I.選擇題(30%)

Select the one choice that best completes the statement or answer that question

1. The statement "The energy is the universe is constant" is a tenet of
(A) The second law of thermodynamics, (B) Thermodynamics spontaneity, (C) The first law of thermodynamics, (D) Entropy, (E) Enthalpy

2. In biochemical reaction, reactants may be converted into products. The extent to which this occurs spontaneously is expressed as which of the following?
(A) ΔG, (B) Keq, (C) ΔS, (D) Temperature, (E) None of the above

3. Which of the following is NOT true of the ΔH?
(A) ΔH is change in heat content, (B) ΔH is change in enthalpy, (C) In biology, is basically the same as ΔE, (D) A reaction with a positive value is exothermic, (E) $\Delta H = \Delta E + \Delta(PV)$

4. An ideal gas expands adiabatically against external pressure of 1 atm. What kinds of thermodynamic quantities q, w, ΔE and ΔH are equal to zero?
(A) q, (B) ΔE, (C) ΔH, (D) Both w & ΔE, (E) Both q & ΔH

5. An ideal gas expands isothermally against external pressure of 1 atm. What kinds of thermodynamic quantities q, w, ΔE and ΔH are equal to zero?
(A) q, (B) ΔE, (C) w, (D) Both ΔH & ΔE, (E) Both q & w

6. For which of the following sets of values of ΔH and ΔS will a reaction be spontaneous only at high temperature?

	ΔH(kj)	ΔS (J/K)
(A)	+80	-10
(B)	-80	-10
(C)	-80	+10
(D)	0	-10
(E)	+80	+10

7. For a triprotic acid, H_3A, K_{a1} is 1.0×10^{-2}, K_{a2} is 1.0×10^{-6}, and K_{a3} is 1.0×10^{-10}. The pH range in which HA^{-2} is the predominant form is a pH between
$H_3A \rightarrow H_2A^- + H^+ \rightarrow H_1A^{-2} + H^+ \rightarrow A^{-3} + H^+$
(A) 1 and 3, (B) 5 and 7, (C) 7 and 9, (D) 9 and 11, (E) 3 and 5

8. At 298K and 1 atmosphere, the closed system shown above is at equilibrium. If the equilibrium is perturbed by isothermally decreasing the volume of the system, which of the following is NOT correct?

$$Cu_2O(s) + \frac{1}{2} O_2(g) \rightleftarrows 2\,CuO(s) \qquad \Delta H^\circ = -11.3 \text{ kJ}$$
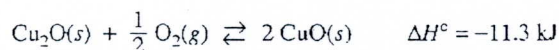
(A) More products will be present after equilibrium is reestablished., (B) ΔG Is less than zero for the process of reestablishing equilibrium, (C) The equilibrium constant, K_{eq} will decrease, (D) The temperature will remain constant, (E) ΔG° will remain unchanged.
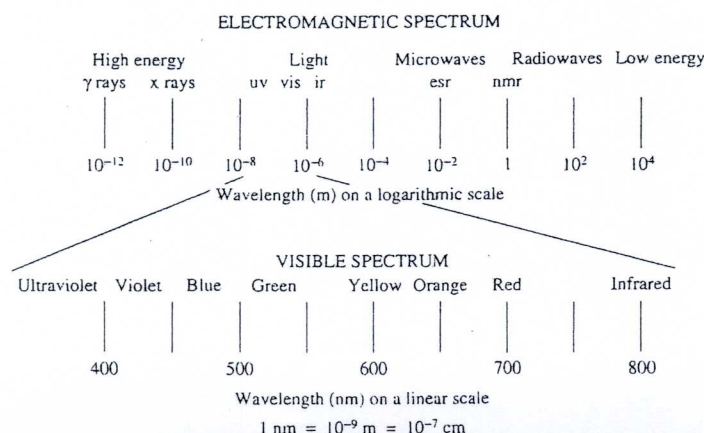
9. One mole of an ideal gas expands isothermally until its volume is doubled. What is the change in Gibbs energy, ΔG for the process?
(A) R ln 1/2, (B) R ln 2, (C) RT ln 1/2, (D) RT ln2, (E) $e^{-2/RT}$

10. In which of the following processes is energy transferred into the substance by work (w>0)?
(A) Expansion of a gas against the surroundings
(B) Expansion of a gas into a vacuum
(C) Vaporization of one mole of water at $70^{\circ}C$ in an open container
(D) Combustion of ethane in a constant-volume container
(E) Melting of 100 g of ice on a laboratory bench top

11. Which of the following partial derivatives is zero for an ideal gas?
(A) $(\partial U/\partial T)_v$, (B) $(\partial H/\partial T)_p$, (C) $(\partial S/\partial T)_p$, (D) $(\partial U/\partial V)_T$, (E) $(\partial S/\partial V)_T$

12. All are true for the Second Law of Thermodynamics EXCEPT:
(A) Systems tend to proceed from ordered states to disordered states.
(B) The entropy of the system plus surroundings is unchanged by reversible processes
(C) The entropy of the system plus surroundings increases for irreversible processes.
(D) All naturally occurring processes proceed toward equilibrium.
(E) None, all are true.

13. Entropy change, ΔS, is
(A).the sum of heat absorbed and work, (B).not a thermodynamic state function, (C).a measure of disorder in a system, (D).determined by pressure change at a constant temperature, (E) equal to the heat transferred at constant pressure and volume.

14.Thermodynamic parameters (entropy, enthalpy, free energy, and internal energy) are given for an unknown enzyme. Explain which results would be expected for the breaking of hydrogen bonds and the exposure of hydrophobic groups from the interior during the unfolding process of a protein.
(A).Entropy change, ΔS, is zero, (B).Enthalpy change, ΔH, is positive, (C).The reaction is spontaneous, (D).Enthalpy change, ΔH, is negative, (E).Entropy change, ΔS, is positive

15. If 4.0 g of a gas occupies 11.2 L at 0.00 C and 0.125 atmosphere, then the molecular mass of the gas is
(A) 8 g, (B) 16 g, (C) 32 g, (D) 48 g, (E) 64 g

II.計算題(70%)

1. (a) For a light-penetrable solution (no scatting), if it shows red color, can you predict the wavelength (nm) with maximum absorption (ε_{max}) in VIS spectrum? Explain the reason. (3 %) (b) In enzyme mechanism, why "induced fit" is more accurate than "key and lock" hypothesis. Explain according to the concept that enzyme-substrate complex favors formation of transition state ($EX^{\ddagger}$). (4 %)

ELECTROMAGNETIC SPECTRUM

High energy　　　Light　　Microwaves　Radiowaves　Low energy
γ rays　x rays　　uv vis ir　　　esr　　nmr

10^{-12}　10^{-10}　10^{-8}　10^{-6}　10^{-4}　10^{-2}　1　10^2　10^4
Wavelength (m) on a logarithmic scale

VISIBLE SPECTRUM
Ultraviolet Violet Blue Green Yellow Orange Red　　Infrared

400　　　500　　　600　　　700　　　800
Wavelength (nm) on a linear scale
1 nm = 10^{-9} m = 10^{-7} cm

2. (a) Describe Micaelis-Menten equation. Please make plots of (i) regular substrate saturation curve; (ii) Lineweaver-Burk and (iii) Hanes-Woolf plots, and label the critical parameters, such as V_{max}, K_M, x- and y-intercepts and slope in the plots. (9 %) (b) There is a example that the following data represents on the rate of formation of product (d[P]/dt). Plot these data according to the Lineweaver-Burk plot and determine values of K_M and V_{max}. (9 %)

Substrate concentration (mM)	2.5	5.0	10.0	15.0	20.0
Rate, d[P]/dt (mM·S^{-1})	0.024	0.036	0.053	0.060	0.064

3. A protein binds to a target ligand by the equation.

[Protein] + [ligand] → [complex]
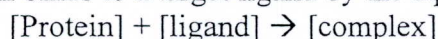
For understanding the binding behavior in solution, we measured the extinction coefficients of individual components at 280 nm: ε(protein) = 25000 M^{-1} cm^{-1}; ε(ligand) = 1000 M^{-1} cm^{-1}; ε(complex) = 30000 M^{-1} cm^{-1}. A solution contained 10 μM total protein and we titrated 5-fold molar excess of ligand into the solution. It shows an absorbance of OD_{280} = 0.324 in a 1-cm cell. If we ignore the volume change from titration, please answer the following questions by employing Beer's law, A = εcL, where ε is extinction coefficient, c is concentration and L is optical path length.
(a) The individual concentrations of complex, free protein and free ligand. (6%)
(b) The dissociation constant K_d (with unit μM). (4%)

4. Use the free energy of hydrolysis of ATP under standard conditions at 25℃, 1 atm, to answer the following questions (take R as 8.314 J/mol K). (15%)
   (a) Calculate the $\triangle G$ for the reaction when [ATP]=$10^{-2}M$, [ADP]=$10^{-4}M$, and [phosphate]=$10^{-1}M$.
   (b) Calculate the maximum available work under the conditions of part (a) when 1 mol of ATP is hydrolyzed. This work can be used, for example, to contract muscle and raise a weight.
   (c) Calculate $\triangle G$ and the maximum available work if [ATP]=$10^{-7}M$, [ADP]=$10^{-1}M$, and [phosphate] =2.5 x $10^{-1}M$.

5. When cells of the skeletal vacuole of a frog were placed in a series of aqueous NaCl solutions of different concentrations at 25℃, it was observed microscopically that the cells remained unchanged in 0.7 wt% NaCl solution, shrank in more concentrated solutions, and swelled in more dilute solutions. Water freezes from the 0.7% salt solution at -0.406℃ (take R as 82.05 ml atm deg^{-1} mol^{-1}, K_{freeze} for water as 1.86, and molar volume of water as 18). (10%)
(a) What is the osmotic pressure of the cell cytoplasm relative to that of pure water at 25℃?
(b) Suppose that sucrose (mol wt 342) was used instead of NaCl (mol wt 58.5) to make the isoosmotic solution. Estimate the concentration (wt%) of sucrose that would be sufficient to balance the osmotic pressure of the cytoplasm of the cell. Assume that sucrose solutions behave ideally.

6. Magnesium ion and other divalent ions form complexes with adenosine triphosphate, ATP. (10%)

ATP + Mg^{2+} → complex
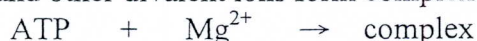
(a) Describe an electrochemical cell that would allow you to measure the activity of Mg^{2+} at any concentration in a 0.100 M ATP solution.
(b) Describe how you could measure the thermodynamic equilibrium constant for binding Mg^{2+} by ATP with an electrochemical cell.