

Code: 9A23404

B.Tech II Year II Semester (R09) Regular & Supplementary Examinations, April / MAY 2012

THERMODYNAMICS IN BIOPROCESS SYSTEMS

(Biotechnology)

Time: 3 hours

Max Marks: 70

Answer any FIVE questions

All questions carry equal marks

- 1 (a) Discuss the scope of thermodynamics.
(b) State first law of thermodynamics and state its limitations.
(c) Give mathematical equations for first law for non-flow process.
- 2 (a) Define second law of thermodynamics. List alternative statements.
(b) A reversible engine operating between a reservoir at 605 K and the ambient atmosphere at 305 K drives a refrigerator operating between 245 K and the ambient atmosphere. Determine the ratio of energy rejected by both the devices to the ambient atmosphere to the energy absorbed by the engine from the reservoir at 605 K.
- 3 (a) Show that chemical potential of component in all phases are equal at equilibrium.
(b) Define the terms : (i) Ideal liquid solution (ii) Raoult's law,
- 4 (a) Obtain the relation for calculation of fugacity coefficient of component in solution of binary system.
(b) Explain the procedure for the estimation of fugacity at any condition by knowing the fugacity coefficient at saturation condition.
- 5 (a) Show that $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$.
(b) Define availability and the does the availability depends upon the conditions of system and surroundings.

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- 6 (a) Calculate the total pressure and the composition of the vapors in contact with a solution at 100°C , containing 30% benzene (C_6H_6), 45% toluene ($\text{C}_6\text{H}_5\text{CH}_3$) and 25% o-xylene ($\text{C}_6\text{H}_4(\text{CH}_3)_2$) by weight. (Data: Vapor pressure at 100°C is Benzene – 1340 mm Hg, toluene – 560 mm Hg and o-xylene – 210 mm Hg.)

- (b) Estimate the vapor phase composition at 60°C in equilibrium with a liquid mixture containing 40 mole % benzene and 60 mole% toluene. Also calculate the composition of the liquid mixture, which boils at 90°C and 101.32 kPa. Vapor pressure data is given as:

Temp. $^{\circ}\text{C}$	Vapor pressure of Benzene, kPa	Vapor pressure of toluene, kPa
60	51.3	18.7
90	135.05	54.4

- 7 Define and explain the terms: Molar Gibbs energy, standard state Gibbs energy, partial Gibbs energy, excess Gibbs energy and residual Gibbs energy. Bring out the differences amongst them with simple thermodynamic relations.
- 8 (a) A mixture of N_2 , H_2 , and Argon in the mole ratio 1:3:2 enters in a catalytic reactor for the synthesis of ammonia. The reactor is maintained at 400°C and 20 MPa. Estimate the degree of conversion and the equilibrium constant is given as $K=1096 \times 10^4$.
- (b) Derive the expression for equilibrium constant for liquid phase reactions and simplify the expression for ideal solutions.

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- 1 (a) What you understand about the term temperature.
(b) The properties of a closed system undergo change following the relation $PV = 4$ and P is in bar and V in metre^3 . Calculate the work done when P increases from 2.5 bar to 8 bar.
(c) Differentiate between intensive and extensive properties with suitable example.
- 2 (a) Discuss how limitations of first law disappear in second law of thermodynamics.
(b) A Carnot engine (i) Operates between two reservoirs at temperature 1920 K and $T^0\text{K}$ while a second Carnot engine (ii) Operates between $T^0\text{K}$ and 302 K. It is found that both the engines have the same efficiency. Determine the value of T .
- 3 (a) Derive fundamental property relation and explain its significance
(b) Differentiate between ideal and non-ideal solutions.
- 4 (a) Derive an equation to find the fugacity and fugacity coefficient of a gas from its compressibility factor data.
(b) State and explain Gibbs theorem.
- 5 (a) Show that $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$.
(b) A system has the equation of state as $PV = ZRT$, show that $\left(\frac{\partial H}{\partial P}\right)_T = \{ - RTT|P \} \left(\frac{\partial Z}{\partial T}\right)_P$.

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- 6 Assuming the validity of Raoult's law, prepare a p-x-y for 80°C and a t-x-y for 80 KPa for chlorobutne (1) = chlorobenzene (2) system. Antoine parameters are as follows: $\log_{10}P = A-B/(t + c)$ where pin torr and t is in °C.
 Chlorobutane: A = 13.96 B = 28866.26 C = 224.10
 Chlorobenzene: A = 13.993 B = 3295.12 C = 217.55.
- 7 Define Henrys law, Lewis/Randall rule, excess property, residual property, fugacity, activity, activity coefficient, fugacity coefficient.
- 8 (a) A gaseous mixture containing 7.8% SO₂, 10.8% O₂ and the rest N₂ is fed to a converter at 500°C and 1 bar. Find the equilibrium conversion if $K_p = 85 \text{ (bar)}^{1/2}$ for the reaction $\text{SO}_2 + 1/2 \text{ O}_2 \longrightarrow \text{SO}_3$ at 500 C.
 (b) Write the effect of temperature and pressure on equilibrium constant.

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- 1 (a) Define open, closed and isolated systems with suitable examples. Show energy of an isolated system is conserved.
(b) What is work? Show that work in changing volume of a PVT system $\int_{V_1}^{V_2} P dv$.
- 2 (a) Write short notes on entropy from microscopic view point.
(b) A reversible heat engine interact with four reservoirs at 1000 K, 600 K, 400 K and 300K. It absorbs 2000 kJ energy as heat from the reservoir at 1000K, rejects 600 kJ energy as heat to the reservoir at 300 K and delivers 1200 kJ work. Determine the energy interaction with the other two reservoirs.
- 3 Derive the relation for the calculation of Gibbs free energy of ideal gas mixture, starting from fundamental property relation.
- 4 (a) Define and explain the terms: fugacity, fugacity coefficient, activity and activity coefficient.
(b) Discuss the variation of activity in liquid mixtures with temperature and pressure.
- 5 A particular thermodynamic system has the following fundamental relation $U = CS^2 / VN$, where C is a constant. Transform the given fundamental relation into the enthalpy representation.

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- 6 (a) Prepare a t-x-y diagram for the ideal binary system benzene (i) –ethyl benzene (2) at 101.3 KPa. Vapour pressures of the pure species are given by
 $\ln P_1^{\text{sat}} = 13.8858 - 2788.51 / (t+220.79)$
 $\ln P_2^{\text{sat}} = 14.0045 - 3279.47 / (t+213.20)$

 (b) Explain briefly solid-liquid equilibriums.

- 7 (a) What does Gibbs/Duhem equation relate?
 (b) State Gibbs theorem and obtain expressions for excess properties for enthalpy, entropy and Gibbs free energy.

- 8 (a) In a laboratory investigation acetylene is catalytically hydrogenated to ethylene at 1120 K and 1 bar. If the feed is an equimolar mixture of acetylene and hydrogen, what is the composition of the product stream at equilibrium? The equilibrium constant at this conditions is one.
 (b) Write the effect of inerts on equilibrium constant.

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- 1 (a) Give the relationships between $^{\circ}\text{C}$, $^{\circ}\text{F}$, $^{\circ}\text{K}$ and $^{\circ}\text{R}$.
(b) Classify the following in to intensive and extensive properties with reasons, total energy, temperature, specific heat, volume, specific volume.
(c) Differentiate between open system and closed system.
- 2 (a) Derive the expression for change of entropy for an ideal gas.
(b) An inventor claims to have developed an engine that takes in 25,000 J/s at a temperature of 300 K and the rejects 12,000 J/s at temperature of 200 K and delivers 15 kW of mechanical power. Would you advice investing, put this engine on the market.
- 3 (a) Show that Raoult's law is valid for component A of a binary solution over the range of composition for which Henry's law holds for component.
(b) Define chemical potential and show that equality of chemical potential is criteria for phase equilibrium.
- 4 (a) Derive the fundamental excess property relation.
(b) Write and explain the expression to calculate volume and enthalpy of ideal solution.
- 5 (a) What is equation of state and how it is used in estimation of thermodynamic properties?
(b) Prove that $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$.

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- 6 (a) Explain briefly liquid-liquid equilibrium.
- (b) Mixture of n-pentene and n-heptane obeys ideal solution behavior. Prepare p-x-y diagram at 70°C. Antoine equation may be to calculate the vapor pressure: $\log_{10} P = A - B / (t + c)$ where pin torr and t is in °C.

Component	A	B	C
n-Pentene	6.87632	1075.780	233.205
n-heptane	6.89386	1264.370	216.640

- 7 (a) Define partial molar property.
- (b) Explain briefly various types models for estimation of activity coefficients.
- 8 (a) In the reaction $\text{CO}_2 (\text{g}) + \text{H}_2 (\text{g}) \longrightarrow \text{CO} (\text{g}) + \text{H}_2\text{O} (\text{g})$. Equilibrium is reached at 1538 K when the four gases have the partial pressures 0.1, 0.1, 0.1 and 0.24 atm. Calculate the equilibrium constant and the standard free energy at 1538 K.
- (b) For chemical reaction equilibrium, show that $-RT \ln K = \Delta G^0$ terms have their usual meaning.
