Name : ....

Roll No. : ....

Invigilator's Signature : ....

CS/B.Tech/BT(N)/SEM-3/BT-301/2012-13

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) In cases 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 zero   d) zero and first.

   ii) Enthalpy can be expressed as

   a) $H = U - PV$ b) $H = U + PV$

   c) $H = U/PV$ d) none of these.

3160 (N)   [Turn over

iii) The order of the reaction whose rate equation is $r = kC_A^{0.8} C_B^{1.2}$ is

   a)   0.8   b)   1.2

   c)   2.0   d)   0.4.

iv) 1 ton of refrigeration is equivalent to

   a)   3.517 kW   b)   35.17 kW

   c)   351.7 kW   d)   3517 kW.

v) Unit of rate constant for an nth order reaction is

   a) $(\text{concentration})^{1-n} (\text{time})^{-1}$

   b) $(\text{concentration})^{n-1} (\text{time})^{-1}$

   c) $(\text{concentration})^{-1} (\text{time})^{1-n}$

   d) $(\text{concentration})^{n} (\text{time})^{1-n}$

vi) Which of the following influences the rate of a chemical reaction performed in solution ?

   a)   Temperature

   b)   Activation energy

   c)   Presence of a catalyst

   d)   None of these.

vii) In terms of the "Collision Theory of Chemical Kinetics", the rate of a chemical reaction is proportional to

    a) the change in free energy per second

    b) the change in temperature per second

    c) the number of collisions per second

    d) none of these.

viii) The time taken for 10% completion of a first order reaction is 20 min. Then, for 19% completion, the reaction will take

    a) 30 min   b) 40 min

    c) 50 min   d) 60 min.

ix) Compressibility factor of an ideal gas is

    a) 0   b) 1

    c) ∞ d) -1.

x) Allosteric enzymes contain

    a) one substrate binding site

    b) no substrate binding site

    c) more than one binding site

    d) none of these.

xi) Henry's law is applicable for

   a) gas-liquid system

   b) gas-gas system

   c) liquid-liquid system

   d) solid-liquid system.

xii) Michaelis-Menten equation is a kinetic model of
………………… system.

   a) linear   b) parabolic

   c) asymptotic   d) sigmoidal.

GROUP – B
(Short Answer Type Questions)
Answer any *three* of the following. $3 \times 5 = 15$

2. Show that $ln\ (\ f/P\ ) = BP/RT$, where B is the second virial coefficient.

3. Determine the value of ΔH and ΔE for the reversible isothermal evaporation of 90.0 gm of water at 100˚C. Assume that water vapour behaves as an ideal gas and heat of evaporation of water is 540cal/gm.

4. a) Write down the difference between order and molecularity of the reaction.

   b) In a Batch reactor liquid A decomposes by first order kinetics. The conversion is 50% of A in a 5 minute run. What will be the time taken for 80% conversion of A ?

   $2 + 3$

5. Define mathematically the combined form of the 1st and 2nd laws of thermodynarmics.

6. The l/v axis of a reciprocal plot is labelled v^{-1}

   (n moles × litre^{-1} × min^{-1} × min^{-1})$^{-1}$ × 10^2 . The plot $l/[S]$ axis is labelled $[S]^{-1}$: (M)$^{-1}$ × 10^{-4}. The plot intersects the two axes at 2 and – 4, respectively. What are V_{max} and K_m ?

GROUP – C
(Long Answer Type Questions)
Answer any *three* of the following. $3 × 15 = 45$

7. a) State Raoult's law.

   b) Binary system acetonitrile (1)/nitromethane (2) conforms closely to Raoult's law. Vapour pressures for pure species are given by the following Antoine equations :

   $$ln\ P_1{}^{sat} / kPa = 14.2724 - \frac{2945.47}{t/°C + 224}$$

   $$ln\ P_2{}^{sat} / kPa = 14.2043 - \frac{2972.64}{t/°C + 209}$$

   Prepare a graph showing P vs x_1 and P vs y_1 for a temperature of 25°C. $5 + 10$

8. a) Derive Michaelis-Menten equation of competitive enzyme inhibition.

b) At what substrate concentration will an enzyme with a k_{cat} of 30/sec and k_m of 0.005 M show $\frac{1}{4}$ of its mixmum rate ? Determine the fraction of V_{max} that would occur at the following substrarte concentration : $S = 1/2 \, k_m$. 5 + 10

9. a) Derive an expression for heat transfer and work done for an isothermal process.

b) Air enters a compressor at 10^5 Pa and 25˚C having volume of 1.8 m^3/kg and is compressed to 5×10^5 Pa isothermally. Determine

i) Work done

ii) Change in internal energy

iii) Heat transferred. 3 + 12

10. a) A 10-minute experimental run shows that 75% of liquid is converted to product by a $\frac{1}{2}$ order rate. What would be the fraction converted in a half-hour run ?

b) A constant density first order reaction $A \rightarrow P$ is carried out in a batch reactor. Data obtained are given in Table below :

Time (sec)	30	60	90	120	150	180	600
Concentration of A (kmol/m^3)	0·74	0·55	0·42	0·29	0·24	0·16	0·0025

If C_{A0} = 1 kmol/m^3, calculate the rate constant for the reaction. Also calculate time reequired for 50% conversion.
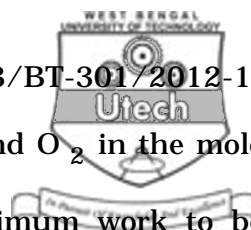
11. a) Atmospheric air is a mixture of N_2 and O_2 in the mole ratio of 79 : 21. Calculate the minimum work to be done to separate one k.mole of air at 0.1 MPa and 300 K into pure N_2 & O_2 at the same temperature & pressure. Treat air as an ideal gas.

   b) A refrigeration system requires 1.5 kW of power for a refigeration in rate of 4 kW.

   i) What is the coefficient of performance ?

   ii) How much heat is rejected in the condenser ?

   iii) If the heat is rejected at 313 K, what is the lowest temperature the system can possibly maintain ?

   $8 + (2 + 2 + 3)$

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