1. (a) A typical melting curve for a pure component is given in the adjacent figure (1) where pressure is held constant. Schematically plot μ for the same as a function of T. (3 points)

b obtain $\underline{G}_n$, $\bar{G}_n$, and ΔG_{mix}.

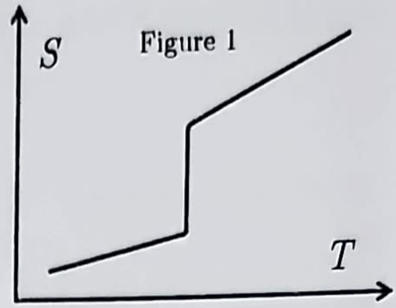


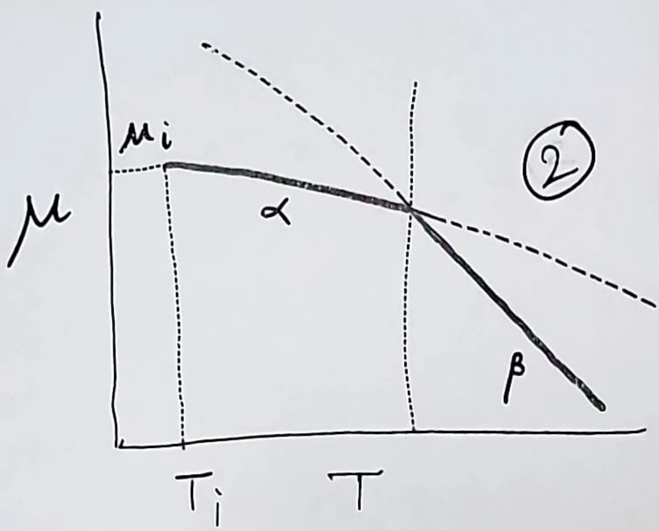
Figure 1

We know that,

for a single pure component:

$$d\mu = -s\,dT \qquad T_i \equiv \text{initial}$$

$$\mu - \mu_i = -\int_{T_i}^{T} s\,dT \quad (1)$$



(b) The Gibbs energy [in kJ/mol] of a binary mixture of species a and species b at 300 K and 10 bar is given by the following expression:

$$\underline{G} = -40x_a - 60x_b + RT\left(x_a \ln x_a + x_b \ln x_b\right) + 5x_a x_b$$

For a mixture containing 1 mol of species a and 4 mol of species

To obtain $\underline{G}_a$, $x_a = 1$ and $x_b = 0$

$$\boxed{\underline{G}_a = 40 \text{ kJ/mol}} \quad 2$$

For

$$\bar{G}_a = \underline{G} - x_b \frac{d\underline{G}}{\partial x_b} \quad 1$$

$$\frac{d\underline{G}}{\partial x_b} = 40 - 60 + RT\left(-\ln x_a - 1 + \ln x_b + 1\right) + 5x_a - 5x_b$$

$$\bar{G}_a = -40 + RT \ln x_a + 5x_b^2$$

$$x_a = \frac{1}{5} = 0.2 \qquad x_b = \frac{4}{5} = 0.8$$

$$\bar{G}_a = -40 + \frac{8.314\,(300)}{1000} \ln(0.2) + 5(0.64)$$

$$\boxed{\bar{G}_a = -40.8 \text{ kJ/mol}} \quad 1$$

$$\Delta G_{mix} = n\left(\underline{G} - x_a \underline{G}_a - x_b \underline{G}_b\right)$$

$$= \left(RT\left(x_a \ln x_a + x_b \ln x_b\right) + 5x_a x_b\right) n \quad 1$$

$$\Delta G_{mix} = -2.2 \text{ kJ}. \quad 1$$

(c) Consider that the pure species are mixed at the same T and P. Assume that the work done in the process of mixing is negligible. If the entropy of mixing ΔS_{mix} is assumed to be identical to that associated with ideal mixtures, estimate the heat interaction (write in words whether heat is needed to be supplied or removed). (6 points)

The heat interaction for mixing is given by (for ideal mixing)

$$\Delta H^{IM}_{mix} = \Delta G^{IM}_{mix} + T \Delta S^{IM}_{mix}$$

For ideal mixtures

$$\Delta G^{IM}_{mix} = RT \sum_i N_i \ln x_i \quad 2$$

$$\Delta S^{IM}_{mix} = -R \sum N_i \ln x_i \quad 2$$

Consequently,

$$\Delta H^{IM}_{mix} = \Delta G^{IM}_{mix} + T \Delta S^{IM}_{mix} = 0 \quad 1$$

For ideal mixing neither heat will be supplied nor will be removed. 1

(d) Define fugacity from the first principles. How much is the fugacity of an ideal gas. (5 points)

The fugacity is defined as: 3

$$f = P \exp\left(\frac{\mu(T,P) - \mu^{IG}(T,P)}{RT}\right)$$

For an ideal gas $\mu(T,P) = \mu^{IG}(T,P)$

Hence $f = P$.

For ideal gases fugacity is equal to P. 2

[2.]

(a) At equilibrium,

$$\hat{f}_a^{\alpha} = \hat{f}_a^{\beta}$$

→ Applying Lewis/Randall reference state;

→ $x_a^{\alpha} \gamma_a^{\alpha} f_a = x_a^{\beta} \gamma_a^{\beta} f_a$ (For species a)

$$\therefore \boxed{x_a^{\alpha} \gamma_a^{\alpha} = x_a^{\beta} \cdot \gamma_a^{\beta}}$$ ✓1

→ $x_b^{\alpha} \gamma_b^{\alpha} f_b = x_b^{\beta} \gamma_b^{\beta} f_b$ (For species b)

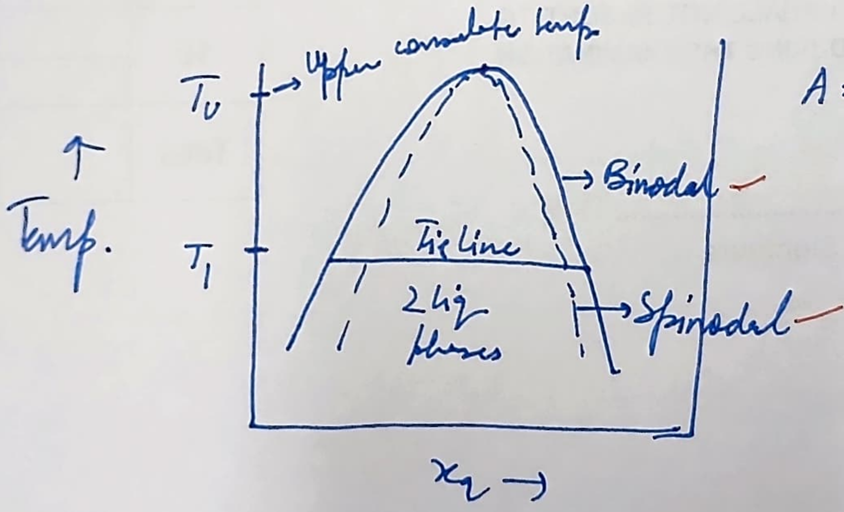
$$\therefore \boxed{x_a^{\alpha} \gamma_a^{\alpha} = x_a^{\beta} \cdot \gamma_a^{\beta}}$$ ✓1

2

(b) Using the relations derived in (a);

$$\boxed{x_a^{\alpha} \cdot \exp\left(\frac{A(1-x_a)^2}{RT}\right) = x_b \cdot \exp\left(\frac{A(1-x_b)^2}{RT}\right)}$$

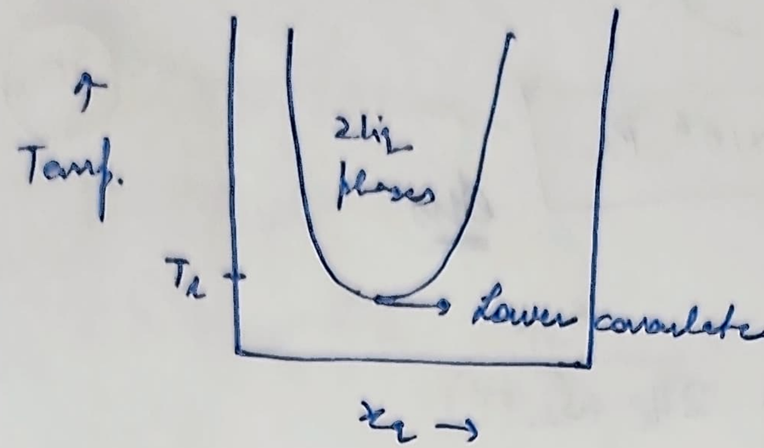
(c)



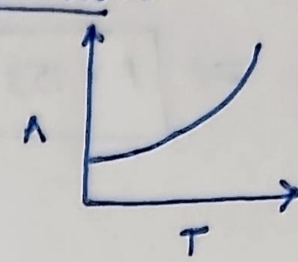
A = constant ✓

3

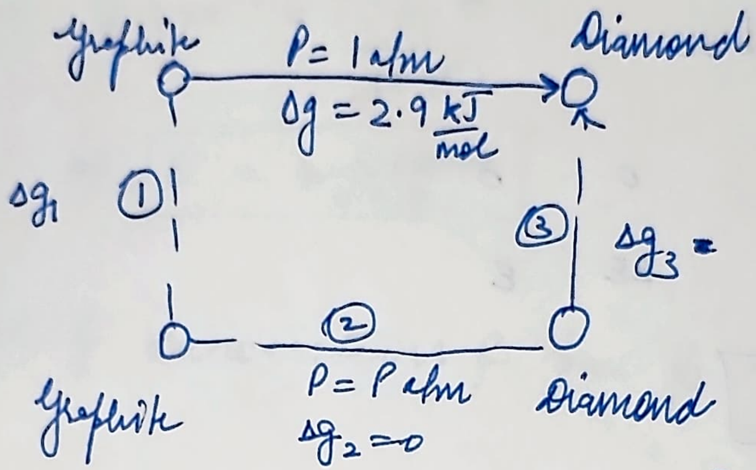
(d)



→ A increases with temperature



$\boxed{3}$



→ At constant T :- $dg_i = v_i dP - \cancel{s_i dT}^{\,0}$ — 1

→ From the above diagram;

$$\Delta g = \Delta g_1 + \Delta g_2 + \Delta g_3 \quad \text{— 2}$$

$$2.9 \frac{kJ}{Mol} = \int_1^P V_{graphite}\, dP + 0 + \int_P^1 V_{dia} \cdot dP \quad \text{— 2}$$

As both graphite & Diamond are incompressible; 1

$$2.9 = (V_{graphite} - V_{dia})(P - 1) \quad \text{— 2}$$

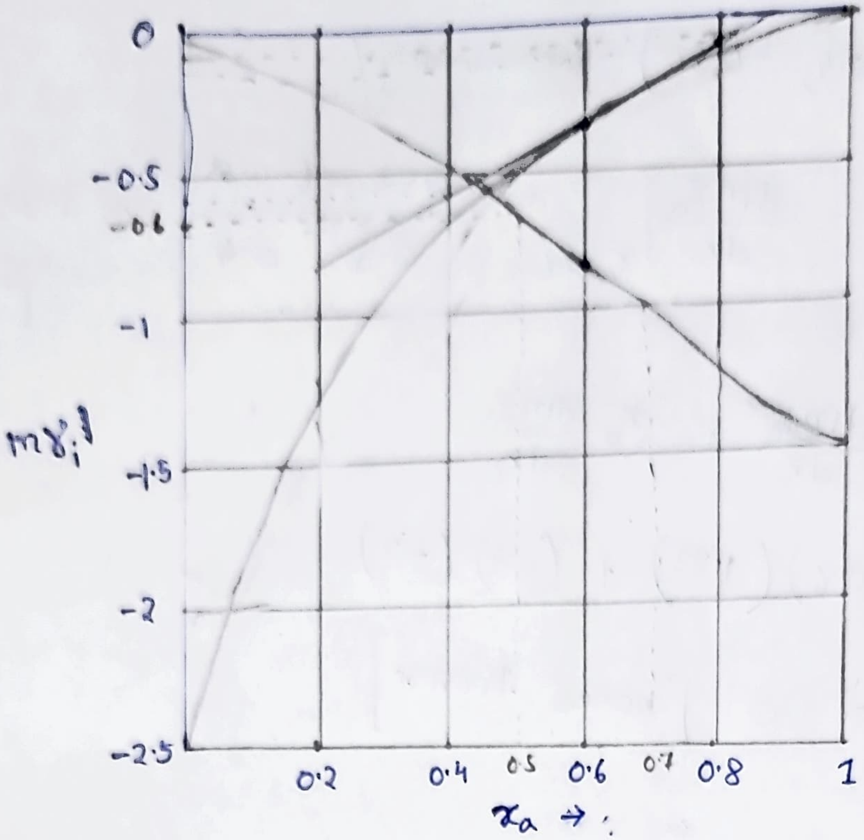
$$2.9 \times 10^3 \frac{J}{mol} = \left(\frac{1}{2.26} - \frac{1}{3.51}\right)\left(12 \times \frac{1}{10^6}\right)\left(P - 1.01 \times 10^5\right)$$

10

$$\Rightarrow \boxed{P = 1533.7 \times 10^6 \ Pa}$$ -2

Ans

4. (a)



Given: $T = 300\ K$, $x_a = 0.6$.

Gibbs-Duhem equation:- $RT\,\Sigma\, x_i d(\ln\gamma_i) = 0$

$$\Rightarrow x_a\, d\ln\gamma_a + x_b\, d\ln\gamma_b = 0$$

$$\Rightarrow x_a \frac{d\ln\gamma_a}{dx_a} + x_b \frac{d\ln\gamma_b}{dx_a} = 0$$ ✓ 1

↳ This we have to prove from the graph.

We need to calculate slope near $x_a = 0.6$.

$\ln\gamma_b$ vs x_a plot has a constant slope between $x_a = 0.5$ and $x_a = 0.7$

$$\therefore \frac{d\ln\gamma_b}{dx_a} = \frac{-1-(-0.6)}{0.7-0.5} = \frac{-0.4}{0.2} = 2$$ ✓ 2

$\ln \gamma_a$ vs x_a Plot has varying slope, near $x_a = 0.6$

We construct a tangent at $x_a = 0.6$. It cuts at $(0.8, -0.02)$

and at $(0.4, -0.55)$ [approximately].

Hence, $$\left.\frac{d\ln\gamma_a}{dx_a}\right|_{x_a=0.6} = \frac{-0.02-(-0.55)}{0.8-0.4} \approx 1.33$$ ✓ 2

$$\therefore\ x_a \frac{d\ln\gamma_a}{dx_a} + x_b \frac{d\ln\gamma_a}{dx_b}$$

$$= (0.6)(1.33) + (0.4)(-2)$$ ✓ 1

$$\approx 0 \text{ [hence, Proved]}$$

(b) We can't conclude whether species a and species b can be separated by distillation or not, because we don't know from the given data whether they are forming azeotrope or not.

4

If they form azeotrope, $y_a P = x_a \gamma_a P_a^{sat}$ and $y_b P = x_b \gamma_b P_b^{sat}$

and at azeotropic point, $y_a = x_a$ and $y_b = x_b$, in that case,

$$\gamma_a P_a^{sat} = \gamma_b P_b^{sat}.$$

$$\Rightarrow \frac{\gamma_a}{\gamma_b} = \frac{P_b^{sat}}{P_a^{sat}}$$

We don't have information about P_b^{sat} and P_a^{sat}, we only have idea about γ_a and γ_b. Hence, we don't know whether they will form azeotrope or not.

(5)

At 60°C ethanol (1) and ethyl acetate (2) exhibit an azeotrope at a pressure of 0.64 bar and x_1 =0.4.

(a) Use Margules equation as a model for G^{ex} determine the Margules parameter C. (5 Points)

(b) At 60°C, what is the composition of the vapor in equilibrium with a liquid of composition x_1 =0.8 (5 Points)

Use Antoine's equation to obtain the saturation pressures

$\ln\left(P^{sat}[\text{bar}]\right) = A - \left[B/(T[K]+C)\right]$	A	B	C
Ethanol	12.2917	3803.98	- 41.68
Ethyl acetate	9.5314	2790.5	- 57.15

(c) Do you think Margules equation is sufficient to model this system? (2 Points)

At the azeotrope, we have,

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

P_1^{sat} and P_2^{sat} can be obtained from Antonine's equation as:

For ethanol: $P_1^{sat} = \exp\left(A - \dfrac{B}{T+C}\right)$

$$= \exp\left(12.2917 - \frac{3803.98}{60+273.17-41.68}\right)$$

$$= 0.468 \text{ bar}$$

For ethyl acetate

$$P_2^{sat} = \exp\left(9.5314 - \frac{2790.5}{60+273.15-57.15}\right)$$

$$= 0.56 \text{ bar} \quad (1)$$

Hence

$$\gamma_1 = \frac{0.64}{0.468} = 1.37 \text{ and}$$

$$\gamma_2 = \frac{0.64}{0.56} = 1.142 \quad (1)$$

For 2 suffix Margulus equation

$RT \ln \gamma_1 = A x_2^2$ and $RT \ln \gamma_2 = A x_1^2$

For specie 1

$$8.314 \frac{J}{mol\,K} \times 333.15\,K \times \ln(1.37) = A(0.6)^2$$

$$A = 2422 \frac{J}{mol}$$ (1)

For specie 2

$$8.314 \times 333.15 \times \ln(1.14) = A(0.4)^2$$

$$A = 2311 \frac{J}{mol}$$ (1)

Therefore average value of $A = 2366 \frac{J}{mol}$. (1)

(b). We have at $60°C$, $x_1 = 0.8$,

hence $\gamma_2 = \exp\left(\frac{A x_1^2}{RT}\right) = \exp\left(\frac{2366\,(0.8)^2}{8.314 \times 333.15}\right) = 1.73$ (1)

$$\gamma_1 = \exp\left(\frac{A x_2^2}{RT}\right) = \exp\left(\frac{2366\,(0.2)^2}{8.314 \times 333.15}\right) = 1.03$$ (1)

y_1 is given by

$$y_1 = \frac{x_1 \gamma_1 P_1^{sat}}{x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat}} = \frac{0.8\,(1.03)\,(0.468)}{0.8 \times 1.03 \times 0.468 + 0.2 \times 1.73 \times 0.56}$$ (2)

$$= 0.67$$ (1)

$$y_2 = 1 - y_1 = 0.33$$

(c) Margulus (2 suffix) equation is sufficient to model the system as value of A obtained from 2 ways is not very different. (2)

6

$$2H_2S \rightleftharpoons 2H_2 + S_2$$

$\rightarrow$ $K_{eq} = 2.17 \times 10^{-5}$ bar

$\rightarrow$ $P = 1$ bar

Initial :	1	0	0
ξ^m :	$1-2\varepsilon$	2ε	ε

✓ 1

$$\boxed{N_T = 1+N+\varepsilon}$$

✓ 2

$\rightarrow$ $y_{H_2S} = \dfrac{1-2\varepsilon}{1+N+\varepsilon}$, $y_{H_2} = \dfrac{2\varepsilon}{1+N+\varepsilon}$, $y_{S_2} = \dfrac{\varepsilon}{1+N+\varepsilon}$ ✓ 1

For gas phase :-

$$K = \pi (y_i \hat{\phi}_i)^{\nu_i} \cdot P^{\nu}$$

✓ 2

$$2.17 \times 10^{-5} = \left(\frac{\varepsilon}{1+N+\varepsilon}\right) \cdot \left(\frac{2\varepsilon}{1+N+\varepsilon}\right)^2 \cdot \left(\frac{1+N+\varepsilon}{1-2\varepsilon}\right)^2 \cdot (P)^1$$

$$\boxed{2.17 \times 10^{-5} = \frac{4\varepsilon^3 P}{(1+N+\varepsilon)(1-2\varepsilon)^2}} \quad \text{— (1)}$$

✓ 1

(b) For $N = 0$, $P = 1$ bar, $T = 700°C$

→ Using ①;

$$2.17 \times 10^{-5} = \frac{4\varepsilon^2}{(1+\varepsilon)^2 \cancel{(1-2\varepsilon)}} \times 1$$

$$\therefore\ 2.17 \times 10^{-5} = \frac{4\varepsilon^3}{\cancel{1+\varepsilon}\ 1}$$

$$\Rightarrow \boxed{\varepsilon = \cancel{2.3 \times 10^{-3}}\ 0.018}$$ ✓ 2

→ Extent of dissociation of pure $H_2 = 2\varepsilon$ ✓ 1

$= \underline{\underline{0.036}}$ $\underline{\underline{\text{Ans}}}$

(7) Given,

$$P = \frac{RT}{V} - \frac{A}{\sqrt{TV^3}} \quad \text{——} \ (1)$$

& $$A = a_1 y_1 + a_2 y_2$$

for ϕ_1 $\quad y_1 = 1$ & $y_2 = 0$

$$\Rightarrow A = a_1$$

Now,

$$P = \frac{RT}{V} - \frac{a_1}{T^{1/2} V^{3/2}} \quad \text{——} \ (2)$$

$$dp = \left(-\frac{RT}{V^2} + \frac{3}{2} \frac{a_1}{T^{1/2} V^{5/2}} \right) dv \quad \text{——} \ (3)$$

1

We know that

$$RT \ln\left(\frac{f_1}{P_{low}}\right) = \int_{RT/P_{low}}^{V} \bar{V} \, dP \quad \text{——} \ (4)$$

—— 1

Now

$$RT \ln\left(\frac{f_1}{P_{low}}\right) = \int_{RT/P_{low}}^{V} V \left(-\frac{RT}{V^2} + \frac{3}{2} \frac{a_1}{T^{1/2} V^{5/2}} \right) dV$$

$$RT \ln\left(\frac{f_1}{P_{low}}\right) = \int_{RT/P_{low}}^{V} \left(-\frac{RT}{V} + \frac{3}{2} \frac{a_1}{T^{1/2} V^{3/2}} \right) dV$$

—— 1

$$RT\ln\left(\frac{f_1}{P_{low}}\right) = \left[-RT\ln(\underline{V}) - 3\frac{a_1}{T^{1/2}\underline{V}^{1/2}}\right]_{\frac{RT}{P_{low}}}^{\underline{V}}$$ (1)

$$\ln\left(\frac{f_1}{P_{low}}\right) = \left[-\ln\left(\frac{\underline{V}P_{low}}{RT}\right) - \frac{3a_1}{RT^{3/2}}\left(\frac{1}{\underline{V}^{1/2}} - \frac{\sqrt{P_{low}}}{\sqrt{RT}}\right)\right]$$

$$\ln f_1 - \cancel{\ln P_{low}} = -\ln\left(\frac{\underline{V}}{RT}\right) - \cancel{\ln P_{low}} - \frac{3a_1}{RT^{3/2}}\left(\frac{1}{\underline{V}^{1/2}} - \frac{\sqrt{P_{low}}}{\sqrt{RT}}\right)$$

for $P_{low} = 0$

(1)

$$\ln f_1 = \ln\left(\frac{RT}{\underline{V}}\right) - \frac{3a_1}{R\sqrt{T^3\underline{V}}}$$

$$\ln f_1 - \ln P = \ln\left(\frac{RT}{\underline{V}}\right) - \ln P - \frac{3a_1}{R\sqrt{\underline{V}T^3}}$$

$$\ln\left(\frac{f_1}{P}\right) = \ln\left(\frac{RT}{P\underline{V}}\right) - \frac{3a_1}{R\sqrt{\underline{V}T^3}}$$ (1)

$$\ln(\phi_1) - \ln\left(\frac{RT}{P\underline{V}}\right) = -\frac{3a_1}{R\sqrt{\underline{V}T^3}}$$ (1)

$$\ln\left(\phi_1\frac{P\underline{V}}{RT}\right) = -\frac{3a_1}{R\sqrt{\underline{V}T^3}}$$

$$\phi_1 \left(\frac{PV}{RT} \right) = \exp\left(- \frac{3a_1}{R\sqrt{VT^3}} \right)$$

$$\boxed{\phi_1 = \left(\frac{RT}{PV} \right) \exp\left(- \frac{3a_1}{R\sqrt{VT^3}} \right)} \quad (1)$$

Similarly, for species 2

$$\boxed{\phi_2 = \left(\frac{RT}{PV} \right) \exp\left(- \frac{3a_2}{R\sqrt{VT^3}} \right)} \quad (2)$$

(7) Given.

EOS $\quad P = \dfrac{RT}{\underline{V}} - \dfrac{A}{\sqrt{T\underline{V}^3}}$ ——— (1)

& $\quad A = a_1 y_1 + a_2 y_2$ ——— (2)

We know that

$$RT \ln\left[\frac{\hat{f}_i^v}{y_i P_{low}}\right] = -\int_{\frac{nRT}{P_{low}}}^{V} \left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} dV \quad \text{——— (3)}$$

(1)

Rewrite the equation (1) in terms of V, n_1 & n_2.

$$P = \frac{RT(n_1+n_2)}{V} - \frac{(n_1 a_1 + n_2 a_2)(n_1+n_2)^{3/2}}{(n_1+n_2)\sqrt{TV^3}}$$

$$P = \frac{RT(n_1+n_2)}{V} - \frac{(n_1 a_1 + n_2 a_2)(n_1+n_2)^{1/2}}{V^{3/2} T^{1/2}} \quad \text{——— (4)}$$

(1)

$$\left(\frac{\partial P}{\partial n_1}\right)_{T,P,n_2} = \frac{RT}{V} - \frac{a_1(n_1+n_2)^{1/2}}{V^{3/2}T^{1/2}} - \frac{(n_1 a_1 + n_2 a_2)}{2V^{3/2}T^{1/2}(n_1+n_2)^{1/2}}$$

$$\boxed{\left(\frac{\partial P}{\partial n_1}\right)_{T,P,n_2} = \frac{RT}{V} - \frac{1}{V^{3/2}T^{1/2}}\left\{a_1(n_1+n_2)^{1/2} + \frac{n_1 a_1 + n_2 a_2}{2(n_1+n_2)^{1/2}}\right\}}$$

(1)

Similarly

$$\boxed{\left(\frac{\partial P}{\partial n_2}\right)_{T,P,n_1} = \frac{RT}{V} - \frac{1}{V^{3/2}T^{1/2}}\left\{a_2(n_1+n_2)^{1/2} + \frac{n_1 a_1 + n_2 a_2}{2(n_1+n_2)^{1/2}}\right\}}$$

(1)

Now, from equation (3)

$$RT \ln\left[\frac{\hat{f}_1^v}{y_1 P_{low}}\right] = -\int_{\frac{nRT}{P_{low}}}^{V} \left\{\frac{RT}{V} - \frac{1}{V^{3/2} T^{1/2}}\left(a_1(n_1+n_2)^{1/2} + \frac{n_1 a_1 + n_2 a_2}{2(n_1+n_2)^{1/2}}\right)\right\} dV$$

$$= -\left[RT \ln V + \frac{2}{V^{1/2} T^{1/2}}\left\{a_1(n_1+n_2)^{1/2} + \frac{n_1 a_1 + n_2 a_2}{2(n_1+n_2)^{1/2}}\right\}\right]_{\frac{nRT}{P_{low}}}^{V}$$ 1

$$= -\left\{RT \ln\left[\frac{V P_{low}}{nRT}\right] + \frac{2}{T^{1/2}}\left(a_1(n_1+n_2)^{1/2} + \frac{(n_1 a_1 + n_2 a_2)}{2(n_1+n_2)^{1/2}}\right)\left(\frac{1}{V^{1/2}} - \left(\frac{P_{low}}{nRT}\right)^{1/2}\right)\right\}$$

$$RT \ln\left(\frac{\hat{f}_1}{y_1}\right) - \cancel{RT \ln P_{low}} = -RT \ln\left(\frac{V}{nRT}\right) - \cancel{RT \ln P_{low}}$$

$$- \frac{2}{T^{1/2}}\left(a_1(n_1+n_2)^{1/2} + \frac{n_1 a_1 + n_2 a_2}{2(n_1+n_2)^{1/2}}\right)\left(\frac{1}{V^{1/2}} - \left(\frac{P_{low}}{nRT}\right)^{1/2}\right)$$

P_{low} is very small $\Rightarrow P_{low} \to 0$, then ~~the~~ the above equation becomes. 1

$$RT\ln\left(\frac{f_1^v}{y_1}\right) = RT\ln\left(\frac{nRT}{V}\right) - \frac{2}{V^{1/2}T^{1/2}}\left(a_1(n_1+n_2)^{1/2} + \frac{n_1a_1+n_2a_2}{2(n_1+n_2)^{1/2}}\right)$$

$$RT\ln\left(\frac{f_1^v}{y_2}\right) = RT\ln\left(\frac{RT}{\underline{V}}\right) - \frac{2}{\sqrt{T\underline{V}}}\left(a_1 + \frac{y_1a_1+y_2a_2}{2}\right)$$

$$\ln\left(\frac{f_1^v}{y_1}\right) = \ln\left(\frac{RT}{\underline{V}}\right) - \frac{2}{RT\sqrt{T\underline{V}}}\left(a_1 + \frac{y_1a_1+y_2a_2}{2}\right)$$

substract lnp on both sides.

$$\ln\left(\frac{f_1^v}{y_1}\right) - \ln P = \ln\left(\frac{RT}{\underline{V}}\right) - \ln P - \frac{2}{RT\sqrt{T\underline{V}}}\left(a_1 + \frac{A}{2}\right)$$

1

$$\ln\left(\frac{f_1^v}{y_1P}\right) = \ln\left(\frac{RT}{P\underline{V}}\right) - \frac{2}{RT\sqrt{\underline{V}T}}\left(a_1 + \frac{A}{2}\right)$$

$$\ln\phi_1^v = \ln\left(\frac{RT}{P\underline{V}}\right) - \frac{2}{RT\sqrt{\underline{V}T}}\left(a_1 + \frac{A}{2}\right)$$

$$\boxed{\phi_1^v = \exp\left[\ln\left(\frac{RT}{P\underline{V}}\right) - \frac{2}{RT\sqrt{\underline{V}T}}\left(a_1 + \frac{A}{2}\right)\right]} \quad 1$$

Similarly

$$\boxed{\phi_2 = \exp\left[\ln\left(\frac{RT}{P\underline{V}}\right) - \frac{2}{RT\sqrt{\underline{V}T}}\left(a_2 + \frac{A}{2}\right)\right]} \quad 2$$