THERMODYNAMICS & KINETICS
(BTC2102)

Time Allotted : 2½ hrs **Full Marks : 60**

Figures out of the right margin indicate full marks.

Candidates are required to answer Group A and any 4 (four) from Group B to E, taking one from each group.

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

Group – A

1. Answer any twelve: **12 × 1 = 12**

Choose the correct alternative for the following

(i) Which of the following is true for a closed system?
(a) mass entering = mass leaving
(b) mass does not enter or leave the system
(c) mass entering can be more or less than the mass leaving
(d) none of the mentioned

(ii) Carnot engine has an efficiency of 50% when its source is at a temperature of 327°C. The temperature of the sink is
(a) 27°C (b) 15°C (c) 100°C (d) 200°C

(iii) What is the significance of triple point in phase diagram
(a) It represents highest temperature in the system.
(b) It is the point where all phases coexists.
(c) It marks the lowest pressure at which a gas phase can exist.
(d) It is unrelated to the equilibrium condition.

(iv) The Gibbs free energy is positive when a change in enthalpy and change in entropy are positive at _____
(a) high temperatures (b) low temperature
(c) all temperatures (d) only at 0 Kelvin

(v) The locus of standard liquid line and standard vapour line meets at
(a) Boiling point (b) Critical point
(c) Ice point (d) Triple point.

(vi) 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

(vii) What is the unit of rate constant for a 1/2 order reaction?
(a) $(\text{time})^{-1}$ (b) $(\text{time})^{-1}\,(\text{concentration})^{3/4}$
(c) $(\text{time})^{-1}\,(\text{concentration})^{-3/4}$ (d) $(\text{time})^{-1}\,(\text{concentration})^{1/2}$

(viii) A batch reactor is a reactor
(a) At steady state
(b) Where composition changes with location and time
(c) At an unsteady state
(d) none

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

(x) Lower 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

Fill in the blanks with the correct word

(xi) An example of extensive property is _____

(xii) Degree of freedom on fusion curve is _____.

(xiii) The first law of thermodynamics is conservation of _____.

(xiv) Unit of rate constant (k) for n^{th} order reaction is _____.

(xv) The time needed to reduce the concentration of the reactant to half its initial value is called_____

Group - B

2. (a) Write three differences between heat engine and heat pump with schematic diagram clearly mentioning the direction of heat flow in each case. *[(CO2)(Analyse/IOCQ)]*

(b) Briefly explain the steps of a refrigeration cycle with diagram. *[(CO2)(Remember/IOCQ)]*

5 + 7 = 12

3. (a) Define entropy. Prove that entropy change of universe is always positive. *[(CO2)(Analyse/IOCQ)]*

(b) Calculate the least work needed to produce 1 kg ice from 0^oC water, if the cooling engine gives up the heat to the surrounding at 27.3 ^oC. Given, latent heat of fusion is 80 cal/gm? *[(CO3)(Compute/IOCQ)]*

(c) Define enthalpy. *[(CO2)(Remember/IOCQ)]*

5 + 6 + 1 = 12

Group - C

4. (a) Define (i) fugacity co-efficient (ii) Helmholtz free energy. *[(CO3)(Remember/LOCQ)]*

(b) What is the osmotic work A for transfer of 1 mole of protons by respiratory chain complexes through the inner mitochondrial membrane, from matrix side (pH =

7) to the inter-membrane space (pH = 6) at 37°C? What is the corresponding difference in membrane potential ΔE (expressed in V)?
(R = 8.3143 J $K^{-1}mol^{-1}$, F = 96 487 J V^{-1} mol^{-1}). *[(CO3)(Compute/HOCQ)]*

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

5. (a) Write van-der –Walls equation and explain significance of each term in it. State the applicability of the equation? *[(CO3)(Analyse/HOCQ)]*
   (b) Explain why a non ideal solution show positive deviation from ideality? Give two examples of such solution. *[(CO3)(Remember/LOCQ)]*

(6 + 2) + (2 + 2) = 12

Group - D

6. (a) The maximum allowable temperature for a reactor is 800K. At present our operating set point is 780K, the 20K 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 792K 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 175kJ/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

[(CO4)(Calculate/HOCQ)]

12

Group - E

8. (a) Derive a kinetic equation for non-competitive inhibition. *[(CO5) (Remember/LOCQ)]*
   (b) Derive Briggs and Haldane equation for enzyme substrate reaction. *[(CO5)(Analyse/HOCQ)]*

6 + 6 = 12

9. Decarboxylation of glyoxalate(S) by mitochondria is inhibited by malonate(I). Using the following data obtained in batch experiments, determine the following:

S, mM		0.25	0.33	0.4	0.5	0.6	0.75	1.00
V, mM/h	I=0	1.02	1.39	1.67	1.89	2.08	2.44	2.5
V, mM/h	I=1.26mM	0.73	0.87	1.09	1.3	1.41	1.82	2.17
V, mM/h	I=1.95mM	0.56	0.75	0.85	1	1.28	1.39	1.82

(i) What type of inhibition is this?

(ii) Determine the constants V_{max}, K_m' and K_I. *[(CO5)(Analyse/HOCQ)]*

12

Cognition Level	LOCQ	IOCQ	HOCQ
Percentage distribution	27.08	25	47.72