1)

(a) For Lewis - Randall reference state,

As $x_1 \longrightarrow 1 \implies r_1 \longrightarrow 1$

$$\implies \ln(r_1) \longrightarrow 0$$

∴ The curve passing through origin should be labelled with r_2 and the other curve should be r_1.

(b) From the graph, we observe than $\ln(r_\infty) > 0$

$\implies r > 1$

Activity coefficient $> 1 \implies$ like forces are stronger

Activity coefficient $= \dfrac{\text{fugacity}}{p^{sat}} > 1$

fugacity $> p^{sat} \implies$ in mixture, more molecules are volatilizing

$\implies$ unlike interactions are weak

(c)

$P = $ Total pressure

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

$x_1 = 0.2$

$x_2 = 0.8$

$P_1^{sat} = 1.12 \text{ bar (given)}$

$P_2^{sat} = 1.013 \text{ bar}$

(saturation Pressure of water at $100°c = 1 atm$)

γ_1 and γ_2 can be found from the graph

(Corresponding to $x_1 = 0.2$)

We approximate from the graph as:

$\ln \gamma_1 \cong 1.05 \qquad \Rightarrow \quad \gamma_1 = 2.86$

$\ln \gamma_2 \cong 0.15 \qquad \Rightarrow \quad \gamma_2 = 1.16$

Substituting all values.

$P = 0.2 \times (2.86) \times (1.12) + 0.8 \times (1.16) \times (1.013)$

$\boxed{P = 1.58 \text{ bar}}$

(d)

We observe that pressure P is relatively low

∴ We assume that vapour phase is ideal

At equilibrium

$$f_i^v = f_i^l$$

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

$$y_1 = \frac{0.2 \times (2.86) \times 1.12}{1.58} = \underline{\underline{0.41}}$$

(e) We can find r_1^α from the graph
(activity coefficient of species 1 at infinite dilution)

$$\ln r_1^\alpha = 2.6$$

$$\Rightarrow r_1^\alpha = 13.5$$

Now calculate H_1 (Henry's law const of n-propanol)

We know,

$$r_1^\alpha = \frac{H_1}{P_1^{sat}}$$

$$\Rightarrow H_1 = (1.12) \times 13.5 = \underline{\underline{15.1 \text{ bar}}}$$

(f) This system exhibits an azeotrope

Explanation:

$$P \text{ (Total pressure)} > P_1^{sat}$$

$$P > P_2^{sat}$$

$\Rightarrow$ P should go through a maximum

$\Rightarrow$ an azeotrope is formed

2)
a and b exhibits azeotrope

$$\Rightarrow x_a = y_a \qquad\qquad x_b = y_b$$

Also, since pressure is relatively low, we assume vapour phase is ideal for both a d b

At equilibrium,

$$f_a^l = f_a^v \qquad\qquad f_b^l = f_b^v$$

$$y_a P = x_a r_a P_a^{sat} \qquad\qquad y_b P = x_b r_b P_b^{sat}$$

$$P = r_a P_a^{sat} \longrightarrow (1) \qquad\qquad P = r_b P_b^{sat} \longrightarrow (2)$$

Finding r_a and r_b

Given: liq- phase non-idially is represented by

two suffix Margules equation

$$\Rightarrow r_a = e^{\left(\frac{A}{RT} x_b^2\right)} = e^{\left(\frac{A}{RT} (1-x_a)^2\right)}$$

$$\Rightarrow r_b = e^{\left(\frac{A}{RT} x_a^2\right)}$$

Substituting into (1) & (2) and equating them

$$\Rightarrow P_a^{sat} e^{\left(\frac{A}{RT} x_b^2\right)} = P_b^{sat} e^{\left(\frac{A}{RT} x_a^2\right)}$$

$$(68.8) \, e^{\left(\frac{2900 \, (1-x_a)^2}{(8.314)(328.15)}\right)} = (46.5) \, e^{\left(\frac{2900 \, x_a^2}{(8.314)(328.15)}\right)}$$

$$\Rightarrow \underline{\underline{x_a = 0.68}}$$

$$\Rightarrow r_a = e^{\left(\frac{2900 \, (0.32)^2}{8.314 \times 328.15}\right)} = \underline{\underline{1.11}}$$

Substituting in (1)

$$\Rightarrow P = r_a P_a^{sat} = (1.11)(68.8) = \underline{\underline{76.4 \ kPa}}$$

∴ Pressure = 76.4 kPa $\qquad$ T = 55°C

$x_a = 0.68$ $\qquad$ $x_b = 0.32$

Azeotropic pressure $> P_a^{sat}$ and P_b^{sat}

⇒ minimum boiling azeotrope (+ve deviations from Raoult's law)

3) To find x_1, we need to find H_1.

For that, we need a reference state : 1 atm pressure, 25°C

Assumptions :

→ gas is ideal

→ liquid is ideal

$1 \rightarrow$ oxygen

$2 \rightarrow$ methanol

We have,

H_1 (at 1 bar) = 3179.4 bar (from table 8.2 in Koretsky)

We use the eqn :

$$d(\ln H_1) = \frac{\overline{V}_1^{\,\alpha}}{RT} \, dP$$

Integrating from reference 1 bar to 100 bar

$$\textcircled{a} \int_{\text{re}}^{\text{??}} d(\ln H_1) = \int_1^{100} \frac{\overline{V}_1^{\,\alpha}}{RT} \, dP$$

$$\ln\left(\frac{H_1}{3179.4}\right) = \frac{4.5 \times 10^{-5}}{8.314 \times 298.15} \left(100 \times 10^5 - 1 \times 10^5\right)$$

$$\Rightarrow \quad H_1 = 3805.7 \text{ bar}$$

given the assumptions, we use:

$$P = x_1 H_1 + x_2 P_2^{sat} = x_1 H_1 + (1-x_1) P_2^{sat} \rightarrow (1)$$

Finding P_2^{sat} $(T = 25°C = 298.15 \text{ K})$

We use Antoine eqn for $(2) \rightarrow$ methanol

$$A = 11.9673 \qquad\qquad B = 3626.55 \qquad\qquad C = -34.29$$

$$\ln\left(P_2^{sat} \text{ (bar)}\right) = A - \frac{B}{T+C}$$

$$\Rightarrow \quad P_2^{sat} = 0.169 \text{ bar}$$

Substituting $P = 100 \text{ bar}$, $P_2^{sat} = 0.169 \text{ bar}$

$$H_1 = 3805.7 \text{ bar} \qquad\qquad \text{in} \qquad (1)$$

$$100 = x_1(3805.7) + (1-x_1) 0.169$$

$$\Rightarrow \quad \boxed{x_1 = 0.0263}$$

$$\downarrow$$

solubility of ~~metha~~ O_2 in methanol

in terms of mole fraction of O_2

4)

(a) To determine which species is on top, we need to calculate the density of both species
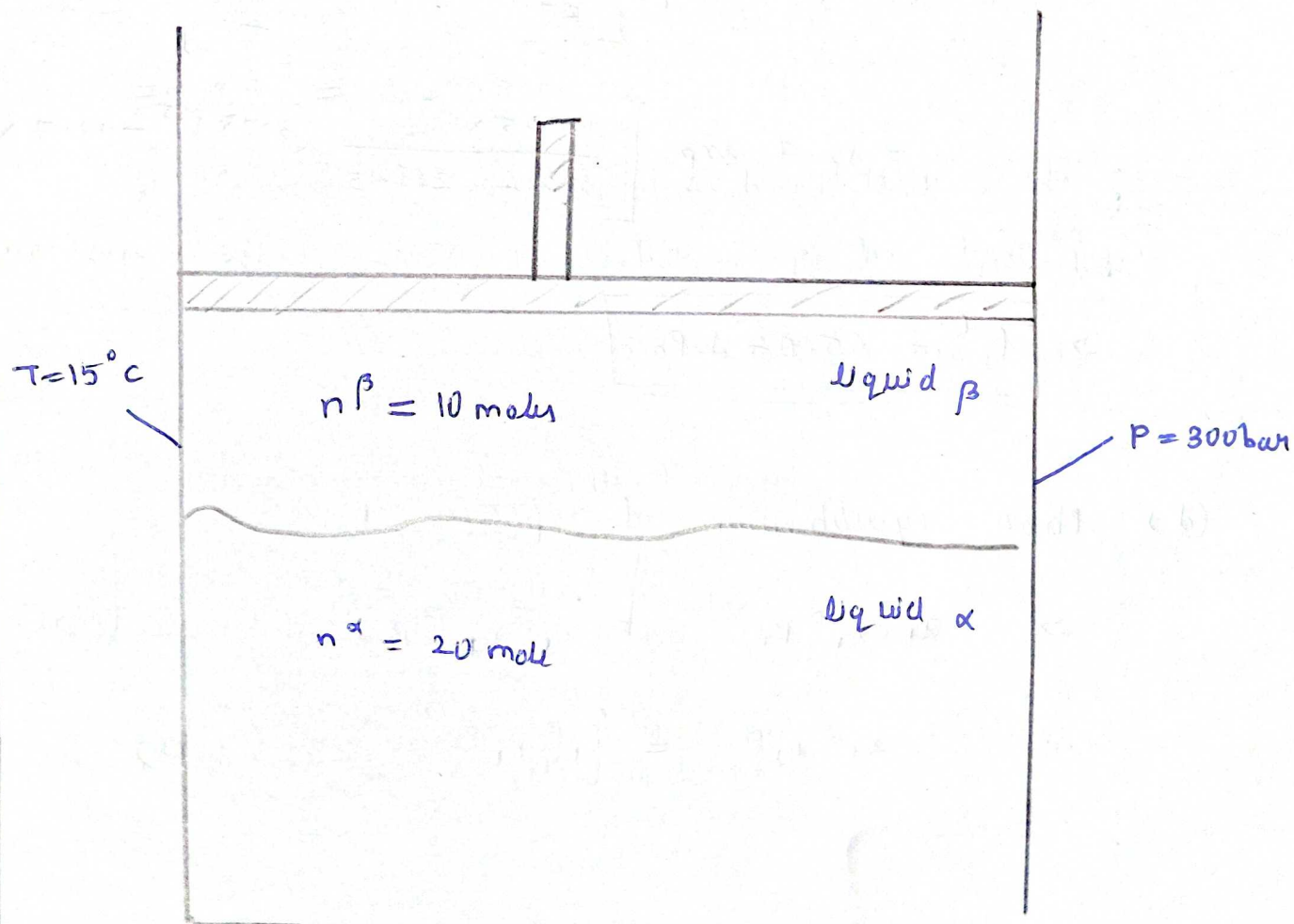
$$\rho_i = \frac{MW_i}{V_i}$$

$$\rho_1 = \frac{86}{130.5} = 0.659 \ g/cm^3 \quad (hexane)$$

$$\rho_2 = \frac{58}{73.4} = 0.79 \ g/cm^3 \quad (acetone)$$

Since phase β has more of the less dense component (hexane), it will be on top.

∴ Schematic looks like:

$T = 15°C$

$n^\beta = 10 \ moles$

liquid β

$P = 300 \ bar$

liquid α

$n^\alpha = 20 \ moles$

(b) Because the mixture separates into two phases, it means that mixture is not as stable as individual species. That is, like interactions are stronger than unlike interactions.

(c) $f_i^l \rightarrow$ pure species fugacity

$$f_i^l = f_i^v = \varphi_i^{sat} P_i^{sat} \exp\left[\int_{P_i^{sat}}^{P} \frac{v_i^{sat}}{RT} dP\right]$$

$P_i^{sat} = 12.7 \, kPa$ (low value)

$$\Downarrow$$

we assume $\varphi_i^{sat} \approx 1$

We also assume the v_i^{sat} is independent of pressure P.

$$\Rightarrow f_i^l = P_i^{sat} \exp\left[\frac{v_i^{sat}}{RT}(P - P_i^{sat})\right]$$

$$= 12.7 \exp\left[\frac{130.5 \times 10^{-6}}{2.314 \times 288.15}(300 \times 10^5 - 12.7 \times 10^3)\right]$$

$$\Rightarrow \boxed{f_i^l = 65.04 \, kPa}$$

(d) Phase equilibrium of species 1

$$\Rightarrow x_1^\alpha \gamma_1^\alpha P_1^{sat} = x_1^\beta \gamma_1^\beta P_1^{sat}$$

$$\therefore \quad x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta \qquad \longrightarrow (1)$$

For the two suffix Margules equation,

$$r_1^\alpha = \exp\left[\frac{A(x_2^\alpha)^2}{RT}\right]$$

$$r_2^\beta = \exp\left[\frac{A(x_2^\beta)^2}{RT}\right]$$

Substituting the above two equations in (i)

$$\Rightarrow x_1^\alpha \exp\left[\frac{A(x_2^\alpha)^2}{RT}\right] = x_1^\beta \exp\left[\frac{A(x_2^\beta)^2}{RT}\right]$$

$$x_1^\alpha = 0.2 \qquad\qquad x_2^\alpha = 0.8 \qquad\qquad T = 15^\circ C$$

$$x_1^\beta = 0.8 \qquad\qquad x_2^\beta = 0.2$$

Using above values,

$$\boxed{A = 5535 \ \frac{J}{mol}}$$

(e) The lowest temperature at which the two species are completely miscible occurs at

$$\frac{RT}{x_1 x_2} = 2A$$

Assumption : A is independent of temperature

$$x_1, x_2 \rightarrow \text{mole fractions of completely miscible solutions}$$

$$x_1 = \frac{x_1^\alpha (n^\alpha) + x_1^\beta (n^\beta)}{n^\alpha + n^\beta} = \frac{0.2(20) + 0.8(10)}{30}$$

$\Rightarrow x_1 = 0.4$ and $x_2 = 0.6$

$A = 5535$ J/mol

Substituting these values us

$$T = \frac{2A \, x_1 x_2}{R}$$

$$\Rightarrow T = \frac{2 \times 5535 \times 0.4 \times 0.6}{8.314} = 320 \, k$$

(f) We have,

$$r_1 = \exp\left[\frac{A \, (x_2)^2}{RT}\right]$$

At r_1^{α} $x_2 \rightarrow 1$

$$\Rightarrow r_1^{\alpha} = \exp\left[\frac{A \, (1)^2}{RT}\right]$$

$$= \exp\left[\frac{5535}{8.314 \times 288.15}\right]$$

$$r_1^{\alpha} = 10.1$$

We know, $r_1^{\alpha} = \frac{H_1}{f_1}$

$$\Rightarrow H_1 = r_1^{\alpha} \times f_1 = 10.1 \times 65.04 = 656.9 \, kPa$$

5:

$\gamma_a^\infty = 7.02$ $\qquad$ $\gamma_b^\infty = 72.37$

We can use 3-suffix Margules equation to model the non-ideality.

At infinite dilution,

$$RT \ln(\gamma_a^\infty) = A - B = 8.314 \times (298.15) \ln(7.02)$$

$$RT \ln(\gamma_b^\infty) = A + B = 8.314 \times (298.15) \ln(72.37)$$

solving,

$$A = 7720 \frac{J}{mol} \qquad B = 2890 \frac{J}{mol}$$

At equilibrium, fugacity of liquid phase α, liquid phase β and vapor phase are equal

ie

$$x_a^\alpha \gamma_a^\alpha P_a^{sat} = x_a^\beta \gamma_a^\beta P_a^{sat} = y_a P \longrightarrow (1)$$

$$x_b^\alpha \gamma_b^\alpha P_b^{sat} = x_b^\beta \gamma_b^\beta P_b^{sat} = y_b P \longrightarrow (2)$$

We use the 3-suffix Margules eqn:

$$RT \ln(\gamma_a) = (A + 3B) x_b^2 - 4B x_b^3$$

$$RT \ln(\gamma_b) = (A - 3B) x_a^2 + 4B x_a^3$$

Substituting above equations in (1) and (2)

$$\Rightarrow x_a^\alpha \exp\left[\frac{(A+3B)(1-x_a^\alpha)^2}{RT} - \frac{4B}{RT}(1-x_a^\alpha)^3 \right]$$

$$= x_a^\beta \exp\left[\frac{(A+3B)(1-x_a^\beta)^2}{RT} - \frac{4B}{RT}(1-x_a^\beta)^3 \right] = \frac{y_a P}{P_a^{sat}}$$

$$\longrightarrow (3)$$

and

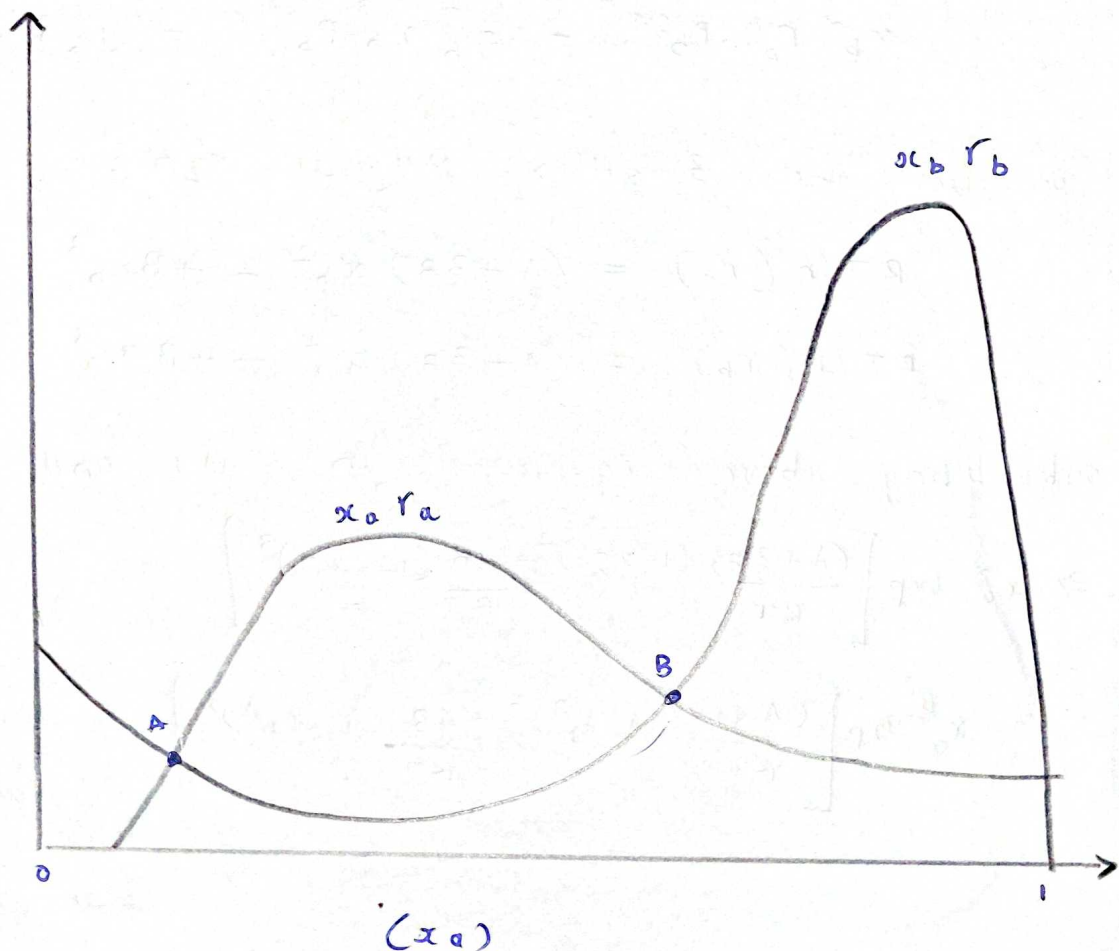$$(1-x_a^\alpha) \exp\left[\frac{(A-3B)}{RT}(x_a^\alpha)^2 + \frac{4B}{RT}(x_a^\alpha)^3\right]$$

$$= (1-x_a^\beta) \exp\left[\frac{(A-3B)}{RT}(x_a^\beta)^2 + \frac{4B}{RT}(x_a^\beta)^3\right] = \frac{y_b P}{P_b^{sat}}$$

$$\hookrightarrow (4)$$

If we plot the quantities $x_a \, r_a$ and $(1-x_a) \, r_b$ vs x_a, the solution for the composition is the two liquid phases occurs at the two compositions of x_a where (3) and (4) are simultaneously satisfied.

We can use online software to graph and then find the solution. The rough graph is shown below:

$x_b \, r_b$

$x_a \, r_a$

B

A

(x_a)

0   1

A and B are the points where the two graphs meet.

We can find (using online plotter),

$$x_a^\alpha r_a^\alpha = x_a^\beta r_a^\beta = 0.987$$

$$x_b^\alpha r_b^\alpha = x_b^\beta r_b^\beta = 0.860$$

$\Rightarrow$

$$\boxed{\begin{array}{l} x_a^\alpha = 0.986 \\[4pt] x_a^\beta = 0.145 \end{array}}$$

To solve for pressure, we can add (1) and (2)

$$\Rightarrow P = x_a^\alpha r_a^\alpha P_a^{sat} + x_b^\alpha r_b^\alpha P_b^{sat}$$

At 25°C

$$P_a^{sat} = 3169 \ Pa \quad (\text{from steam table})$$

$$P_b^{sat} = 875 \ Pa \quad (\text{Given})$$

$$\Rightarrow \boxed{P = 3880 \ Pa}$$

From (1),

$$y_a^\alpha P = x_a^\alpha r_a^\alpha P_a^{sat}$$

$$\Rightarrow y_a^\alpha = \frac{x_a^\alpha r_a^\alpha P_a^{sat}}{P}$$

(r_a^α can be found using 3-suffix Margules eqn)

$$\Rightarrow \boxed{y_a^\alpha = 0.8}$$

∴ Composition of three phases

Phase α : $x_a{}^\alpha = 0.986$ $x_b{}^\alpha = 0.014$

Phase β : $x_a{}^\beta = 0.145$ $x_b{}^\beta = 0.855$

Vapor $\cdot$ $y_a = 0.8$

$y_b = 0.2$

System pressure $(P) = 3880$ Pa

6) The purpose of applying salt to the road is to lower the freezing point of water.

∴ We want to find the lowest temperature at which liquid water exists.

From the phase diagram, the lowest temperature is

$\boxed{-21.12\,°C}$ and the corresponding composition ≈ 24 wt %

(from the graph)

∴ The smallest composition of salt required to lower the freezing point to this temperature is appr. 24 wt %

∴ $\boxed{T = -21.12\,°C}$ $\boxed{\text{Concentration} = 24 \text{ wt \% of NaCl}}$