# III B.Tech I Semester Examinations,May 2011 CHEMICAL ENGINEERING THERMODYNAMICS - II <br> Chemical Engineering 

Time: 3 hours
Max Marks: 80

## Answer any FIVE Questions

All Questions carry equal marks

1. For steady flow through a heat exchanger at approximately atmospheric pressure, determine the final temperature when 2500 KJ of heat is added to 15 mol of i -butene initially at $260^{\circ} \mathrm{C}$
2. Derive $\ln \frac{f}{f^{s a t}}=\frac{V^{l}}{R T}\left(\mathrm{p}-\mathrm{p}^{\text {sat }}\right)$ where $\mathrm{f}=$ fugacity of liquid at given pressure P . write the assumption used.
3. (a) Under what conditions a solution behaves ideally? How it is different from ideal gas model? Discuss the validity of Lewis Randall rule.
(b) What is excess property? Derive the relationship between excess Gibbs energy and activity coefficient. Derive Lewis Randall rule from that. $\quad[6+10]$
4. (a) What are the usual standard states employed in the study of chemical reaction equilibrium? How do they differ from the standard states used in the study of phase equilibrium?
(b) The equilibrium constant for the reaction
$2 \mathrm{H}_{2} \mathrm{O}_{(g)} \rightarrow 2 \mathrm{H}_{2(g)}+\mathrm{O}_{(g)}$
At 2000 K and 1 atm is given by $\mathrm{K}_{p}=6.45 \times 10^{-8}$. Determine the partial pressure of $\mathrm{O}_{2}$ if water vapor at 2000 K and 1 atm is allowed to come to equilibrium.
5. (a) Discuss the use of Pitzer's correlations to estimate vapor-liquid equilibrium state.
(b) Briefly explain the flash calculations and VLE using Redlich-Kwong equation of state.
6. Prove Cpm $=\frac{\int_{T 1}^{T 2} C p d T}{T_{2}-T_{1}}$
7. An example of a partially miscible system is diethyl ether \& water. At $60^{\circ} \mathrm{C}$ ether dissolves to the extent of 0.9 mole $\%$ in water and water dissolves to the extent of 6.7 $\mathrm{mole} \%$ in ether. The vapor pressures of ether and water at $60^{\circ} \mathrm{C}$ are 2.27 bar and 0.2 bar respectively. Construct $y$-x diagram for this system at a constant temperature of $60^{\circ} \mathrm{C}$. Assume Henry's law is followed by each component at concentrations below the lower solubility limit and that Raoult's law is followed at concentrations above the upper solubility limit.
8. Wilson's parameters for the system chloroform (1) - methanol (2) at 35 oC are given by $\left(\lambda_{12}-\lambda_{11}\right)=-1.552 \frac{\mathrm{~kJ}}{\mathrm{molK}}$ and $\left(\lambda_{12}-\lambda_{22}\right)=7.559 \frac{\mathrm{~kJ}}{\mathrm{molK}}$

Estimate the VLE data for the system at 350 C
if $V_{1}^{L}=80.67 \times 10^{-6} \frac{\mathrm{~m}^{3}}{m o l}$ and $V_{2}^{L}=40.73 \times 10^{-6} \frac{\mathrm{~m}^{3}}{m o l}$
Vapor pressures are calculated from the Antonie equation $\log _{10}^{p}=A-\frac{B}{t+C}$, where P is in Torr and t is in ${ }^{0} \mathrm{C}$ whose constants are given as follows:

A B C
Chloroform $9.95465 \quad 1170.966 \quad 226.322$
$\begin{array}{llll}\text { Methanol } & 8.08097 & 1582.271 & 239.726\end{array}$

* $\begin{aligned} & \\ & \text { * } \star \star\end{aligned}$


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1. (a) What do you understand by standard free energy change? How is equilibrium constant ' K ' related to standard free energy change ?
(b) Determine the equilibrium constant at $25^{\circ} \mathrm{C}$ for the reaction

$$
\mathrm{CH}_{4(g)}+\mathrm{H}_{2} \mathrm{O}_{(l)} \rightarrow \mathrm{CO}_{(g)}+3 \mathrm{H}_{2(g)}
$$

Data:

| Component | $\Delta G_{f(298)}^{0}, \mathrm{~K} \mathrm{cal} / \mathrm{g}-\mathrm{mol}$ |
| :---: | :---: |
| $\mathrm{CO}_{(g)}$ | -32.81 |
| $\mathrm{CH}_{4(g)}$ | -12.14 |
| $\mathrm{H}_{2} \mathrm{O}_{(l)}$ | -56.7 |

2. Determine expressions for $\mathrm{G}^{R}, \mathrm{H}^{R}$ and $\mathrm{S}^{R}$ implied by the equation of state $P=\frac{R T}{V-b} \exp \left(\frac{-a}{V R T}\right)$ where $a$ and $b$ are functions of composition only.
3. (a) Define standard heat of formation? Why is it important? Discuss it with an example. Why the concept of standard heat of combustion has been introduced
(b) The gross heating value of n - butane gas at $25^{\circ} \mathrm{C}$ is $2880.44 \mathrm{~kJ} / \mathrm{mol}$. Calculate the standard enthalpy of its formation at $298.15 \mathrm{~K} \Delta H_{f 298}^{0}\left(\mathrm{CO}_{2}\right)(\mathrm{g})=$ $-393.978 \mathrm{~kJ} \Delta H_{f 298}^{0}\left(\mathrm{H}_{2} \mathrm{O}\right)((\mathrm{l})=-285.9 \mathrm{~kJ}$
Data: $\Delta H C^{0} \mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})=-1299.61 \mathrm{~kJ} / \mathrm{mol}$
$\Delta H C^{0} C_{3} H_{8}(c)=-2204.0 \mathrm{~kJ} / \mathrm{mol}$
$\Delta H C^{0} C O(g)=-282.9 \mathrm{~kJ} / \mathrm{mol}$
4. A rigid vessel contains 50 kg of saturated liquid water and 4.3 kg of saturated vapor. The system pressure is at 10 KPa . What is the minimum amount of heat needed to evaporate all the liquid (Use steam table)
5. Calculate the fugacity of liquid water at $30^{\circ} \mathrm{C}$ and at the following pressure
(a) saturation pressure.
(b) 10 bar (c) 100 bar.

Data: At $30^{\circ} \mathrm{C}$, saturation pressure $=0.0424$ bar
Sp.vol of liquid water at saturation $=0.001004 \mathrm{~m}^{3} / \mathrm{kg}$
6. (a) Write the equation which define property change of mixing of volume, enthalpy entropy and Gibbs free energy entropy relation of change of mixing.
(b) Derive the relation ship for determineing change in Gibbs free energy of an ideal solution.
$[12+4]$
7. Show that Wilson activity coefficient model cannot predict the existence of two liquid phases for any values of its parameters.
8. The excess Gibbs energy for a binary system is given by $\frac{G^{E}}{R T}=0.45 x_{1} x_{2}$. The pure component vapor pressures are given by:
$\ln P_{1}^{\text {sat }} / k P a=14.39-\frac{2795.8}{t /{ }^{0} C^{+230}}$ and $\ln P_{2}^{\text {sat }} / k P a=16.59-\frac{3644.2}{t /{ }^{3} C^{+239}}$
Obtain pressure - composition diagram for this system at $60^{\circ} \mathrm{C}$.

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1. Derive the Henry's from Lewis Randall rule. Write the condition in which Henry's law is applicable.
2. (a) Write the general equation for determining the fugacity of a component in a gaseous mixture. Show that component fugacity is directly proportional to its mole fraction if this mixture is assumed to be an ideal solution.
(b) The Henry's law constant for energy in water at 298 K is $4.4 \times 10^{\wedge} 4$ bar. Estimate the solubility (in mass unit) of oxygen in water at 298 K for a partial pressure of oxygen at 0.25 bars.
[8+8]
3. Determine expressions for $\mathrm{G}^{R}, \mathrm{H}^{R}$ and $\mathrm{S}^{R}$ implied by the three-term virial equation in volume.
4. (a) Discuss how free energy change of reaction indicates the feasibility of reaction?
(b) The water gas reaction is represented by the equation.
$\mathrm{CO}_{2(g)}+\mathrm{H}_{2(g)} \rightarrow+\mathrm{H}_{2} \mathrm{O}_{(g)}+\mathrm{CO}_{(g)}$

At $127^{\circ} \mathrm{C}$. Find the value of Kp. The Gibbs free energy of formation at $127^{\circ} \mathrm{C}$ are as follows:
-35.01 K cal/mol for CO
$-94.33 \mathrm{~K} \mathrm{cal} / \mathrm{mol}$ for $\mathrm{CO}_{2}$
$-53.22 \mathrm{~K} \mathrm{cal} / \mathrm{mol}$ for $\mathrm{H}_{2} \mathrm{O}$
Also comment on feasibility of the reaction.
5. Explain LLE with the help of temperature-composition diagrams. Explain the terms island, upper and lower consulate temperatures, critical solution temperature and binodal curves.
6. The enthalpy of a binary liquid solution of species 1 and 2 at fixed T and P is represented by the following equation $H=400 x_{1}+600 x_{2}+x_{1} x_{2}\left(40 x_{1}+20 x_{2}\right)$ where $H$ is in $\mathrm{J} / \mathrm{mol}$. Determine expressions for $\bar{H}_{1}$ and $\bar{H}_{2}$ as function of $\mathrm{x}_{1}, \mathrm{H}_{1}$ and $\mathrm{H}_{2}$ and numerical values for the partial enthalpies at infinite dilution $\left(\bar{H}_{1}^{\infty}, \bar{H}_{2}^{\infty}\right)$.
7. Test whether the following Isobaric VLE data for the system acetone (1) - carbon tetrachloride (2) at 450 Torr is thermodynamically consistent.

Code No: 07A50803
R07

## Set No. 1

| $T\left({ }^{0} C\right)$ | $X$ | $Y$ |
| :---: | :---: | :---: |
| 55.29 | 0.0490 | 0.1890 |
| 49.50 | 0.1625 | 0.3930 |
| 46.26 | 0.2970 | 0.5150 |
| 44.06 | 0.4470 | 0.6100 |
| 43.05 | 0.5650 | 0.6770 |
| 42.42 | 0.6525 | 0.7280 |
| 41.92 | 0.7480 | 0.7840 |
| 41.54 | 0.8955 | 0.9015 |
| 41.53 | 0.9260 | 0.9220 |
| 41.46 | 0.9450 | 0.9450 |

The pure component vapor pressures are calculated by the following Antonie equations. $\log P_{1}^{\text {sat }} /$ Torr $=7.117-\frac{1210.595}{t / 0 C^{+229.664}}$ and
$\log P_{2}^{\text {sat }} /$ Torr $=6.841-\frac{1177.910}{t^{t} C^{+220.526}}$
[16]
8. A heat exchanger is to be designed to raise the temperature of $10 \mathrm{kmol} / \mathrm{hr}$ of ammonia from 300 K to 400 K . The inlet and exit pressure of ammonia in the heat exchangers are almost identical. Determine the amount of energy to be transferred to ammonia in the heat exchanger, if the isobaric molar heat capacity of ammonia is given by $\mathrm{Cp}=29.747+25.108 \mathrm{X} 10^{-3} \mathrm{~T}-4.546 \mathrm{X} 10^{5} \mathrm{~T}^{-2}$

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1. The liquid phase in a binary system of species 1 and 2 , exhibits partial miscibility. In the regions of miscibility, the excess Gibbs energy is expressed by the following equation:
$G^{E} / R T=2.25 x_{1} x_{2}$
Given the vapor pressures of pure species are $P_{1}^{\text {sat }}=75 \mathrm{kPa} ; P_{2}^{\text {sat }}=110 \mathrm{kPa}$. Making the usual assumption for low-pressure VLE, prepare a pressure-composition diagram for this system at a temperature of $66^{\circ} \mathrm{C}$.
2. Estimate $\mathrm{H}^{R}$ and $\mathrm{S}^{R}$ for an equimolar mixture of methyl ethyl ketone (1) and Toluene (2) at $50^{\circ} \mathrm{C}$ and 25 kPa using van der Waats equation. The constants for van der Waals equation are (in SLunits)

$$
\begin{align*}
a_{1}=2.01 \times 10^{6} & b_{1}=0.1341 \\
a_{2}=2.487 \times 10^{6} & b_{2}=0.149 \tag{16}
\end{align*}
$$

3. (a) Define activity coefficient. Derive an equation which shows a solution departure from its ideality.
(b) Derive the Lewis Randall rule and in turn Raults law. Why Raoult's law is valid for solvent.
4. How fugacity of a compressed liquid is determined? What is the basic principle behind this. Derive the equation for them.
5. (a) Write Gibbs Duhem equation at a constant temperature and pressure in terms of fugacity. What are the limitations of this equation?
(b) Write the modified Raoult's law. Write the steps to calculate activity coefficient using experimental low pressure VLE isothermal data. [6+10]
6. For the binary system 1-Propanol (1) Water (2) $V_{1}=75.14$ and $V_{2}=18.07$ $\mathrm{cm}^{3} \mathrm{~mol}^{-1}$. The Wilson parameters are $\mathrm{a}_{12}=775.48$ and $\mathrm{a}_{21}=1351.9 \mathrm{cal} / \mathrm{mol}$. The pure component vapor pressures of 1-Propanol and water are given by the following Antonie equations.
$\ln P_{1}^{\text {sat }} / k P a=16.0962-\frac{3448.66}{t /{ }^{0} C^{+204.09}}$ and $P_{2}^{\text {sat }} / k P a=16.262-\frac{3799.89}{t /{ }^{0} C^{+226.35}}$
Prepare a T - xy diagram for $\mathrm{P}=101.33 \mathrm{kPa}$.

Code No: 07A50803
R07
7. What is the temperature at which $50 \%$ of 1 - butene may be dehydrogenated according to the following reaction, if the operating pressure is 2 atm and 15 moles of steam per mole of butadiene is supplied to the dehydrogenated tower $\mathrm{C}_{4} \mathrm{H}_{8(g)} \rightarrow$ $\mathrm{C}_{4} \mathrm{H}_{6(g)}+\mathrm{H}_{2(g)}$

|  | 1,3 - Butadiene | 1-Butene | H2 |
| :---: | :---: | :---: | :---: |
| $\Delta H_{f(298)}^{0}, \mathrm{cal} / \mathrm{g}-\mathrm{mol}$ | 26,330 | -30 | - |
| $\Delta G_{f(298)}^{0}, \mathrm{cal} / \mathrm{g}-\mathrm{mol}$ | 36,010 | 17,090 | - |
| $\alpha$ | 5.432 | 3.909 | 6.937 |
| $\beta \times 10^{3}$ | 53.224 | 62.848 | -0.200 |
| $\gamma \times 10^{6}$ | -17 | -19.517 | 0.481 |

8. Calculate the standard enthalpy change of 298.15 K for the reaction of butane $\mathrm{C}_{4} \mathrm{H}_{10}(\mathrm{~g})+\frac{13}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}+5 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ From the standard enthalpy of formation of the compounds at 298.15K $\Delta H_{f 298}^{0}(\mathrm{KJ})$ of $\mathrm{C}_{4} \mathrm{H}_{10}(\mathrm{~g}), \mathrm{CO}_{2}(\mathrm{~g}), \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ are respectively $-74,943,-393.978$ and -241.997 .
