Problem Set I

Problem 29

a) $$\ln\phi = \frac{G^R}{RT}$$

$$= \int_0^{\rho} (Z-1)\,\frac{d\rho}{\rho} + Z - 1 - \ln Z$$

$$= \int_0^{\rho} \left[\frac{b}{V-b} - \frac{a}{RT^{1.5}(V+b)} \right] \frac{d\rho}{\rho} + Z - 1 - \ln Z$$

using $\rho = \frac{1}{V}$, ie $V = 1/\rho$

$$= \int_0^{\rho} \left[\frac{b}{1/\rho - b} - \frac{a}{RT^{1.5}(1/\rho + b)} \right] \frac{d\rho}{\rho} + Z - 1 - \ln Z$$

$$= \int_0^{\rho} \left[\frac{b}{1-b\rho} - \frac{a}{RT^{1.5}(1+b\rho)} \right] d\rho + Z - 1 - \ln Z$$

$$= \left[-\ln(1-b\rho) - \frac{a}{bRT^{1.5}} \ln(1+b\rho) \right]_0^{\rho} + Z - 1 - \ln Z$$

$$= -\ln(1-b\rho) - \frac{a}{bRT^{1.5}} \ln(1+b\rho) + Z - 1 - \ln Z$$

$$= -\ln\left(1-\frac{b}{V}\right) - \frac{a}{bRT^{1.5}} \ln\left(1+\frac{b}{V}\right) + Z - 1 - \ln Z$$

QED

b) n-butane at 500K and 50 bar

$$\ln\phi = -\ln\left(1-\frac{b}{V}\right) - \frac{a}{bRT^{1.5}}\ln\left(1+\frac{b}{V}\right) + Z-1-\ln Z$$

from $P = \dfrac{RT}{V-b} - \dfrac{a}{T^{0.5}V(V+b)}$

and $T_c = 425.1\,K$ $P_c = 37.96$ bar $P = 50$ bar $T = 500K$

$\therefore$ $a = 29$ $b = 8.07 \times 10^{-5}$

$\Longrightarrow$ $V = 5.70 \times 10^{-4}$ m³/mol

$\therefore$ $Z = 1 + \dfrac{b}{V-b} - \dfrac{a}{RT^{1.5}(V+b)} = 0.685$

hence $\ln\phi = -0.296$ using eqn. from a)

$\phi = 0.7436$

$\phi = \dfrac{f}{P}$ $\therefore$ $f = \phi P = 0.7436 \times 50$ bar

$$\boxed{f = 37.18 \text{ bar}}$$

c) $G^R = H^R - TS^R$

$G^R = (-4.51 \times 1000) - (500 \times -6.55) = -1235 \text{ J/mol}$

$\ln\phi = \frac{G^R}{RT} = \frac{-1235}{8.314 \times 500} = -0.297$

$\therefore \phi = 0.743$

$$\boxed{f = 37.15 \text{ bar}}$$

d) using $\ln\phi = \ln\phi_0 + \omega \ln\phi_1$

or $\phi = \phi_0 \cdot \phi_1^{\omega}$

at $P_r = \frac{50}{37.96} = 1.317$ $T_r = \frac{500}{425.1} = 1.176$

and $\omega = 0.200$

$\Longrightarrow \phi_0 \approx 0.7462$ $\phi_1 \approx 1.072$

$\therefore \phi = 0.7462 \times 1.072^{0.2} = 0.756$

$$\boxed{\therefore f = 37.83 \text{ bar}}$$

Problem 30

(a) $$\frac{G^E}{RT} = (-2.6x_1 - 1.8x_2)x_1x_2$$

$$\therefore \frac{\bar{G}_1^E}{RT} = \frac{G^E}{RT} + x_2\frac{d}{dx_1}(G^E/RT)$$

$$= (-2.6x_1 - 1.8x_2)x_1\cdot x_2 + x_2\frac{d}{dx_1}[(-1.8 - 0.8x_1)\cdot x_1\cdot(1-x_1)]$$

$$= (-2.6x_1 - 1.8x_2)x_1x_2 + x_2\frac{d}{dx_1}[0.8x_1^3 + x_1^2 - 1.8x_1]$$

$$= (-2.6x_1 - 1.8x_2)x_1x_2 + x_2(2.4x_1^2 + 2x_1 - 1.8)$$

since $\ln\gamma_1 = \frac{\bar{G}_1^E}{RT}$

$$\therefore \ln\gamma_1 = (-2.6x_1 - 1.8x_2)x_1x_2 + x_2(2.4x_1^2 + 2x_1 - 1.8)$$

$$\ln\gamma_2 = \frac{\bar{G}_2^E}{RT} = \frac{G^E}{RT} - x_1\frac{d(G^E/RT)}{dx}$$

$$= (-2.6x_1 - 1.8x_2)x_1x_2 - x_1\frac{d}{dx}[(-1.8 - 0.8x_1)\cdot x_1\cdot(1-x_1)]$$

$$= (-2.6x_1 - 1.8x_2)x_1x_2 - x_1\frac{d}{dx}[0.8x_1^3 + x_1^2 - 1.8x_1]$$

$$\ln\gamma_2 = (-2.6x_1 - 1.8x_2)x_1x_2 - x_1(2.4x_1^2 + 2x_1 - 1.8)$$

(b) $\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$

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

$= \overset{\textcircled{A}}{x_1(-2.6x_1 - 1.8x_2)x_1x_2} + \overset{\textcircled{B}}{x_1x_2(2.4x_1^2 + 2x_1 - 1.8)}$

$+ \overset{\textcircled{C}}{x_2(-2.6x_1 - 1.8x_2)x_1x_2} - \overset{\textcircled{D}}{x_1x_2(2.4x^2 + 2x_1 - 1.8)}$

term Ⓐ + Ⓒ gives $(-2.6x_1 - 1.8x_2)x_1x_2$ as $x_1 + x_2 = 1$

↗ this is G^E/RT

$\therefore$ Ⓑ + Ⓓ must equal to zero, which it does.

QED

(c) $\sum_i x_i \, d\ln\gamma_i = 0$ Gibbs-Duhem eqn.

$x_1 \, d\ln\gamma_1 + x_2 \, d\ln\gamma_2 = 0$

$x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d}{dx_1}\ln\gamma_2 = 0$

$\therefore x_1 \frac{d}{dx_1}(0.8x_1^3 + x_1^2 - 1.8x_1 + 0.4x_1^2 + 3.8x_1 - 1.8 - 2.4x_1^3)$

$+ x_2 \frac{d}{dx_1}(0.8x_1^3 + x_1^2 - 1.8x_1 - 2.4x_1^3 - 2x_1^2 + 1.8x_1)$

$= x_1 \frac{d}{dx_1}(-1.6x_1^3 + 1.4x_1^2 + 2x_1 - 1.8) + x_2 \frac{d}{dx_1}(-1.6x_1^3 - x_1^2)$

$= x_1(-4.8x_1^2 + 2.8x_1 + 2) + (1-x_1)(-4.8x_1^2 - 2x_1)$

$= 0$ QED

(d) $\frac{d \ln \gamma_1}{dx_1} = -4.8x_1^2 + 2.8x_1 + 2$ From part (c)

$\therefore$ at $x_1 = 1$ $\frac{d \ln \gamma_1}{dx_1} = 0$ QED

$\frac{d \ln \gamma_2}{dx_1} = -4.8x_1^2 - 2x_1$ From part (c)

$\therefore$ at $x_1 = 0$ $\frac{d \ln \gamma_2}{dx_1} = 0$ QED

* PS, I've notice that most of you use the relation

$$\frac{\bar{G}_i^E}{RT} = \left[\frac{\partial}{\partial n_i}\left(n\frac{G^E}{RT}\right)\right]_{T, P, n_{j \neq i}}$$

to do part (a) - (d)

So I've included the solution of part (a) and (b) using this method also, in case you prefer it that way

$\Rightarrow$ see next page

(a)

$$\frac{\overline{G_1^E}}{RT} = \left[\frac{\partial(nG^E/RT)}{\partial n_1}\right]_{T,P,n_2} = \ln\gamma_1$$

$$= \frac{\partial}{\partial n_1}\left\{ n\cdot\left(-2.6\frac{n_1}{\cancel{n}} - 1.8\frac{n_2}{\cancel{n}}\right)\frac{n_1}{n}\cdot\frac{n_2}{n}\right\}_{T,P,n_2}$$

$$= \frac{\partial}{\partial n_1}\left\{\frac{-2.6n_1^2n_2 - 1.8n_1n_2^2}{(n_1+n_2)^2}\right\}$$

$$= \frac{(n_1+n_2)^2\frac{\partial}{\partial n_1}(-2.6n_1^2n_2-1.8n_1n_2^2) - (-2.6n_1^2n_2-1.8n_1n_2^2)\frac{\partial}{\partial n_1}(n_1+n_2)^2}{(n_1+n_2)^4}$$

$$= \frac{-5.2n_1n_2 - 1.8n_2^2}{(n_1+n_2)^2} + \frac{(2.6n_1^2n_2+1.8n_1n_2^2)\cdot 2\cdot(n_1+n_2)}{(n_1+n_2)^4}$$

$$= \frac{-5.2n_1n_2-1.8n_2^2}{(n_1+n_2)^2} + \frac{5.2n_1^2n_2+3.6n_1n_2^2}{(n_1+n_2)^3}$$

$$\ln\gamma_1 = -5.2x_1x_2 - 1.8x_2^2 + 5.2x_1^2x_2 + 3.6x_1x_2^2$$

similarly $\ln\gamma_2 = \frac{\overline{G_2^E}}{RT} = \left[\frac{\partial(nG^E/RT)}{\partial n_2}\right]_{T,P,n_1}$

$$= \frac{\partial}{\partial n_2}\left\{\frac{-2.6n_1^2n_2 - 1.8n_1n_2^2}{(n_1+n_2)^2}\right\}$$

$$= \frac{(n_1+n_2)^2\frac{\partial}{\partial n_2}(-2.6n_1^2n_2-1.8n_1n_2^2) - (-2.6n_1^2n_2-1.8n_1n_2^2)\frac{\partial}{\partial n_2}(n_1+n_2}{(n_1+n_2)^4}$$

$$= \frac{-2.6 n_1^2 - 3.6 n_1 n_2}{(n_1+n_2)^2} + \frac{5.2 n_1^2 n_2 + 3.6 n_1 n_2^2}{(n_1+n_2)^3}$$

$$\ln \gamma_2 = -2.6 x_1^2 - 3.6 x_1 x_2 + 5.2 x_1^2 x_2 + 3.6 x_1 x_2^2$$

(b) show that $\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$

$$= x_1(-5.2 x_1 x_2 - 1.8 x_2^2) + \overset{\textcircled{A}}{x_1(5.2 x_1^2 x_2 + 3.6 x_1 x_2^2)}$$

$$+ x_2(-2.6 x_1^2 - 3.6 x_1 x_2) + \overset{\textcircled{B}}{x_2(5.2 x_1^2 x_2 + 3.6 x_1 x_2^2)}$$

$$= -5.2 x_1^2 x_2 - 1.8 x_1 x_2^2 - 2.6 x_1^2 x_2 - 3.6 x_1 x_2^2 + \underbrace{5.2 x_1^2 x_2 + 3.6 x_1 x_2^2}_{\substack{\textcircled{A} + \textcircled{B} \\ \text{since } x_1 + x_2 = 1}}$$

$$= -1.8 x_1 x_2^2 - 2.6 x_1^2 x_2$$

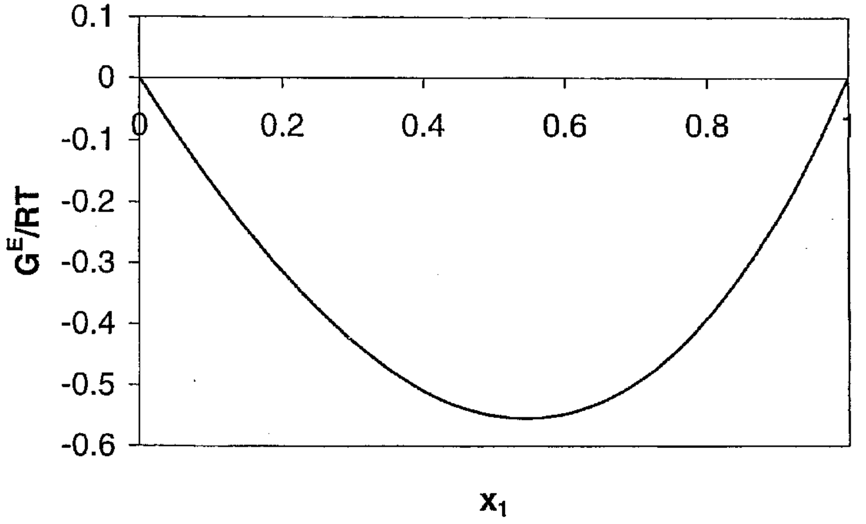
$$= (-2.6 x_1 - 1.8 x_2) x_1 x_2$$

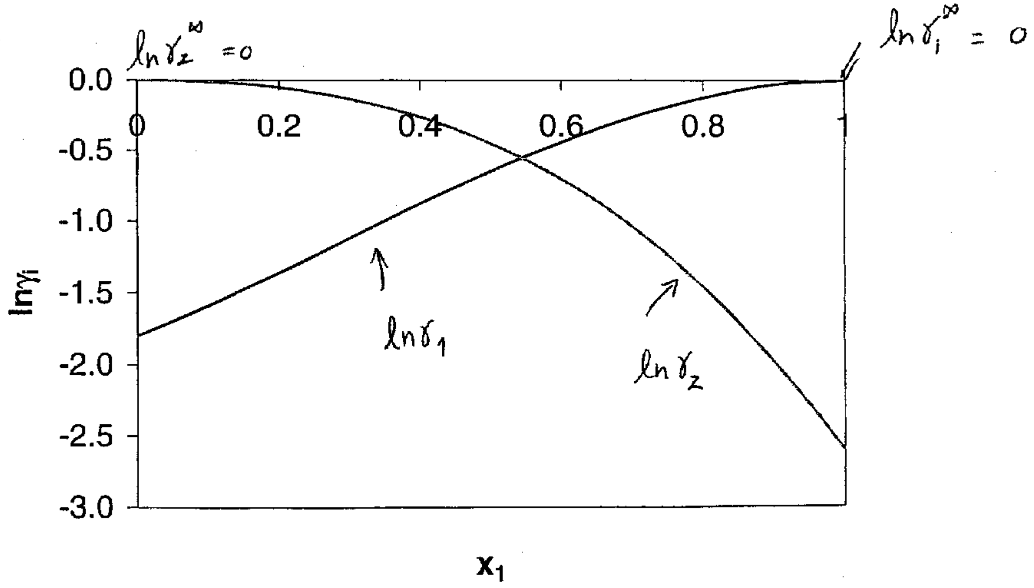
QED

etc....

(e)

x_1	G^E/RT	$\ln\gamma_1$	$\ln\gamma_2$
0	0	-1.8	0
0.05	-0.0874	-1.6967	-0.0027
0.1	-0.1692	-1.5876	-0.0116
0.15	-0.2448	-1.4739	-0.0279
0.2	-0.3136	-1.3568	-0.0528
0.25	-0.375	-1.2375	-0.0875
0.3	-0.4284	-1.1172	-0.1332
0.35	-0.4732	-0.9971	-0.1911
0.4	-0.5088	-0.8784	-0.2624
0.45	-0.5346	-0.7623	-0.3483
0.5	-0.55	-0.65	-0.45
0.55	-0.5544	-0.5427	-0.5687
0.6	-0.5472	-0.4416	-0.7056
0.65	-0.5278	-0.3479	-0.8619
0.7	-0.4956	-0.2628	-1.0388
0.75	-0.45	-0.1875	-1.2375
0.8	-0.3904	-0.1232	-1.4592
0.85	-0.3162	-0.0711	-1.7051
0.9	-0.2268	-0.0324	-1.9764
0.95	-0.1216	-0.0083	-2.2743
1	5.77E-16	0	-2.6



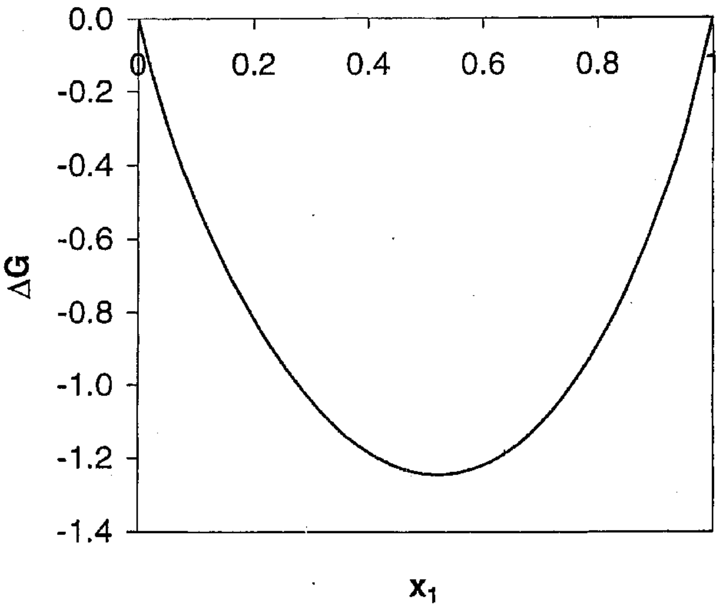


(f)

x_1	G^E/RT	ΔG
0	0	0
0.05	-0.0874	-0.285915
0.1	-0.1692	-0.494283
0.15	-0.2448	-0.667509
0.2	-0.3136	-0.814002
0.25	-0.375	-0.937335
0.3	-0.4284	-1.039264
0.35	-0.4732	-1.120647
0.4	-0.5088	-1.181812
0.45	-0.5346	-1.222739
0.5	-0.55	-1.243147
0.55	-0.5544	-1.242539
0.6	-0.5472	-1.220212
0.65	-0.5278	-1.175247
0.7	-0.4956	-1.106464
0.75	-0.45	-1.012335
0.8	-0.3904	-0.890802
0.85	-0.3162	-0.738909
0.9	-0.2268	-0.551883
0.95	-0.1216	-0.320115
1	5.77E-16	0

$$G^E = \Delta G - RT \sum_i x_i \ln x_i$$

$$\frac{\Delta G}{RT} = \frac{G^E}{RT} + \sum_i x_i \ln x_i$$



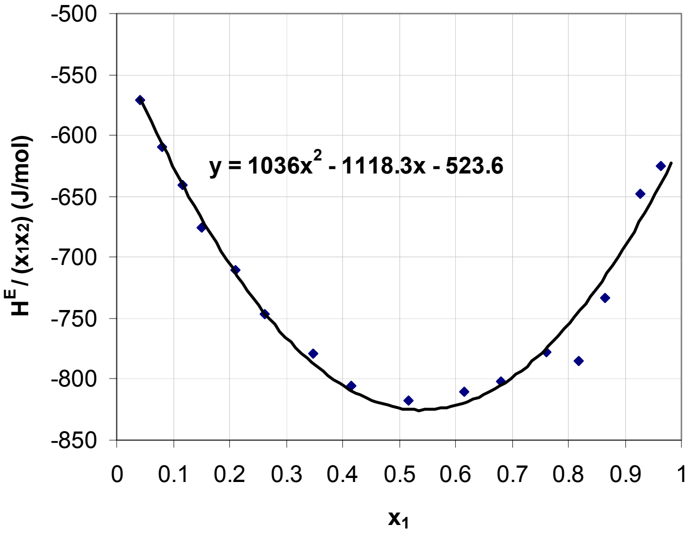
31)

We are given H^E data for 1,2-dicholorethane(1) and dimethyl carbonate (2) at 313.15 K and 1 atm.

a) We fit the data to the expression:

$$H^E = x_1 x_2 (a + bx_1 + cx_1^2) \qquad [1]$$

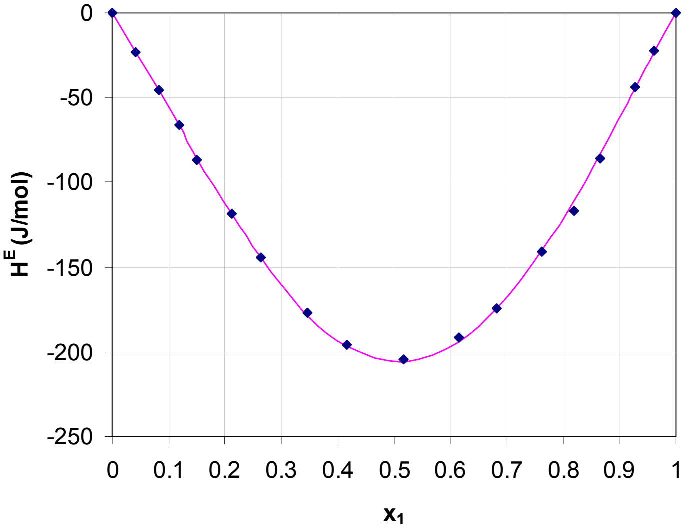
This solution uses a spreadsheet program. We can plot $H^E/(x_1x_2)$ and get the best fit quadratic curve.



From the quadratic equation, we get

a = **-523.6 J/mol**,
b = **-1118.3 J/mol**,
c = **1036 J/mol**.

b) We plotted $H^E/(x_1x_2)$. Now plotting H^E vs x_1, we get:



The points are data from the table.
The line is the best-fit expression calculated using equation [1] and the a, b, and c values above.

The minimum appears to be
$\mathbf{H^E_{min} = -206\ J/mol}$ **at** $\mathbf{x_1 \approx 0.51}$.

A more rigorous approach is to calculate x_1 at which $\frac{dH^E}{dx_1} = 0$.

$H^E = x_1(1-x_1)(a + bx_1 + cx_1^2) = (x_1 - x_1^2)(a + bx_1 + cx_1^2)$

$$\frac{dH^E}{dx_1} = (1-2x_1)(a + bx_1 + cx_1^2) + (x_1 - x_1^2)(b + 2cx_1) = -4cx_1^3 + 3(c-b)x_1^2 + 2(b-a)x_1 + a \qquad [2]$$

Setting $(dH^E/dx_1) = 0$ and using the values of a, b, and c above, we get three solutions:
$x_1 = -0.199$, $x_1 = 0.509$, $x_1 = 1.249$. The only one that makes sense: $\mathbf{x_1 = 0.509}$
At this x_1, $H^E = \mathbf{H^E_{min} = -206.0\ J/mol}$

c) To get expressions for $\overline{H}_1^E$ and $\overline{H}_2^E$, we use the equations for binary systems:

$$\overline{H}_1^E = H^E + x_2 \frac{dH^E}{dx_1} \quad [3] \qquad \text{and} \qquad \overline{H}_2^E = H^E - x_1 \frac{dH^E}{dx_1} \quad [4]$$

We calculated (dH^E/dx_1) already, see equation [2] above:

$$\frac{dH^E}{dx_1} = -4cx_1^3 + 3(c-b)x_1^2 + 2(b-a)x_1 + a$$

So, plugging this into equations [3] and [4], we get:

$$\overline{H}_1^E = H^E + x_2 \frac{dH^E}{dx_1} = (x_1 - x_1^2)(a + bx_1 + cx_1^2) + [1 - x_1]\left[-4cx_1^3 + 3(c-b)x_1^2 + 2(b-a)x_1 + a\right]$$

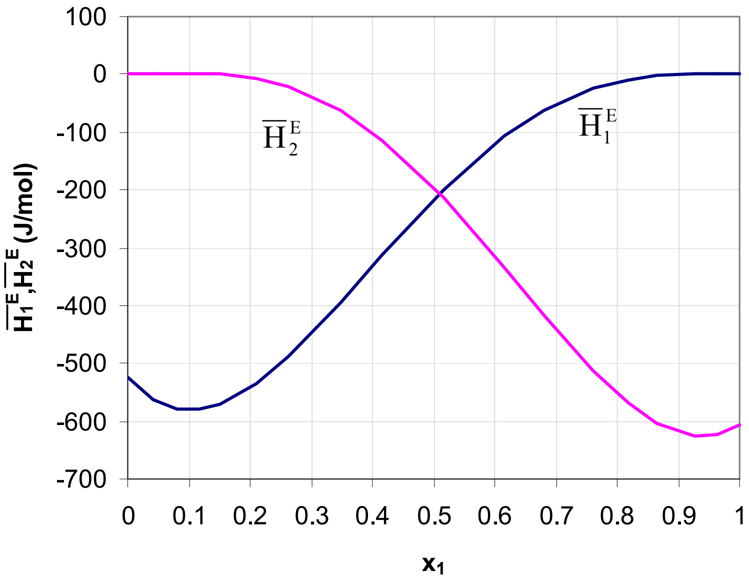
$$\overline{H}_2^E = H^E - x_1 \frac{dH^E}{dx_1} = (x_1 - x_1^2)(a + bx_1 + cx_1^2) - x_1\left[-4cx_1^3 + 3(c-b)x_1^2 + 2(b-a)x_1 + a\right]$$

The above can be simplified by collecting the x_1 terms to give us:

$$\overline{H}_1^E = 3cx_1^4 + (-6c + 2b)x_1^3 + (3c - 4b + a)x_1^2 + (2b - 2a)x_1 + a$$
$$\overline{H}_2^E = 3cx_1^4 + (-2c + 2b)x_1^3 + (b + a)x_1^2$$

(ans)

Plotting these vs. x_1:



Both curves are non-monotonic with a minimum near $x_i = 0.1$. The infinite dilution values are the values at which $x_i = 0$:

$\overline{H}_1^{E,\infty} = -524$ J/mol

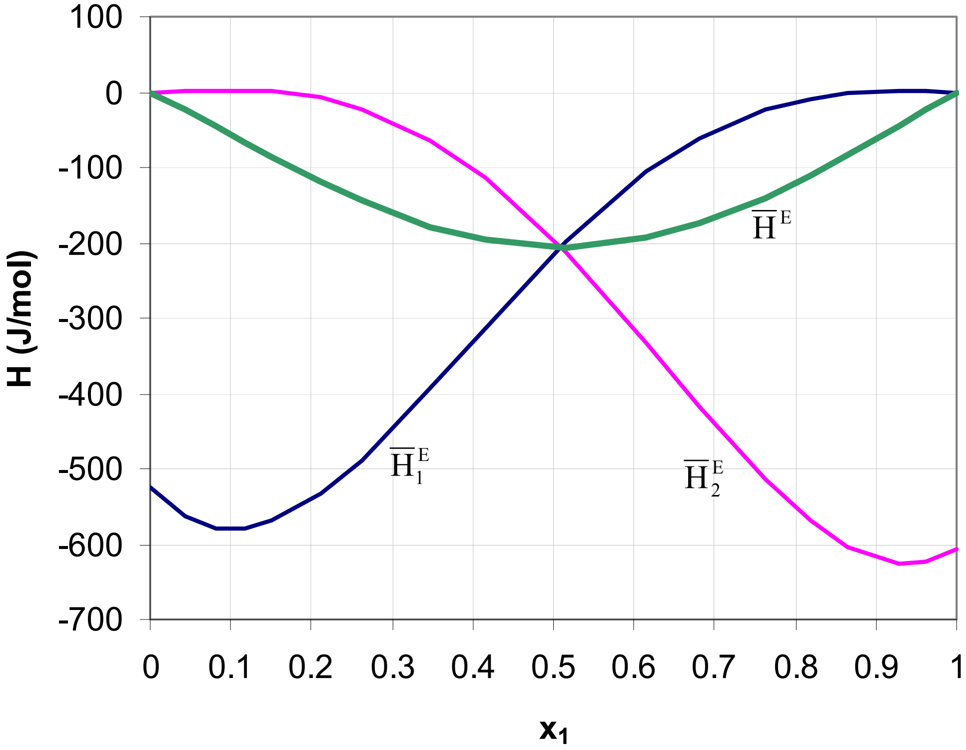
$\overline{H}_1^{E,\infty} = -606$ J/mol

For $x_i = 1$, see part e).

The curves intersect ($\overline{H}_1^E = \overline{H}_2^E$) at $x_1 \sim 0.51$, which is where the minimum of H^E occurs; see part b). '$\overline{M}_1 = \overline{M}_2$ where a minimum of M occurs' is always true for binary systems. See equation [3] and [4] to convince yourself why.

d) $\Delta H = H - \Sigma x_i H_i = H^E$ (p. 436)

So plotting ΔH is the same as plotting H^E, which was done in part b. But just to put together the results, below are H^E, $\overline{H}_1^E$, and $\overline{H}_2^E$ in the same plot.



e) $x_1 = 0$: $H^E = 0$, $\overline{H}_1^E = -524$ J/mol , $\overline{H}_2^E = 0$

$x_1 = 1$: $H^E = 0$, $\overline{H}_1^E = 0$, $\overline{H}_2^E = -606$ J/mol

$$H^E = x_1\overline{H}_1^E + x_2\overline{H}_2^E$$

At $x_1 = 0$, even if $\overline{H}_1^E \neq 0$, as long as $\overline{H}_2^E = 0$, H^E will be 0. Similarly, at $x_1 = 1$.

At $x_1 = 0$ $H^E = (0)\ \overline{H}_1^{E,\infty} + (1)\ (0) = 0$

At $x_1 = 1$ $H^E = (1)\ (0) + (1)\ \overline{H}_2^{E,\infty} = 0$

Physically: At $x_1 \rightarrow 0$, component 2 behaves ideally. Component 1 does not behave ideally but there is so little of component 1 that it does not matter. So overall, we get ideal behavior ($H^E = 0$).

32)

Initial (state 1): $P_1 = 9000$ kPa, $T_1 = 400^oC$
Final (state 2): $P_2 = 300$ kPa, $T_2 = T_1 = T = 400^oC$

$f_2/f_1 = ?$

From definition of fugacity eq (11.30), dropping the subscripts i:

$$G = \Gamma(T) + RT \ln f$$

So at state 2: $G_2 = \Gamma(T) + RT \ln f_2$
at state 1: $G_1 = \Gamma(T) + RT \ln f_1$

the constant of integration Γ only depends on T, which is constant

Subtracting the two equations:

$$G_2 - G_1 = RT(\ln f_2 - \ln f_1) = RT\ln\left(\frac{f_2}{f_1}\right) \qquad \rightarrow \qquad \frac{f_2}{f_1} = \exp\left(\frac{G_2 - G_1}{RT}\right)$$

Mind here that the subscripts refer to states here, not to components.
We only have one component: steam.

From steam table, at 9000 kPa and 400°C,

$H_1 = 3121.2$ kJ/kg; $S_1 = 6.2915$ kJ/kg K

$G_1 = H_1 - TS_1 = 3121$ kJ/kg $-$ (673 K) (6.2915 kJ/kg K) $= -1113$ kJ/kg

From steam table, at 300 kPa and 400°C,

$H_2 = 3275.2$ kJ/kg; $S_2 = 8.0338$ kJ/kg K

$G_2 = H_2 - TS_2 = 3275.2$kJ/kg $-$ (673 K) (8.0338 kJ/kg K) $= -\ 2131$ kJ/kg

$$\frac{f_2}{f_1} = \exp\left(\frac{-2131\,\text{kJ/kg} - (-1113\,\text{kJ/kg})}{(8.314\,\text{J/mol K})(673)}\frac{1000\,\text{J}}{1\,\text{kJ}}\frac{18\,\text{g}}{1\,\text{mol}}\frac{1\,\text{kg}}{1000\,\text{g}}\right) = \mathbf{0.0378}$$