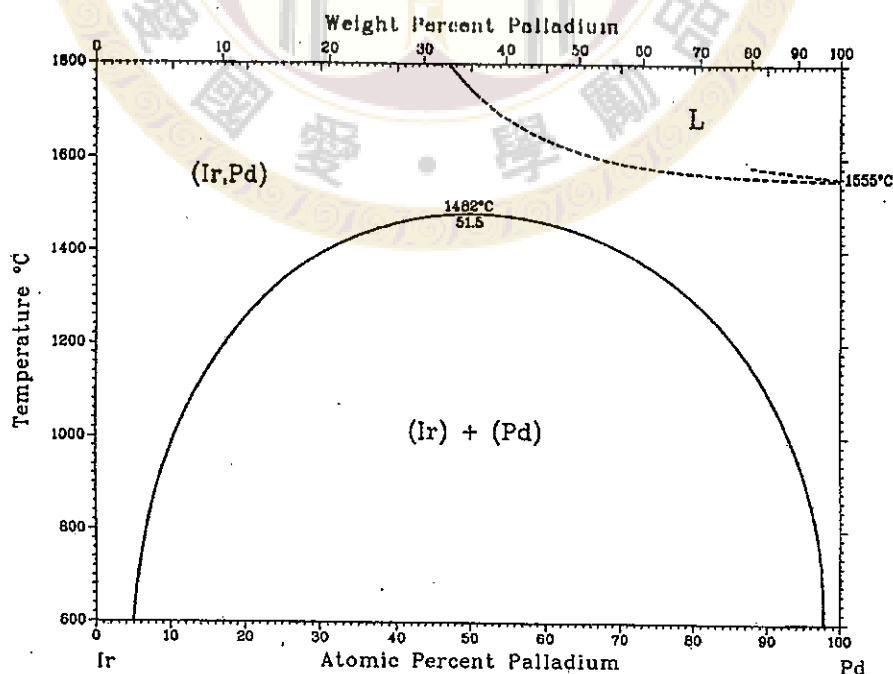


1. Please reply the following questions: (5% each, 15% in total)
  - (a) Explain why the change in the Gibbs free energy,  $\Delta G$ , (as opposed to the change in internal energy,  $\Delta U$ , or entropy,  $\Delta S$ ) is often used as a criterion for equilibrium?
  - (b) Explain Henrian standard state. Why is it often used?
  - (c) What distinguishes critical phenomena such as order-disorder transitions from first order phase transitions such as melting and vaporization?
  
2. Miscibility gaps are observed in the binary phase diagrams among the platinum group metals. The phase diagram for Ir-Pd is given below.
  - (a) Can the miscibility gap in the Ir-Pd system be represented by the regular solution model? Plot the values for the miscibility gap assuming a regular solution model on the phase diagram below. Indicate the value of the  $\Omega$  used in your model. (5%)
  - (b) Draw the spinodal curve predicted by a regular solution model on the phase diagram. Within the miscibility gap label the metastable and unstable regions. In addition, indicate the mechanism of phase transformation associated with these regions. (10%)
  - (c) Briefly explain why a relative simple phase diagram is observed for a pair of metals such as Ir-Pd, but very different behavior is found for the binary systems Al-Pd, Sn-Pd and Zn-Pd. In these systems, more limited regions of solid solution and intermetallic compounds are observed. (5%)



見背面

3. Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is to be electrolyzed to metallic aluminum in an electrochemical cell. The electrodes of the cell are made of graphite. The products of the reaction are metallic aluminum and carbon dioxide. Metallic aluminum does not react with the graphite.

(a) Write the chemical reaction that takes place in the cell. (5%)

(b) Calculate the minimum voltage at which the electrolysis may be carried out at 650 °C. (10%)

Data:  $2\text{Al} + 1.5\text{O}_2 = \text{Al}_2\text{O}_3$ ,  $\Delta G^\circ = -1,676,000 + 320T$  (J/mole)

$\text{C} + \text{O}_2 = \text{CO}_2$ ,  $\Delta G^\circ = -394,100 - 0.84T$  (J/mole)

Faraday's constant is 96500

4. Briefly answer the following questions and reason your answers (15%)

(1) Can the change in a state function be equal to the difference of two nonstate functions?

(2) Can entropy be negative?

(3) What are the considerations that the van der Waals equation was derived from?

5. At  $T = 25^\circ\text{C}$ ,  $1000\text{ cm}^3$  of nitrogen ( $\text{N}_2$ ) at pressure  $P_1 = 1\text{ atm}$  is mixed with  $2000\text{ cm}^3$  of oxygen ( $\text{O}_2$ ) at pressure  $P_2 = 2\text{ atm}$ . The volume of the mixture is then changed such that the temperature and pressure in the final state are  $T = 25^\circ\text{C}$  and  $P = 1\text{ atm}$ , respectively. Calculate the change of entropy associated with this two-step process if both nitrogen and oxygen behavior as ideal gas. (15%)

Note the gas constant  $R = 0.082\text{ liter}\cdot\text{atm}/\text{degree}\cdot\text{mole} = 8.314\text{ joules}/\text{degree}\cdot\text{mole}$

6. Calcium boils at  $1440^\circ\text{C}$ . The standard free energy of vaporization of liquid calcium at temperature  $T$  is given by

$$\Delta G_T^\circ = 41030 + 2.53T \ln(T) - 42.23T \quad (\text{cal/mol})$$

(a) Find the linear Gibbs free energy equation of the form

$$\Delta G_T^\circ = a + bT \quad (\text{cal/mol})$$

which approximates the above equation as closely as possible near 1500 K. (12%)

(b) Calculate the boiling point from the linear equation and compare with the actual value. (8%)

試題隨卷繳回