



SUMMER-22 EXAMINATION
Model Answer

Subject title: Chemical Engineering Thermodynamics

Subject code

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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.
- 8) As per the policy decision of Maharashtra State Government, teaching in English/Marathi and Bilingual (English + Marathi) medium is introduced at first year of AICTE diploma Programme from academic year 2021-2022. Hence if the students in first year (first and second semesters) write answers in Marathi or bilingual language (English +Marathi), the Examiner shall consider the same and assess the answer based on matching of concepts with model answer.



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Q No.	Answer	Marking scheme
1	Attempt any five	10
1	a Isochoric process Isochoric process (constant volume process) in thermodynamics is the process in which the volume of closed system remains constant.	2
1	b Adiabatic process If there is no heat interaction between the system and the surroundings, then such a process is known as an adiabatic process. i.e. Heat is neither absorbed from the surrounding nor given out to the surrounding.	2
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 Heat capacity The heat capacity of a substance is the quantity of heat to be supplied to effect a temperature rise of one degree. Specific heat The specific heat is the amount of heat to be supplied per unit mass of the substance to raise the temperature by one degree.	1 1
1	e 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. Sign convention used for heat	1



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		Heat (Q) flow in to system is taken as positive and heat flow out of the system is taken as negative.	1
1	f	Gibb's Phase rule: The phase rule states that number of degree of freedom of the system is related to the number of components and number of phases by the equation $F = C - P + 2$ for any system at equilibrium at a definite temperature and pressure.	2
1	g	Third law of thermodynamics: The law states that absolute entropy is zero for a perfect crystalline substance at absolute zero temperatures	2
2		Attempt any three	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.	1 1
		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
2	b	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, $W_s = 0$,	4



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horizontal apparatus, therefore $Z_i = Z_e$.

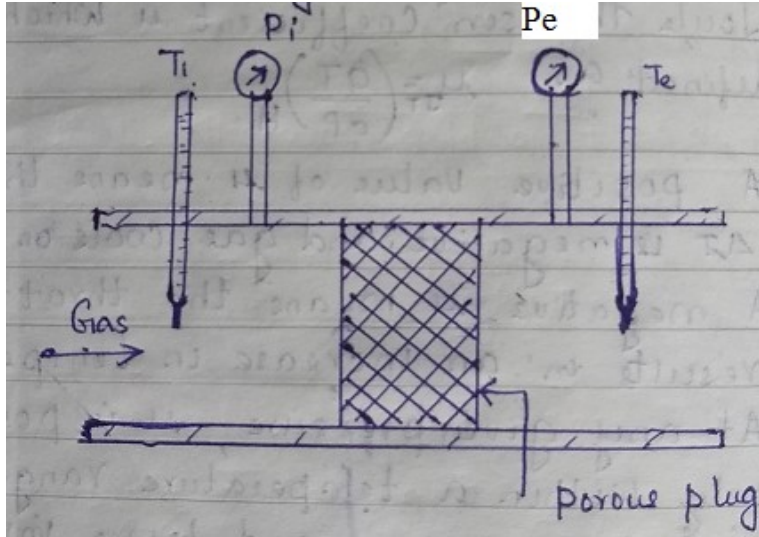
Ignore the change in velocity due to the flow through the porous plug,

$V_i = V_e$, therefore $h_e = h_i$.

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 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

c

$P_1 = 1.5 \text{ bar}$

$T_1 = 65^\circ\text{C} = 338 \text{ K}$

$P_2 = 9 \text{ bar}$

$\gamma = 1.23$



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		For adiabatic process $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\gamma-1/\gamma}$ $\frac{T_2}{338} = \left(\frac{9}{1.5}\right)^{1.23-1/1.23}$ $T_2 = 472.52 \text{ K} = 199.52^\circ\text{C}$ Temperature at the end of compression $T_2 = 472.52 \text{ K} = 199.52^\circ\text{C}$	2 2
2	d	$X_1 = 21\% = 0.21$ $X_2 = 79\% = 0.79$ $R = 8.314 \text{ J/molK}$ $\Delta S = -R \sum X_i \ln X_i$ $\Delta S = -R(X_1 \ln X_1 + X_2 \ln X_2)$ $\Delta S = -8.314*(0.21* \ln 0.21 + 0.79* \ln 0.79) = 4.273 \text{ kJ / kmolK}$	2 2
3		Attempt any three	12
3	a	Definition: i. Isothermal process A process which is carried out at a constant temperature is called as an isothermal process. It is the process in which temperature is maintained constant. ii. Cyclic process A process or a series of processes, undergone by a system as a result of which the system is returned to its exact original state. iii. Irreversible process A process which goes from initial state to the final state in a finite time and cannot be carried in the reverse order is called as irreversible process OR A process which is carried out with a finite driving force is called as irreversible process.	1 mark each



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		<p>iv. Quasistatic process</p> <p>A process which takes place very slowly and with infinitesimal driving force is called quasi static process. OR It is the thermodynamic process that occurs infinitely slowly so that the system remains in internal equilibrium during the process.</p>	
3	b	<p>Data:</p> <p>Number of moles= $n = 1 \text{ mol}$</p> <p>$R = 8.314 \text{ J/mol K}$</p> <p>Initial volume = V_1</p> <p>Final volume = $V_2 = 10V_1$</p> <p>$T = 300 \text{ K}$</p> <p>The work done by an ideal gas in isothermal reversible expansion is</p> $W = nRT \ln\left(\frac{V_2}{V_1}\right)$ $W = 1 \times 8.314 \times 300 \ln\left(\frac{10V_1}{V_1}\right)$ $W = 1 \times 8.314 \times 300 \ln(10)$ $W = 2494.2 \times 2.304$ <p>$W = 5746.6 \text{ J}$</p> <p>From First Law of Thermodynamics</p> $\Delta U = Q - W$ <p>For isothermal process, $\Delta U = 0$</p> <p>Therefore $Q = W$</p> <p>$Q = 5746.6 \text{ J}$</p> <p>As per definition of enthalpy H</p> $\Delta H = \Delta U + \Delta(PV)$	<p>2</p> <p>1</p>

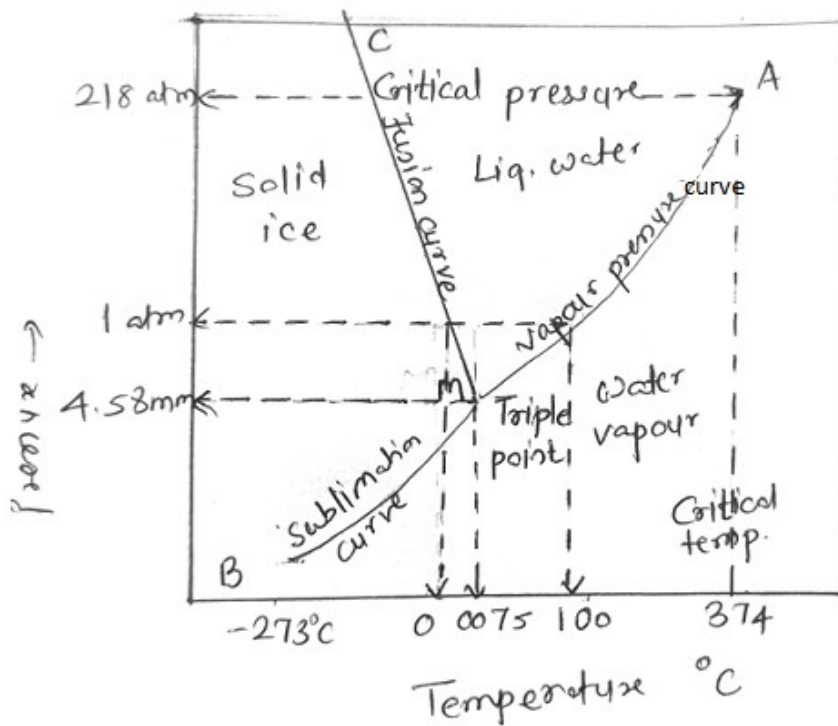


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2

It is a one component system. Water exists in three possible phases viz. ice (solid), water (liquid), and vapour (gas). These three single phases may form four possible equilibria.

- (i) Solid \rightleftharpoons Liquid
- (ii) Liquid \rightleftharpoons Vapour
- (iii) Solid \rightleftharpoons Vapour
- (iv) Solid \rightleftharpoons Liquid \rightleftharpoons Vapour

At low temperature, solid (ice) is the stable phase. At moderate temperature and pressure, liquid water is the stable phase and at high temperature and low pressure, water vapour is the stable phase.

Curves MA, MB and MC separate these phases and indicate equilibrium

2



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	<p>between two phases. Thus, along the curve MA, the phases liquidwater and water vapour coexist in equilibrium.</p> <p>A plot of the saturation pressure of a liquid as a function of temperature gives the vaporisation curve MA as shown in Fig. Similarly, a plot of melting point of ice at several pressures gives the curve MC and a plot of the vapour pressure of ice as a function of temperature gives the curve MB as shown in above figure.</p> <p>The curve MA is called the vaporisation curve or vapour pressure curve of water along which the phases liquidwater and water vapour coexist in equilibrium.</p> <p>The curve MB is called the sublimation curve of ice along which the phases-ice and water vapour coexist in equilibrium. This curve separates ice from water vapour.</p> <p>The curve MC is called the melting curve of ice or fusion curve of water along which the ice and liquid water phases coexist in equilibrium.</p> <p>Along the curves MA, MB and MC, since $C = 1$ and $P = 2$, we have $F = 1$ ($F = C - P + 2$). Thus, when one variable either P or T is specified, the other is fixed automatically.</p> <p>The curves MA, MB and MC on the phase diagram meet at a common point (point M) called the triple point. At the triple point all the three phases-ice, liquid water and water vapour coexist in equilibrium and the system is invariant since $C = 1$ and $P = 3$, we have $F = 0$. The point M is thus invariant and at this point both the temperature and pressure are fixed.</p>	
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4	b	<p>Data:</p> <p>Number of moles of ideal gas = $n = 2$ mols</p> <p>$T_1 = 300$ K</p> <p style="text-align: center;">$T_2 = 325$ K</p> <p>$V_1 = 2 \text{ dm}^3 = 0.2\text{m}^3$</p> <p>$V_2 = 4\text{dm}^3 = 0.4 \text{ dm}^3$</p> <p>$C_v = 12.5 \text{ J/mol.K}$</p> <p>$R = 8.314 \text{ J/mol.K}$</p> <p>The relationship between the entropy change for an ideal gas is</p> $\Delta S = nC_v \cdot \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$ $\Delta S = 2 * 12.5 \cdot \ln\left(\frac{325}{300}\right) + 2 * 8.314 \ln\left(\frac{0.4}{0.2}\right)$ $\Delta S = 25 \cdot (0.0797) + 16.62 * (0.6931)$ $\Delta S = 1.9925 + 11.52$ $\Delta S = 13.5125\text{J/K}$	2
4	c	<p>Data:</p> <p>Number of moles of ideal gas = $n = 5$ gmols</p> <p>Temperature = $27^{\circ}\text{C} = 300$ K</p> <p>$V_1 = 5 \text{ lit}$</p> <p>$V_2 = 50 \text{ lit}$</p> <p>$R = 1.987 \text{ cal/mol.K}$</p> <p>For an isothermal expansion of an ideal gas ,the entropy change is</p> $\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$	2



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		$\Delta S = 5 * 1.987 \ln\left(\frac{50}{5}\right)$ $\Delta S = 9.935 \ln(10)$ $\Delta S = 22.87 \frac{\text{cal}}{\text{K}} = 22.87 \text{eu} = 95.72 \text{J/K}$	2
4	d	<p>Relation between ΔG and K</p> <p>Consider the reaction $aA + bB \rightarrow rR + sS$</p> <p>$\Delta G$ reaction = ΔG product - ΔG reactant.</p> $= (r \mu_R + s \mu_S) - (a \mu_A + b \mu_B).$ <p>At equilibrium there is no Gibb's free energy change, $\Delta G = 0$</p> $(r \mu_R + s \mu_S) - (a \mu_A + b \mu_B) = 0$ $(r \mu_R + s \mu_S) = (a \mu_A + b \mu_B)$ <p>But $\mu_i = \mu_i^0 + RT \ln p_i$</p> <p>Therefore $r(\mu_R^0 + RT \ln p_R) + s(\mu_S^0 + RT \ln p_S) = a(\mu_A^0 + RT \ln p_A) + b(\mu_B^0 + RT \ln p_B)$</p> $RT \ln \left(\frac{p_R^r p_S^s}{p_A^a p_B^b} \right) = (a \mu_A^0 + b \mu_B^0) - (r \mu_R^0 + s \mu_S^0)$ $= -(\Delta G \text{ product} - \Delta G \text{ reactant})$ $= -\Delta G \text{ reaction.}$ $\ln \left(\frac{p_R^r p_S^s}{p_A^a p_B^b} \right) = \frac{-\Delta G \text{ reaction}}{RT} \text{ But } \left(\frac{p_R^r p_S^s}{p_A^a p_B^b} \right) = K_p$ <p>K_p is a function of temperature only. So at constant temperature</p> $\Delta G = -RT \ln K$ <p>OR</p> <p>Let us consider the following chemical reaction</p> $aA + bB \rightleftharpoons rR + sS$ <p>The free energy of reactant mixture consisting of 'a' moles of A & 'b' moles</p>	2



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of B in terms of chemical potential at constant pressure, temperature and composition is

$$G(\text{reactants}) = a\mu_A + b\mu_B$$

The free energy of product mixture consisting of 'r' moles of R & 's' moles of S in terms of chemical potential at constant pressure, temperature and composition is

$$G(\text{reactants}) = r\mu_R + s\mu_S$$

The free energy (ΔG) accompanying the above reaction at constant temperature & pressure is

$$\Delta G = G(\text{products}) - G(\text{reactants})$$

$$\Delta G = (r\mu_R + s\mu_S) - (a\mu_A + b\mu_B) \quad \text{eq1}$$

The chemical potential μ of any constituent of a mixture is given by

$$\mu = \mu^0 + RT \ln a$$

μ^0 = chemical potential of a substance in standard state of unit activity & **a** is the activity of the substance in mixture under consideration.

On substituting chemical potential in above equation 1,

$$\Delta G = (r\mu_R^0 + s\mu_S^0) - (a\mu_A^0 + b\mu_B^0) + RT(r \ln a_R + s \ln a_S - a \ln a_A - b \ln a_B)$$

$$\text{As } \Delta G^0 = (r\mu_R^0 + s\mu_S^0) - (a\mu_A^0 + b\mu_B^0)$$

$$\Delta G = \Delta G^0 + RT \ln(a_R^r \cdot a_S^s / a_A^a \cdot a_B^b) \quad \text{eq2}$$

The free energy change accompanying a chemical reaction under equilibrium conditions must be equal to zero. i.e. $\Delta G = 0$

Eq 2 becomes $0 = \Delta G^0 + RT \ln(a_R^r \cdot a_S^s / a_A^a \cdot a_B^b)$ **a** indicates activity at equilibrium

$$\Delta G^0 = -RT \ln(a_R^r \cdot a_S^s / a_A^a \cdot a_B^b)$$

$$\text{As } K = (a_R^r \cdot a_S^s / a_A^a \cdot a_B^b)$$



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		$\Delta G^0 = - RT \ln K \qquad \text{eq3}$ <p>Eq3 relates std. free energy change of the reaction at a specified temperature T to the thermodynamic equilibrium constant.</p>	
4	e	<p>Feasibility of a chemical reaction from Gibb's free energy:</p> <p>To predict the feasibility of chemical reaction & equilibrium condition at constant temperature & pressure, the criteria is</p> $\Delta G^0 \leq 0$ <p>1) At a chemical equilibrium $\Delta G^0 = 0$. For a chemical reaction at equilibrium at a given temperature & pressure, the free energy must be minimum.</p> <p>2) If $\Delta G^0 < 0$ i.e. it is negative, the reaction can take place spontaneously. (Reaction is possible under a given set of reactions). For spontaneous reaction, there should be decrease in Gibb's free energy change.</p> <p>3) If $\Delta G^0 > 0$ is positive, the reaction cannot take place under the given conditions</p>	4
5		Attempt any two	12
5	a	<p>Cp - Cv = R (proof)</p> <p>$C_p = dH / dT$ and $C_v = dU / dT$</p> $C_p - C_v = \frac{dH}{dT} - \frac{dU}{dT} = \frac{d(H - U)}{dT} \dots\dots(1)$ <p>$H = U + PV$</p> <p>$dH = dU + d(PV)$</p> <p>$dH - dU = d(PV) \dots\dots\dots(2)$</p> <p>Substituting (2) in (1)</p> $C_p - C_v = \frac{d(PV)}{dT} \dots\dots(3)$ <p>For ideal gas $PV = RT$</p>	2
			2



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		<p>Equation (3) becomes $C_p - C_v = \frac{d(RT)}{dT} = R \frac{d(T)}{dT} = R$</p> <p>Therefore $C_p - C_v = R$</p>	2
5	b	<p>P-H diagram</p> <p>On the P-H diagram, pressure is indicated on the y-axis and enthalpy is indicated on the x-axis. The upside down U figure shown on the diagram designates the points at which the refrigerant changes phase. The left vertical curve indicates the saturated liquid curve and the right vertical curve indicates the saturated vapor curve. The region in between the two curves describes refrigerant states that contain a mixture of both liquid and vapor. The locations to the left of the saturated liquid curve indicate that the refrigerant is in liquid form and locations to the right of the saturated vapor curve indicate that the refrigerant is in vapor form. The point at which the two curves meet is called the critical point. The importance of this point is that at any point above, no</p>	2
			4



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		<p>additional pressure will change the vapor into a liquid.</p> <p>The curves break up the diagram into three regions (1) Liquid, (2) Vapor and (3) Mix.</p> <p>(1) Liquid Region: The liquid region is also known as the sub-cooled region. In this region there are vertical temperature lines, which increase as enthalpy is increased. Figure illustrating the constant temperature lines.</p> <p>(2) Vapor Region: The vapor region is also known as the super heated region. In this region there are vertical temperature lines, which increase as enthalpy is increased. There are also lines of constant entropy, which are also important. Entropy is the measure of the amount of disorder in the system.</p> <p>(3) Liquid-Vapor Mix Region: In this region, the P-H diagram shows horizontal temperature lines, which indicate constant temperature. The mix region is the phase change region, where any addition of enthalpy will cause additional liquid to vaporize instead of raising the temperature. Figure illustrates the horizontal temperature lines in the mix region. There are also upward sloping curves which indicate quality. Quality is a measure of the ratio of vapor mass to total mass.</p>	
5	c	$\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$ $K_c = \frac{C_{\text{NH}_3}^2}{(C_{\text{N}_2} \cdot C_{\text{H}_2}^3)}$ $C_{\text{NH}_3} = 0.105 \text{ mol/lit}$ $C_{\text{N}_2} = 1.10 \text{ mol/lit}$ $C_{\text{H}_2} = 1.5 \text{ mol/lit}$ $K_c = \frac{(0.105 \text{ mol/lit})^2}{(1.10 \text{ mol/lit} \cdot 1.5 \text{ mol/lit})} = 2.97 \times 10^{-3} \text{ mol}^{-2} \cdot \text{l}^2$ $K_p = K_c (RT)^{\Delta n}$ $\Delta n = 2 - (3+1) = -2$	3



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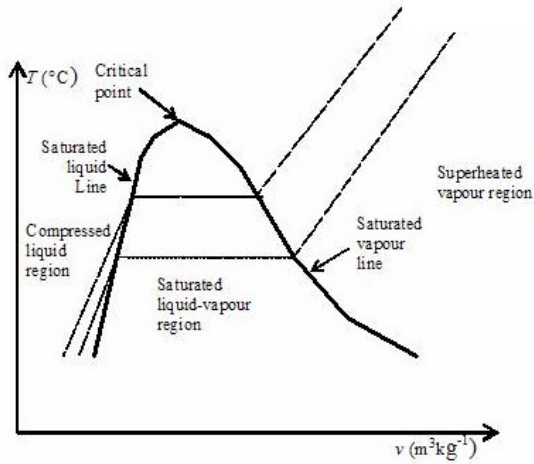
		R= 0.08206 l.atm./mol.K T=1000K $K_p = (2.97 \times 10^{-3} \text{ mol}^{-2} \cdot \text{l}^2) (0.08206 \text{ l.atm./mol.K} * 1000\text{K})^{\Delta(-2)}$ $= 4.42 * 10^{-7} \text{ atm}^{-2}$	3
6		Attempt any TWO of the following	12
6	a	T-V diagram The TV diagram contains three single phase regions (liquid, vapour, and supercritical fluid), a two-phase (liquid+vapour) region, and two important curves - the saturated liquid and saturated vapour curves. The number of regions and curves will increase when we consider solids. The saturated liquid and vapor curves meet at the critical point, which represents the highest temperature and pressure in which vapour and liquid phases can coexist. The single phase liquid region is also called sub cooled liquid because, at a given pressure, temperature will be below the boiling temperature. The single phase vapor region is also called superheated vapor because, at a given pressure, temperature will always be above the boiling temperature. An isotherm is a line of constant temperature. The PVT surface can be generated from a TV diagram by imagining each of the isobars to be at a different level on the new Pressure axis.	3



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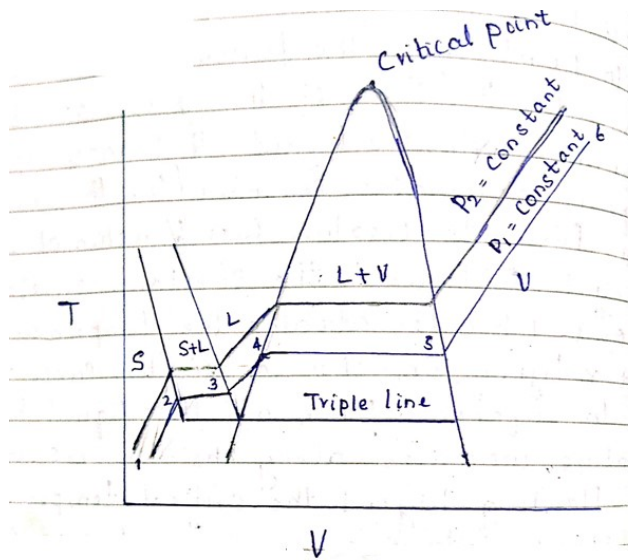
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OR



Consider a solid substance at a given temperature (Point 1). If it is heated at constant pressure, the solid expands and the specific volume of the solid increases with increase of temperature as shown by the path 1-2 in the diagram. At point 2, the solid



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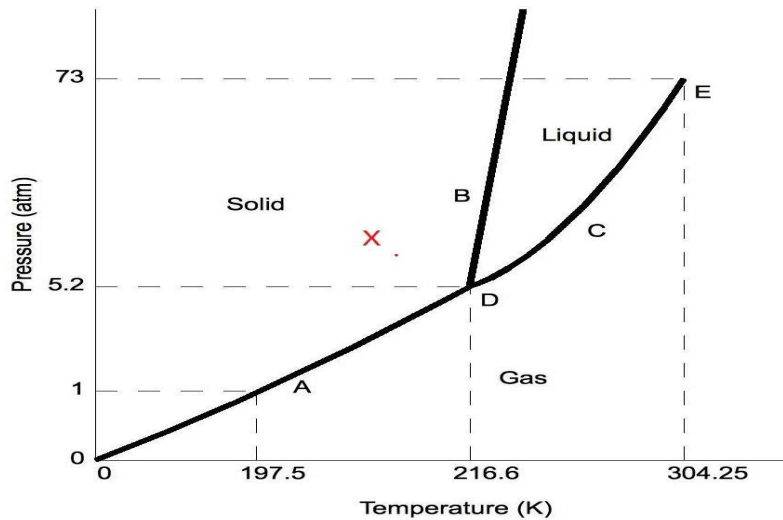
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starts melting. At this stage, the system contains two phases – solid and liquid which are in equilibrium with each other. If heating is continued, more and more of the solid converts in to liquid, the temperature remains constant and the specific volume increases till the state 3(heat supplied from state 2 to state 3 is called latent heat or enthalpy of fusion) is reached where the substance is present only in liquid phase. With further heating, the temperature and specific volume of liquid increases till state 4 is reached, at which point the liquid begins to boil. If heating is continued, more and more of the liquid converts in to liquid, the temperature remains constant and the specific volume increases till the state 5(heat supplied from state 4 to state 5 is called latent heat or enthalpy of vaporization) is reached where the substance is present only in vapour phase. Upon further heating at constant pressure, the system follows the path 5-6 and the substance is superheated vapour.

6 b

Phase diagram of carbon dioxide system:



It has three distinct phases- solid, liquid and gas. AD is the sublimation curve

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		<p>along which solid CO₂ is in equilibrium with the gas. DE is the vaporization curve along which liquid CO₂ is in equilibrium with the gas. DB is the fusion curve along which solid CO₂ and liquid CO₂ are in equilibrium with each other. Fusion curve slopes away from the pressure axis which indicates that increase in pressure raises the meltingpoint of solid CO₂. Along all these curves, the system are univariant (degree of freedom is 1). D is the triple point where the three phases of CO₂ coexist at equilibrium. The temperature at this point is -57⁰ C 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 DB while a slight decrease in temperature will result in the disappearance of liquid phase and the equilibrium will shift along the curve DA.</p>	3
6	c	<p>$2\text{NaHSO}_4 \leftrightarrow \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$</p> <p>$\Delta H = 19800 \text{ cal}$</p> <p>$\Delta G = 9000 \text{ cal}$</p> <p>$T = 298\text{K}$</p> <p>$R = 1.987 \text{ cal/gmole K}$</p> <p>$\Delta G = -RT \ln K$</p> <p>$9000 = -1.987 * 298 \ln K$</p> <p>$\ln K = -15.199$ $K = 2.51 * 10^{-7}$</p> <p>$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H}{R} * \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$</p> <p>$T_1 = 298 \text{ K}$ $T_2 = 700\text{K}$ $K_1 = 2.51 * 10^{-7}$</p> <p>$\ln K_2 - \ln K_1 = \frac{-1980}{1.987} * \left(\frac{1}{700} - \frac{1}{298}\right)$</p> <p>$\ln K_2 - \ln 2.51 * 10^{-7} = 19.2$</p>	3



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	$\ln K_2 = 4$	$K_2 = 54.598$	
	Dissociation pressure at 700K = 54.598		3