國 立 清 華 大 學 命 題 紙

八十六學年度 工程與系統科學 系（所） 組碩士班研究生入學考試

科目 冶金熱力學 科號 4013 共 3 頁第 1 頁 *請在試卷【答案卷】內作答

Work all problems:

1. From the Second Law of Thermodynamics:" In an isolated system, the entropy is a maximum at equilibrium," show that the conditions for thermodynamic equilibrium in a one-component, two phase (α and β), nonreacting otherwise simple system are:

   $T_\alpha = T_\beta$, $P_\alpha = P_\beta$ and $\mu_\alpha = \mu_\beta$.

   where T is temperature, P is pressure and μ is chemical potential. (15%)

2. At a pressure of 1 atm the equilibrium melting temperature of lead is 600 K, and, at this temperature, the latent heat of melting of lead is 4810 J/mole. Calculate the entropy produced of system and surrounding when 1 mole of supercooled liquid lead spontaneously freezes at 590 K and 1 atm pressure. The constant-pressure molar heat capacity of liquid lead, as a function of temperature, at 1 atm pressure is given by

   $$c_{p(l)} = 32.4 - 3.1 \times 10^{-3} T \text{ J/K}$$

   and the corresponding expression for solid lead is

   $$c_{p(s)} = 9.75 \times 10^{-3} T \text{ J/K}$$

   (a) From statistical considerations, would you expect the entropy to increase or decrease on freezing?
   (b) Does the answer to (a) violate predictions of the Second Law of Thermodynamics? Explain it. (20%)

3. Show that $c_p - c_v = VT\alpha^2/\beta$,

   where c_p is constant pressure molar heat capacity
   c_v is constant volume molar heat capacity
   V is molar volume
   T is absolute temperature
   α is thermal expansion coefficient
   β is isothermal compressibility coefficient (15%)

4. You are given an Ellingham diagram as shown in Fig.1.
   (a) If a pure Ti specimen is heat treated at 800°C, refer to the Ellingham diagram, would you select a quartz (SiO_2) tube to contain the specimen? If your answer is no, please explain the reason and suggest a material that may contain the specimen for heat treatment.
   (b) Using Ellingham diagram to estimate the partial pressure of oxygen for the oxidation of Cr at 800°C. Provide a method to prevent oxidation during heat treatment of Cr at 800°C. (20%)

5. One mole of silver is taken at constant pressure from T=0°K, to temperature above 1235°K, where it is molten.
   (a) Plot the Gibbs free energy, the enthalpy, as well as the entropy, as a function of the temperature. The graph should be schematic, but should reflect the physically important trends.
   (b) Justify, using quantitative thermodynamic arguments, the curves you have drawn. (15%)

6. Consider the dilute solid solution of A in B.
   (a) Prove that if the solute obeys Henry's law then the solvent obeys Raoult's law.
   (b) Prove that complete insolubility is not possible. State any assumptions you make in the proof. (15%)

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科目 冶金熱力學 科號 403 共 3 頁第 3 頁 *請在試卷【答案卷】內作答

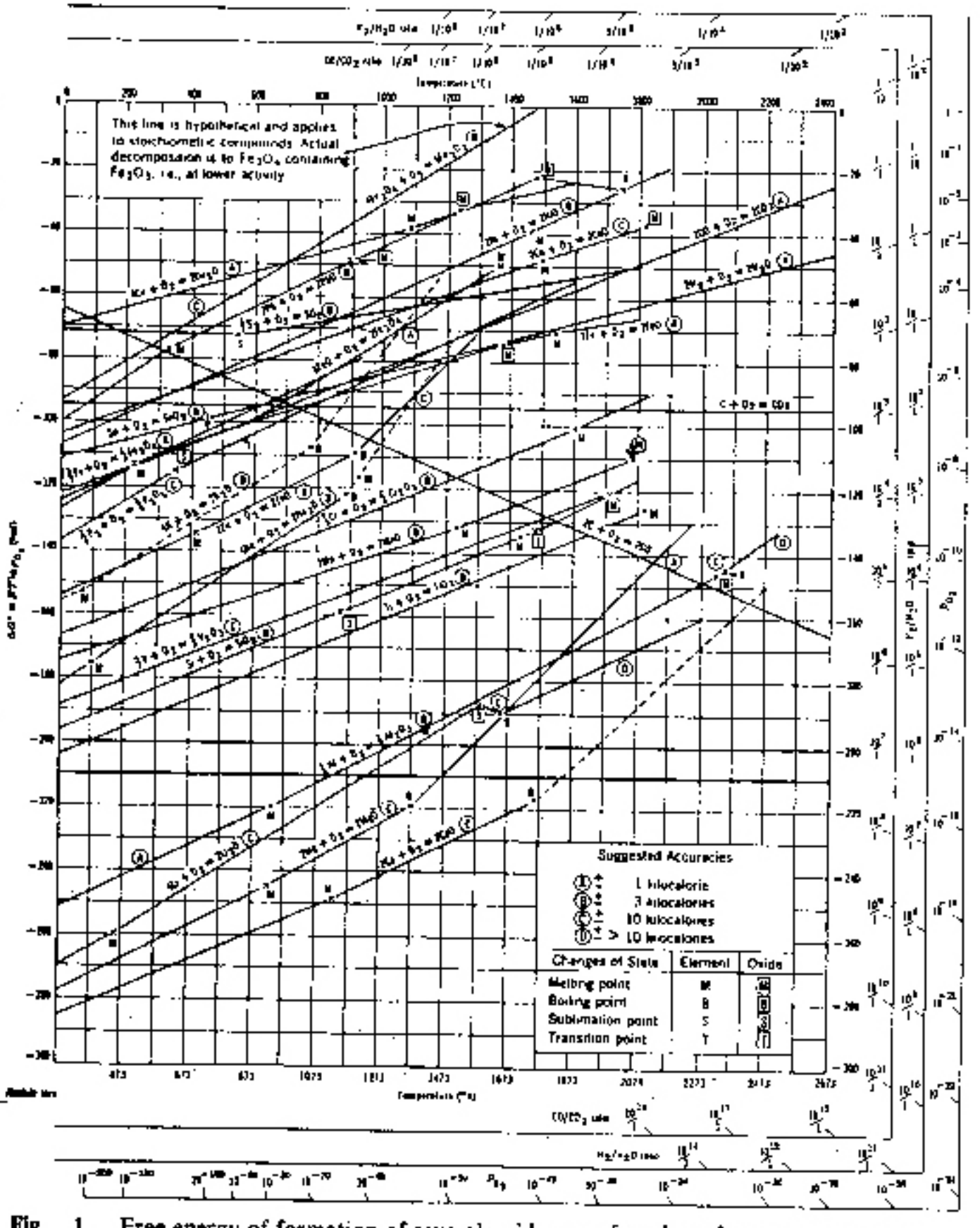

Fig. .1 Free energy of formation of several oxides as a function of temperature. From L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, 1953.