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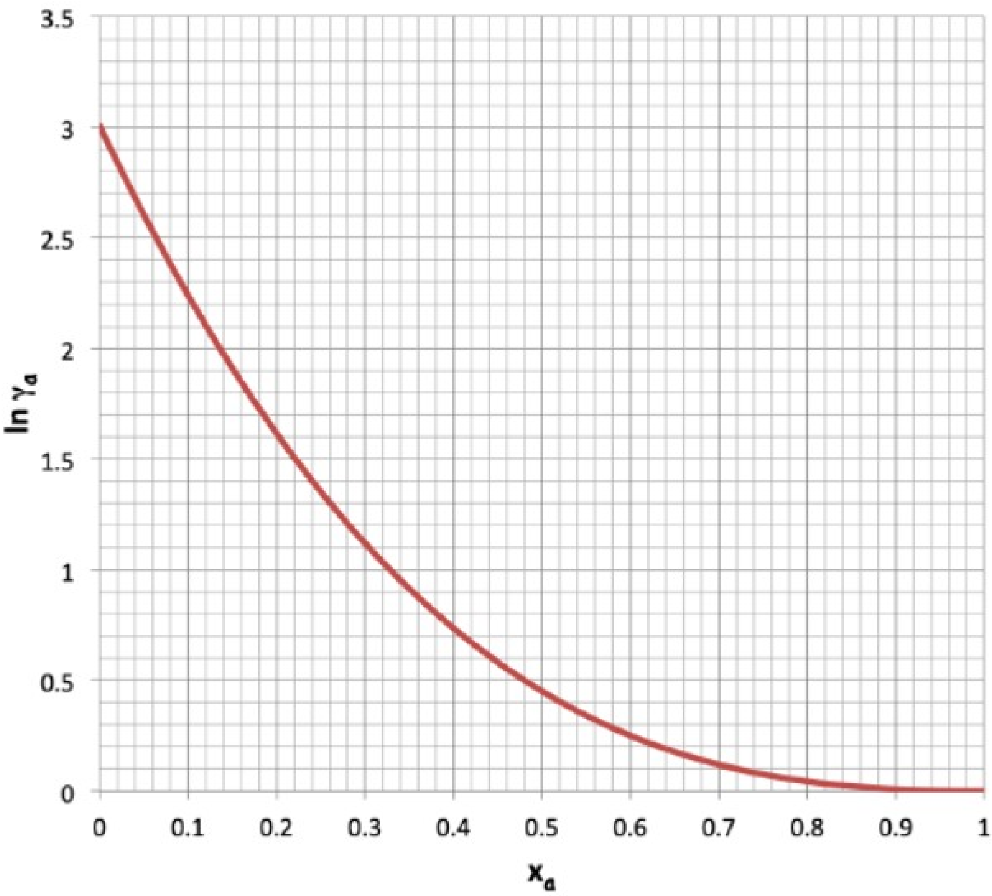
CH19B072

FUGACITY

ASSIGNMENT

30-11-20

1: The plot is given below: ($\ln \gamma_a$ vs x_a)



For the plot,

$$\ln(\gamma_a) \rightarrow 0 \quad \text{as} \quad x_a \longrightarrow 1$$

ie $\gamma_a \longrightarrow 1$ as $x_a \longrightarrow 1$

This is a characteristic of Lewis-Randall reference state.

$\therefore$ Species a is based on $\boxed{\text{Lewis-Randall}}$ reference state

At equilibrium (species a):

$$f_a = f_a^l = f_a^v = \varphi_a^{sat} P_a^{sat} \exp\left[\int_{P_a^{sat}}^{P} \left(\frac{V_a^l}{RT}\right) dP \right]$$

Assumptions:

→ $\varphi_a^{sat} \approx 1$ since $P_a^{sat} = 80$ kPa is low

→ Poyting correction $\left[\exp\left[\int_{P_a^{sat}}^{P} \left(\frac{V_a^l}{RT}\right) dP \right] \right]$ is also assumed to be 1 since P_{system} is low and therefore, P is near to P_a^{sat}

$$\therefore f_a = f_a^l = P_a^{sat} = \boxed{80 \text{ kPa}}$$

From the graph, $\ln(\gamma_a^\infty) = 3$

(the value of $\ln(\gamma_a)$ at $x_a \rightarrow 0$)

⇓

infinite dilution

$$\Rightarrow \gamma_a^\infty = e^3 = 20.08$$

We know.

$$\gamma_a^{\infty} = \frac{H_a}{f_a}$$

$$\Rightarrow H_a = \gamma_a^{\infty} f_a = 20.08 \times 80 \text{ kPa} = \boxed{1606 \text{ kPa}}$$

2) (a) γ_a^{∞} = (already found in qn 1)

$$\boxed{\gamma_a^{\infty} = 20.08}$$

(b) The relation between γ_a^{∞} and $\gamma_a^{\text{Henry's, pure a}}$:

$$\gamma_a^{\text{Henry's, pure a}} = \frac{1}{\gamma_a^{\infty}} = \frac{f_a}{H_a}$$

$$= \frac{1}{20.08}$$

$$= \boxed{0.0498}$$

3) Gibbs - Duhem equation

$$\sum n_i \, d\bar{K}_i = 0$$

For activity coefficient,

$$\sum x_i \, d(\ln \gamma_i) = 0$$

$$\Rightarrow x_a \frac{\partial(\ln \gamma_a)}{\partial x_a} + (1-x_a)\frac{\partial(\ln \gamma_b)}{\partial x_a} = 0$$

$$\Rightarrow \frac{d(\ln \gamma_b)}{dx_a} = \frac{-x_a}{1-x_a}\frac{d(\ln \gamma_a)}{dx_a}$$

Approximating, we get

$$\boxed{(\ln(r_b))_{i+1} = (\ln(r_b))_i - \left(\frac{x_a}{1-x_a} \cdot \frac{\partial(\ln(r_a))}{\partial x_a}\right)_i (\Delta x_a)_i} \rightarrow (1)$$

where $(\Delta x_a)_i = x_{i+1} - x_i$

we find $\frac{\partial(\ln(r_a))}{\partial x_a}$ using centered difference method

$$\left(\frac{\partial(\ln(r_a))}{\partial x_a}\right)_i = \frac{(\ln(r_a))_{i+1} - (\ln(r_a))_{i-1}}{2(\Delta x_a)_i}$$

Reference point : $x_a = 0 \rightarrow$ pure b $(i=0)$ $x_a = 0$

If I choose Lewis-Randall reference state,

As $x_a \rightarrow 0$ $r_b \rightarrow 1$

$$\therefore \boxed{x_a = 0 \quad (\ln(r_b))_0 = 0}$$

$\therefore$ We can use the relation (1) to find $\ln(r_b)$ at all points. First one is shown as example

$\underline{i=1}$: $x_a = 0.02$

$$(\ln(r_b))_{0.02} = (\ln(r_b))_0 - \left(\frac{x_a}{1-x_a}\right)_0 [\quad\quad]$$

$$\quad\quad\quad\quad\quad\quad \downarrow \quad\quad\quad\quad \downarrow$$

$$\quad\quad\quad\quad\quad\quad 0 \quad\quad\quad\quad 0 \quad (x_a \text{ at } i=0 \Rightarrow 0)$$

$$\Rightarrow (\ln(r_b))_{0.02} = 0$$

$\underline{i=2}$: $(x_a)_2 = 0.04$

$$(\ln(r_b))_{0.04} = \underbrace{(\ln(r_b))_{0.02}}_{0} - \left(\frac{x_a}{1-x_a} \cdot \frac{\partial(\ln(r_a))}{\partial x_a}\right)_{0.02} (\Delta x_a)_{0.02}$$

$(\Delta x_a)_{0.02} = 0.04 - 0.02 = 0.02$

$$\left(\frac{\partial(\ln \gamma_a)}{\partial x_a}\right)_{0.02} = \frac{(\ln(\gamma_a))_{0.04} - (\ln(\gamma_a))_{0}}{2 \times 0.02} = \frac{2.7 - 3}{0.04}$$

$$\left(\frac{x_a}{1-x_a}\right)_{0.02} = \frac{0.02}{1-0.02} = \frac{0.02}{0.98}$$

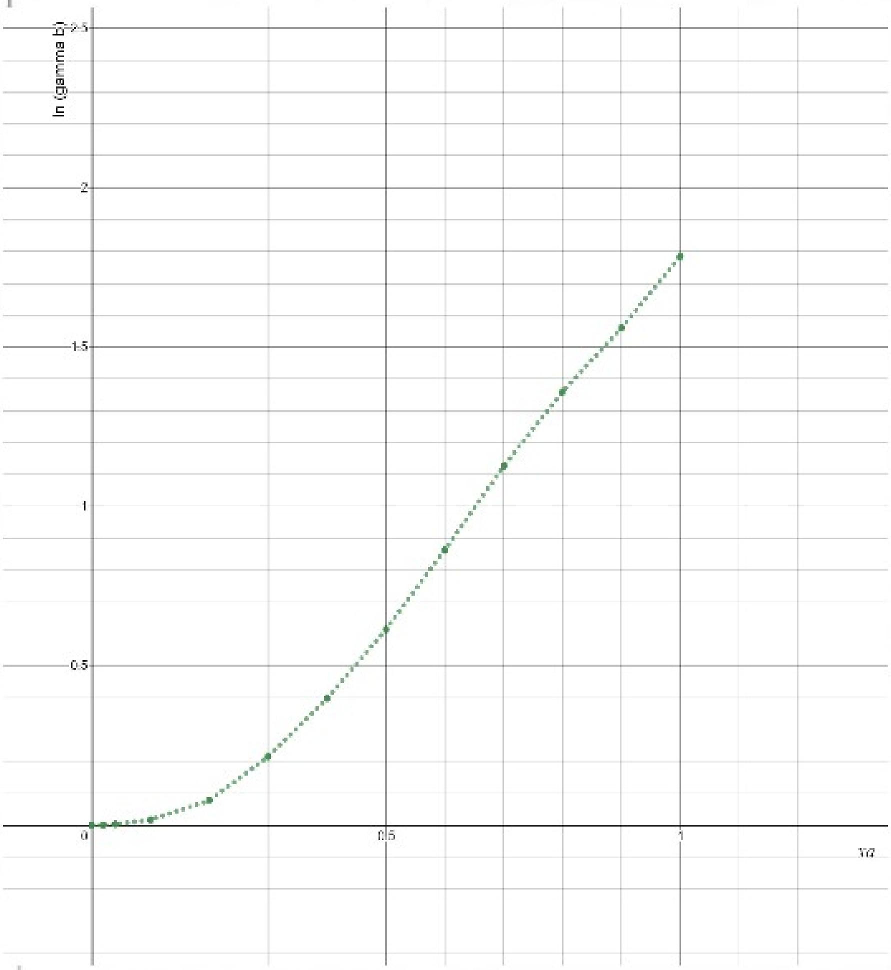
Substituting,

$$(\ln(\gamma_b))_{0.04} = \underline{0.003061}$$

Table:

xa	ln (gamma a)	ln (gamma b)
0	3	0
0.02	2.85	0
0.04	2.7	0.00306122449
0.1	2.2	0.01660289116
0.2	1.6	0.07771400227
0.3	1.1	0.2152140023
0.4	0.75	0.3973568594
0.5	0.45	0.6140235261
0.6	0.25	0.8640235261
0.7	0.1	1.126523526
0.8	0.05	1.359856859
0.9	0	1.559856859
1	0	1.784856859

Plot : $\ln(\gamma_b)$ vs x_a



4) We know,

$a_i = x_i \gamma_i$

$\Rightarrow a_a = x_a \gamma_a$

$\Rightarrow a_b = x_b \gamma_b = (1-x_a)\gamma_b$

We know γ_a and γ_b at different x_a values

$\therefore$ We can find a_a and a_b

$\boxed{a_a = x_a \gamma_a}$ $\boxed{a_b = (1-x_a)\gamma_b}$

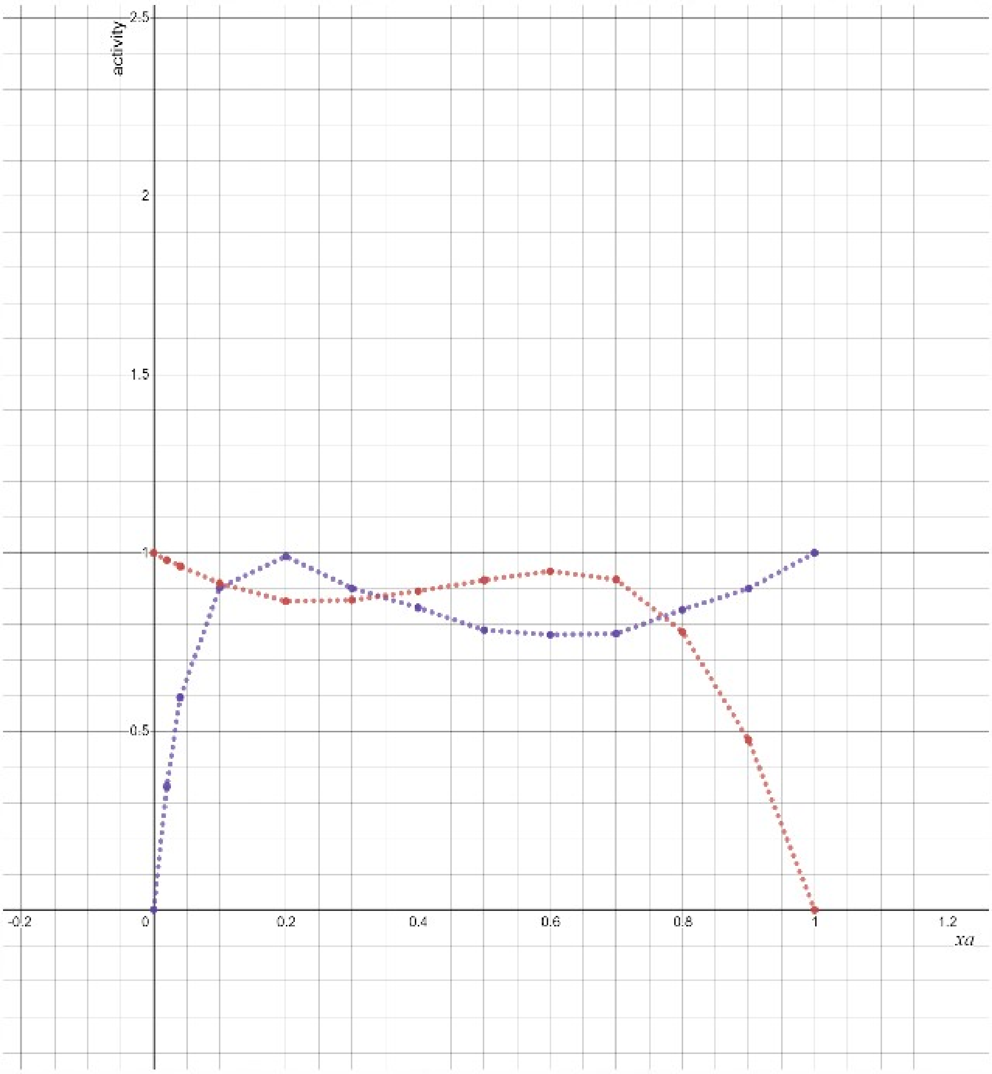
Table showing $a_a \rightarrow$ activity (a) and $a_b \rightarrow$ activity (b):

xa	ln (gamma a)	ln (gamma b)	gamma a	gamma b	activity(a)	activity(b)
0	3	0	20.08553692	1	0	1
0.02	2.85	0	17.28778184	1	0.3457556368	0.98
0.04	2.7	0.00306122449	14.87973172	1.003065915	0.595189269	0.9629432782
0.1	2.2	0.01660289116	9.025013499	1.016741485	0.9025013499	0.9150673366
0.2	1.6	0.07771400227	4.953032424	1.080813504	0.9906064849	0.8646508034
0.3	1.1	0.2152140023	3.004166024	1.240127259	0.9012498072	0.868089081
0.4	0.75	0.3973568594	2.117000017	1.487886802	0.8468000066	0.892732081
0.5	0.45	0.6140235261	1.568312185	1.84785134	0.7841560927	0.9239256698
0.6	0.25	0.8640235261	1.284025417	2.372688086	0.77041525	0.9490752346
0.7	0.1	1.126523526	1.105170918	3.084913216	0.7736196427	0.9254739649
0.8	0.05	1.359856859	1.051271096	3.895635638	0.8410168771	0.7791271277
0.9	0	1.559856859	1	4.758140113	0.9	0.4758140113
1	0	1.784856859	1	5.958726951	1	0

Plot: a_a vs x_a and a_b vs x_a

~~red line~~ → a_b → activity (b) → red line

~~black line~~ → a_a → activity (a) → violet line



5) We know,

$$\gamma_a = \gamma_a^{\infty} \gamma_a^{Henry's}$$

$$\gamma_b = \gamma_b^{\infty} \gamma_b^{Henry's}$$

In (1), we found $\gamma_a^{\infty} = e^3 = 20.08 \Rightarrow \ln(\gamma_a^{\infty}) = \underline{3}$

From Q(3), (plot) $\longrightarrow$ $\ln(\gamma_b^{\infty}) = \underline{1.7848}$

(value of $\ln(\gamma_b)$ at $x_a \to 1$)

$\downarrow$
infinite dilution of b

$$\Rightarrow \ln(\gamma_a^{Henry's}) = \ln(\gamma_a) - \ln(\gamma_a^{\infty}) = \boxed{\ln(\gamma_a) - 3}$$

$$\Rightarrow \ln(\gamma_b^{Henry's}) = \ln(\gamma_b) - \ln(\gamma_b^{\infty}) = \boxed{\ln(\gamma_b) - 1.7848}$$

We know, γ_a and γ_b as a function of x_a.

Therefore, the below table shows the data:

xa	ln (gamma a)	ln (gamma b)	ln (gamma a, Henry's)	ln (gamma b, Henry's)
0	3	0	0	-1.784856859
0.02	2.85	0	-0.15	-1.784856859
0.04	2.7	0.00306122449	-0.3	-1.781795635
0.1	2.2	0.01660289116	-0.8	-1.768253968
0.2	1.6	0.07771400227	-1.4	-1.707142857
0.3	1.1	0.2152140023	-1.9	-1.569642857
0.4	0.75	0.3973568594	-2.25	-1.3875
0.5	0.45	0.6140235261	-2.55	-1.170833333
0.6	0.25	0.8640235261	-2.75	-0.9208333333
0.7	0.1	1.126523526	-2.9	-0.6583333333
0.8	0.05	1.359856859	-2.95	-0.425
0.9	0	1.559856859	-3	-0.225
1	0	1.784856859	-3	0

~~Plot :~~

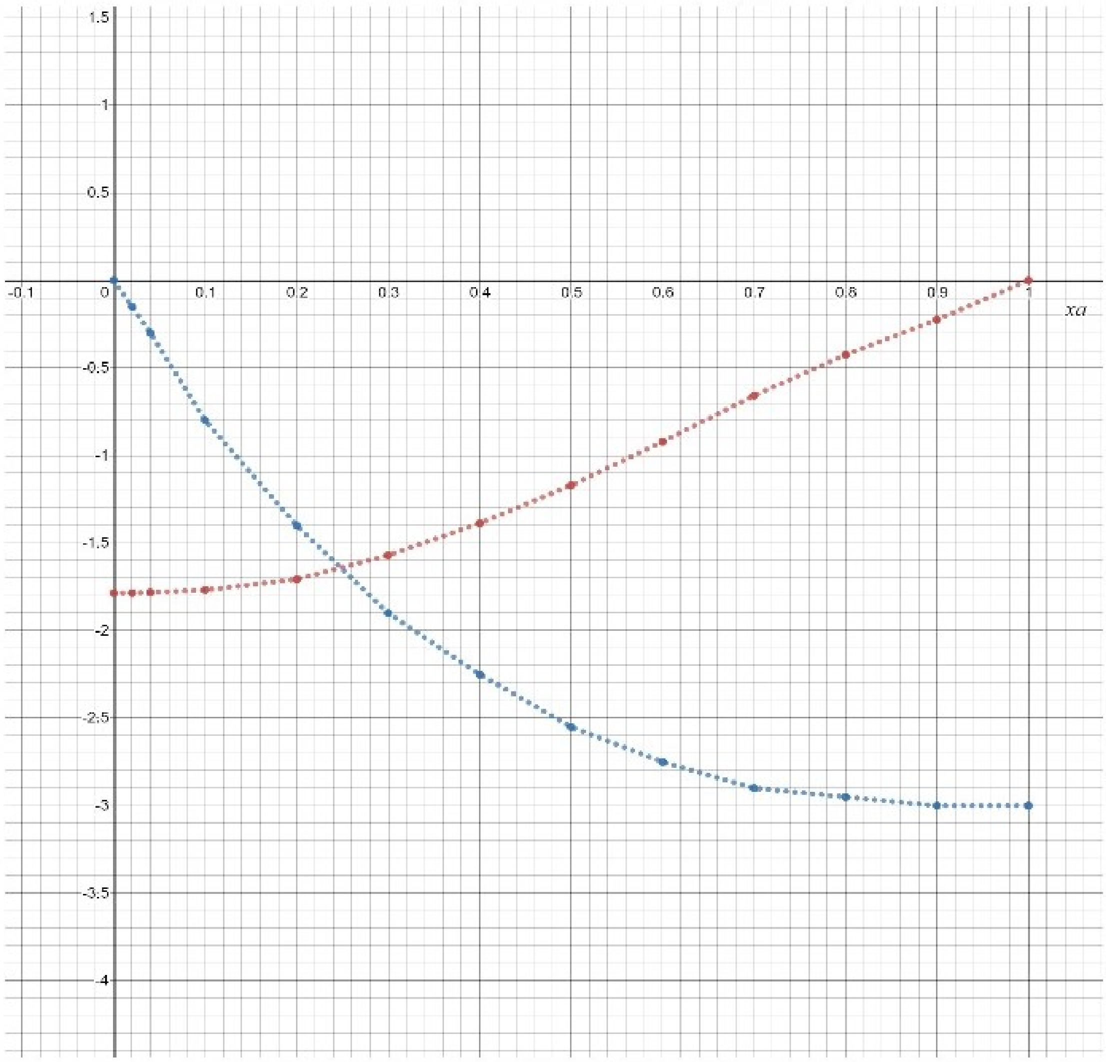
~~green line $\rightarrow \ln(r_a^{Henry's})$~~

~~violet line $\rightarrow \ln(r_b^{Henry's})$~~

Plot : $\ln r_a^{Henry's}$ vs x_a and $\ln r_b^{Henry's}$ vs x_a

$\ln(r_a^{Henry's}) \longrightarrow$ blue line

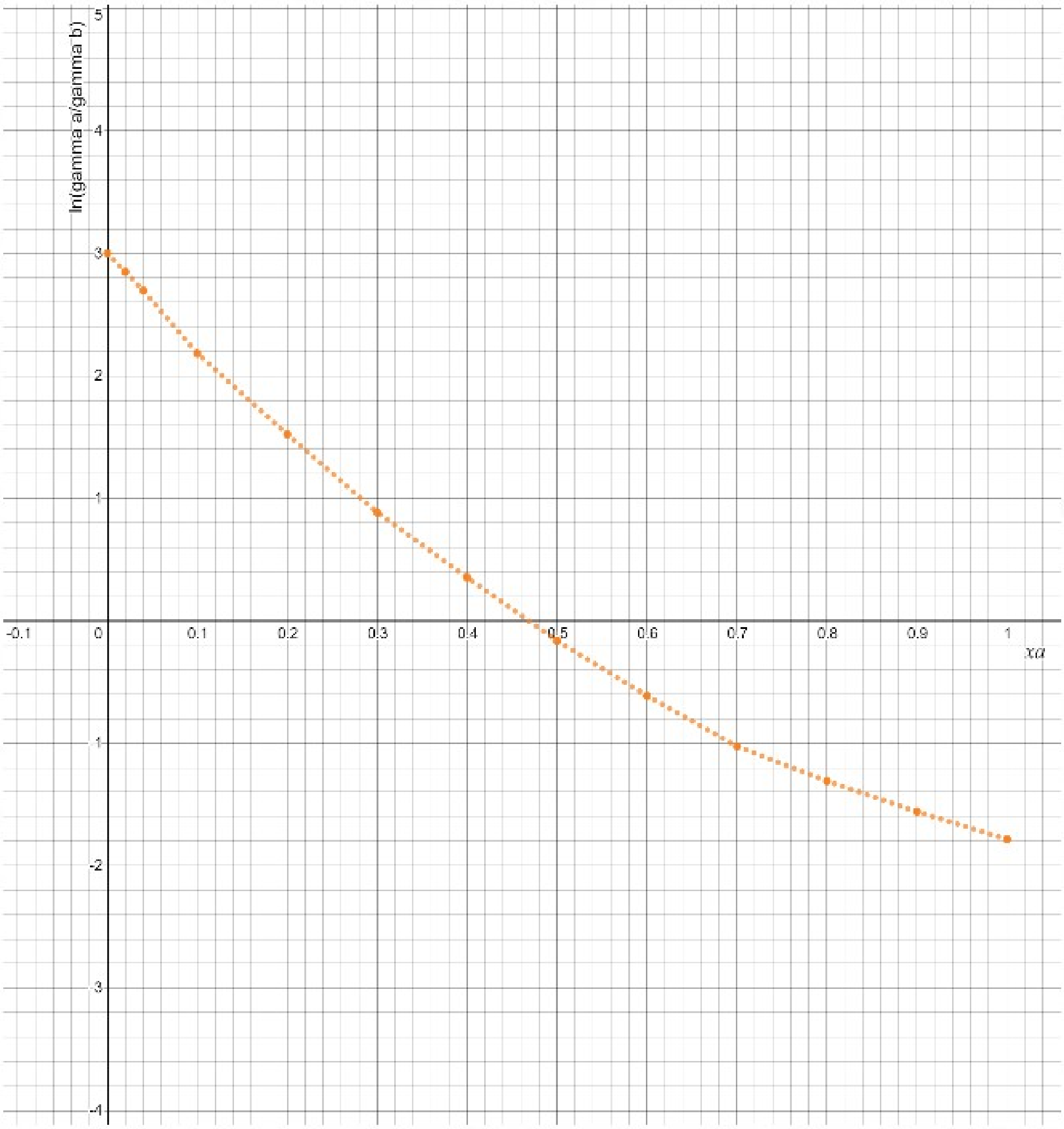
$\ln(r_b^{Henry's}) \longrightarrow$ red line



6) $\ln\left(\frac{\gamma_a}{\gamma_b}\right) = \ln(\gamma_a) - \ln(\gamma_b)$ vs x_a

we have values of $\ln(\gamma_a)$ and $\ln(\gamma_b)$ at various x_a values :

Plot : $\left[\ln\left(\frac{\gamma_a}{\gamma_b}\right) \text{ vs } x_a \right]$



$\int_0^1 \ln\left(\frac{\gamma_a}{\gamma_b}\right) dx_a$ = area enclosed by the above graph and x-axis

We can find this area by ~~counting no. of squares.~~

Trapezoidal rule:

$$\text{Area} \cong \frac{1}{2} \times 0.1 \left[3 + (2.18)2 + (1.52)2 + (0.88)2 + 0.35\right]$$
$$+ \frac{1}{2} \times 0.4 \times 0.06 \quad - \frac{1}{2} \times 0.04 \times 0.25$$
$$- \frac{1}{2} \times 0.1 \left[0.16 + (0.614)2 + (1.023)2 + (1.31)2 + (1.56)2 + 1.78\right]$$

Area $\cong$ 0.0848 $\rightarrow$ close to zero

$\Rightarrow$ quality of experimental data is fairly right

7) $x_a = \frac{8}{10} = 0.8$ $\qquad$ $x_b = 0.2$

From, the graph, we can find $\ln(\gamma_a)$ at $x_a = 0.8$

$$\ln(\gamma_a) = 0.05 \quad \Rightarrow \quad \gamma_a = 1.05$$

At equilibrium,

$$\hat{f}_a^{v} = \hat{f}_a^{l} = x_a \gamma_a f_a^{o} = 0.8 \times 1.05 \times 80\,\text{kPa}$$
$$\hat{f}_a^{v} = 67.2\,\text{kPa}$$

The vapor mole fraction can be determined from the definition of fugacity in the vapor phase if we assume ideal gas behaviour (reasonable at 1 bar)

$\hat{f}_a^{\,v} = y_a P$ $\quad\quad$ $P = 1$ bar (given)

$y_a = \dfrac{67.2 \text{ kPa}}{100 \text{ kPa}} = \cancel{0.6656}$ $\quad$ $\underline{\underline{0.672}}$

8) Assume the two-suffix Margules equation :

$$g^E = A x_a x_b$$

$$\therefore \quad \overline{G}_a^E = RT \ln(\gamma_a) = A x_b^2 = A(1-x_a)^2$$

$$\boxed{RT \ln(\gamma_a) = A(1-x_a)^2}$$

$T = 300$ K $\quad\quad$ $R = 8.314$ J/mol K

We know $\ln(\gamma_a)$ vs x_a

$\therefore$ We can calculate A as

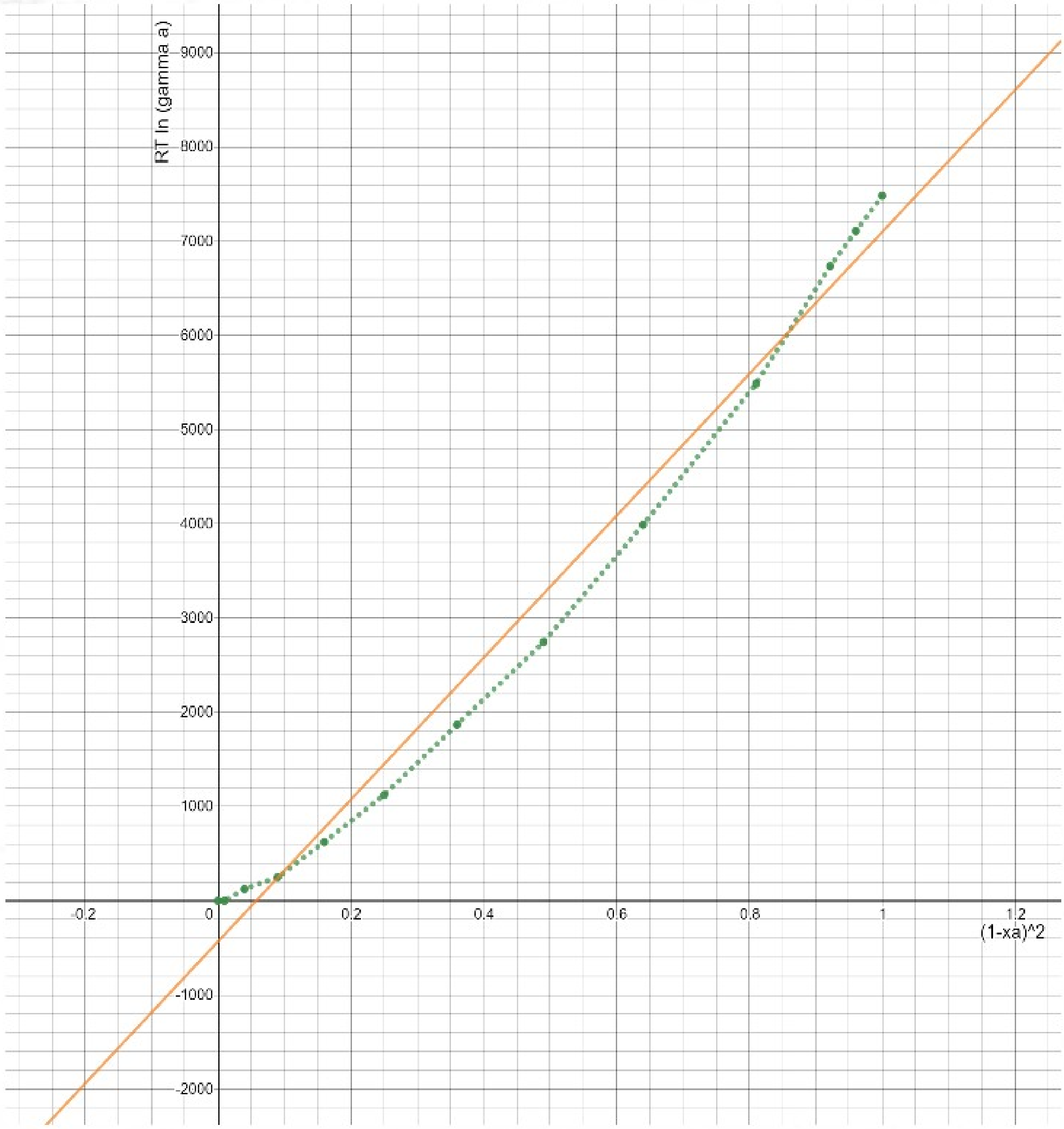
$$\boxed{A = \text{slope of } RT\ln(\gamma_a) \text{ vs } (1-x_a)^2}$$

Table:

xa	(1-xa)^2	ln (gamma a)	RT ln (gamma a)
0	1	3	7482.6
0.02	0.9604	2.85	7108.47
0.04	0.9216	2.7	6734.34
0.1	0.81	2.2	5487.24
0.2	0.64	1.6	3990.72
0.3	0.49	1.1	2743.62
0.4	0.36	0.75	1870.65
0.5	0.25	0.45	1122.39
0.6	0.16	0.25	623.55
0.7	0.09	0.1	249.42
0.8	0.04	0.05	124.71
0.9	0.01	0	0
1	0	0	0

Plot: $RT\ln(\gamma_a)$ vs $(1-x_a)^2$

Orange-line $\Rightarrow$ curve-fit line



slope of fitted line = A = ~~7495~~ ~~75319~~ 7531.9

$\therefore$ ~~A = 7495 J/mol~~

$\boxed{A = 7531.9 \text{ J/mol}}$

9) 3-suffix Margules eqn:

$$g^E = x_a x_b [A + B(x_a - x_b)]$$

$$\Rightarrow \boxed{RT \ln \gamma_a = (A+3B)(1-x_a)^2 + \cancel{\phi} -4B(1-x_a)^3}$$

In this case, we plot $\underline{\underline{RT \ln \gamma_a \text{ vs } (1-x_a)}}$

$RT \ln \gamma_a \rightarrow y$, $(1-x_a) \rightarrow x$

Table:

xa	(1-xa)	RT ln (gamma a)
0	1	7482.6
0.02	0.98	7108.47
0.04	0.96	6734.34
0.1	0.9	5487.24
0.2	0.8	3990.72
0.3	0.7	2743.62
0.4	0.6	1870.65
0.5	0.5	1122.39
0.6	0.4	623.55
0.7	0.3	249.42
0.8	0.2	124.71
0.9	0.1	0
1	0	0

Plot:

The plot is $RT \ln \gamma_a$ vs $(1-x_a)$

$RT \ln \gamma_a \rightarrow y$, $(1-x_a) \rightarrow x$

~~Green~~ Orange - line : cubic regression line

~~Green~~ Orange - line is represented as

$$y = ax^3 + bx^2 + cx + d$$

As expected, c and d are close to 0

$a = 6400$

$b = 933.63$

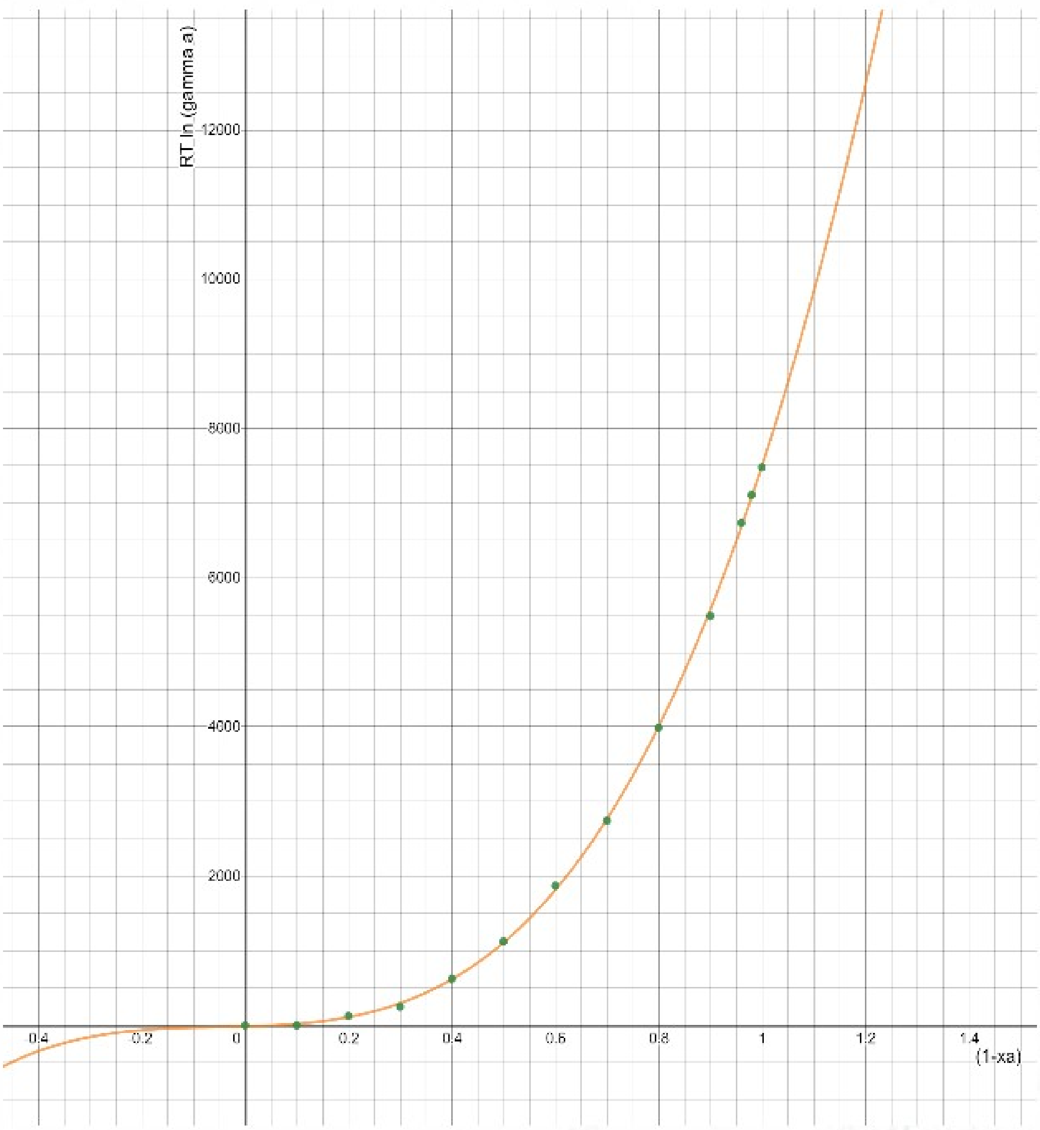
$\therefore$ orange line: $y = 6400x^3 + 933.63x^2$

org eqn: $y = (A+B)x^3 + -4Bx$

Comparing,

$$\boxed{A = 6633.4075 \text{ J/mol} \qquad B = -233.4075 \text{ J/mol}}$$

Plot:



10) $g_a = 50\ J/mol \qquad g_b = 100\ J/mol$

$$x_a g_a + x_b g_b = 50 x_a + (1 - x_a)\,100$$

$$\Delta g_{mix}^{ideal} = RT(x_a \ln x_a + x_b \ln x_b)$$

$$g^E = A x_a x_b = A x_a (1 - x_a) = 7531.9\,(x_a(1 - x_a))$$

Table with values:

$$\left(g^{total} = x_a g_a + x_b g_b + \Delta g_{mix}^{ideal} + g^E \right)$$

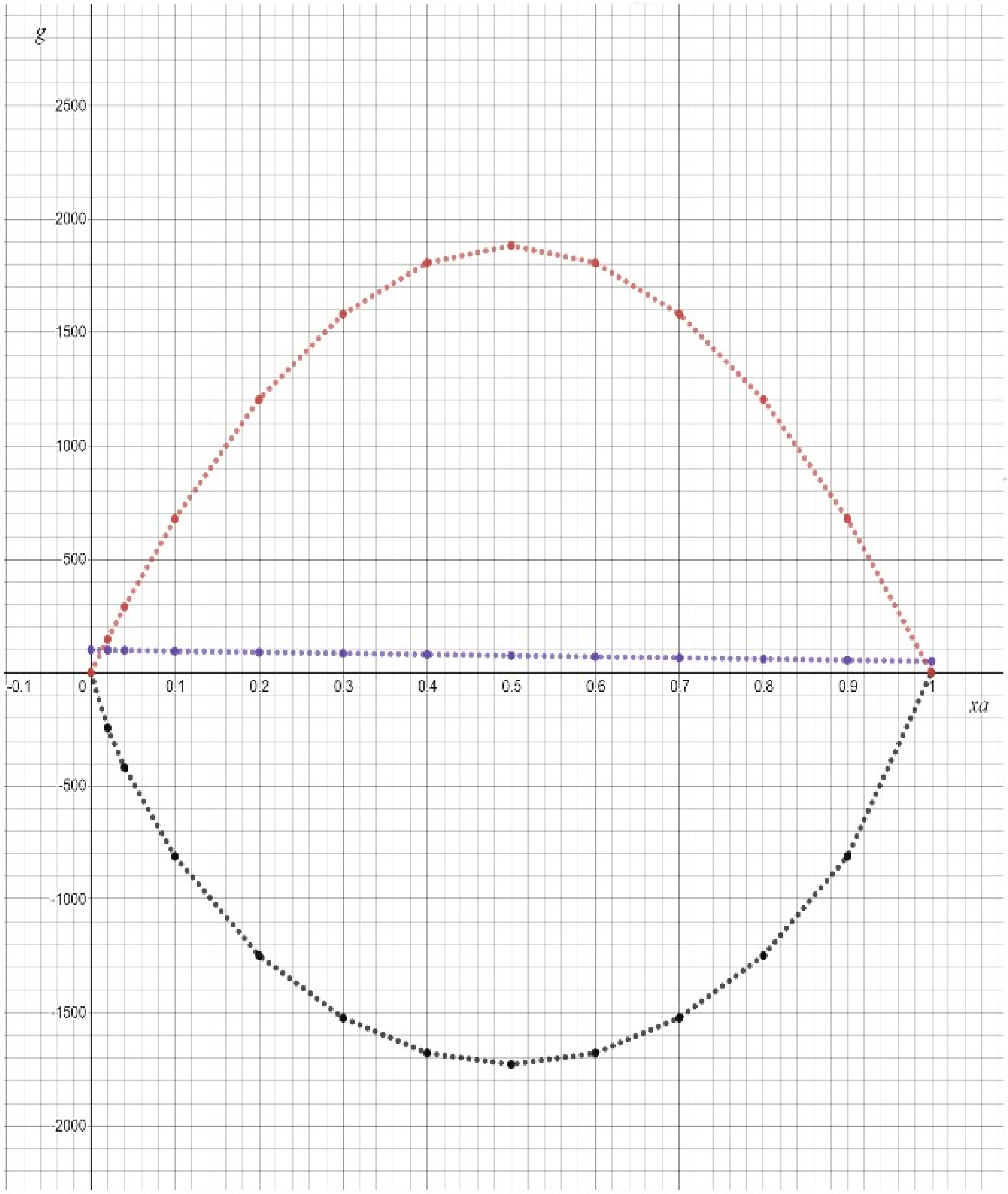
xa	xaga+xbgb	delta(g-mix, ideal)	gE, excess energy	gT, total energy
0	100	0	0	100
0.02	99	-244.5291563	147.62524	2.096083658
0.04	98	-418.8862933	289.22496	-31.66133328
0.1	95	-810.8219522	677.871	-37.95095223
0.2	90	-1248.103725	1205.104	47.00027521
0.3	85	-1523.617742	1581.699	143.0812578
0.4	80	-1678.6257	1807.656	209.0303001
0.5	75	-1728.847698	1882.975	229.1273022
0.6	70	-1678.6257	1807.656	199.0303001
0.7	65	-1523.617742	1581.699	123.0812578
0.8	60	-1248.103725	1205.104	17.00027521
0.9	55	-810.8219522	677.871	-77.95095223
1	50	0	0	50

Plot :

$x_a g_a + x_b g_b \longrightarrow$ violet line

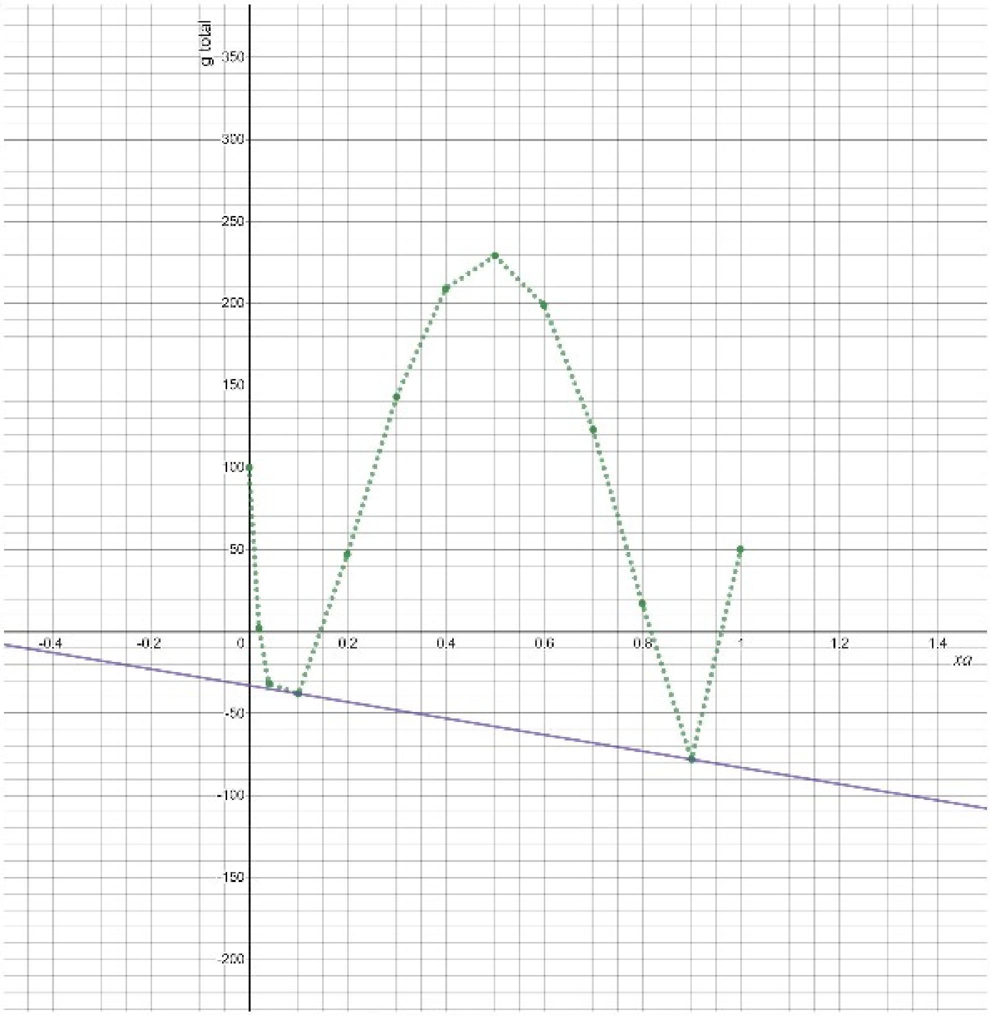
$\Delta g_{mix}^{ideal} \longrightarrow$ black line

$g^E \longrightarrow$ red line



11) Plot of g^{total} vs x_a :

violet line → required tangent



OBSERVATIONS

→ 2 minima and 1 maxima

→ Tangent joining two minima

↓

this tangent shows the g value of phase-separated mixtures. The mixture will exist with two compositions in this area because, in this case, the total gibbs free energy is smaller than any point on the curve (between these 2 minima)

12) Assume $A = \cancel{7531.9}$ -7531.9 J/mol

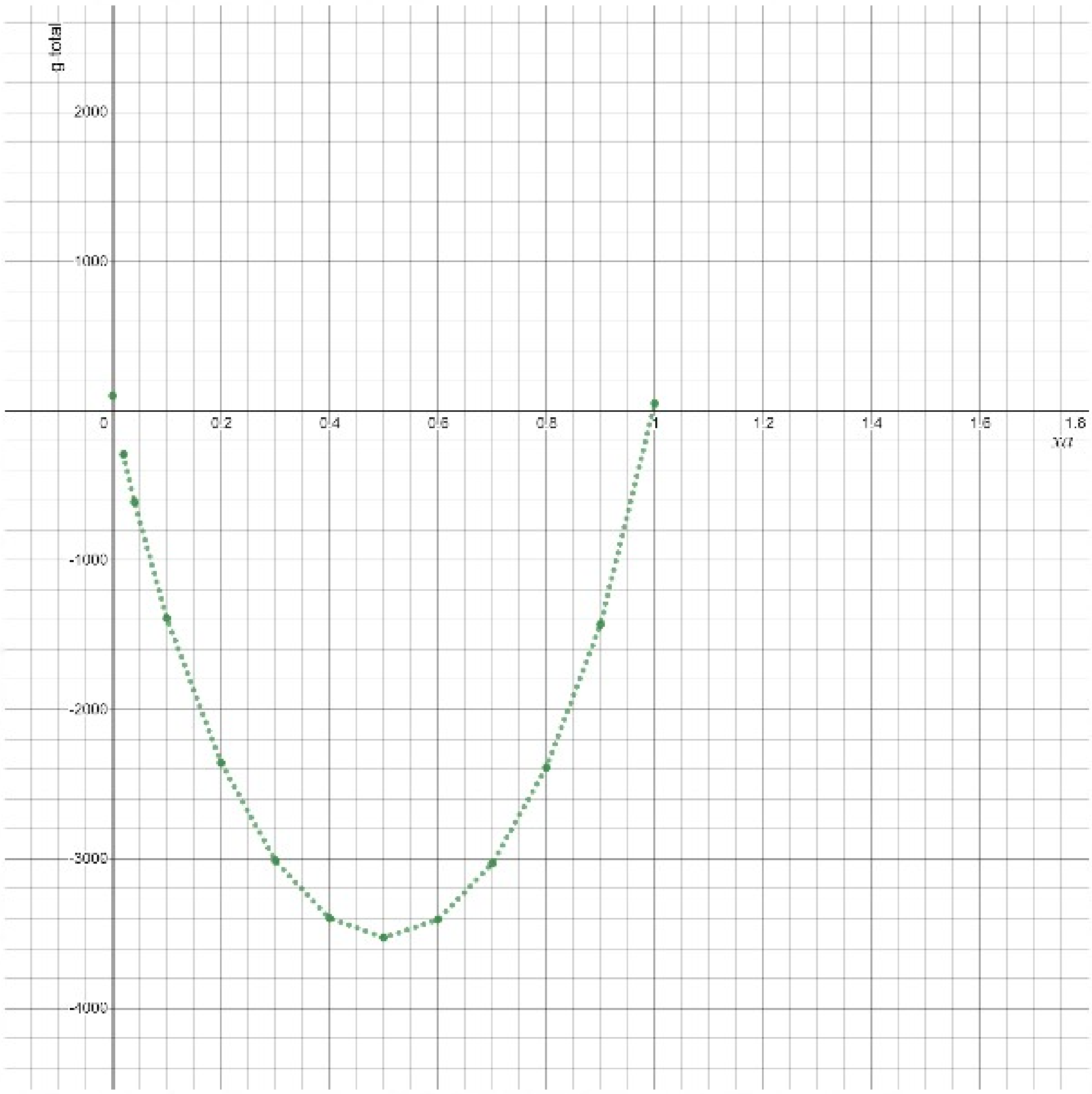
$$g^{total} = g_a x_a + g_b x_b + \Delta g_{mix}^{ideal} + g^E$$

(same as previous case → except A is -ve)

Table:

xa	xaga+xbgb	delta(g-mix, ideal)	gE, excess energy	gT, total energy
0	100	0	0	100
0.02	99	-244.5291563	-146.902	-292.4311563
0.04	98	-418.8862933	-289.22496	-610.1112533
0.1	95	-810.8219522	-674.55	-1390.371952
0.2	90	-1248.103725	-1199.2	-2357.303725
0.3	85	-1523.617742	-1573.95	-3012.567742
0.4	80	-1678.6257	-1798.8	-3397.4257
0.5	75	-1728.847698	-1873.75	-3527.597698
0.6	70	-1678.6257	-1798.8	-3407.4257
0.7	65	-1523.617742	-1573.95	-3032.567742
0.8	60	-1248.103725	-1199.2	-2387.303725
0.9	55	-810.8219522	-674.55	-1430.371952
1	50	0	0	50

Plot : (g_{total} vs x_a) : A is negative



Observations

→ The plot is concave parabolic in this case

→ Here, there is only one minima, so phase separation does not occur.