# LUKHDHIRJI ENGINEERING COLLEGE MORBI CHEMICAL ENGINEERING DEPARTMENT 

## 3140507: Chemical Engineering Thermodynamics - II

## Tutorial 01:

## Q.1:

Will it be possible to prepare $0.1 \mathrm{~m}^{3}$ of alcohol-water solution by mixing $0.03 \mathrm{~m}^{3}$ alcohol with $0.07 \mathrm{~m}^{3}$ pure water? If not possible, what volume should have been mixed in order to prepare a mixture of the same strength and of the required volume? Density of ethanol and water are 789 and $997 \mathrm{~kg} / \mathrm{m}^{3}$ respectively. The partial molar volumes of ethanol and water at the desired compositions are: Ethanol = $53.6 \times 10^{-6} \mathrm{~m}^{3} / \mathrm{mol} ;$ water $=18 \times 10^{-6} \mathrm{~m}^{3} / \mathrm{mol}$.

## Q.2:

At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are represented by

$$
\mathrm{V}=109.4 * 10^{-6}-16.8 * 10^{-6} \mathrm{x}_{1}-2.64 * 10^{-6} \mathrm{x}_{1}^{2}
$$

where $\mathrm{x}_{1}$ is the mole fraction of benzene and V has the units of $\mathrm{m}^{3} / \mathrm{mol}$. Find expressions for the partial molar volumes of benzene and cyclohexane.

## Q.3:

If the molar density of a binary mixture is given by the empirical expression:

$$
\rho=a_{0}+a_{1} x_{1}+a_{2} x_{1}^{2}
$$

find the corresponding expressions for $\overline{\mathrm{V}}_{1}$ and $\overline{\mathrm{V}_{2}}$.
Q.4:

A $30 \%$ by mole methanol-water solution is to be prepared. How many cubic meters of pure methanol (molar volume, $40.727 \times 10-6 \mathrm{~m} 3 / \mathrm{mol}$ ) and pure water (molar volume, $18.068 \times 10-6 \mathrm{~m} 3 / \mathrm{mole}$ ) are to be mixed to prepare 2 m 3 of desired solution? The partial molar volumes of methanol and water in a $30 \%$ solution are $38.632 \times 10-6 \mathrm{~m} 3 / \mathrm{mol}$ and $17.765 \times 10-6 \mathrm{~m} 3 / \mathrm{mol}$, respectively.

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## Tutorial 02:

From the following compressibility-factor data for $\mathrm{C}_{2}$ at $423.15 \mathrm{~K}\left(150^{\circ} \mathrm{C}\right)$ prepare plots of the fugacity and fugacity coefficient of $\mathrm{CO}_{2}$ vs. P for pressures up to 500 bar Compare results with those found from the generalized correlation represented by Eq

$$
\phi=\exp \left[\frac{P_{r}}{T_{r}}\left(\boldsymbol{B}^{0}+\omega B^{1}\right)\right]
$$

| $P$ (bar) | $Z$ |
| :---: | :---: |
| 0 | 1 |
| 10 | 0.985 |
| 20 | 0.97 |
| 40 | 0.942 |
| 60 | 0.913 |
| 80 | 0.885 |
| 100 | 0.869 |
| 200 | 0.765 |
| 300 | 0.762 |
| 400 | 0.824 |
| 500 | 0.91 |

$$
\ln \phi_{i}=\int_{0}^{P}\left(L_{i}-1\right) \frac{d P}{P}
$$

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## Tutorial 03:

1. Calculate bubble point pressure for binary mixture of Benzene (1)/Toluene (2) at $\mathrm{T}=\mathbf{4 0 0} \mathbf{7 0 0}$ and $1000 \mathrm{~K} \& \mathrm{x}_{1}=0.4$. Draw P-x1y1 diagram at different T .
2. Then generate $T$-xy diagram at pressure $\mathbf{P}=1,10$ and 100 atm.

Antoine equation: $\ln P=A-\frac{B}{T+C}$ where, P in $\mathrm{kPa}, \mathrm{T}$ in K
$\mathrm{A} 1=14.1603, \mathrm{~B} 1=2948.78, \mathrm{C} 1=-44.5633$
$\mathbf{A 2}=14.2515, \mathbf{B 2}=3242.38, \mathbf{C 2}=-47.1806$

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## Tutorial 04:

Q.1:

Estimate the values for the fugacity of 1-butane vapor at 473.15 K and 70 bar.
Data given: $\operatorname{Tr}=1.127, \quad \operatorname{Pr}=1.731$ and $\omega=0.191$

## Q.2:

The saturation pressure of n-octane at 427.85 K is 215 Mpa . Estimate the fugacity of liquid n-octane at 427.85 K and 1 Mpa .

## Data given:

For n -octane: $\mathrm{f}_{\mathrm{i}}{ }^{\text {sat }}=0.2368 \mathrm{MPa}$ and $\mathrm{v}_{\mathrm{i}}{ }^{\mathrm{L}}=0.2003 \times 10^{-3} \mathrm{~m}^{3} / \mathrm{mol}$

## Q.3:

Describe a graphical interpretation of following equations:

$$
\overline{\mathrm{M}}_{1}=\mathbf{M}+\mathrm{x}_{2} \frac{\mathbf{d M}}{\mathbf{d x}_{1}}
$$

$$
\bar{M}_{2}=M-x_{1} \frac{d M}{d x_{1}}
$$

## Q.4:

At $25{ }^{\circ} \mathrm{C}$ the density of a methanol (1) - water (2) solution at $\mathrm{x}_{1}=0.7779$ is $825.959 \mathrm{~kg} / \mathrm{m}^{3}$. Partial molar volume of water in this solution is $15.686 \times 10^{-6} \mathrm{~m}^{3} / \mathrm{mol}$. Determine the partial molar volume of methanol in the solution.

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## Tutorial 05:

## Q.1:

Ternary equimolar mixture is flashed at $110{ }^{\circ} \mathrm{C}$ to carry out $30 \%$ vaporization. Determine equilibrium pressure, vapor and liquid composition.

Data Given:
At $110{ }^{\circ} \mathrm{C}$ :

$$
\begin{aligned}
& \mathrm{P}_{1}{ }^{\text {sat }}=224 \mathrm{kPa} \\
& \mathrm{P}_{2}{ }^{\text {sat }}=98.6 \mathrm{kPa} \\
& \mathrm{P}_{3}{ }^{\text {sat }}=48 \mathrm{kPa}
\end{aligned}
$$

## Q.2:

A mixture containing equimolar amounts of benzene(l), toluene(2), and ethylbenzene(3) is flashed to conditions $T$ and $P$. For one of the conditions following determine the equilibrium mole fractions $\left\{x_{i}\right\}$ and $\left\{y_{i}\right\}$ of the liquid and vapor phases formed and the molar fraction $V$ of the vapor formed. Assume that Raoult's law applies.
(a) $\mathrm{T}=383.15 \mathrm{~K}, \mathrm{P}=90 \mathrm{kPa}$.
(b) $\mathrm{T}=383.15 \mathrm{~K}, \mathrm{P}=100 \mathrm{kPa}$.
(c) $\mathrm{T}=383.15 \mathrm{~K}, \mathrm{P}=110 \mathrm{kPa}$.
(d) $\mathrm{T}=383.15 \mathrm{~K}, \mathrm{P}=120 \mathrm{kPa}$.

## Q.3:

For a perticular binary system, the activity coefficients are adequately represented by following equations:

$$
\ln \gamma_{1}=0.6 \mathrm{x}_{2}^{2} \text { and } \ln \gamma_{2}=0.6 \mathrm{x}_{1}^{2}
$$

The saturation pressures of the components at $80^{\circ} \mathrm{C}$ are given by $\mathrm{P} 1 \mathrm{sat}=900 \mathrm{mmHg}$ and $\mathrm{P} 2 \mathrm{sat}=600 \mathrm{mmHg}$. Is it possible for the system to exhibit azeotropy at 80 C ? If yes, calculate azeotropic pressure and composition.

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## Tutorial 06:

## Q.1:

Water (1) - hydrazine (2) system forms an azeotrope containing $58.5 \%$ (mol) hydrazine at 393 K and 101.3 kPa . Calculate the equilibrium vapour composition for a solution containing $20 \%$ (mol) hydrazine. The relative volatility of water with reference to hydrazine is 1.6 and may be assumed to remain constant in the temperature range involved. The vapour pressure of hydrazine at 393 K is 124.76 kPa .

## Q.2:

Using van Laar constants and the vapour pressures of the pure substances how would you prove whether a given binary system forms an azeotrope or not?

## Q.3:

From vapour-liquid equilibrium measurements for ethanol-benzene system at 318 K and 40.25 kPa it is found that the vapour in equilibrium with a liquid containing $38.4 \%$ (mol) benzene contained $56.6 \%$ (mol) benzene. The system forms an azeotrope at 318 K . At this temperature, the vapour pressures of ethanol and benzene are 22.9 and 29.6 kPa respectively. Determine the composition and total pressure of the azeotrope. Assume that van Laar equation is applicable for the system.

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## Tutorial 07:

## Q.1:

Using the criterion of phase equilibrium, show that the change in entropy during phase changes can be calculated from the latent heat of phase change and the absolute temperature as $\Delta \mathrm{S}=\Delta \mathrm{H} / \mathrm{T}$.

## Q.2:

Using van Laar constants and the vapour pressures of the pure substances how would you prove whether a given binary system forms an azeotrope or not?

## Q.3:

The following results were obtained by experimental VLE measurements on the system, ethanol (1)benzene (2) at 101.3 kPa . Test whether the data are thermodynamically consistent or not.

| $x_{1}$ | 0.003 | 0.449 | 0.700 | 0.900 |
| :--- | :--- | :--- | :--- | :--- |
| $y_{1}$ | 0.432 | 0.449 | 0.520 | 0.719 |
| , kPa | 65.31 | 63.98 | 66.64 | 81.31 |
| , kPa | 68.64 | 68.64 | 69.31 | 72.24 |

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## Tutorial 08:

## Q.1:

Develop expressions for the mole fractions of reacting species as functions of the reaction coordinate for: (a) A system initially containing $2 \mathrm{~mol} \mathrm{NH}_{3}$ and $5 \mathrm{~mol} \mathrm{O}_{2}$ and undergoing the reaction:

$$
4 \mathrm{NH}_{3}(g)+5 \mathrm{O}_{2}(g) \rightarrow 4 \mathrm{NO}(g)+6 \mathrm{H}_{2} \mathrm{O}(g)
$$

(b) A system initially containing $3 \mathrm{~mol}_{\mathrm{H}_{2} \mathrm{~S}}$ and $5 \mathrm{~mol} \mathrm{O}_{2}$ and undergoing the reaction:

$$
2 \mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})+2 \mathrm{SO}_{2}(\mathrm{~g})
$$

(c) A system initially containing $3 \mathrm{~mol} \mathrm{NO}_{2}, 4 \mathrm{~mol} \mathrm{NH}_{3}$, and $1 \mathrm{~mol}_{2}$ and undergoing the reaction:

$$
6 \mathrm{NO}_{2}(g)+8 \mathrm{NH}_{3}(g) \rightarrow 7 \mathrm{~N}_{2}(g)+12 \mathrm{H}_{2} \mathrm{O}(g)
$$

Q.2:

A system initially containing $2 \mathrm{~mol}_{2} \mathrm{H}_{4}$ and $3 \mathrm{~mol} \mathrm{O}_{2}$ undergoes the reactions:

$$
\begin{gathered}
\mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow\left\langle\left(\mathrm{CH}_{2}\right)_{2}\right\rangle \mathrm{O}(\mathrm{~g}) \\
\mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{~g})+3 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
\end{gathered}
$$

Develop expressions for the mole fractions of the reacting species as functions of the reaction coordinates for the two reactions.
Q.3:

A system formed initially of $2 \mathrm{molCO}_{2}, 5 \mathrm{molH}_{2}$, and 1 molCO undergoes the reactions:

$$
\begin{gathered}
\mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \\
\mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
\end{gathered}
$$

Develop expressions for the mole fractions of the reacting species as functions of the reaction coordinates for the two reactions.

