Name : .....

Roll No. : .....

Invigilator's Signature : .....

CS/B.TECH(BT-OLD)/SEM-4/BT-401/2012

2012

THERMODYNAMICS AND KINETICS

Time Allotted : 3 Hours *Full Marks* : 70

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

GROUP – A

(Multiple Choice Type Questions)

1. Choose the correct alternatives for any *ten* of the following : $10 \times 1 = 10$

   i) How many degrees of freedom has the following systems ?

   A liquid solution of alcohol in water in equilibrium with its vapor.

   a) 1 b) 2

   c) 3 d) 0.

   ii) Higher possible value of C.O.P. is attained in

   a) air cycle

   b) vapour compression cycle by expansion value

   c) Carnot cycle

   d) vapour compression cycle by expansion engine.

iii) An ideal refrigerant should have

a) low vapour pressure in condenser

b) vapour pressure in evaporator a bit higher than the atmospheric pressure

c) constant entropy of saturated vapour

d) all of these.

iv) Henry's law is applicable for

a) gas-liquid system b) gas-gas system

c) liquid-liquid system d) solid-liquid system.

v) For an ideal gas, the fugacity coefficient is

a) 0 b) 1

c) <1 d) >1.

vi) Residual and excess properties of a fluid

a) are same by magnitude

b) may be correlated

c) are applicable for ideal system

d) none of these.

vii) The order of the reaction whose rate equation is $r = kCA\,0\cdot 8.CB^{1\cdot 2}$ is

a) 0·4 b) 0·8

c) 1·2 d) 2·0.

viii) Standard free energy change (ΔG^o) of a chemical reaction is given by the relation

a) $\Delta G° = -RlnK$ b) $\Delta G° = -RTlnK$

c) $\Delta G° = RlnK$ d) $\Delta G° = RTlnK$.

ix) The plot of reaction velocity and pH for an enzymatic reaction is

a) a straight line through origin

b) a bell shaped curve

c) an asymptotic curve

d) a straight line parallel to *x*-axis.

x) An enzyme does which the following in catalyzing a reaction ?

a) Stabilizes the substrate

b) Decreases the equilibrium constant

c) Increases the forward reaction rate

d) Accelerates the approach to equilibrium.

xi) In case of enzymatic reactions occurring respectively at high and low substrate concentrations, the reaction orders are respectively

a) first and zero b) pseudo first and zero

c) second and first d) zero and first.

xii) Km is a measure of

a) the rate of the reaction

b) the affinity of the enzyme for the substrate

c) the concentration of the enzyme-substrate (ES) intermediate

d) none of these.

GROUP – B

(Short Answer Type Questions)

Answer any *three* of the following. 3 × 5 = 15

2. The rate of decomposition of a gas A was 7·25 in some unit when 5% had reached and it was 5·14 in the same unit when, 20% had undergone decomposition. Calculate the order of reaction.

3. Derive an expression for the fugacity coefficient of a gas obeying the equation of state $P(V-b)=RT$ and estimate the fugacity of ammonia at 10 bar and 298 K, given that $b = 3 \cdot 707 \times 10^{-5}\,\mathrm{m}^3/\mathrm{mol}$.

4. Prove that $C_p - C_v = R$.

5. Write short notes on allosteric enzyme.

6. Define C.O.P. and write a note on choice of refrigerant. 2 + 3

GROUP – C

(Long Answer Type Questions)

Answer any *three* of the following. 3 × 15 = 45

7. The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the Antoine equations

$$\ln P_1^s = 14 \cdot 5463 - 2940 \cdot 46 / T - 35 \cdot 93$$

$$\ln P_1^s = 14 \cdot 2724 - 2945 \cdot 47 / T - 49 \cdot 15$$

Where *T, K* and *P* is in kPa. Assuming that the solutions formed by these are ideal, calculate

a) x_1 and y_1 at 327 K and 65 kPa

b) T and y_1 at 65 kPa and $x_1 = 0{\cdot}4$

c) P and y_1 at 327 K and $x_1 = 0{\cdot}4$

d) T and x_1 at 65 kPa and $y_1 = 0{\cdot}4$

e) P and x_1 at 327 K and $y_1 = 0{\cdot}4$.

8. a) State phase rule. For a closed system how this rule gets modified ? Explain with deduction. 2 + 4

b) For acetone at 293·150 K and 1 bar,

$$\beta = 1 \cdot 487 \times 10^{-3} K^{-1}$$

$$\kappa = 62 \times 10^{-6} \text{ bar}^{-1}$$

$$V = 1 \cdot 287 \times 10^{-3} m^3 kg^{-1}$$

Find

i) The value of $\left(\frac{\partial P}{\partial T}\right) v$

ii) The pressure generated when acetone is heated at constant volume from 293·150 K and 1 bar to 303·15 K.

iii) The volume change when acetone is changed from 293·150 K and 1 bar to 273·15 K and 10 bar. 6

c) Explain Boiling Point Diagram. 3

9. a) Write virial equation of state with its implication.

Reported values for the virial coefficients of isopropanol vapour at 473·15 K are :

$B = -0 \cdot 388 \text{ m}^3 \text{ kmol}^{-1}$

$C = -26 \times 10^{-3} \text{ m}^6 \text{ kmol}^{-2}$

Calculate V and Z for isopropanol vapor at 473·15 K and 10 bar by the ideal gas equation. 1 + 2 + 3

b) State briefly the salient features of Transition state Theory. Explain why activated state entropy (S^*) is negative. 6 + 3

10. a) A vapour compression refrigeration system with ammonia as the working fluid is to operate between 266 K and 300 K. Determine the following :

i) COP, given that the enthalpy of saturated vapour at 266 K = 656 kJ/kg and enthalpy of superheated vapour leaving the compressor = 724 kJ/kg, enthalpy of saturated liquid at 300 K = 144 kJ/kg.

ii) COP, if a temperature approach of 5 K is necessary in the evaporator and condenser, and the efficiency of compressor is 75%. Enthalpy of saturated vapour at 261 K = 652 kJ/kg and the enthalpy of superheated vapour entering the condenser = 758 kJ/kg, enthalpy of saturated liquid at 305 K = 159 kJ/kg.

iii) COP of an ideal Carnot refrigerator.

b) A vapour compression cycle using ammonia as refrigerant is employed in an ice manufacturing plant. Cooling water at 288 K enters the condenser at a rate of 0·25 kg/s and leaves at 300 K. Ammonia is 294 K condenses at a rate of 0·5 kJ/kg/minute. Enthalpy of liquid ammonia at 294 K is 281·5 kJ/kg. The compressor efficiency is 90%. Saturated ammonia vapour at 258 K and enthalpy of 1426 kJ/kg enters the compressor. What is the power requirement of the compressor and refrigeration capacity in tons ?

11. The following data were obtained from enzymatic oxidation of phenol by phenol oxidase at different phenol concentrations :

S (mg/l)	10	20	30	50	60	80	90	110	130	140	150
Rate (mg/l-h)	5	7·5	10	12·5	13·7	15	15	12·5	9·5	7·5	5·7

a) Identify the type of inhibition.

b) Determine the constants V_m, K_m, K_{si}.

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