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106 學年度研究所碩士班招生考試
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物理化學

注意：a.本試題共 5 題，每題 20 分，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 J $K^{-1}mol^{-1}$ = 0.08314 L bar $K^{-1}mol^{-1}$ = 0.08206 L atm $K^{-1}mol^{-1}$, 1 atm = 1.013 bar, 1 bar = 10^5 Pa, 1 kPa = 1000 Pa, 1 Torr = 133.32237 Pa.

1. A system composed of an ideal gas expands reversibly and isothermally at 300 K from the initial volume of 1 m^3 to the final volume of 10 m^3. Calculate the changes in molar internal energy ($\Delta\bar{U}$), molar enthalpy ($\Delta\bar{H}$), molar Gibbs energy ($\Delta\bar{G}$), molar Helmholtz energy ($\Delta\bar{A}$), and molar entropy ($\Delta\bar{S}$) of the system.

2. **(a)** Show that the change in Helmholtz energy (ΔA) for a reversible process at constant temperature is equal to the total work done on the system by the surroundings.

(b) The PV work means the pressure-volume work. When the PV work and non-PV work are involved, show that the change in Gibbs energy (ΔG) for a reversible process at constant temperature and pressure is equal to the non-PV work done on the system by the surroundings.

3. Consider the following reaction:

$$3C(graphite) + 2H_2O(g) = CH_4(g) + 2CO(g)$$

The $\Delta_r G^o$ (standard Gibbs energy of reaction) and $\Delta_r H^o$ (standard enthalpy of reaction) for the reaction at 1000 K are 4.122 kJ mol^{-1} and 181.899 kJ mol^{-1}, respectively. Assuming that $\Delta_r H^o$ is independent of temperature. At what temperature will the reaction have an equilibrium constant (***K***) of unity (***K*** = 1)?

4. A ternary liquid mixture of A, B, and C is in equilibrium with its vapor at a constant temperature of 300 K, where A, B, and C represent different chemical species. Assuming that the liquid phase is an ideal solution and the vapor phase obeys the ideal gas law. The vapor pressures of the pure A, B, and C are 0.3 bar, 0.5 bar, and 0.7 bar, respectively. The mole fractions of A, B, and C in the vapor are 0.3, 0.4, and 0.3, respectively.

(a) Calculate the total pressure of the vapor.

(b) What are the mole fractions of A, B, and C in the solution?

5. Consider a first-order chemical reaction:

$$A \rightarrow B$$

where A and B represent different chemical species. The activation energy and pre-exponential factor in Arrhenius equation for the reaction are found to be 105000 J mol^{-1} and 5×10^{13} s^{-1}, respectively. At what temperature will the reaction have a half-life ($t_{½}$) of 100 s?