SUMMER-19 EXAMINATION

Model Answer

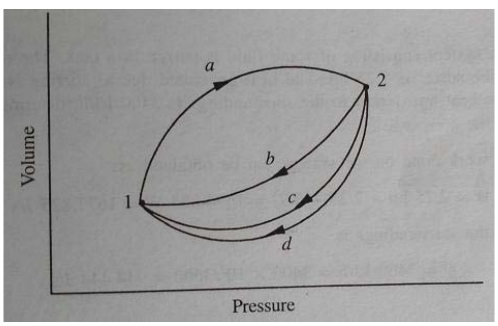
Subject title: Chemical Engineering Thermodynamics Subject code 22406

Important Instructions to examiners:

1) The answers should be examined by key words and not as word-to-word as given in the model answer scheme.
2) The model answer and the answer written by candidate may vary but the examiner may try to assess the understanding level of the candidate.
3) The language errors such as grammatical, spelling errors should not be given more Importance (Not applicable for subject English and Communication Skills.
4) While assessing figures, examiner may give credit for principal components indicated in the figure. The figures drawn by candidate and model answer may vary. The examiner may give credit for any equivalent figure drawn.
5) Credits may be given step wise for numerical problems. In some cases, the assumed constant values may vary and there may be some difference in the candidate's answers and model answer.
6) In case of some questions credit may be given by judgement on part of examiner of relevant answer based on candidate's understanding.
7) For programming language papers, credit may be given to any other program based on equivalent concept.

Q No.		Answer	Marking scheme
1		**Attempt any FIVE of the following**	10
1	a	**System:** It is the part of the universe which is set apart for the process to takes place. **Surroundings:** The part of the universe outside the system and separated from the system by boundaries is called surroundings.	1 1
1	b	**Open system:** Systems which can exchange both mass and energy across the boundaries are known as open system. **Closed system:** Systems that can exchange energy with the surroundings but which cannot transfer mass across the boundaries are known as closed system.	1 1
1	c	**Zeroth law of thermodynamics:** It states that if body A is in thermal equilibrium with body B and B is in thermal equilibrium with body C, then C is also in thermal equilibrium with A.	2
1	d	**Sign convention used for work done:** W is positive when work is done by the system and W is negative when work is done on the system.	2
1	e	**Relation between C_p and C_v for ideal gas:** $C_p - C_v = R$	2
1	f	**Formula to calculate Vander Waals constant in Vander Waals equation:** Vander Waals equation is $\left(P + \frac{a}{V^2}\right)(V-b) = RT$	

		Where a and b are constants. $a = \frac{27R^2 T_C^2}{64P_C}$ and $b = \frac{RT_C}{8P_C}$ where T_c and P_c are critical temperature and critical pressure respectively.	 1 1
1	g	**Equation for calculating entropy change during isothermal mixing of ideal gases.** $\Delta S = -R \sum x_i \ln x_i$ where x_i is the mole fraction of i^{th} component in the gas mixture and R is the universal gas constant.	2
2		**Attempt any THREE of the following**	**12**
2	a	**Extensive property:** If the property of the system depend on the quantity of matter present in the system , then it is known as extensive property. Eg Volume, mass. **Intensive property:** If the property of the system does not depend on the quantity of matter present in the system, then it is known as intensive property. Eg. Temperature, Pressure.	1 1 1 1
2	b	**Internal energy is a state function:** Consider a system undergoing a series of changes from state 1 to state 2 along [illegible] If the surrounding remain unchanged, the change in internal energy ΔU along [illegible] the other hand, if [illegible] would be a residuum of energy resulting from cyclic process. Energy would	4

		have been created without the loss of an equivalent amount of another kind, which is in contrast to the first law of thermodynamics. As per first law, [illegible] means that internal energy accompanying a given change of state depends only on the end state and not on the path followed. ie internal energy is a state function. 	
2	c	Work done on the system = - 1678J/S Heat given out to the surroundings = -3400kJ/ hour = -3400* 1000/ 3600 = - 944.44J/S From first law of thermodynamics , $\Delta U = Q - W$ = - 944.44-(-1678) = **733.56 J/S**	1 1 2
2	d	Let T_1, T_2 and T be the temperature of hot water, cold water and the final temperature of the mixture respectively. Let m_1 and m_2 be the mass of hot water and cold water respectively. $T_1 = 375K$ $T_2 = 275$ K $m_1 = 10$ kg $m_2 = 30$kg C_p of water = 4.2kJ/ kg K Heat lost by hot water = Heat gained by cold water	

		$m_1C_p(T_1-T)$ hot water = $m_2C_p(T-T_2)$ cold water . 10 * 4.2* (375 − T) = 30* 4.2* (T-275) T = **300K**	2
		Let ΔS_1 be the entropy change of hot water and ΔS_2 be the entropy change of cold water. $\Delta S_1 = m_1 \int_{T_1}^{T} C_P \frac{dT}{T}$ = $m_1 C_P \ln\frac{T}{T_1}$ = 10* 4.2 * ln($\frac{300}{375}$) = -9.37 kJ / K $\Delta S_1 = m_2 \int_{T_2}^{T} C_P \frac{dT}{T}$ = $m_2 C_P \ln\frac{T}{T_2}$ = 30* 4.2 * ln($\frac{300}{275}$) = 10.96 kJ / K Total entropy change = $\Delta S_1 + \Delta S_2$ = -9.37 + 10.96 = **1.593 kJ/K**	2
3		**Attempt any THREE of the following**	**12**
3	a	**Criteria for thermal, mechanical, chemical and thermodynamic equilibrium:** **Thermal equilibrium:** A system is said to be in thermal equilibrium if there is no flow of heat from one portion of system to another. The temperature remains uniform or unchanged throughout the system. In thermal equilibrium there is no thermal gradient within the system and there is no temperature difference between system and its surrounding.	1
		Mechanical equilibrium: A system is said to be in mechanical equilibrium if there is no imbalance of forces within the system. The pressure is uniform throughout the system or there are no unbalanced forces within the system. In mechanical equilibrium there is no pressure difference or unbalanced forces between two interacting systems.	1
		Chemical equilibrium: A system is said to be in chemical equilibrium if the composition of components present in the system is uniform throughout the system. The concentration or chemical potential remains constant throughout	1

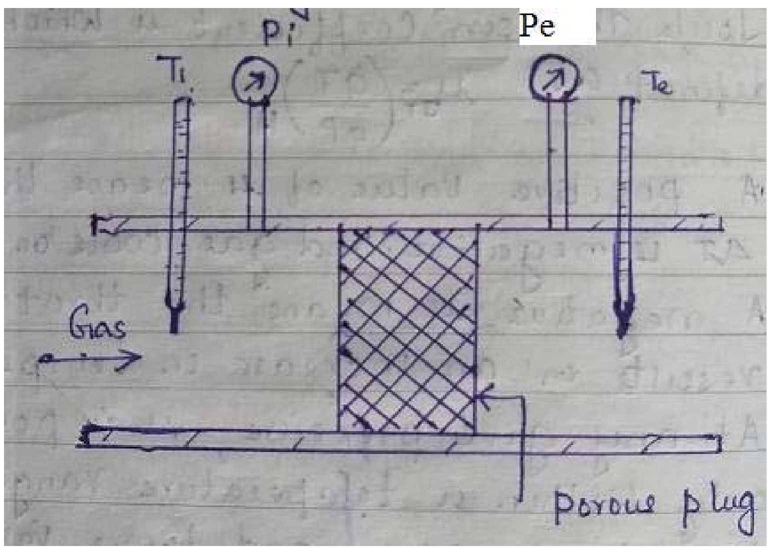
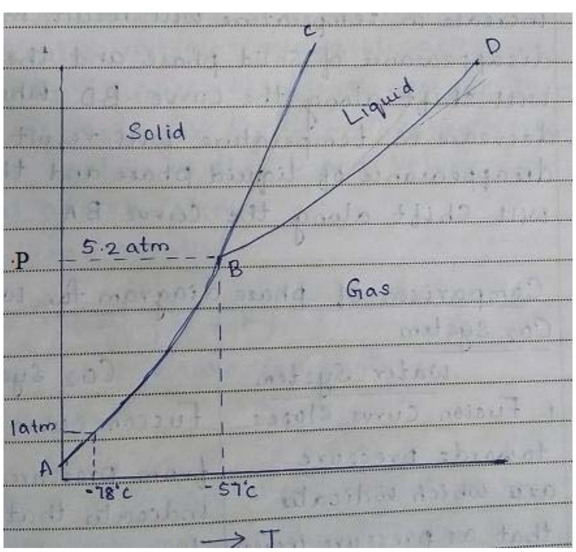
		the system. In chemical equilibrium there is no tendency for the chemical reaction to occur when the system is isolated. **Thermodynamic equilibrium**. If a system is simultaneously in state of thermal equilibrium, mechanical equilibrium and chemical equilibrium, then it is said to be in state of thermodynamic equilibrium.	1
3	b	Data: $P_1 = 0.1$ MPa $T_1 = 300K$ $V_2 = V_1 / 15$ $n = 1.2$ PV^n = constant $P_1 V_1^n = P_2 V_2^n$ $0.1 * V_1^{1.2} = P_2 (V_1 / 15)^{1.2}$ $P_2 = 0.1 * 15^{1.2} =$ **2.578 M Pa.** $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$ $\frac{T_2}{300} = \left(\frac{2.578}{0.1}\right)^{\frac{0.2}{1.2}}$ T_2= **515.63K**	2 2
3	c	**Equation for entropy change of an ideal gas in terms of temperature and volume:** From first law of thermodynamics, dU = dQ [illegible]dW [illegible] [illegible] dW = PdV [illegible] For ideal gas dU= n C_v[illegible] [illegible] Substituting ii,iii and iv in i	

		$TdS = n\,C_v dT + PdV$ $dS = \frac{n\,C_v dT}{T} + \frac{PdV}{T}$ For ideal gas $P = \frac{nRT}{V}$ Substituting $dS = \frac{n\,C_v dT}{T} + \frac{nRdV}{V}$ Integrating between limits (Assuming C_v is independent of temperature) $\int_{S_1}^{S_2} dS = nC_v\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V}$ $\Delta S = nC_v \ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$	2 2
3	d	n = 2 moles C_p of water = 4.2 kJ/kg K = 4.2*18 *1000 / 1000 = 75.6 J / mol K C_p of steam = 1.9 kJ/kg K = 1.9*18*1000/ 1000 = 34.2 J / mol K ΔH vaporization = 2257 kJ/ kg = 2257*18* 1000 / 1000 = 40626 J /mole Water at 273 K to steam at 473K. Entropy change when 2 moles of water at 273K is heated to water at 373K $\Delta S_1 = n\int_{T_1}^{T_2} C_{P\,liquid}\frac{dT}{T} = nC_{p\,water}\ln(T_2 / T_1)$ = 2*75.6 * ln(373 / 273) = **47.19 J / K** Entropy change when 2 moles of water at 373K is converted to steam at 373K $\Delta S_2 = n * \frac{\Delta H_{Vaporization}}{T_b}$ = 2 * 40626 / 373 = **217.83 J / K** Entropy change when 2 moles of steam at 373K is heated to steam at 473K $\Delta S_3 = n\int_{T_1}^{T_2} C_{P\,Vapour}\frac{dT}{T} = nC_{p\,steam}\ln(T_2 / T_1)$ = 2* 34.2 * ln(473 / 373) = **16.25 J / K** Total entropy change = $\Delta S_1 + \Delta S_2 + \Delta S_3$ = 47.19 + 217.83 + 16.25 = **281.27 J /K**	 1 1 1 1

4		**Attempt any THREE of the following**	**12**
4	a	[illegible] The phase rule states that number of degree of freedom in a physical system at equilibrium is equal to the number of components in the system minus the number of phases plus the constant 2. Mathematically, it is stated as follows: $F = C - P + 2$ where C is the number of components, P is the number if phases in thermodynamic equilibrium with each other and F is the number of degrees of freedom or variance of the system. **Degree of freedom for a binary mixture of benzene and toluene in equilibrium with its own vapour** $C = 2$ $P = 2$ $F = C - P + 2 = 2 - 2 + 2 =$ **2**	2 2
4	b	Reaction is $CO + \frac{1}{2} O_2 \rightarrow CO_2$ Entropy of CO = 198 J/ mol K Entropy of O_2 = 205.2 J / mol K Entropy of CO_2 = 213.8 J / mol K [illegible] ΔS products = **213.8 J / mol K** ΔS reactants = 198 + (205.2 / 2) = **300.6 J / mol K** ΔS reaction = 213.8 - 300.6 = **86.8 J / mol K**	1 1 2
4	c	**Entropy change during isothermal mixing is R ln 2** When two distinct intermingling ideal gases are mixed, the resulting entropy change is given by $\Delta S = -R\sum x_i \ln x_i$ The given mixture is an equimolar mixture of two distinct ideal gases,	2

		therefore $x_i = 0.5$ [illegible] = -[illegible] $\ln x_i$ = $-R(0.5 \ln 0.5 + 0.5 \ln 0.5)$ $= -R \ln 0.5 = -R \ln(1/2) =$ **R ln 2**	2
4	d	[illegible] [illegible] [illegible] [illegible] $_R$ [illegible] $_S$) - [illegible] $_A$ [illegible] $_B$). At equilibrium there is no [illegible] [illegible] $_R$ [illegible] $_S$) - [illegible] $_A$ [illegible] $_B$) = 0 [illegible] $_R$ [illegible] $_S$ [illegible] $_A$ [illegible] $_B$) [illegible] ^{0} + RT $\ln p_i$ [illegible] $_R^0$ + RT $\ln p_R$ [illegible] $_S^0$ + RT $\ln p_S$ [illegible] $_A^0$ + RT $\ln p_A$) + [illegible] $_B^0$ + RT $\ln p_B$) RT ln $\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = (a\,\mu_A^0 + b\,\mu_B^0) - (r\,\mu_R^0 + s\,\mu_S^0)$ = - [illegible] = - [illegible] $\ln\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = \frac{-\Delta G\ \text{reaction}}{RT}$ But $\left(\frac{p_R^r\, p_S^s}{p_A^a\, p_B^b}\right) = K_p$ [illegible] RT $\ln K_p$	2 2
4	e	[illegible] Le-[illegible]f we induce a stress on a system at equilibrium, then the equilibrium will shift so as to relieve that stress. The stress may be a change in concentration, temperature or pressure. As per this principle, the equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium in the reaction shifts in the direction	2

	a	that tends to nullify the effect of the change. **Effect of change in pressure on the dissociation reaction $N_2O_4 \rightleftharpoons 2NO_2$** According to Le Chateliers principle, increase in pressure favours the reaction in the direction which takes place with a decrease in the total number of moles. Similarly decrease in pressure favours the reaction in the direction which takes place with an increase in the total number of moles. For the above reaction , increase in pressure favours the backward reaction since backward reaction is taking place with a decrease in the number of moles and decrease in pressure favours the forward reaction since forward reaction is taking place with an increase in the number of moles (ie more NO_2 will be formed).	2
5		**Attempt any TWO of the following**	**12**
5	a	**Joule Thomson porous plug experiment:** This experiment is used to measure the change in temperature of a gas when it flows steadily through a porous plug. The apparatus consists of a long, horizontal and insulated pipe at the center of which a porous plug is inserted. On either side of the porous plug, provision is made to measure the temperature and pressure of the flowing fluid. The pipe is insulated, therefore Q = 0, no shaft work is involved ,Ws = 0, horizontal apparatus , therefore Zi = Ze. Ignore the change in velocity due to the flow through the porous plug, Vi = Ve, therefore he = hi. Ie whenever a fluid flows steadily from high pressure to low pressure through a porous plug or partially opened valve inserted in a long horizontal and insulated pipe, the enthalpy of fluid remains constant. Such a flow is called	4

		throttling. Therefore a throttling process is an isenthalpic process. The slope of the isenthalpic curve is defined as Joule- Thomson or Joule-Kelvin coefficient μ_{JT}. $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$ 	2
5	b	**Phase diagram of carbon dioxide system:** 	3

		It has three distinct phases- solid, liquid and gas. AB is the sublimation curve along which solid CO_2 is in equilibrium with the gas. BD is the vaporization curve along which liquid CO_2 is in equilibrium with the gas. BC is the fusion curve along which solid CO_2 and liquid CO_2 are in equilibrium with each other Fusion curve slopes away from the pressure axis which indicates that increase in pressure raises the melting point of solid CO_2. Along all these curves, the system are univariant (degree of freedom is 1). B is the triple point where the three phases of CO_2 coexist at equilibrium. The temperature at this point is -57^0C and pressure is 5.2 atm. A slight variation in temperature or pressure at this point may result in the disappearance of one of the three phases. A slight increase in temperature will result in the disappearance of solid phase and the equilibrium will shift along the curve BD while a slight decrease in temperature will result in the disappearance of liquid phase and the equilibrium will shift along the curve BA.	3
5	c	$N_2 + 3H_2 \rightleftharpoons 2NH_3$ P = 30 atm Let there be 1 mol of N_2 and 3 mol of H_2 present initially. Let x moles of NH_3 be produced at equilibrium	2

	N_2	H_2	NH_3	
Moles present initially	1	3	0	
Moles reacted / produced at equilibrium	x/2	3x/2	x	

Moles present at equilibrium	1-(x /2)	3-(3x /2)	x	Total moles = 4-x
Mole fraction	$\frac{1-\frac{x}{2}}{4-x}$	$\frac{3-\frac{3x}{2}}{4-x}$	$\frac{x}{4-x}$	
Partial pressure	$30*\left(\frac{1-\frac{x}{2}}{4-x}\right)$	$30*\left(\frac{3-\frac{3x}{2}}{4-x}\right)$	$\frac{30x}{4-x}$	

% of NH_3 at equilibrium = 10% = 0.1 — 2

$\frac{x}{4-x}$ = 0.1

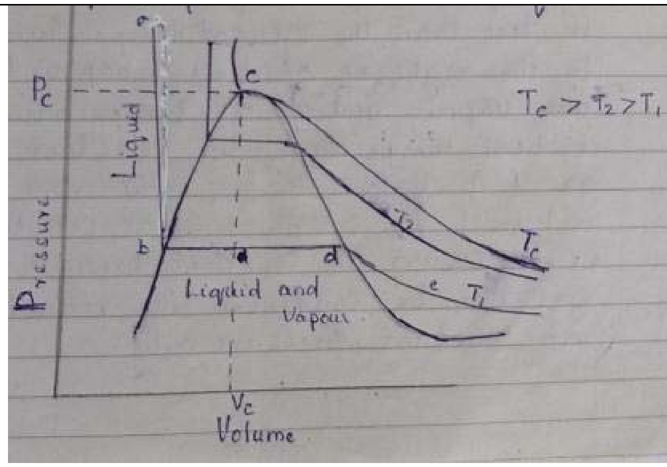
x = 0.3636

Substitute the value of x in the equation for partial pressure

Then P_{N2} = 6.75atm, P_{H2} = 20.25atm P_{NH3} = 2.996atm — 2

$K_p = \frac{P_{NH3}^2}{P_{N2}\ P_{H2}^3}$ = $2.996^2 /(6.75 * 20.25^3)$ = **$1.6014*10^{-4}$ atm^{-2}**

6		**Attempt any TWO of the following**	**12**
6	a	**P-V diagram of water.** Consider the thermodynamic state of water represented as a function of pressure and volume.	



3

[illegible]

change in volume of water with pressure at constant temperature T_1 is along the isotherm a-b-d-e. Since liquid water is almost incompressible, the

[illegible]

[illegible]

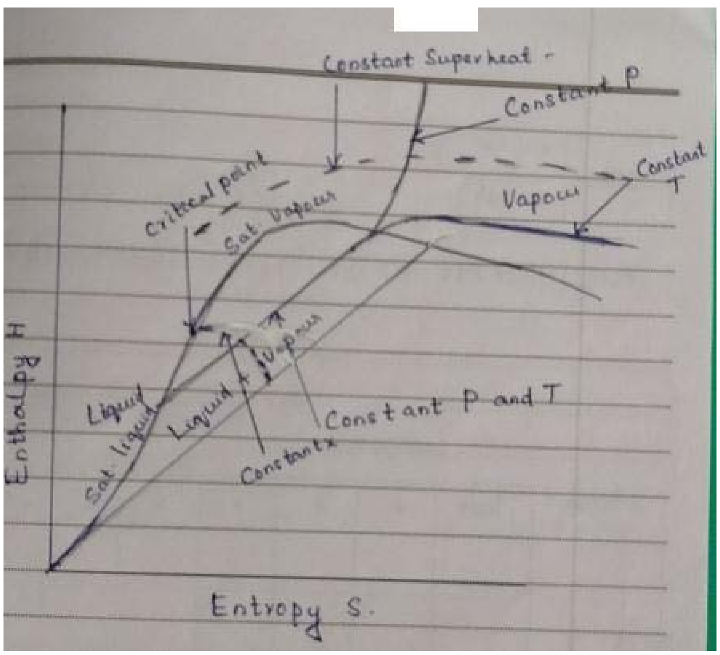
[illegible]

liquid and vapour are in equilibrium. The temperature and pressure remains constant during the phase change as indicated by the horizontal portion of the isotherm b-d. Saturated liquid state is represented by point b and saturated vapour state by point d. The temperature and pressure at which the liquid and vapour phases coexist at equilibrium is called saturation temperature and pressure. Further reduction in pressure increases the volume along the curve d-e. When the pressure over the system is brought down to below saturation pressure at constant temperature (or when the temperature is increased above saturation temperature at constant pressure), the vapour gets superheated. The locus of the saturated phases is represented by the dome shaped curve b-c-d. the area under the dome represents two phase region, the area to the left of the

3

curve b-c is the liquid region and the area to the right of the curve c-d is the vapour region. When the temperature of the system is increased to T_c, the critical temperature , the saturated liquid and saturated vapour phases become indistinguishable. The properties of the substance at the critical point are known as critical properties.

6 b **Mollier diagram**



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The Enthalpy-Entropy diagram is known as Mollier diagram.

$\left(\frac{\partial H}{\partial S}\right)_P = T$. This equation forms the basis of Mollier diagram. The energy requirement in flow process in general and the temperature changes involved in isentropic and isenthalpic processes are easily determined using these charts. The lines of constant T and P shown within the two phase region separates in the vapour region in to pressure lines that rise continuously and temperature lines that drop and eventually become horizontal. Lines of

2

constant quality are also shown in the two phase region.

6 c **Relation between conversion and thermodynamic equilibrium constant for 2nd order reversible reaction**

Reaction is [illegible]

Let 1 mole of A and 1 mole of B is present initially.

x mole of A reacts at equilibrium

P is the total pressure.

	A	B	R	S	
Moles present initially	1	1	0	0	
Moles reacted / produced at equilibrium	x	x	x	x	
Moles present at equilibrium	1-x	1-x	x	x	Total moles = 2
Mole fraction	(1-x)/2	(1-x)/2	x/2	x/2	
Partial pressure	P(1-x)/2	P(1-x)/2	Px/2	Px/2	

3

$$K_p = \frac{P_{R*}P_S}{P_{A*}P_B} = \frac{\frac{Px}{2}*\frac{Px}{2}}{\frac{P(1-x)}{2}*\frac{P(1-x)}{2}} = \frac{x^2}{(1-x)^2} = \frac{x^2}{1-2x+x^2}$$

$K_p\ (1-2x+x^2) = x^2$

$K_p - 2K_p x + K_p x^2 = x^2$

$K_p - 2K_p x + K_p x^2 - x^2 = 0$

$x^2 (K_p - 1) - 2K_p x + K_p = 0$

$$x = \frac{2K_P \pm \sqrt{4K_P^2 - 4(K_P-1)K_P}}{2(k_P-1)}$$

3