

B. E. (MET) 3rd Semester Examination, December 2013

Subject: METALLURGICAL THERMODYNAMICS AND KINETICS

Code: MT 302

Time: Three hours

Full marks: 70

Use separate answer scripts for different sections

Section A

Answer all questions

1. Say whether the following statements are True (T) or False (F). Write nothing else
- For a normal reaction activation energy (E) cannot be zero
 - For a first order reaction α increases by 50 percent at equal intervals
 - Jander's eq. i.e. $[1-(1-\alpha)^{1/3}] = kt$ is a special case of the Ginstling – Brownstein eq.
 $1-2/3\alpha - (1-\alpha)^{2/3} = kt$
 - For nth order of reaction the rate constant equals the reaction rate at the very beginning.
 - A reduced time plot can be used to evaluate the activation energy.
 - During a reaction the temperature varies at a steady rate from 50 k to 1050 k. The average reaction rate will correspond to 500 k.
 - A cementation reaction: $Fe + Cu^{2+} = Cu + Fe^{2+}$ involves four reaction steps
 - A catalyst increases reaction rate by spreading on a surface to increase the surface area.
 - The α -t plot for a reaction during steady increase in temperature must look like a Johnson- Mehl equation plot, but is not identical.
 - In DTA one obtains two successive endothermic peaks. On subsequent cooling the peaks will be reversed always.

10×1=10

2. Discuss the basis of your answer for any five questions given in Q.1

5×2=10

3. Answer **any three** of the following questions.

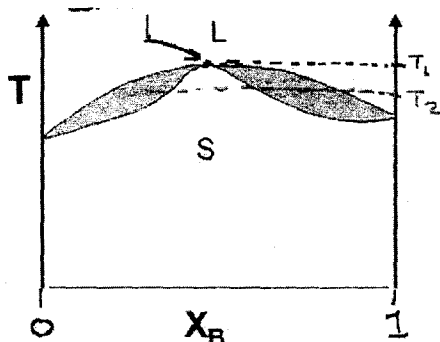
- How does one evaluate the value when the X-T plot follows a Johnson-Mehl eq.?
- Calculate values of α for the reduced time plot for the parabolic equation for $t/t_{0.5}$ values of 0.4, 0.6, 1.2, and 1.4.
- A solid cube is dissolving in a liquid and the reaction rate is controlled by solid surface area. Derive the kinetic equation.
- How does one obtain the basic kinetic equation when the temperature increases at a steady rate?
- Show how the TG, DTG and DTA plots differ between those for dolomite ($CaCO_3.MgCO_3$) and an equimolar mixture of $CaCO_3$ and $MgCO_3$.
- Discuss any two methods of evaluating the activation energy from a α -t plot for a reaction.

3×5=15

Section B

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

4. a. Draw free energy vs composition curves for the following system at T_1 and T_2 temperatures



- b. Discuss the significance of intermediate compound in a phase diagram
- c. Interaction parameter (Ω) plays an important role in calculating the free energy change for a regular binary solution – justify.
- d. How can you construct phase diagram from free energy composition diagram?
- e. With the help of free energy vs temperature diagram explain the driving force for solidification.

(5 x 3)

5. a. Define excess function. How does excess free energy related with change of enthalpy for regular solution?

b. The partial molar free energy of Zinc in liquid Cu-Zn alloys at 1027°C can be represented as:

$$G_{\text{Zn}}^{\text{XS}} \quad (\text{cal/mole}) = -5150 (1 - X_{\text{Zn}})^2$$

Calculate the activity of copper at 1027°C in an equiatomic solution.

(2+3) + 5

- a. Explain thermodynamic system with a suitable example.
- b. State combined first and second law of thermodynamics.
- c. Internal energy is a function of temperature only – justify.
- d. Relate heat capacity and enthalpy.

(2.5 x 4)

- a. A spontaneous process can be made reversible – comment
- b. Express the concept of equilibrium in the light of entropy and free energy
- c. When a system undergoes a process at a constant pressure, does the entropy change depend on temperature?
- d. Discuss the importance of Helmholtz's free energy.

8. a. How does third law of thermodynamics differs from other two laws?

b. The definition of entropy from Nernst and Max Planck are different – comment.

c. Derive the statistical expression for entropy.

d. Substances usually expand with increase in temperature at constant pressure. Is C_p usually larger than C_v ?

[2.5 x 4]