

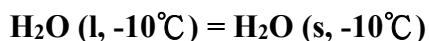
國立高雄應用科技大學  
107 學年度研究所碩士班招生考試  
化學工程與材料工程系碩士班  
物理化學

試題 共 2 頁，第 1 頁

- 注意：a. 本試題共 題，共 100 分  
b. 作答時不必抄題  
c. 考生作答前請詳閱答案卷之考生注意事項

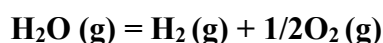
Given:  $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1} = 8.314 \times 10^{-2} \text{ L bar K}^{-1}\text{mol}^{-1} = 8.206 \times 10^{-2} \text{ L atm K}^{-1}\text{mol}^{-1}$ ;  $1 \text{ atm} = 1.013 \text{ bar}$ ;  $1 \text{ bar} = 10^5 \text{ Pa}$ ;  $1 \text{ F} = 96485 \text{ C mol}^{-1}$ .

1. What is the molar volume of methane at 300 K and 50 bar according to (a) the ideal gas law and (b) the virial equation? The second virial coefficient  $B$  of methane is  $-0.04 \text{ L mol}^{-1}$  at 300 K. 10%
2. The combustion of ethanol in a constant-volume calorimeter produces  $1364.34 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . What is the value of  $\Delta_r H^\circ$  for this combustion reaction? Assuming that the combustion reaction produces water is liquid state. (The quantity  $\Delta_r H^\circ$  is the reaction enthalpy) 8%
3. Calculate the  $\Delta_{\text{mix}} S$  and  $\Delta_{\text{mix}} G$  for the formation of a quantity of air containing 1 mol of gas by mixing nitrogen and oxygen at  $30^\circ\text{C}$ . Air may be taken to be 80% nitrogen and 20% oxygen. (The quantity  $\Delta_{\text{mix}} S$  and  $\Delta_{\text{mix}} G$  is the mixing entropy and mixing Gibbs energy) 8%
4. A mole argon is allowed to expand adiabatically and reversibly from a pressure of 10 bar and 300 K to 2 bar. Calculate the final temperature and the molar quantities of  $\Delta U$  and  $\Delta H$ . (The quantity  $U$  is the internal energy,  $\bar{C}_V = 2/3 R$ ). 12%
5. The transition of one mole of supercooled water at  $-10^\circ\text{C}$  and 1 bar to ice at  $-10^\circ\text{C}$  and 1 bar is given as:



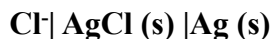
For the crystallization of liquid water at  $0^{\circ}\text{C}$ ,  $\Delta H = -6004 \text{ J mol}^{-1}$ . The heat capacity of water may be taken to be  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , and that of ice may be taken to be  $36.8 \text{ J K}^{-1} \text{ mol}^{-1}$  over this range. (a) What is the molar quantity of  $\Delta S$  for the water (denoted as system)? (b) What is the molar quantity of  $\Delta S$  for the heat reservoir at  $-10^{\circ}\text{C}$  (denoted as surrounding)? (c) Is the process reversible or irreversible? 12%

6. For the reaction



At  $2000^{\circ}\text{C}$  water is 4% dissociated into oxygen and hydrogen at a total pressure of 1 bar. (a) Calculate the equilibrium constant  $K$  and  $\Delta_r G^{\circ}$ . (b) Will the extent of reaction increase or decrease if the pressure is reduced? Why? (c) Will the extent of reaction increase or decrease if argon is added, when the total pressure is held equal to 1 bar? Why? (d) Will the extent of reaction change if pressure is raised by the addition of argon at constant volume to the closed system containing partially dissociated water vapor? Why? (The quantity  $\Delta_r G^{\circ}$  is the reaction Gibbs energy) 16%

7. For the cell



Chemical thermodynamic properties at 298 K and 1 bar are given as:

|               | $\Delta_f H^{\circ} / \text{kJ mol}^{-1}$ | $\Delta_f G^{\circ} / \text{kJ mol}^{-1}$ |
|---------------|---|---|
| $\text{Cl}^-$ | -167.159                                  | -131.228                                  |
| $\text{AgCl}$ | -127.068                                  | -109.789                                  |

(a) What is the cell reaction? (b) Calculate the molar quantities of  $\Delta H^{\circ}$  and  $\Delta G^{\circ}$  for the cell reaction at  $25^{\circ}\text{C}$ . (c) What is the standard electromotive force of the cell at  $25^{\circ}\text{C}$ ? (d) Calculate the molar quantity of  $\Delta G^{\circ}$  for the cell reaction at  $100^{\circ}\text{C}$  by using Gibbs-Helmholtz equation ( $[\partial(\Delta G^{\circ}/T)/\partial T]_p = -\Delta H^{\circ}/T^2$ ) if  $\Delta_r C_p^{\circ} = 0$ . (e) What is the standard electromotive force of the cell at  $100^{\circ}\text{C}$ ? 20%

8. For the decomposition reaction



At  $508^{\circ}\text{C}$  has a half-life of 135 min when the initial pressure of HI is 0.1 atm and 13.5 min when the pressure is 1 atm. (a) Show that this proves that the reaction is second order. (b) What is the value of the rate constant in  $\text{L mol}^{-1} \text{ s}^{-1}$ ? 14%