國 立 清 華 大 學 命 題 紙

98 學年度_____生命科學院_____系（所）____乙、丙____組碩士班入學考試

科目___物理化學__科目代碼____0303、0403____共__2__頁第__1__頁 *請在【答案卷】內作答

(log2 = 0.301, ln2=0.693, ln10=2.303)

1. For the process A ⇆ B, K_{eq}(AB) is 0.2 at 37°C. For the process B ⇆ C, K_{eq}(BC) is 100 at 37°C. (gas constant = 8.314J/mol K)
   (a) Determine K_{eq}(AC), the equilibrium constant for the overall process A ⇆ C from K_{eq}(AB) and K_{eq}(BC). (6 points)
   (b) Determine standard state free energy changes for all three processes (6 points)
   (c) Use $\Delta G°$(AC) to determine K_{eq}(AC). (3 points)

2. Calculate the pH at which the ε-amino group of lysine is 20% dissociated. (For the lysine side chain, pK_a = 10.5.) (9 points)

3. Explain the first, second and third laws in the Thermodynamics (6 points)

4. Explain the following terms
   (a) An isolated system; A closed system; An open system (6 points)
   (b) State variables (2 points)
   (c) Entropy (2 points)
   (d) Free energy (2 points)
   (e) Chemical potential (2 points)
   (f) Transition state (2 points)
   (g) Activation energy (2 points)
   (h) Michaelis-Menten Kinetics (2 points)

5. Consider the process where n_A mol of gas A initailly at 1 atm pressure mix with n_B mol of gas B also at 1 atm to form 1 mol of a uniform mixture of A and B at a final total pressure of 1 atm, and all at constant temperature. Assume that all gases behave ideally.
   (a) What is the entropy change for this process? What is the sign of the entropy change? (5 points)
   (b) What is the change of Gibbs free energy? What is the sign of the change of Gibbs free energy? (5 points)

6. A reaction is zero order in substance S. Starting with the differential rate law, derive an expression for $t_{1/2}$ (half life) in terms of the starting concentration $[S]_0$ and the zero-order rate constant k. (5 points)

7. According to Boltzmann distribution law, please calculate the ratio of molecules in the upper energy states to those in the lower energy states. (5 points) The energy difference between two energy states is
   a. 1.2×10^{-2} J • mol^{-1}
   b. 12 J • mol^{-1}
   c. 12 kJ • mol^{-1}
   d. 120 kJ • mol^{-1}

   In these energy states, which transition will give rise to the most intense absorption spectrum, and please also describe why NMR method gives us very insensitive signal of absorption where NMR resonance is in the range of 300 -900 MHz. (3 points)

8. An interesting protein with molecular weight 10 kDa can form two structural isoforms in solution. A and B. The two formations can easily interconvert to each other in solution. Protein with the two states has very different UV absorption: at wavelength of 280 nm, the molar extinction coefficient for formation A is 1.0×10^4 M^{-1} cm^{-1} and that for formation B is 4-fold higher, 4.0×10^4 M^{-1} cm^{-1}. We dissolved 1 mg protein into 1 ml buffer, and allow protein isoforms reach their equilibrium. We measure the absorbance of the protein sample at 280 nm in a 1 cm pathlength cuvette at various temperatures. Here is the result:

Temp	298	A_{280}	1.4848
	303		1.5193
	308		1.5468
	313		1.5760

(a) Can you calculate the individual concentrations of formation A and B at different temperatures by using the equation $A = \varepsilon CL$ (A: absorption; ε: molar extinction coefficient; C: concentration; L: pathlength). (5 points)

(b) Please derive the equation to calculate the equilibrium constant *Kc* for the interconversion of A and B. (2 points) According to the calculated protein concentrations, please estimate *Kc* values at different temperatures. (5 points)

(c) Please also derive the equation to calculate the free energy ΔG^0 for the reaction. (3 points). Calculate corresponding ΔG^0 and ΔH^0 and ΔS^0 at different temperatures, if we assume that ΔH^0 and ΔS^0 are constant with respect to temperature. (5 points)

9. The diffusion coefficient for glucose ($C_6H_{12}O_6$) in water is 6.81×10^{-10} m^2 s^{-1} at 25°C. The water viscosity at the temperature is 8.937×10^{-4} kg m^{-1} s^{-1} and the density of glucose is 1.55 g cm^{-3}. Please use Stokes-Einstein equation to estimate the molar mass of glucose and compare to the true molar mass. (7 points)