last homework problem of them all…

Unfortunately (or perhaps rather suitably) it is a rather long one. However, let's see if we can break it down to several parts that are easier to understand.

We have the reaction: **$CH_4 + CO \leftrightarrow CH_3CHO$**

at 260°C and 100 bar. Gases are non-ideal but form ideal solution.

To save time, let's abbreviate: **Me + CO ↔ Ac**

Information given: 1 mole of CO enters with 1 mole of Me and 4 moles of N_2.

a) Final compositions of reaction mixture as a function of ε.

$$y_i = \frac{n_i}{n} = \frac{n_{i,o} + \nu_i \varepsilon}{n_o + \nu\varepsilon} \qquad \text{(derived in lecture)}$$

y_i = mole fraction of component i; ν_i = stoichiometric coef. of component *i*;

$n_{i,o}$ = initial number of moles of component i; n_o = initial total number of moles = $\Sigma\, n_{i,o}$; $\nu = \Sigma\, \nu_i$

Making a table like the following usually helps:

Component	**$n_{i,o}$ (moles)**	**ν_i** (from rxn)	**$n_i = n_{i,o} + \nu_i\varepsilon$ (moles)**	**$y_i = n_i/n$**
Me	1	-1	1-ε	(1-ε) / (6-ε)
CO	1	-1	1-ε	(1-ε) / (6-ε)
Ac	0	1	ε	ε / (6-ε)
N_2	4	0	4	4 / (6-ε)
Total	**n_o** = 6	ν = -1	**n** = 6-ε	1

The answers for this part are in the rightmost column of the above table

.

b)

For reaction equilibrium:
$$\exp\left(-\frac{\Delta G^o_{rxn}(T)}{RT}\right) = K = \prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i}$$

Most problems require us to 'fill in the blanks' for both sides of the equations. Let's start with the right hand side.

For all gas reaction, we derived in class, for standard reference of pure species at 1 atm:

$$\prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = \prod_i \left(\frac{y_i \hat{\phi}_i P}{1\,\text{bar}}\right)^{\nu_i} \qquad \text{This is a general expression for gas-phase reaction.}$$

The problem states that the gases are not ideal ($\hat{\phi}_i$ is not 1); but the gases form ideal solution. This allows us to say that $\hat{\phi}_i = \phi_i$. This is because for ideal solution of gases, $\hat{f}_i = y_i f_i = y_i \phi_i P$ (The fugacity of comp. *i* in the mixture is fugacity of pure *i* multiplied by its fraction in the mixture). So rewriting the expression above:

$$\prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = \prod_i \left(\frac{y_i\,\phi_i\,P}{1\,\text{bar}}\right)^{\nu_i}$$ expression for ideal solution of non-ideal gases

We have the y_i and ν_i for all the species (done in part a). P = 100 bar (given). T = 260°C = 533 K. What about the ϕ_i's? ϕ of pure species; we can get through generalized correlation.

Component	**Pc (bar)**	**Tc (K)**	ω	$\mathbf{P_r}$ $\mathbf{(P/P_c)}$	$\mathbf{T_r}$ $\mathbf{(T/T_c)}$	(ϕ^o)	(ϕ^1)	$\phi = (\phi^o)(\phi^1)^\omega$
Me	45.99	190.6	0.012	2.17	2.80	1.01	1.14	1.01
CO	34.99	132.9	0.048	2.86	4.01	1.04	1.13	1.04
Ac	55.50	466.0	0.291	1.80	1.14	0.63	1.11	0.65

from Appendix B

P = 100 bar
T = 533 K

App. E
(with interpolations)

We see that even at this high pressure, but because the temperature is also high, we have almost ideal behavior for methane and CO. The acetaldehyde cannot be assumed to be ideal however, since $\phi_{Ac} = 0.65$.

Now we can write down all the knowns for the right hand side of our equilibrium equation:

$$\prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = \prod_i \left(\frac{y_i\,\phi_i\,P}{1\,\text{bar}}\right)^{\nu_i} = \left(\frac{y_{Me}\,\phi_{Me}\,P}{1\,\text{bar}}\right)^{\nu_{Me}} \left(\frac{y_{CO}\,\phi_{CO}\,P}{1\,\text{bar}}\right)^{\nu_{CO}} \left(\frac{y_{Ac}\,\phi_{Ac}\,P}{1\,\text{bar}}\right)^{\nu_{Ac}}$$

with $\nu_{Me} = -1$, $\nu_{Me} = -1$, $\nu_{Ac} = 1$ (and re-arranging):

$$\prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = \left(\frac{y_{Ac}\,\phi_{Ac}}{(y_{Me}\,\phi_{Me})(y_{CO}\,\phi_{CO})}\right)\left(\frac{1\,\text{bar}}{P}\right)$$

Writing in expressions for y_i from part a, and also ϕ_i values from the table above:

$$\prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = \left(\frac{\frac{\varepsilon}{6-\varepsilon}(0.65)}{\frac{1-\varepsilon}{6-\varepsilon}(1.01)\,\frac{1-\varepsilon}{6-\varepsilon}(1.04)}\right)\left(\frac{1\,\text{bar}}{P}\right) = \left(\frac{(0.65)\varepsilon 0.-\varepsilon)}{(1.01)(1.04)(1-\varepsilon)^2}\right)\left(\frac{1\,\text{bar}}{P}\right)$$

$$\prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i} = \frac{0.618\,\varepsilon\,(6-\varepsilon)}{(1-\varepsilon)^2}\left(\frac{1\,\text{bar}}{P}\right) \qquad \textbf{(*)}$$

Why isn't N_2 included in the expression above? We can include it, but $\nu_{N2} = 0$. So the term drops out anyway.

Not so bad now, was it? Okay… now for the other part of the equation.

Reminder: $$\boxed{\exp\left(-\frac{\Delta G^o_{rxn}(T)}{RT}\right) = K = \prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i}}$$

We know how to get ΔG^o_{rxn} at 298 K (from data in Appendix C). To get ΔG^o_{rxn} at a different temperature, we derived in class (and also in the textbook equation 13.18):

$$\frac{\Delta G^o(T)}{RT} = \frac{\Delta G^o(To) - \Delta H^o(To)}{RTo} + \frac{\Delta H^o(To)}{RT} + \frac{1}{T}\int_{To}^{T}\frac{\Delta C_p^o}{R}dT - \int_{To}^{T}\frac{\Delta C_p^o}{R}\frac{dT}{T}$$

(where the Δ's means Δ_{rxn}) To = T reference = 298 K for our case. $\Delta Cp = \Sigma \nu_i Cp_i$.

From appendix C:

$Cp^{ig}/R = A + BT + CT^2 + DT^{-2}$

Component	ΔH^o_f at To=298 K (J/mol)	ΔG^o_f at To=298 K (J/mol)	A	B	C	D
Me	-74,520	-50,460	1.702	$9.081\cdot10^{-3}$	$-2.164\cdot10^{-6}$	0
CO	-110,525	-137,169	3.376	$0.557\cdot10^{-3}$	0	-3,100
Ac	-166,190	-128,860	1.693	$17.978\cdot10^{-3}$	$-6.158\cdot10^{-6}$	0
Δ	$\Delta H^o_{rxn}(To)$ =18,855	$\Delta G^o_{rxn}(To)$ = 58,769	ΔA= -3.385	ΔB= $8.340\cdot10^{-3}$	ΔC= $-3.994\cdot10^{-6}$	ΔD= 3,100

Explanation on the Δ row: Just a shorthand where $\Delta M = \Sigma \nu_i M_i$ where M is variable of interest.
e.g. $\Delta G^o_{rxn} = \Delta(\Delta G^o_f) = \Sigma \nu_i \, \Delta G^o_{f,i}$.

$$\frac{\Delta G^o(T)}{RT} = \frac{\Delta G^o(To) - \Delta H^o(To)}{RTo} + \frac{\Delta H^o(To)}{RT} + \frac{1}{T}\int_{To}^{T}\frac{\Delta C_p^o}{R}dT - \int_{To}^{T}\frac{\Delta C_p^o}{R}\frac{dT}{T}$$

$$\frac{\Delta G^o(T)}{RT} = \frac{\Delta G^o(To) - \Delta H^o(To)}{RTo} + \frac{\Delta H^o(To)}{RT} + \frac{1}{T}\int_{To}^{T}(\Delta A + \Delta B\cdot T + \Delta C\cdot T^2 + \Delta D\cdot T^{-2})\,dT - \int_{To}^{T}(\Delta A + \Delta B\cdot T + \Delta C\cdot T^2 + \Delta D\cdot T^{-2})\frac{dT}{T}$$

$$\frac{\Delta G^o(T)}{RT} = \frac{\Delta G^o(To) - \Delta H^o(To)}{RTo} + \frac{\Delta H^o(To)}{RT} + \frac{1}{T}\left[\Delta A(T - To) + \frac{\Delta B}{2}(T^2 - T_o^2) + \frac{\Delta C}{3}(T^3 - T_o^3) - \Delta D(\frac{1}{T} - \frac{1}{To})\right] - \left[\Delta A\ln(\frac{T}{To}) + \Delta B(T - To) + \frac{\Delta C}{2}(T^2 - T_o^2) - 2\Delta D(\frac{1}{T^2} - \frac{1}{To^2})\right]$$

Long, but doable. We know all the values for the above equation. T=298 K and To = 533 K.
If we do the calculation, we get:

$$\frac{\Delta G^o(533\,K)}{RT} = 20.47 \quad \textbf{(**)}$$

Having calculated this, we can return to our equilibrium equation:

$$\exp\left(-\frac{\Delta G^o_{rxn}(T)}{RT}\right) = K = \prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i}$$

Putting together what we calculated before, **(*)** and **(**)** above:

$$\exp\left(-\frac{\Delta G^o_{rxn}(T)}{RT}\right) = K = \frac{0.618\,\varepsilon\,(6-\varepsilon)}{(1-\varepsilon)^2}\left(\frac{1\,\text{bar}}{P}\right)$$

$$\exp(-20.47) = 1.29\cdot 10^{-9} = \frac{0.618\,\varepsilon\,(6-\varepsilon)}{(1-\varepsilon)^2}\left(\frac{1\,\text{bar}}{100\,\text{bar}}\right)$$

This is a quadratic equation in ε which we can solve:

ε = 3.50 ·10^{-8} … practically ≈ 0. What does this mean? Why?

$CH_4 + CO \leftrightarrow CH_3CHO$

This means our reaction does not proceed very far before it reaches equilibrium. The equilibrium constant K = 1.29 ·10^{-9} is quite small, suggesting reaction to the left (producing methane and CO) is favored over reaction producing acetaldehyde.

We could not have known this before we calculated the K and ε. So it's not really pointless. Besides, the point is to make sure you know how to do this type of calculation. Anyway, for the mole fraction, we can calculate using ε (using expressions we got in part a):

$y_{methane}$ = 0.167; y_{CO} = 0.167; y_{Ac} = 6 ·10^{-8} ≈ 0; y_{N2} = 0.666.

Recapping:

1) We write the reaction equilibrium equation: $\boxed{\exp\left(-\frac{\Delta G^o_{rxn}(T)}{RT}\right) = K = \prod_i \left(\frac{\hat{f}_i}{f_i^o}\right)^{\nu_i}}$

2) We figure out both sides of the equation, writing in terms of what we know (given or data from back of the book) and what we don't know (what we try to solve).

3) If the temperature is not 298 K and the value for ΔG^orxn or K are not given, $\Delta G^o_{rxn}(T)$ must be calculated using the Cp's like above.

4) For the right hand side, we express the fugacities depending on the phase of the species (liquid, gas, solid, solution).

5) The expression of fugacities will usually involve some molar fraction (y_i, x_i). Usually it's easier to write down the molar fraction in terms of one variable (for one reaction), namely ε. This requires some stoichiometry and, sometimes, material balance.

6) Finally, if we have reaction equilibrium, we equate the lefthand side and the righthand side, and solve for what we don't know.

(For the case of more than one reactions (say *n* reactions), we have *n* equilibrium equations. Also, we have *n* of ε: $\varepsilon_{rxn\,1}$, $\varepsilon_{rxn\,2}$, … $\varepsilon_{rxn\,n.}$ We haven't practiced with this. We may do this to study for the final)