Group - D

6. (a) An ampoule of radioactive Kr-89 (half life=76 min) is set aside for a day. What does this do to the activity of the ampoule? Note that radioactive decay is a first order process.

   (b) Define the terms limiting reactant, order and molecularity.

9 + 3 = 12

7. Find the overall order of the irreversible reaction $2H_2 + 2NO \rightarrow N_2 + 2H_2O$ From the following constant volume data using equimolar amounts of hydrogen and nitric oxide.

Total pressure, mm Hg	200	240	280	320	360
Half-life, sec	265	186	115	104	67

12

Group - E

8. In a number of separate runs different concentrations of substrate and enzyme are introduced into a batch reactor and allowed to reactor. After a certain time the reaction is quenched and the vessel contents analyzed. From the results found below find a rate equation to represent the action of enzyme on substrate.

Run	C_{E0}, mol/m^3	C_{A0}, mol/m^3	C_A, mol/m^3	t, h
1	3	400	10	1
2	2	200	5	1
3	1	20	1	1

12

9. Enzyme E catalyzes the decomposition of substrate S. To see whether substance B acts as inhibitor we make two kinetic runs in a batch reactor, one with B present, the other without B. From the data recorded below
   (i) Find a rate equation to represent the decomposition of S.
   (ii) What is the role of B in this decomposition?
   (iii) Suggest a mechanism for the reaction.

   Run 1: S_0=600mol/m^3, E_0= 8gm/m^3, no B present

S	350	160	40	10
t, h	1	2	3	4

   Run 2: S_0=800mol/m^3, E_0= 8gm/m^3, $C_B = C_{B0}$= 100mol/m^3

S	560	340	180	80	30
t, h	1	2	3	4	5

12

THERMODYNAMICS & KINETICS
(BIOT 2201)

Time Allotted : 3 hrs **Full Marks : 70**

Figures out of the right margin indicate full marks.

Candidates are required to answer Group A and any 5 (five) from Group B to E, taking at least one from each group.

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

Group – A
(Multiple Choice Type Questions)

1. Choose the correct alternative for the following: **10 × 1 = 10**

   (i) The change in internal energy of a closed system during a certain reversible process equals the net heat transferred, provided the process is
   (a) isothermal (b) isobaric
   (c) isochoric (d) isenthalpic.

   (ii) A piston cylinder contains air at 600 kPa, 290 K and a volume of 0.01m^3. A constant pressure process gives 54 kJ of work out. Find the final volume of the air.
   (a) 0.05 m^3 (b) 0.01 m^3
   (c) 0.10 m^3 (d) 0.15 m^3.

   (iii) Which of the following represents the numerator for the expression used to determine the equilibrium constant for the hydrolysis of ATP to yield AMP

   $$ATP \rightarrow AMP + 2Pi$$

   (a) $[ATP] \times [H_2O]$ (b) $[AMP] \times [Pi]^2$
   (c) $[AMP] + [Pi]^2$ (d) $[AMP] \times 2[Pi]$.

   (iv) Which of the following best characterizes the free energy change ΔG for an endothermic reaction under physiological conditions?
   (a) The sign of ΔG is positive
   (b) The sign of ΔG is negative
   (c) The sign of ΔG cannot be determined without knowing more information
   (d) ΔG is zero.

(v) If a reaction is exergonic under standard biochemical conditions, what must be true of the equilibrium constant for this reaction?
(a) 1<Keq (b) Keq=0
(c) 0<Keq<1 (d) −1<Keq<0.

(vi) An elementary reaction has the kinetic equation $-r_A = kC_A^{2.5}C_B^{-2.5}$. What is the order of reaction?
(a) 0 (b) 2.5
(c) 5 (d) none.

(vii) For the enzyme substrate reaction, the rate of disappearance of substrate is given by $-r_A = \frac{k[A][E_0]}{M+[A]}$ mol/m^3.s. What are the units of the k and M?
(a) s^{-1}, mol/m^3 (b) mol/m^3.s, mol/m^3
(c) mol/L, s^{-1} (d) none.

(viii) Reactions with order n<1
(a) can go into completion within a finite time
(b) never go into completion within a finite time
(c) do not have any limiting reactant
(d) none of the above.

(ix) Higher value of Michaelis constant signifies
(a) increased substrate affinity of the enzyme
(b) reduced substrate affinity of the enzyme
(c) decreased enzyme reaction rate
(d) none of the above.

(x) Carboxypeptidase is an example of
(a) co-factor (b) ribozyme
(c) allosteric enzyme (d) apoenzyme.

Group - B

2. (a) Write down the Virial Equation of state. Define Compressibility factor.

(b) Draw and explain the P-V diagram of a pure substance *other than water* and show the saturated liquid line, triple point line and saturated vapor line.

(c) Define (i) fugacity co-efficient (ii) Reduced temperature of a gas.

(2 + 1) + (3 + 3) + (1.5 + 1.5) = 12

3. (a) Air flows steadily at a rate of 0.5 kg/s, through an air compressor, entering at 7 m/sec velocity, 100 KPa pressure, 0.95 m^3/kg volume and leaving at 5m/sec velocity, 700 KPa pressure 0.19 m^3/kg volume. The internal energy of the air leaving is 90KJ/kg greater than that of the air entering. Cooling water in the compressor absorbs the heat from the air at a rate of 58 KW.
(i) Compute the Rate of shaft work input to the air in KW.
(ii) Find the ratio of inlet pipe diameter to outlet pipe diameter.

(b) Define critical temperature and pressure of a pure substance. Show the critical point on T-S diagram.

(c) What are the differences between reversible process and irreversible process?

(5 + 2) + (2 + 1) + 2 = 12

Group - C

4. (a) The equilibrium constant Kp for a reaction is 3.0 at 400 ^{o}C and 4.0 at 500 ^{o}C. Calculate the value of ΔH^o for the reaction.

(b) Write two applications of Gibbs –Helmoltz equation.

6 + 6 = 12

5. (a) Calculate the standard free energy changes of the following metabolically important enzyme catalysed reaction at 25^{o}C and pH 7.0, using equilibrium constant given

(i) Glutamate + oxaloacetate $\xrightleftharpoons{\text{Aspartate aminotransferase}}$ aspartate + α ketogluterate (K_{eq} = 6.8).

(ii) Di-hydroxyacetone hosphate $\xrightleftharpoons{\text{Triose phosphate isomerase}}$ glyceraldehyde-3-phosphate(K_{eq}= 0.0475).

(iii) Fructose 6 phosphate +ATP $\xrightleftharpoons{\text{Phosphofructokinase}}$ Fructose 1,6 bisphosphate+ADP(K_{eq}= 254).

(b) Derive the expression of Vant't Hoff isochore.

(2 + 2 + 2) + 6 = 12