國　立　清　華　大　學　命　題　紙

95 學年度_生命科學院、生命科學院醫學生物科技學程_系（所）_乙、丙_組碩士班入學考試

科目___物理化學__科目代碼__0903、1003、1107__共___6_頁第_1_頁 *請在【答案卷卡】內作答

Gas constant R= 8.31 J/K mol, Boltzmann constant k=1.38x10^{-23} J/K, Planck's constant h=6.62 x10^{-34} J s
ln2=0.693, ln10=2.3 .

Part I. Select the best answer from each question. If there is no suitable answer, choose "(E) None of the above".

1. Which of the following statements is FALSE? (3 points)
   (A) Kinetics tells us when and how fast a reaction can occur.
   (B) Thermodynamics tells us whether a reaction can occur.
   (C) All reactions rates increase with increasing temperature and concentration.
   (D) Many reaction mechanisms can be proposed to be consistent with a given set of experimental observed rates.
   (E) None of the above.

2. Which of the following statements about transition state is FALSE? (3 points)
   (A) The transition state corresponds to an energy minimum between two stable species (reactant and product) along the reaction pathway.
   (B) The transition state energy is the energy difference between the transition state and reactants.
   (C) The magnitude of the transition state energy characterizes the temperature dependence of the rate of the reaction.
   (D) The transition state is an unstable state that exists only for the time of a molecular vibration.
   (E) None of the above.

3. The rate for the reaction catalyzed by liver enzyme that converts C2H5OH into CH3CHO is observed to be constant. The kinetic order of the reaction is (3 points)
   (A) 1/2
   (B) 0
   (C) 1
   (D) 2
   (E) None of the above.

4. Which of the following is FALSE? (3 points)
   (A) An enzyme can increase the rate of a biological reaction by many orders of magnitude, and its structure changed at the end of the reaction.
   (B) Most enzymes are proteins.
   (C) Some RNA molecules can act as enzymes.
   (D) Antibodies can be catalytic if they are made to stabilize the transition state and reduce the activation energy of a reaction.
   (E) None of the above.

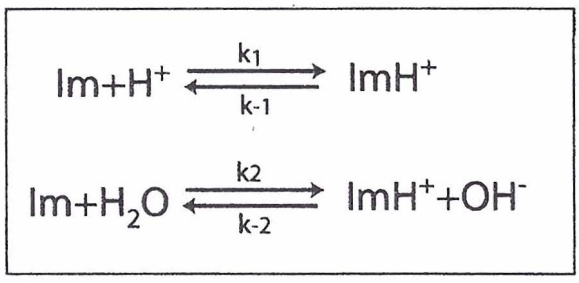
5. Consider an elementary particle in a one-dimensional box described by quantum mechanics. Which of the following is FALSE? (3 points)
   (A) The energy gap between two adjacent energy levels decreases as the dimension of the box increases.
   (B) The energy gap between two adjacent energy levels decreases as the mass of the particle increases.
   (C) The energy gap between two adjacent energy levels decreases as the quantum number increases.
   (D) The probability of finding the particle in the central half (between x=a/4 and x=3a/4, where "a" is the dimension of the box) is independent of the dimension of the box.
   (E) None of the above

6. Which of the following statement is FALSE? (3 points)
   (A) Infrared absorption is associated with molecular vibration.
   (B) Radio frequency radiation is associated with the spin transition in the nuclear magnetic resonance.
   (C) Fluorescence is associated with electron spin transition under magnetic field..
   (D) UV/Vis radiation is associated with electron transition.
   (E) None of the above.

7. Which of the following statement about IR (Infrared) and Raman spectroscopy is FALSE? (3 points)
   (A) O_2 is IR inactive.
   (B) CO_2 is IR active
   (C) CO_2 is Raman active
   (D) For a molecule to be Raman active, it must possess permanent dipole moment.
   (E) None of the above.

Part II.

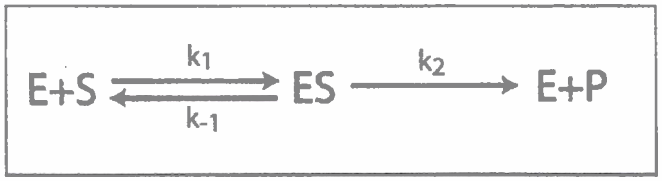
1. Imidazole (Im) can react with H^+ or H2O to form positively charged imidazole (ImH^+). The reaction mechanisms are



The rate constants in aqueous solution are: $k_1=1.5\times10^{10}M^{-1}s^{-1}$; $k_{-1}=1.5\times10^{3}s^{-1}$; $k_2=2.5\times10^{3}s^{-1}$; $k_{-2}=2.5\times10^{10}M^{-1}s^{-1}$.

(a) What is the value of the equilibrium constant for the ionization of imidazole ($ImH^+ \Longleftrightarrow Im + H^+$)? (2 points)
(b) Write the differential equation for the net rate of formation of ImH^+. (2 points)
(c) If the pH is suddenly changed for a solution of 0.1 M imidazole in water from pH7 to pH4, what is the rate-determining step for the appearance of ImH^+ at pH4? (2 points)
(d) What is the value of the initial rate of increase of ImH^+ at pH4? (2 points)
(e) The rate constant k_1 and k_{-1} both depend on temperature. Would you expect them to decrease or increase with increasing temperature? Which would you expect to change most with temperature and why? (2 points)
(f) Predict the sign of the heat of ionization for imidazole based on your answer to part (e). (2 points)

2. Consider the simple Michaelis-Menten mechanism for an enzyme-catalyzed reaction:



The following data were obtained:
k_1, k_{-1} very fast
k_2=100 s^{-1}, K_M=1.0x10^{-4} M at 280K
k_2=200 s^{-1}, K_M=1.5x10^{-4} M at 300K
(a) for [S]=0.10 M and $[E]_0$=1.0x10^{-5}M, calculate the rate of formation of product at 280 K. (3 points)
(b) Calculate the activation energy for k_2. (3 points)
(c) What is the value of the equilibrium constant at 280 K for the formation of the enzyme-substrate complex ES from E and S? (3 points)
(d) What is the sign and magnitude of the standard thermodynamic enthalpy ΔH^0 for the formation of ES from E and S? (3 points)

3. The fluorescence lifetime of benzene in cyclohexane is 29 ns when air is completely removed. In the presence of 0.0072 M dissolved O_2, the measured fluorescence lifetime is 5.7 ns because of quenching. Calculate the rate constant k_Q for the quenching reaction (3 points). If the relative fluorescence intensity is 100 for pure benzene, what is the relative fluorescence intensity of benzene containing 0.0072 M dissolved O_2? (2 points)

Part III.

Select the one choice that best completes the statement or answer that question. (20 points/2 points each)

1. 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

2. 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

3. 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

4. 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)	-80	+10
(E)	0	-10

5. 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°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

6. If nitrogen gas trapped in a cylinder with a movable position undergoes an adiabatic expansion, which of the following statements is true for the expansion/

(A) $q = w$
(B) $w = 2q$
(C) $\Delta U=0$
(D) $\Delta U=w$
(E) $\Delta U=q$

7. Living systems are:

(A) closed systems exchanging only energy with the surroundings.
(B) isolated systems that are totally contained.
(C) open systems exchanging only energy with the surroundings.
(D) open systems exchanging both energy and matter with their surroundings.
(E) none of the above.

8. Which equation defines a system at equilibrium?

(A) $\Delta G > 0$
(B) $\Delta G^\circ = \Delta G$
(C) $\Delta G = 0$
(D) $\Delta G^\circ = 0$
(E) $\Delta G = RT \ln ([\text{products}]/[\text{reactants}])$

9. To predict whether pairs of coupled reactions will proceed spontaneously:

(A) Subtract the smaller from the larger ΔG.
(B) Sum the $\Delta G^{o\prime}$s for each reaction.
(C) Add the ΔS values for each reaction at constant temperature.
(D) The absolute value of the positive $\Delta G^{o\prime}$ must be larger than the value of the negative $\Delta G^{o\prime}$.
(E) None are true.

10. 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

Part IV.

1. (20%)

The Na^+-K^+ pump uses the free energy of hydrolysis of ATP to pump Na^+ ions out of the cell and K^+ ions into the cell at 300°K. The chemical potential $\Delta\mu°$ is -40 KJ for ATP hydrolyses at 300°K; the ratio of ATP to ADP in cells is 100. There is also a voltage difference of –100mV across the membrane. The inside membrane is negative relative to the outside membrane. The $[Na^+]_{in}$= 10mM, $[Na^+]_{out}$= 100mM, $[K^+]_{in}$=100mM, $[K^+]_{out}$= 1mM. (ln10= 2.3, R= 8.314 J/K mol, Faraday constant= 96.485 KJ/mol)

(a) What is the free energy to transport 3 mol Na^+ out the membrane?
(b) What is the free energy to transport 2 mol K^+ into the membrane?
(c) What is the total free energy cost of transporting 3 mol Na^+ ions out the membrane and 2 mol of K^+ ions into the membrane in Na^+-K^+ pump?
(d) What is the free energy for the hydrolysis of ATP (ATP → ADP + P)?
(e) Weather this active transport reaction Na^+-K^+ pump can occur using the free energy of hydrolysis of ATP?

2. (10%)

In general, native proteins are in equilibrium with denatured forms:

Protein(native) → Protein(denatured)

For ribonuclease, the following concentration data for the two forms were experimentally determined for a total protein concentration of 1x 10^{-3}. Determine ΔH for the reaction, assuming it to be independent for the temperature.

Temperature (℃)	Native	Denatured
27	9.97×10^{-4} mol L^{-1}	2.5×10^{-6} mol L^{-1}
127	8×10^{-4} mol L^{-1}	2×10^{-4} mol L^{-1}