## SAINTGITS COLLEGE OF ENGINEERING (AUTONOMOUS)

(AFFILIATED TO APJ ABDUL KALAM TECHNOLOGICAL UNIVERSITY, THIRUVANANTHAPURAM)

\section*{FOURTH SEMESTER B.TECH DEGREE EXAMINATION (S), SEPT 2022 CHEMICAL ENGINEERING <br> (2020 SCHEME)

## Course Code : <br> 20CHT202

 <br> 20CHT202}Course Name:
Max. Marks :

## Chemical Engineering Thermodynamics

100
Duration: 3 Hours

## PART A <br> (Answer all questions. Each question carries 3 marks)

1. State mathematically the first law of thermodynamics for an open, closed and isolated system.
2. The $\mathrm{P}-\mathrm{V}$ diagram of an ideal gas is shown in the figure. What is the change in internal energy, entropy and the work done by the gas when it completes one cycle starting from point A in antilock wise direction.

3. Assuming that the properties of a pure fluid can be expressed as T (temperature), P (pressure), V (volume) and S (entropy) derive the following expression from the definitions of change in internal energy.

$$
\left(\frac{\partial T}{\partial V}\right)_{S}=-\left(\frac{\partial P}{\partial S}\right)_{V}
$$

4. Explain the Joule Thomson's effect.
5. Explain the term partial molar quantities, how are they different from molar quantities.
6. Write down the Gibbs Duhem equation in terms of activity coefficient. Mention two applications of the same.
7. Draw the T-x-y diagram of a binary solution. Highlight bubble point, dew point and tie line of the diagram.
8. Draw the T-x-y diagram for positive deviations from ideality, as well as minimum boiling azeotropes.
9. A gas mixture containing 2 moles nitrogen, 7 moles hydrogen and 1 mole ammonia initially, is undergoing the following reaction.

$$
\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightarrow 2 \mathrm{NH}_{3}
$$

Derive expressions for the mole fractions of ammonia in the reaction mixture in terms of the extent of reaction.
10. Write down the Van't Hoff equation and describe the terms.

## PART B

## (Answer one full question from each module, each question carries 14 marks)

## MODULE I

11. a) A system containing 2.5 mol of ideal gas for which molar $\mathrm{C}_{\mathrm{V}}$ is $20.71 \mathrm{~J} \mathrm{~mol}^{-1}$ $\mathrm{K}^{-1}$ is taken through a cycle indicated in the diagram below, in the direction indicated by arrow. Path 3-1 is an isothermal process. Calculate $\mathrm{q}, \mathrm{w}, \Delta \mathrm{U}$ and $\Delta \mathrm{H}$ for each segment and for the cycle, assuming that the specific heat is constant.

b) Define Carnot's principle and find the efficiency of a Carnot engine working between 10 K and 300 K .

## OR

12. a) Show that for an open system at steady state the mechanical energy balance can be written in the following form (here $u$ denote the velocity, $Z$ the elevation of the fluid from a reference, V the control volume, P is the pressure of the fluid in the control volume, $\mathrm{W}_{\mathrm{s}}$ is the shaft work, F is the frictional losses)

$$
\begin{equation*}
d\left(\frac{u^{2}}{2}\right)+g d Z+V d P+W_{s}=0 \tag{14}
\end{equation*}
$$

For a isentropic flow through a convergent - divergent nozzle show that the velocity of fluid inside the nozzle varies with cross section area as,

$$
\frac{d u}{d A}=\frac{u}{A}\left(\frac{1}{M a^{2}-1}\right)
$$

## MODULE II

13. a) Draw the P-V diagram (isotherms) of water and explain the diagram. Mark the liquid, vapor and liquid - vapor mixture regions. Mark the critical properties. Explain the difference between a gas and a vapor.
b) For a pure fluid with volume V , temperature T , specific heats at constant
pressure and volume as $C_{P}$ and $C_{V}$, coefficient of volume expansivity $\beta$ and coefficient of volume compressibility $\kappa$
Show that

$$
\begin{gathered}
C_{P}-C_{V}=\frac{\beta^{2} V T}{\kappa} \\
\text { OR }
\end{gathered}
$$

14. a) The equation of state of a gas is expressed as follows, $P V(1-b P)=R T$, where $\mathrm{P}, \mathrm{V}, \mathrm{R}$ and T have usual meanings, b is a parameter. For the above gas show that the change in Gibbs free energy of the gas when it moves from state 1 to 2 can be expressed as

$$
\begin{equation*}
\Delta G=R T \ln \left(\frac{P_{2}\left(1-b P_{1}\right)}{P_{1}\left(1-b P_{2}\right)}\right) \tag{7}
\end{equation*}
$$

b) Derive the Gibbs Helmholtz equation

## MODULE III

15. a) For a solution assume the total Gibbs free energy to be a function of $T, P$, and number of moles as follows,

$$
\begin{equation*}
G^{T}=G^{T}\left(T, P, n_{1}, n_{2} \ldots\right) \tag{10}
\end{equation*}
$$

If the solution has a partial molar enthalpy $\bar{H}_{i}$, chemical potential $\mu_{i}$, temperature T. Show that $\boldsymbol{\mu}_{\boldsymbol{i}}=-\boldsymbol{T}\left(\int \frac{\overline{\boldsymbol{H}}_{i}}{\boldsymbol{T}^{2}} \boldsymbol{d} \boldsymbol{T}\right)+$ Constant
b) Explain the Lewis Randall rule, with mathematical expression.

## OR

16. For a solution with N components show that if $\mathrm{M}^{t}$ is any total property then

$$
\begin{equation*}
\sum_{i=1}^{N} n_{i} d \overline{M_{\imath}}=0 \tag{14}
\end{equation*}
$$

Where $n_{i}$ is the number of moles of species i , and $\bar{M}_{i}$ is the partial molar property of species i. For a binary mixture use the above equation and derive the Gibb's Duhem equation in the following form,

$$
x_{1} \frac{\partial \ln \left(\gamma_{1}\right)}{\partial x_{1}}=x_{2} \frac{\partial \ln \left(\gamma_{2}\right)}{\partial x_{2}}
$$

## MODULE IV

17. a) With the help of a neat labelled diagram explain the T-x-y diagram (at constant pressure) of a partially miscible system. Clearly mark the homogenous liquid phase, heterogeneous liquid phase, and the three phase equilibrium temperature. Assume a mixture below the three phase point and explain the various characteristics of the curve that takes place while you heat the system. Using a diagram explain the effect of pressure on the above, also mark the upper critical solution temperature.
b) Write down the Van Lar equations for a binary solution
18. An arbitrary system A-B system forms an azeotrope containing $58.5 \%$ (mol) B at 393 K and 101.3 kPa . Calculate the equilibrium vapour composition for a solution containing $20 \%$ (mol) B. The relative volatility of A with reference to B is 1.6 and may be assumed to remain constant in the temperature range involved. The vapour pressure of B at 393 K is 124.76 kPa .

## MODULE V

19. a) Explain the effect of inert on the chemical conversion.
b) The reaction $\mathrm{N}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}$ takes place in the gas phase at 2975 K and 2025 kPa . The reaction mixture initially comprises 15 mol percent oxygen, 77 mol percent nitrogen and the rest inerts. The standard Gibbs free energy change for the reaction is $113.83 \mathrm{~kJ} / \mathrm{mol}$ at this temperature. Assuming ideal gas behaviour, calculate the partial pressures of all species at equilibrium. How is the conversion of oxygen affected when the initial mixture were free of inert?

## OR

20. a) Methanol is synthesized according to the following reaction.

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

Standard heat of formation of CO and methanol at 298 K are respectively, $-110.6 \mathrm{~kJ} / \mathrm{mol}$ and $-238.64 \mathrm{~kJ} / \mathrm{mol}$. The latent heat of vaporization of methanol at 298 k is 37.98 K . The specific heats in $(\mathrm{J} / \mathrm{mol} \mathrm{K})$ are given by,
$\mathrm{C}_{\mathrm{P}}\left(\mathrm{CH}_{3} \mathbf{O H}\right)=18.382+101.564 \times 10^{-3} T-28.683 \times 10^{-6} T^{2}$
$\mathrm{C}_{\mathrm{P}}(\mathrm{CO})=28.068+4.631 \times 10^{-3} T-2.5773 \times 10^{4} T^{-2}$
$\mathrm{C}_{\mathrm{P}}\left(\mathrm{H}_{2}\right)=\mathbf{2 7 . 0 1 2}+\mathbf{3 . 5 0 9} \times \mathbf{1 0}^{-3} T+6.9006 \times \mathbf{1 0}^{4} T^{-2}$
Calculate the standard heat of reaction at 1073 K
b) Derive an expression for equilibrium criteria for a general reaction

$$
a A+b B \rightarrow c C+d D
$$

