國立中山大學100學年度碩士班招生考試試題

科目：物理化學及分析化學【化學系碩士班】

Physical Chemistry (50 points)

Single choice, 2 points for each question

1. For a ground state free particle in one-dimensional box $(0 \le x \le a)$ the expectation value of the physical quantity p^4 is
    a. $8h^4/a^4$ b. $h^4/16a^4$ c. $h^2/2a^4$ d. 0
    e. none is correct

2. Convert the energy $E = 1.5$ erg into wave number (cm^{-1})
    a. 3.88×10^{26} b. 5.0348×10^{22} c. 4.32×10^5
    d. 7.5522×10^{15} e. none is correct

3. Which of the following statements is correct?
    a. The electron spin has no angular momentum
    b. One can measure all three components of angular momentum simultaneously.
    c. Quantum mechanical expression of angular momentum operator has only angular dependence. .
    d. Electrons at same atomic orbital have identical angular momentum.
    e. All answers are correct.

4. The ground state wave function of hydrogen atom is $\psi = \dfrac{1}{\pi^{1/2}}\left(\dfrac{1}{a}\right)^{3/2} e^{-r/a}$,

    where a is Bohr radius. According to this wave function, the average distance of r for hydrogen atom is
    a. a b. $3a/2$ c. $a/2$ d. $2a$
    e. none is correct

5. Which of the following statements about harmonic oscillator is true?
    a. The vibration of a diatomic molecule is exact harmonic oscillation.
    b. The average kinetic energy is equal to the average of potential energy.
    c. The frequency of harmonic oscillation depends on the equilibrium position.
    d. The ground state energy, $E_0 = h\nu/2$, can be measured experimentally.
    e. None is correct

6. The microwave spectrum of HCl consists of a series of lines with approximately equally spaced. The lines are separated by 6.26×10^{11} Hz. The microwave spectrum of DCl should display lines separated by .

a. 3.13×10^{11} Hz b. 3.22×10^{11} Hz c. 4.27×10^{11} Hz

d. 4.56×10^{11} Hz e. none is correct

7. Which of the following statement is correct?

   a. Hamiltonian operator commutes with all operators.

   b. Quantum mechanical operators are always commute.

   c. For two commute operators $\hat{A}$ and $\hat{B}$, one can always measure their corresponding physical properties simultaneously.

   d. $\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} = \hat{A}\left[\hat{B}, \hat{C}\right]$

   e. None is correct

8. Evaluate $\left[\hat{x}, \hat{p}_x^2\right] =$

   a. $i\hbar$ b. $-i\hbar\dfrac{\partial^2}{\partial x^2}$ c. 0 d. $2\hbar^2\dfrac{\partial}{\partial x}$

   e. none is correct

9. The fundamental of HBr is around 2640 cm^{-1}, then the fundamental of DBr should be around

   a. 1892 cm^{-1} b. 1320 cm^{-1} c. 1867 cm^{-1} d. 3683 cm^{-1}

   e. None is correct.

10. In aqueous ionic solution, the rate constant is

    a. has no relation to ionic strength

    b. proportional to the square root of ionic strength

    c. proportional to the inverse of ionic strength

    d. proportional to the square of ionic strength

    e. proportional to ionic strength

11. For a system with the two competing elementary reactions

$$A \xrightarrow{k_1} C \quad \text{and} \quad A \xrightarrow{k_2} D$$
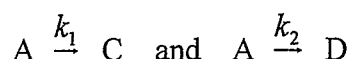
In which E_1 and E_2 are the activation energies correspond to k_1 and k_2 respectively. Then the observed activation energy E_a of the system is

a. $E_a = \ln(k_1 e^{-E_1/RT} + k_2 e^{-E_2/RT})$ b. $E_a = E_1 + E_2$

c. $E_a = (k_1 e^{-E_1/RT} + k_2 e^{-E_2/RT})/(k_1 + k_2)$ d. $E_a = (k_1 E_1 + k_2 E_2)/(k_1 + k_2)$

e. none is correct

12. The reaction between X and Y is second order. If Y is in large excess than X, the following data were obtained:

T(K)	[Y] (mol/dm^3)	rate constant (s^{-1})
300	2.5×10^{-6}	5.0×10^{-4}
500	1.0×10^{-6}	7.5×10^{-3}

According to Arrehnius law, the pre-exponential factor for this reaction is

a. 7.5×10^6 b. 4.42×10^6 c. 3.18×10^6 d. 5.74×10^6

e. None is correct

13. In usual condition, which is the correct order of molecular energies?
(E_{elec}: electronic energy, E_{trans}: translational energy, E_{vib}: vibrational energy, E_{rot}: rotational energy)

a. $E_{elec} > E_{trans} > E_{rot} > E_{vib}$ b. $E_{elec} > E_{vib} > E_{rot} > E_{trans}$

c. $E_{vib} > E_{elec} > E_{rot} > E_{trans}$ d. $E_{trans} > E_{vib} > E_{rot} > E_{elec}$

e. none is true

14. The following data relate to an enzyme reaction

10^3 [S] /mol dm^{-3}	10^5 V /mol dm^{-3} s^{-1}
2.0	13
4.0	20
8.0	29
12.0	33
16.0	36
20.0	38

Base on the data, the Michaelis constant is approximately

a. 8.0×10^{-3} mod dm^{-3} b. 4.0×10^{-3} mod dm^{-3} c. 9.5×10^{-3} mod dm^{-3}

d. 10.0×10^{-3} mod dm^{-3} e. None is true

15. Which of the following relation is correct?

a. $\left[\dfrac{\partial}{\partial T} \left(\dfrac{\Delta G^0}{T} \right) \right]_P = -\dfrac{\Delta H^0}{T^2}$ b. $\left[\dfrac{\partial}{\partial T} \left(\dfrac{\Delta H^0}{T} \right) \right]_P = -\dfrac{\Delta G^0}{T^2}$

c. $\left[\dfrac{\partial}{\partial T} \left(\dfrac{\Delta G^0}{T} \right) \right]_P = -\dfrac{\Delta H^0}{T}$ d. $\left[\dfrac{\partial}{\partial T} \left(\dfrac{\Delta H^0}{T} \right) \right]_P = \dfrac{\Delta S^0}{T^2}$

e. all answers are wrong

16. Which of the following diagram gives correct behavior of G vs. T for a single component system?

a   **b**   **c**   **d**
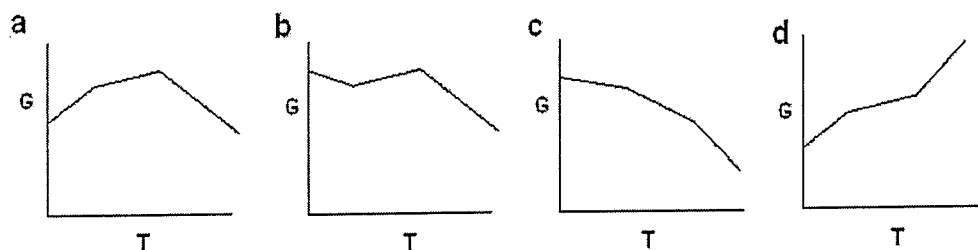
e. none is correct

17. If 3.0 mole of argon is expanded reversibly and isothermally from a volume of 500.0 dm^3 to a volume of 2500.0 dm^3 at 298.15 K, what is the entropy change of the system?
    a. 13.38 J K^{-1} b. 40.14 J K^{-1} c. 31.32 J K^{-1} d. Zero
    e. All answers are wrong

18. For an ideal gas, a typical Carnot cycle undergoes four reversible steps: I. isothermal expansion at T_h from V_1 to V_2, II. adiabatic expansion from T_h to T_c and volume from V_2 to V_3, III. Isothermal compression from V_3 to V_4, IV. adiabatic compression from V_4 to V_1.
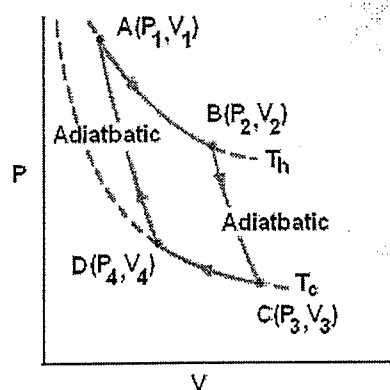
The enthalpy change of step II is
    a. Zero   b. $C_P(T_c - T_h)$ c. $C_V(T_c - T_h)$ d. $C_P ln(V_3 / V_2)$
    e. All answers are wrong

19. Which of the following is the correct expression of thermodynamic equation of state?
    a. $\left(\dfrac{\partial U}{\partial P}\right)_V = -P + T\left(\dfrac{\partial T}{\partial P}\right)_P$ b. $\left(\dfrac{\partial U}{\partial P}\right)_T = -P + T\left(\dfrac{\partial P}{\partial T}\right)_P$

c. $\left(\dfrac{\partial U}{\partial V}\right)_T = -P + T\left(\dfrac{\partial V}{\partial T}\right)_P$ d. $\left(\dfrac{\partial U}{\partial V}\right)_T = -P + T\left(\dfrac{\partial P}{\partial T}\right)_V$

e. All answers are wrong

20. The heat of fusion of water is 333 J/g. The entropy change for melting of 10 g of ice is

     a.   12.2 J K^{-1} b. 23.6 J K^{-1} c. 8.7 J K^{-1} d. 10.4 J K^{-1}

     e.   none is correct

21. Which is the correct conclusion of Joule-Thompson experiment?

     a.   Internal energy of ideal gas is zero.

     b.   The Joule-Thompson coefficient is always greater than zero.

     c.   The adiabatic expansion has no enthalpy change.

     d.   A gas has positive Joule-Thompson coefficient will heat during a Joule-Thompson expansion.

     e.   None is correct.

22. The molar heat capacity (JK^{-1}mol^{-1}) at constant pressure of Al$_2$O$_3$ is

$Cp = a + bT + (c/T^2)$

Where $a = 114.8$, $b = 12.8 \times 10^{-3}$ and $c = -35.4 \times 10^5$.

The enthalpy change for heating one mole Al$_2$O$_3$ from 300 K to 500 K is

     a.   19.56 kJ   b.   19.26 kJ   c. 11.28 kJ   d. 35.6 kJ

     e.   none is correct

23. When acetaldehyde decomposed thermally the main products are methane and carbon monoxide. The experimental evidence has shown that the reaction occurs by the mechanism

     1. $CH_3CHO \xrightarrow{k_1} CH_3 + CHO$

     2. $CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$

     3. $CH_3CO \xrightarrow{k_3} CH_3 + CO$

     4. $CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$

Using steady state approximation, the rate of change of the concentration of acetaldehyde is

a. $v = k_2\left(\dfrac{k_1}{k_4}\right)[CH_3CHO]^{1/2}$ b. $v = k_1\left(\dfrac{k_2}{k_4}\right)[CH_3CHO]^{1/2}$

c. $v = k_2\left(\dfrac{k_1}{k_4}\right)^{1/2}[CH_3CHO]^{3/2}$ d. $v = k_4\left(\dfrac{k_2}{k_4}\right)[CH_3CHO]^{1/2}$

e. none is correct

24. A mole of gas at P_1, V_1, T_1 is expanded isothermally to the condition $P_1/2$, $2V_1$, T_1. The collision number after expansion is

     a. 1/2 as large as before expansion   b. $\sqrt{2}$ as large as before expansion

     c. 1/4 as large as before expansion   d. $1/\sqrt{2}$ as large as before expansion

     e. none is correct

25. The Maxwell distribution function of gaseous molecule is

$$F(v) = \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\cdot 4\pi v^2$$

The average velocity is

     a. $\sqrt{\dfrac{2kT}{\pi m}}$ b. $\sqrt{\dfrac{3kT}{\pi m}}$ c. $\sqrt{\dfrac{8kT}{\pi m}}$ d. $\sqrt{\dfrac{kT}{\pi m}}$

     e. none is correct

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Gas constant: $R = 8.314$ J K^{-1} mol^{-1} = 82.057 cm^3 atm mol^{-1} = 1.987 cal K^{-1} mol^{-1}

1 cal = 4.184 Joule = 41.29 cm^3 atm

	Nm^{-2}	atm	torr	bar
1 pa =	1	9.869×10^{-6}	7.501×10^{-3}	10^{-5}
1 atm =	101325	1	760	1.01325
1 torr =	133.32	1.316×10^{-3}	1	1.3332×10^{-3}
1 bar =	10^5	0.9869	750.1	1

1 bar = 10^5 pa

Planck constant $h = 6.626\times10^{-34}$ J s

$$\int_0^\infty x^n e^{-qx}dx = \frac{n!}{q^{n+1}} \qquad n > -1, \quad q > 0$$

Analytical Chemistry (50 points)

Note: Always use the correct significant figures in your calculation.

26. Define and distinguish between the following;

    (a) t-test and F-test

    (b) standard addition method and internal standard method

    (c) fluorescence and phosphorescence

    (d) Quadrupole ion-trap mass spectrometer and Fourier transform ion cyclotron resonance mass spectrometer (4% each, 16% total)

27. Use van Deemter equation to describe peak broadening in capillary electrophoresis, high-performance liquid chromatography, and gas chromatography. (8%)

28. A typical ICP-MS system has a mass range of 250 amu, whereas a typical GC-MS system has a mass range of 1000 amu. Explain this difference. (4%)

29. Consider the diprotic acid H_2A with $pK_1 = 5.00$ and $pK_2 = 9.00$. Find the pH and concentrations of H_2A, HA^-, and A^{2-} in the 0.100 M NaHA. (4%)

30. Use activities to calculate the solubility of $Ba(IO_3)_2$ in a 0.1 M solution of NaCl. The thermodynamic solubility product for $Ba(IO_3)_2$ is 1.57×10^{-9}. (4%)

Ionic strength (M)	Activity coefficient of Ba^{2+}	Activity coefficient of IO_3^-
0.001	0.869	0.965
0.005	0.743	0.926
0.01	0.668	0.900
0.05	0.46	0.81
0.1	0.38	0.76

31. Describe the operating principle of a pH glass-electrode. (4%)

32. What information can be obtained from the following analytical methods?
    (a) XPS, (b) FTIR, (c) NMR, (d) MALDI-TOF-MS, (e) cyclic voltammetry. (10%)