U.S.N.

B.M.S. College of Engineering, Bengaluru-560019

Autonomous Institute Affiliated to VTU

June 2025 Semester End Main Examinations

Programme: B.E. **Semester: IV**
Branch: Chemical Engineering **Duration: 3 hrs.**
Course Code: 23CH4PCTD2 / 22CH4PCTD2 **Max Marks: 100**
Course: Process Engineering Thermodynamics-II

Instructions: 1. Answer any FIVE full questions, choosing one full question from each unit.
2. Missing data, if any, may be suitably assumed.

Important Note: Completing your answers, compulsorily draw diagonal cross lines on the remaining blank pages. Revealing of identification, appeal to evaluator will be treated as malpractice.

		UNIT - I	*CO*	*PO*	**Marks**
1	a)	Derive Maxwell's equations from fundamental property relations. State its significance.	*CO2*	*PO2*	**8**
	b)	Derive Clausius-Clapeyron equations with assumptions.	*CO2*	*PO2*	**8**
	c)	Determine the increase in entropy of solid magnesium when the temperature is increased from 300 K to 800 K at atmospheric pressure. The heat capacity is given by the following relation $C_P = 26.04 + 5.586 \times 10^{-3}\,T + 28.476 \times 10^{-4}\,T^{-2}$ Where, C_P is in J/mol K and temperature in K.	*CO1*	*PO1*	**4**
		OR			
2	a)	Show that $dU = -\left[P + T\left\{ \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \right\}\right] dV + C_V\, dT$	*CO2*	*PO2*	**12**
	b)	Show that $$\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial C_P}{\partial V}\right)_T = 0$$	*CO2*	*PO2*	**8**
		UNIT - II			
3	a)	Derive an Equation to deduce the effect of temperature and effect of pressure on the activity co efficient using fugacity equations for effect of pressure and temperature respectively.	*CO3*	*PO2*	**10**
	b)	The fugacity of component 1 in binary liquid mixture of components 1 and 2 at 298 K and 20 bar is given by where is in bar and x_1 are the mole fraction of component 1. Determine, (i) The fugacity f_1 of pure component 1; (ii) The fugacity coefficient f_1 ; (iii) The Henry's law constant K_1; (iv) The activity coefficient g_1.	*CO3*	*PO2*	**10**
		OR			

<table>
<tr><td></td><td>4</td><td>a)</td><td>Derive Gibbs-Duhem equation in terms of activity coefficient.</td><td>CO3</td><td>PO2</td><td>10</td></tr>
<tr><td></td><td></td><td>b)</td><td>At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are represented by
$V = 109.4 X 10^{-6} - 16.8 X 10^{-6}x - 2.64 X 10^{-6} x^2$, where x is the mole fraction of benzene and V has the units of m^3/mol. Find the expressions for the partial molar volumes of benzene and cyclohexane.</td><td>CO3</td><td>PO2</td><td>10</td></tr>
<tr><td></td><td></td><td></td><td>UNIT - III</td><td></td><td></td><td></td></tr>
<tr><td></td><td>5</td><td>a)</td><td>Explain the boiling point diagram (T-x-y diagram) along with the effect of pressure on Vapour-Liquid-Equilibria.</td><td>CO4</td><td>PO3</td><td>10</td></tr>
<tr><td></td><td></td><td>b)</td><td>The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the Antoine equations
$$\ln P_1^S = 14.5463 - \frac{2940.46}{T - 35.93}$$
$$\ln P_2^S = 14.2724 - \frac{2945.47}{T - 49.15}$$
Where T is in K and P is in kPa. Assuming that the solutions formed by these are ideal, calculate
(i) x_1 and y_1 at 327 K and 65 kPa
(ii) T and y_1 at 65 kPa and $x_1 = 0.4$</td><td>CO4</td><td>PO3</td><td>10</td></tr>
<tr><td></td><td></td><td></td><td>OR</td><td></td><td></td><td></td></tr>
<tr><td></td><td>6</td><td>a)</td><td>Mixtures of n-Heptane (A) and n-Octane (B) are expected to behave ideally. The total pressure over the system is 101.3 kPa. Using the vapour pressure data given below,
(i) Construct the boiling point diagram and
(ii) The equilibrium diagram
(iii) Deduce an equation for the equilibrium diagram using an arithmetic average “∝” value.
<table>
<tr><td>T, (K)</td><td>371.4</td><td>378</td><td>383</td><td>388</td><td>393</td><td>398.6</td></tr>
<tr><td>P_s^A (kPa)</td><td>101.3</td><td>125.3</td><td>140</td><td>160</td><td>179.9</td><td>205.3</td></tr>
<tr><td>P_s^B (kPa)</td><td>44.4</td><td>55.6</td><td>64.5</td><td>74.8</td><td>86.6</td><td>101.3</td></tr>
</table></td><td>CO4</td><td>PO3</td><td>10</td></tr>
<tr><td></td><td></td><td>b)</td><td>Explain the P-x-y diagram with the effect of temperature near the critical point.</td><td>CO4</td><td>PO3</td><td>10</td></tr>
<tr><td></td><td></td><td></td><td>UNIT - IV</td><td></td><td></td><td></td></tr>
<tr><td></td><td>7</td><td>a)</td><td>Define azeotropes and explain minimum boiling and maximum boiling azeotropes with P-x-y and T-x-y diagrams.</td><td>CO6</td><td>PO3</td><td>10</td></tr>
<tr><td></td><td></td><td>b)</td><td>The following data gives the composition versus total pressure for the system chloroform (1)–ethyl alcohol (2) at 328 K:</td><td>CO4</td><td>PO3</td><td>10</td></tr>
</table>

<table>
<tr><td></td><td></td><td></td><td><table><tr><td>Components</td><td>1</td><td>2</td></tr><tr><td>x_i</td><td>0.0331</td><td>0.0348</td></tr><tr><td>P,kPa</td><td>40.84</td><td>84.88</td></tr></table>
Vapor pressures of chloroform and acetone at 328 K are 82.35 and 37.30 kPa, respectively. Estimate the constants in the Margules equation</td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td>OR</td><td></td><td></td><td></td></tr>
<tr><td></td><td>8</td><td>a)</td><td>Explain the Redlich-Kister method to check the consistency of the given VLE data.</td><td><i>CO6</i></td><td><i>PO3</i></td><td>4</td></tr>
<tr><td></td><td></td><td>b)</td><td>Liquids A and B form an azeotrope containing 46.1 mole per cent A at 101.3 kPa and 345 K. At 345 K, the vapor pressure of A is 84.8 kPa and that of B is 78.2 kPa. Calculate the van Laar constants.</td><td><i>CO4</i></td><td><i>PO3</i></td><td>8</td></tr>
<tr><td></td><td></td><td>c)</td><td>At 318 K and 24.4 kPa, the composition of the system ethanol (1) and toluene (2) at equilibrium is $x_1 = 0.3$ and $y_1 = 0.634$. The saturation pressures at the given temperature for the pure components are $P_1^s = 23.06$ kPa and $P_2^s = 10.05$ kPa, respectively. Calculate the liquid-phase activity coefficients.</td><td><i>CO4</i></td><td><i>PO3</i></td><td>8</td></tr>
<tr><td></td><td></td><td></td><td>UNIT - V</td><td></td><td></td><td></td></tr>
<tr><td></td><td>9</td><td>a)</td><td>Evaluate the equilibrium constant at 600 K for the reaction
$CO (g) + 2H_2 (g) \rightarrow CH_3OH (g)$
Given that the Gibbs free energy function for CO, H_2 and methanol at 600 K are respectively –203.81, –136.39 and –249.83 J/mol K. The heats of formation at 298 K of CO (g) and CH_3OH (g) at 298 K are –110,500 J/mol and –200,700 J/mol.</td><td><i>CO5</i></td><td><i>PO3</i></td><td>10</td></tr>
<tr><td></td><td></td><td>b)</td><td>Derive van ’t Hoff equation from Gibbs–Helmholtz equation.</td><td><i>CO5</i></td><td><i>PO3</i></td><td>10</td></tr>
<tr><td></td><td></td><td></td><td>OR</td><td></td><td></td><td></td></tr>
<tr><td></td><td>10</td><td>a)</td><td>Derive an equation for the standard free energy change using chemical potential relationship
$$\Delta G^0 = -RT \ln K$$</td><td><i>CO5</i></td><td><i>PO3</i></td><td>10</td></tr>
<tr><td></td><td></td><td>b)</td><td><i>n</i>-Butane is isomerised to <i>i</i>-butane by the action of catalyst at moderate temperatures. It is found that the equilibrium is attained at the following compositions.<table><tr><td>Temperature, K</td><td>Mol %, <i>n</i>-butane</td></tr><tr><td>317</td><td>31</td></tr><tr><td>391</td><td>43</td></tr></table>Assuming that activities are equal to the mole fractions, calculate the standard free energy of the reaction at 317 K and 391 K and the average value of the heat of reaction over this temperature range.</td><td><i>CO5</i></td><td><i>PO3</i></td><td>10</td></tr>
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