Dr Vishal Singh 8/12/2022 184

NATIONAL INSTITUTE OF TECHNOLOGY, HAMIRPUR, H.P

Department of Materials Science and Engineering

End Term Examination

Materials Thermodynamics and Kinetics (MS-213)

Duration: 3 hrs ***Maximum Marks***: 50

Attempt all the following questions.

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1. Briefly explain/define any *ten* of the following terms/concepts with suitable examples, wherever required:-

   i. *Zeroth Law of Thermodynamics*
   ii. *Open, Closed and Isolated Systems*
   iii. *Extensive and Intensive Properties*
   iv. *State/Point Functions*
   v. *Hess' Law*
   vi. *Gibbs and Helmholtz Free Energies*
   vii. *Activity and Activity Coefficient*
   viii. *Excess Functions*
   ix. *Subregular Solution*
   x. *The Chemical Potential*
   xi. *Rate of a reaction*
   xii. *Fugacity*

   (10 Marks)

2. State and explain the Kirchhoff's law. Calculate the standard heat of formation of PbO from Pb and O_2 at 227°C from the following date:

   $\Delta H^{\circ}_{298,\,<PbO>} = -52.4$ kcal/mol
   $C_{P,\,<PbO>} = 10.6 + 4.0 \times 10^{-3}\,T$ cal/deg/mol
   $C_{P,\,<Pb>} = 5.63 + 2.33 \times 10^{-3}\,T$ cal/deg/mol
   $C_{P,\,<PbO>} = 7.16 + 1.0 \times 10^{-3}\,T - 0.4 \times 10^{5} T^{-2}$ cal/deg/mol

   (5 Marks)

3. Derive *Gibbs-Helmholtz equation*. Calculate the standard enthalpy and entropy changes at 25°C (298 K) for the reaction:

   $2 <Cu> + \frac{1}{2}\,(O_2) = <Cu_2O>;\ \Delta G^{\circ} = -40{,}500 - 3.92\,T \log(T) + 29.5\,T$ cal.

   (5 Marks)

4. Briefly discuss the *Clausius-Clapeyron equation*. The vapour pressure of liquid titanium at 2227°C is 1.503 mm Hg (200 N/m^2). The heat of vaporization at the normal boiling point of titanium is 104 kcal/mol (435.14 kJ/mol). Calculate its normal boiling point.

   (5 Marks)

5. What is meant by the *order of a reaction*? Derive expressions for the *specific reaction rate (k)* and *half-life* ($t_{0.5}$) for a first order reaction. It is known that the radioactive decay of uranium-238 is a first order reaction and the half-life for this reaction is 4.51×10^9 years. Calculate the specific reaction rate for this reaction. How many days will it take 75 percent of a given amount uranium-238 to disappear?

   (6 Marks)

6. Differentiate between ideal, nonideal and regular solutions. Briefly discuss the properties, viz., volume change, heat of formation and entropy of formation of an ideal solution.

   (5 Marks)

(185)

7. Copper and Gold form complete ranges of solid solution at temperatures between 410°C and 889°C and , at 600°C, the excess molar Gibbs free energy of formation of the solid solution is -28, 280 $x_A x_B$ Joules. Calculate the partial pressure of Au and Cu exerted by the solid solution of $x_{Cu} = 0.6$ at 600°C. The saturated vapour pressures of solid copper and gold are given by

$$\ln p^{o}_{Cu}(atm) = -\frac{40920}{T} - 0.86 \ln T + 21.67$$

$$\ln p^{o}_{Au}(atm) = -\frac{45650}{T} - 0.306 \ln T + 10.81$$

OR

From the e.m.f. measurements at 527°C (800K), the following values of the activity coefficient of cadmium in zinc-cadmium solutions have been obtained:-

x_{Cd} *(Mole fraction of Cd)*	0.2	0.3	0.4	0.5
γ_{Cu} *(Activity coefficient of Cd)*	2.153	1.817	1.544	1.352

(a) Determine whether the Zn-Cd solution exhibits regular behaviour.
(b) Calculate the values of the partial molar heat of mixing of Zn and Cd, integral molar heat of mixing, integral molar entropy of mixing, partial molar free energy of mixing of Cd and integral molar free energy of mixing for an equiatomic solution of Zn-Cd, assuming regular behaviour at 527°C (800K).

(6 Marks)

8. Write short notes on <u>*any two*</u> of the following: -
   (a) Regular Solution Model
   (b) Collision and transition state theory/absolute reaction rate theory
   (c) Maxwell's Relations

(8 Marks)