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) In isothermal process, the internal energy
(a) increases (b) decreases
(c) remains constant (d) first increases, then decreases.

(ii) Which statement is false?
(a) Carnot cycle is reversible
(b) A reversible cycle is more efficient than irreversible one
(c) Carnot cycle is the most efficient among all cycles
(d) All reversible cycle has same efficiency.

(iii) The coefficient of performance of a refrigerator is 5. If the temperature inside said refrigerator is -20^0 C. Calculate the temperature of the surrounding where it releases heat.
(a) 11^0 C (b) 21^0 C (c) 31^0 C (d) 41^0 C.

(iv) 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→ AMP+2Pi

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

(v) V_{max} remains unchanged in value in presence of inhibitor for
(a) Competitive inhibition (b) Uncompetitive inhibition
(c) Non-competitive inhibition (d) All the (a), (b) & (c).

(vi) 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 (a), (b) & (c).

(vii) Conversion of a reactant is independent of initial concentration of the reactant for
(a) First order reaction (b) Second order reaction
(c) Half order reaction (d) Zero order reaction.

(viii) The relationship between rate constant and temperature is given by
(a) Raoult's Law (b) Arrhenius' Law
(c) Henry's Law (d) Boyle's Law.

(ix) A 10 minute experimental run shows that 75% of liquid reactant is converted to product by a ½ order rate. What would be the percentage converted in a 30 minute run?
(a) 95 (b) 80 (c) 90 (d) Reaction completed before 30 minutes.

(x) 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.

Group- B

2. (a) The internal energy of a certain substance is given by the following equation U = 3.56 PV +84
where U is given in KJ/Kg, P is in KPa and V is m^3/Kg.
A system composed of 1 Kg of substance expands from an initial pressure of 500 KPa and volume 0.22 m^3 to a final pressure of 100 KPa in a process in which pressure and volume are related by $PV^{1.2}$ = constant.
(i) If the expansion is quasi-static, find Q , W and ΔU for the process.
(ii) In another process, the same system expands according to the same pressure volume relationship and from the same initial state to same final state, as given above. But the net heat transfer in this in this case is 30 KJ. Find the work transfer in this process. *[(CO2)(Critical/HOCQ)]*

(b) A clump of steel of mass 30 kg at 427°C is dropped in 100 kg of oil at 27 °C. The specific heats of steel and oil is 0.5KJ/kg-K, respectively. Calculate the entropy change of steel and oil. *[(CO3)(Analyse/IOCQ)]*

8 + 4 = 12

3. (a) Refrigeration in an ideal refrigeration system leaves evaporator at -20°C and has a condenser pressure 0.9 MPa. The mass flow rate is 3 Kg/min. Find COP_R and $COP_{R,\ carnot}$ for the same Tmax and Tmin . Also find the tons of refrigeration.
Conditions at different sections of refrigeration cycle are given below:
At compressor inlet:
T= -20°C
Enthalpy h = 235.31 KJ/Kg
At compressor exit:
P= 900 Kpa
Enthalpy h = 275.1 KJ/Kg
T= 44.74°C
At condenser exit:

P = 900 KPa
Enthalpy h = 99.53 KJ/Kg
At expansion valve exit:
T = -20^{o}C
Given: Tons of refrigeration = 211 KJ/min. *[(CO2)(Apply/HOCQ)]*

(b) Derive the equation showing entropy change due to mixing of two ideal gases. *[(CO2)(Derive/IOCQ)]*

6 + 6 = 12

Group - C

4. (a) Define the following:
(i) Chemical potential, (ii) Fugacity, (iii) Activity coefficient. *[(CO3)(Remember/LOCQ)]*

(b) State Raoult's Law. What is meant by vapour pressure of a liquid and how is it related to temperature. *[(CO2)(Understand/IOCQ)]*

(2 + 2 + 2) + (2 + 4) = 12

5. (a) Draw and explain P-T diagram of water. *[(CO2)(Analyse/IOCQ)]*

(b) Derive the relationship to show how does equilibrium constant (Keq) of a reversible reaction changes with change in temperature of reaction. *[(CO2)(Derive/IOCQ)]*

6 + 6 = 12

Group - D

6. (a) The maximum allowable temperature for a reactor is 800K. At present our operating set point is 780 K, the 20 K margin of safety to account for fluctuating feed, sluggish controls etc. Now with a more sophisticated control system we would be able to raise our set point to 792 K with the same margin of safety that we now have. By how much can the reaction rate, be raised by this change if the reaction taking place in the reactor has activation energy of 175 kJ/mol? *[(CO4)(Understand/LOCQ)]*

(b) Derive a kinetic equation for a second order reaction. *[(CO4)(Understand/LOCQ)]*

7 + 5 = 12

7. Reactant A decomposes in a batch reactor A→R. The composition of A in the reactor is measured at various times with results shown in the following columns. Find a rate equation to represent the data by fractional life method.

Time (s)	0	20	40	60	120	180	300
C_A (mol/L)	10	8	6	5	3	2	1

[(CO5)(Calculate/IOCQ)]

12

Group - E

8. (a) Derive a kinetic equation for non-competitive inhibition. *[(CO5)(Remember/LOCQ)]*

(b) Enzyme E catalyzes the transformation of reactant A to product R as follows: A+ E→R+E,

$$-r_A = (200C_AC_{E0})/(2 + C_A), \quad \text{mol/L.min})$$

If we introduce enzyme (C_{E0}= 0.001mol/L) and reactant (C_{A0}= 10mol/L) into a batch reactor and let the reaction proceed, find the time needed for the concentration of reactant to drop to 0.025 mol/L. Note that the concentration of the enzyme remains unchanged during the reaction. *[(CO6)(Understand/LOCQ)]*

6 + 6 = 12

9. During a test of kinetics of an enzyme catalyzed reaction the following data were recorded:

E_0 (g/L)	T (˚C)	I (mmol/mL)	S (mmol/mL)	V (mmol/mL.min)
1.6	30	0	0.1	2.63
1.6	30	0	0.033	1.92
1.6	30	0	0.02	1.47
1.6	30	0	0.01	0.96
1.6	30	0	0.005	0.56
1.6	49.6	0	0.1	5.13
1.6	49.6	0	0.033	3.7
1.6	49.6	0	0.01	1.89
1.6	49.6	0	0.0067	1.43
1.6	49.6	0	0.005	1.11
0.92	30	0	0.1	1.64
0.92	30	0	0.02	0.90
0.92	30	0	0.01	0.58
0.92	30	0.6	0.1	1.33
0.92	30	0.6	0.033	0.80
0.92	30	0.6	0.02	0.57

(i) Determine the Michaelis-Menten constant for the reaction with no inhibitor present at 30°C and 49.6°C.

(ii) Determine the maximum velocity of the uninhibited reaction at 30°C and an enzyme concentration of 1.6 g/L.

(iii) Determine K_I for the inhibitor at 30˚C and decide what type of inhibitor is being used. *[(CO6)(Calculate, Infer/HOCQ)]*

6 + 2 + (3 + 1) = 12

Cognition Level	*LOCQ*	*IOCQ*	*HOCQ*
Percentage distribution	*31.25*	*41.67*	*27.08*

Course Outcome (CO):

After completion of this course, the students will be able to:

1. Comprehend the thermodynamic properties and functions of different systems and processes.
2. Apply the thermodynamic laws in practical problems.
3. Relate the thermodynamic properties and functions to biological systems.
4. Explain effect of temperature on rate of reaction.
5. Determine the order of a reaction using different suitable analytical methods.
6. Understand the kinetic mechanism of enzyme-substrate reactions with/without the presence of inhibitor and solve related problems.

**LOCQ: Lower Order Cognitive Question; IOCQ: Intermediate Order Cognitive Question; HOCQ: Higher Order Cognitive Question.*