淡江大學96學年度碩士班招生考試試題

系別：化學工程與材料工程學系　　科目：物 理 化 學

准帶項目請打「V」	
V	簡單型計算機

本試題共 1 頁

Physical Chemistry

1. (a) Give the classical thermodynamic definition of differential entropy change dS. 5%
   (b) The statistical mechanics defines "W", the weight of configuration $\{n_0, n_1, n_2, n_3, \ldots\}$, as the number of ways in which a system consisting n particles, here $n = \sum n_i$, can be distributed among different energy levels $\varepsilon_0, \varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots$. Knowing that $\frac{\partial \ln W}{\partial n_i} + \alpha - \beta\varepsilon_i = 0$, where $\alpha = \ln \frac{1}{\sum e^{-\varepsilon_i/kT}}$, $\beta = \frac{1}{kT}$ and on assuming that the system volume is kept constant, prove that $S = k \ln W$. 10%
   (c) What could you say about the third law of thermodynamics from $S = k \ln W$? 5%

2. (a) Explain the physical meaning of phase transition. 5%
   (b) Letting H = H(x, y, z, ...), tell your choice for the variables x, y, z, ..., and give the mathematical expression of differential enthalpy change dH for phase transition. 5%
   (c) From the classical definition of differential entropy dS and the chosen function H(x, y, z, ...), prove that the entropy change of phase transition is $\Delta_{trans} S = \frac{\Delta_{trans} H}{T_{trans}}$ 10%

3. (a) What physical significance does the wavefunction in Schrödinger equation tell about the particle? 5%
   (b) The ground-state wavefunction of a hydrogen atom is $\Psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$, where a_0 = 53 pm (the Bohr radius). Calculate the probability that the electron will be found somewhere within a small sphere of radius 1.0 pm centred on the nucleus. 5%
   (c) Now suppose that the same sphere is located at $r = a_0$. What is the probability that the electron is inside it? 10%

4. (a) Give the definition of partial molar Gibbs energy, and describe its physical meaning. 5%
   (b) Explain what the physical meaning of osmotic pressure is. 5%
   (c) Based on the description you give above, try to derive the van't Hoff equation $\Pi = [B]RT$, where [B] = n_B/V is the molar concentration of the solute. 10%

5. (a) In the study of reaction kinetics, we usually use the steady-state approximation to resolve the reaction mechanism. Explain what the so called "steady-state approximation" is, and why we can assume it. 5%
   (b) The Lindemann-Hinshelwood mechanism for unimolecular reactions suppose that a reactant molecule A becomes energetically excited by collision with another A molecule. The energized molecule A* might lose its excess energy by collision with another molecule, or alternatively, the excited molecule might itself apart and form product P. Write down the reaction mechanism based on the description above. 5%
   (c) From the mechanism above derive the rate law for the formation of P. Furthermore, tell the condition under which the reaction can be viewed as first-order rate law. 10%