Section A

Answer all questions

1. Say if these statements are true (T) or False (F). WRITE NOHING ELSE.

a. Rate of exothermic reactions increase with increase in temperature.

b. A catalyst increases reaction rate by decreasing the activation energy.

c. When the reaction temperature oscillates uniformly around a mean, then the average temperature corresponding to the average rate constant is above this mean.

d. In a series of steps in a reaction the Rate Controlling Step is the most efficient.

e. The enthalpy of mixing two components A and B is identical for ideal and regular solutions.

f. When the progress of a reaction is described by a degree of reaction then the dimensions of rate and rate constant are the same.

g. During electrolysis if there is a limiting current then it implies that diffusion of cations to the cathode is the rate controlling step.

h. If, during an isothermal reaction, the reaction rate decreases then it implies decrease in the rate constant also.

i. Favourable kinetics can make a reaction even if it is thermodynamically not feasible.

j. A reduced time plot can be used to derive the activation energy.

k. $CaCO_3$ can decompose below the decomposition temperature.

l. The entropy of a system may not be zero even at zero degree Kelvin.

m. For any reaction, the activation energy can be known only if the kinetic equation is known.

n. If there is a growing layer of oxide on a metal plate undergoing oxidation then the reaction rate must gradually decrease.

o. The efficiency of an engine operating between a heat source at temperature T_1 and a heat sink at temperature T_2 $(T_1 > T_2)$ increases when (T_1, T_2) increases.   **15×1=15**

2. Explain why the following statements are True. ANSWER ANY FIVE BRIEFLY

a. If the reaction temperature rises steadily during a reaction then the α-t plot assumes a S shape.

b. Entropy of mixing A with B is the same of ideal and regular solutions.

c. TG and DTA plots for the compound $CaCO_3$, $MgCO_3$ are different from those of an equimolar mixture of the carbonates.

d. During a phase transformation through nucleation and growth, nuclei are not stable if the size is less than a critical size.

e. The differential form of the Johnson Mehl equation is not a true kinetic equation but the integral form is.

f. The reaction rate increase more significantly with increase in temperature when the activation energy is higher.

g. The rate equation for a reaction governed by the same rate controlling step changes with the shape of a particle.

h. A first order reaction is better characterized by the ' Half Life' than the time for total reaction.

$$3\times5=15$$

3. Answer ANY TWO questions

a. Show that if the Reduced Time Plot (i.e. x versus t/t0.5 plot) is derived from the following equation x2 = 0.25 (t/ t0.5) then it points towards a particular case of diffusion through product layer as rate controlling.

b. Steel is being undergoing through the following reaction. (O_2) + [S] = (S_2) + [o] where
( ) and [ ] denote, respectively the slag and metal phase. Draw the concentration profiles for the different species as they are transferred to and from the slag / metal interface when [S] transfer is the rate controlling step.

c. Derive the kinetic equation for the reaction of a flat surface and of a spherical solid when the reaction is controlled by the surface area . $$2.5\times2=5$$

Section B

Question No. 4 is compulsory. Answer any two from the rest.

4. a. Derive the expression for free energy and composition for ideal and regular solution. Discuss the role of interaction parameter in this relationship.

 b. Draw the free energy vs composition curves for the following phase diagram at three temperatures (horizontal lines) .
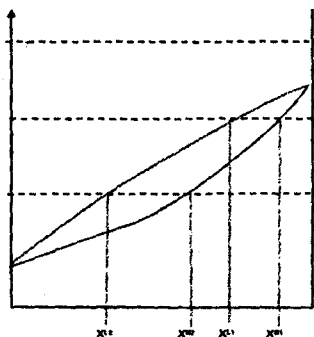
c. Define congruent melting. Draw a phase diagram showing congruent melting with associated free energy composition curve at that point.

[5+5+5]

5. Prove the following

a. For a binary solution: $\Delta S_{mix} = - R(X_A \ln X_A + X_B \ln X_B)$ where ΔS_{mix} is entropy of mixing, X_A and X_B are the mole fractions of A and B atoms respectively.

b.

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial H}{\partial P}\right)_S = V \qquad \left(\frac{\partial H}{\partial S}\right)_P = T$$

[5+5]

6. a. Discuss how the concept of Enthalpy has been evolved in Thermodynamics.

b. Differentiate constant Volume and constant pressure heat capacity.

c. Discuss the effect of pressure in free energy.

[3+4+3]

7. a. Define thermodynamic systems.

b. Discuss the effect of pressure in free energy.

c. For a spontaneous process entropy of the system should increase while free energy should decrease – justify.

[3+4+3]