國　立　清　華　大　學　命　題　紙

97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＿3＿頁第＿1＿頁 *請在【答案卷】內作答

Gas constant $R = 8.314\ \text{J} \cdot \text{mol}^{-1} \cdot K^{-1} = 0.08205\ \text{L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot K^{-1}$

1. For the following processes, state whether each of the thermodynamic quantities q (heat), w (work), ΔE (energy) and ΔH (enthalpy) is greater than, equal to, or less than zero for the system described. Explain your answers briefly. (20 points)
   (a) An ideal gas expands adiabatically against external pressure of 1 atm.
   (b) An ideal gas expands isothermally against external pressure of 1 atm.
   (c) An ideal gas expands adiabatically into a vacuum.
   (d) A liquid at its boiling point is converted reversibly into its vapor, at constant temperature and 1 atm pressure.
   (e) H_2 gas and O_2 gas are caused to react in a closed bomb at 25℃ and the product water is brought back to 25℃.

	q	w	ΔE	ΔH
(a)				
(b)				
(c)				
(d)				
(e)				

(注意: 請勿在此處作答, 請回答在答案卷上!)

2. A study of the temperature-induced reversible denaturation of the protein ribonuclease was carried out. The equilibrium constants for the denaturation over a range of pH and temperatures were measured as T(K)/Keq: 326.1/0.12; 327.5/0.27; 329.0/0.68 for pH 3
   (a) Calculate the ΔH° at 54.5 °C (6 points)
   (b) What does this value of ΔH° mean for the unfolding of the protein? (4 points)

3. Consider a system that undergoes a phase change from phase α to phase β at equilibrium temperature T_m and equilibrium pressure P_m. At these equilibrium conditions, the heat absorbed per mole of material undergoing this transition is q_m, and there is a molar volume change of ΔV_m. The molar heat capacities at constant pressure for the α and β phases are $C_{p,\alpha}$ and $C_{p,\beta}$; they are independent of temperature.
   (a) Evaluate w, ΔE, ΔH, ΔS, and ΔG for converting 1 mole of the system from phase α to phase β at the equilibrium T_m and P_m. (5 points)
   (b) The denaturation transition of a globular protein can be approximated as a phase transition from α to β. Calculate ΔG, ΔH and ΔS for a heat of transition of q_m = 638 kJ/mol at T_m = 70 °C, P_m = 1 atm; $C_{p,\alpha} - C_{p,\beta}$ = 8.37 kJ/mol*K (5 points)

4. The second law of thermodynamics states that entropy increases for spontaneous processes and that an increase in entropy is associated with transitions from ordered to disordered states. Living organisms, even the simplest bacteria growing in cultures, appear to violate the second law because they grow and proliferate spontaneously. They convert simple chemical substances into the highly organized structure of their descendants. Write a critical evaluation of the proposition that living organisms contradict the second law. Be sure to state your conclusion clearly and to present detailed, reasoned arguments to support it. (5 points)

5. In the red blood cell, glucose is transported into the cell against its concentration gradient. The energy for this transport is supplied by the hydrolysis of ATP:
   $ATP + H_2O$ ---> $ADP + Pi$ ($\Delta\overline{G^0} = -31.0kJ$)
   Assume that the overall transport reaction is 100% efficient and given by
   $ATP + H_2O$ + 2 glucose (out) ---> 2 glucose (in) + ADP + Pi

   (a) At 25 °C, under condition where [ATP], [ADP], and [Pi] are held constant at $1x10^{-2}$ M by cell metabolism, find the maximum value of [glucose(in)]/[glucose(out)]. Assume all activity coefficients are equal to 1. (5 points)
   (b) If the stoichiometry of transport were 1 mol of glucose transported per mol of ATP hydrolyzed, what would be the maximum concentration gradient of glucose under the same conditions as part (a)? (5 points)
   (c) In an actual cell, the glucose inside the cell may have an activity coefficient much less than 1 due to nonideal behavior. Would this increase or decrease the maximum concentration gradient obtainable? (Assume that all other activity coefficients are equal to 1.) (5 points)

6. The measured osmotic pressure of seawater is 25 atm at 273 K.
   (a) What is the activity of water in seawater at 273 K? Take the partial molar volume of water in seawater to be 0.018 M^{-1}. (5 points)
   (b) The vapor pressure of pure water at 273 K is 4.6 torr. What is the vapor pressure of water in seawater at this temperature? (5 points)
   (c) What temperature would you expect to find for seawater in equilibrium with the polar ice caps? The melting point of pure water at 1 atm pressure is 0 °C, and $\Delta\overline{H^0_{fus}}$ (enthalpy of fusion) may be taken as 5.86 kJ/mol, independent of temperature. (5 points)

7. An electronically excited molecule A* can either emit fluorescence to return to its ground state, or it can lose its excitation by collision:

$$A^* \xrightarrow{k_r} A + photon$$

$$A^* \xrightarrow{k_T} A + heat$$

(k_r and k_T are rate constants with units of s^{-1})

(a) The fluorescence intensity of A* can be measured as the number of photons emitted per second. Write an equation relating the fluorescence intensity to the concentration of A*. (5 points)

(b) Derive an equation for the concentration of A* as a function of time, k_r, k_T, and $[A^*]_0$ (concentration of A* at zero time). (5 points)

8. A carboxypeptidase was found to have a Michaelis constant K_M of 2.00 μM and a k_{cat} of 150 s^{-1} for its substrate A.

(a) What is the initial rate of reaction for a substrate concentration of 5.00 μM and an enzyme concentration of 0.01 μM? Give units. (5 points)

(b) The presence of 5.00 mM of a competitive inhibitor decreased the initial rate above by a factor of 2. What is the dissociation constant for the enzyme-inhibitor complex, K_I, where K_I=[E][I]/[EI]? (5 points)

(c) A competing substrate B is added to the solution in part (a). Its K_M is 10.00 μM and its k_{cat} is 100 s^{-1}. Calculate the relative rates of substrate reaction for equal concentrations of substrates; that is, calculate v_A/v_B. (5 points)