Name : ....

Roll No. : ....

Invigilator's Signature : ....

CS/INT.PBIR (CHE)/SEM-1/CH-413/2010-11

2010-11

EQUILIBRIUM AND NON-EQUILIBRIUM THERMODYNAMICS

Time Allotted : 3 Hours | Full Marks : 50

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

Answer any *five* questions.

1. In a closed composite system of γ-components a rigid diathermal partition separates the system into two values (1 and 2). The wall is permeable to the component-1 only. Based on the thermodynamic postulates, establish the conditions for equilibrium, assuming that initially the extensive variables of the subsystems 1 and 2 are different in magnitudes and the adaptive and impermeability constraints are relaxed slowly. In which direction will there be a mass flow ? 5

2. Show that entropy maximum and energy minimum postulates for equilibrium in a thermodynamic system are equivalent. 5

3. Explain the idea of Legendre transformation geometrically with reference to a function $y = y(x)$. What is meant by the inverse transformation ? Perform Legendre transformation and the inverse transformation of a function $y = Ae^{Bx}$ taking $A = 2$, $B = 0{\cdot}5$. What are the different Legendre transforms of energy U ? 5

4. Formulate the stability criteria of thermodynamic system in energy representation and extend the results to the Legendre transform of energy. 5

5. Explain what is meant by the critical temperature (T_{cr}) ? Using Landau's theory show that the order parameters spontaneously become non-zero and grow as $(T_{cr} - T)^{\frac{1}{2}}$ for $T < T_{cr}$. What happens to the order parameter for $T > T_{cr}$? 5

6. The fundamental relation for a given thermodynamic system is $S = \left(A\, U^2\, V\, N^2\right)^{\frac{1}{5}}$ with the constant $A > 0$. Find the equation of state. How are the intensive parameters $\frac{\mu}{T}$, $\frac{1}{T}$ and $\frac{\rho}{T}$ are related ? 5

7. Two identical systems, 1 and 2 have heat capacities of the form $C(T) = DT^n$ ($n > 0$). Show that the system which are constrained to have constant volume and mole numbers are characterized by energy $U = U_0 + DT^{(n+1)}/(n+1)$ and entropy $S = S_0 + DT^n/(n)$. If the initial temperatures of the two systems were T_{10} and T_{20}, respectively, what would be the maximum delivered work ? 5

8. A particular system obeys the two equations of state $T = 3As^2/v$ and $P = 3As^3/v^2$ where A is a constant s = molar entropy, v = molar volume. Find the fundamental equation of the system. 5

GROUP – B

Answer any *three* questions.

9. Show that for a chemical reaction the rate of change of entropy density (ρs) is given by $\frac{d}{dt}(\rho s) = \frac{A}{TV}\left(\frac{dz}{dt}\right)$ where A is the affinity and $\left(\frac{dz}{dt}\right)$ is the rate of advancement of the reaction (Ignore all other rate processes like, heat flow, charge flow, mass flow). $8\frac{1}{3}$

10. Starting form $\frac{\partial(\rho s)}{\partial t} = -\vec{\nabla}\cdot\vec{J}_s + \sigma$, where $\vec{J}_s$ is the entropy flux vector and σ is the entropy production. (Ignore mass flow, charge flow and chemical reaction). For a heat flow, show that $ds = đ_e s + đ_i s$ i.e., the total change in entropy is contributed by the two terms. Comment on the second law in this context. $8\frac{1}{3}$

11. Show that for a chemical reaction $\alpha A + \beta B = \gamma D$. The rate of advancement $\left(\frac{dz}{dt}\right)$ is linearly proportional to the affinity A of the chemical reaction. $8\frac{1}{3}$

12. a) Starting from Boltzmann equation for entropy and probability, establish the form of probability distribution of fluctuations $\{\alpha_i\}$ for small deviation from equilibrium. 4

b) Using the above result calculate the average $<\alpha_i, X_j>$ where X_j is the j-th thermodynamic force. $4\frac{1}{3}$