八十五學年度材料科學工程研究所(系)(所) 甲三 組碩士班研究生入學考試

科目 物理化學(II) 科號 2102 2107 共 8 頁第 1 頁 *請在試卷【答案卷】內作答

I.

1. (5%) For a free particle moving between 0 and a in a one-dimension box, find its Hamiltonian, wave function for energy level n = 1 and 2, and energy for n = 1 and 3 in the following choices :

(a) $k \sin(\pi x/a)$, (b) $h^2/8ma^2$, (c) $-\frac{h^2}{2m}\frac{d^2}{dx^2}$, (d) $\frac{-h^2}{2m}\frac{d^2}{dx^2}$, (e) $3h^2/8ma^2$,

(f) $(\frac{2}{a})^{\frac{1}{2}}\sin(2\pi x/a)$, (g) $3h^2/8ma$, (h) $(\frac{2}{a})^{\frac{1}{2}}\sin(3\pi x/a)$, (i) $\frac{-h^2}{2\pi m}\nabla^2$,

(j) $(\frac{2}{a})^{\frac{1}{2}}\sin(\pi x/a)$

2. (6%) For a free particle moving in a one-dimension box, show that (a) the mean value of x is $\bar{x}$=a/2, (b) the mean square deviation is $\overline{(x-\bar{x})^2} = (a^2/12)\left[1-(6/\pi^2 n^2)\right]$, where a is the length of the box and (c) as n becomes very large, this value agrees with the classical one

$$\overline{(x-\bar{x})^2} = a^2/12$$

(*Hint*: $\int_0^{n\pi} y^2 \sin^2 y dy = \frac{n^3\pi^3}{6} - \frac{n\pi}{4}$, $\int_0^{n\pi} y \sin^2 y dy = \frac{(n\pi)^2}{4}$)

3. (2%) Choose the Heisenberg Uncertainty Principle as (a) $\Delta E \cdot \Delta x \geq \hbar$, (b) $\Delta p \cdot \Delta x \geq h/2\pi$, (c) $\Delta p \cdot \Delta x \geq \hbar/2$, (d) $\Delta E \cdot \Delta t \geq h/4\pi$.

4. (6%) (A) Apply the Heisenberg Uncertainty Principle to estimate the kinetic energy of the electron in a hydrogen atom at a distance r from the nucleus as

(a) $E_k = \frac{4\hbar^2}{32\pi^2 m_e r^2}$, (b) $E_k = \frac{h^2}{16\pi^2 m_e r^2}$, (c) $E_k = \frac{h}{8\pi^2 m_e r^2}$.

(B) Calculate the equilibrium distance r_e by minimizing the total energy E (kinetic - potential) with respect to r to be equal to (a) $r_e = h/4\pi^2 m_e e^2$, (b) $r_e = h^2/4\pi^2 m_e e^2$, (c) $r_e = h^2/8\pi^2 m_e e^2$

5. (4%) The eigenvalues for the rigid rotator are $E_J = J(J+1)\hbar^2/2I$ where $I = \mu R^2$

(a) What is the degeneracy of each level?

(b) Prepare a plot of the energy levels expressed in units of $\hbar^2/2I$.

6. (6%) By means of vector diagrams, find the term symbols that can arise from one p and one d electron.

7. (4%) Write electronic configurations for C_2. Which configuration predicts a paramagnetic molecule? If the term for the ground state is $^1\sum_x^+$, which configuration is correct?

8. (3%) Consider an LC electric circuit consisting of a capacitance C in series with a coil of self-inductance L and zero resistance. If Q is the charge of the capacitor, the relation among Q, C and L is $-L\frac{d^2Q}{dt^2}=\frac{Q}{C}$

(a) Calculate Q(i) function

(b) Show that the natural frequency of the circuit is $\omega=(1/LC)^{\frac{1}{2}}$

(c) In the problem of the harmonic oscillator with mass=m, force constant=k, and displacement=x, find the correspondent parameters analogous to the L,Q, and C of the electric problem?

9. (3%) Consider the particle in the one-dimensional well inside which the potential energy is given by $u(x)=c\cdot\frac{x}{a}$ where a is the length of the well, c is the constant and x is any point between 0 and a. What is the first-order estimate of the energy of this system using perturbation theory? (Hint: $\int_0^{n\pi} y\sin^2 y dy=(n\pi)^2/4$)

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10. (5%) Determine the number of molecules in each energy level of the following system if 10^{12} molecules are present at 100K.

$g_4 = 2 \qquad E_4 = 13\times10^{-21}\,J,molecule^{-1}$

$g_3 = 1 \qquad E_3 = 10\times10^{-21}\,J,molecule^{-1}$

$g_2 = 4 \qquad E_2 = 7\times10^{-21}\,J,molecule^{-1}$

$g_1 = 2 \qquad E_1 = 4\times10^{-21}\,J,molecule^{-1}$

$g_0 = 1 \qquad E_0 = 1\times10^{-21}\,J,molecule^{-1}$

Where g_n is the degeneracy, E_n is the corresponding energy level. (Hint: $k=1.38\times10^{-23}JK^{-1}molecule^{-1}$)

11. (4%) (A) Given the probability that the molecule has diffused to a region between x and x+dx as

$P(x)dx = \frac{1}{2(\pi Dt)^{1/2}}\exp(\frac{-x^2}{4Dt})dx$. Choose the mean square distance of diffusion, $\overline{x^2} = (a)4Dt,\ (b)4(Dt)^{3/2},\ (c)2\pi Dt,\ (d)2Dt,\ (e)4\pi\left(\frac{Dt}{2\pi}\right)$.

(Hint: $\int_{-\infty}^{\infty} x^2 e^{-ax^2}dx = \frac{1}{2a}\cdot(\pi/a)^{1/2}$)

(B) What is the relationship among diffusion constant D, average velocity $\bar{c}$ and mean free path λ :

(a) $D = \frac{1}{3}\bar{c}\lambda,\ (b)D = \frac{1}{2}\bar{c}\lambda,\ (c)D = \frac{2}{3}\bar{c}\lambda,\ (d)D = \bar{c}\lambda$.

12. (2%) For each statement in the following, select the correct formula from the lists below:
(A) The number of ways of grouping N distinguishable objects into r groups such that N_i are in group i
(B) The number of ways of putting N distinguishable objects into g locations with no restrictions

(a) $\frac{(N+g-1)!}{N!(g-1)!}$ (b) g^N (c) $\frac{g!}{(g-N)!N!}$, (d) $\frac{N!}{\prod_{i=1}^{r} N_i!}$, (e) $\frac{N!}{(N-r)!r!}$

II. Mono-choice questions (38 %)

1. Potassium metal crystallizes in the body-centered cubic structure. The number of nearest-neighbor atoms for each potassium atom in the solid is
(a) 4 (b) 6 (c) 8 (d) 10 (e) 12

2. If the radius of a metal atom is 2.0 Å and its crystal structure is cubic close-packed (face-centered cubic lattice), what is the volume, in cubic centimeters, of one unit cell?
(a) 8.00×10^{-24} (b) 1.60×10^{-23} (c) 2.26×10^{-23} (d) 3.20×10^{-23} (e) 1.81×10^{-22}

3. For which of the following ionic crystalline solids does the cation–anion bond have the largest amount of covalent character?
(a) CdS (b) NaBr (c) SrS (d) BaO (e) LiF

4. In an experiment to study the reaction A + 2B → C + 2D, the initial rate, $-d[A]/dt$ at $t = 0$, was found to be $2.6 \times 10^{-2}\ M \cdot s^{-1}$. What is the value of $-d[B]/dt$ at $t = 0$ in $M \cdot s^{-1}$?
(a) 2.6×10^{-2} (b) 5.2×10^{-2} (c) 1.3×10^{-2} (d) 1.0×10^{-1} (e) 6.5×10^{-3}

5. The reaction A(g) + 2B(g) → C(g) + D(g) is an elementary process. In an experiment, the initial partial pressures of A and B are $P_A = 0.60$ atm and $P_B = 0.80$ atm. When $P_C = 0.20$ atm, the rate of the reaction, relative to the initial rate, is
(a) $\frac{1}{48}$ (b) $\frac{1}{24}$ (c) $\frac{8}{15}$ (d) $\frac{1}{3}$ (e) $\frac{1}{8}$

6. For the reaction between chlorine and nitric oxide,

$$Cl_2(g) + 2NO(g) \rightarrow 2NOCl(g)$$

it is found that doubling the concentration of both reactants increases the rate by a factor of 8. If only the concentration of Cl_2 is doubled, the rate increases by a factor of 2. The order of this reaction with respect to NO is

(a) 0 (b) 1 (c) 2 (d) 3 (e) $\frac{1}{2}$

The Following Information Is for Use in Questions 7–9

In an "iodine-clock" experiment, the time, t, it takes for the blue color of the starch–iodine complex to appear is a measure of the initial rate of formation of I_3^-. The rate of the reaction

$$3I^- + S_2O_8^{2-} \rightarrow I_3^- + 2SO_4^{2-}$$

was studied using the iodine-clock technique, and the following data were obtained:

Run Number	$[I]_0$ *(M)*	$[S_2O_8^{2-}]_0$ *(M)*	*t (s)*
1	0.0800	0.0400	44.0
2	0.0800	0.0800	22.1
3	0.1600	0.0200	43.9
4	0.0400	0.0400	88.0

7. The order of this reaction with respect to $S_2O_8^{2-}$ is

(a) 0 (b) $\frac{1}{2}$ (c) 1 (d) 2 (e) 3

8. The overall order of this reaction is

(a) 0 (b) $\frac{1}{2}$ (c) 1 (d) 2 (e) 3

9. If a run is made with $[I]_0 = 0.120\ M$ and $[S_2O_8^{2-}]_0 = 0.0400\ M$, you would expect to see the blue color appear in approximately

(a) 29 s (b) 33 s (c) 44 s (d) 66 s (e) 88 s

10. For a hypothetical reaction $A + 2B \rightarrow 3C + D$, $d[C]/dt$ is equal to

(a) $-d[A]/dt$ (b) $-d[B]/dt$ (c) $+3d[A]/dt$ (d) $-\frac{1}{2}d[B]/dt$ (e) $+d[A]/dt$

11. An ionic crystalline solid, MX_3, has a cubic unit cell. Which of the following arrangements of the ions is consistent with the stoichiometry of the compound?

(a) M^{3+} ions at the corners, X^- ions at the face centers.
(b) M^{3+} ions at the corners, X^- ions at the body centers.
(c) X^- ions at the corners, M^{3+} ions at the face centers.
(d) X^- ions at the corners, M^{3+} ions at the body centers.
(e) M^{3+} ions at the corners and the body centers, X^- ions at the face centers.

12. For which of the following crystals would you expect the assumption of anion–anion contact to be valid?

(a) CsBr (b) NaF (c) KCl (d) NaI (e) SrO

13. Which of the following statements about metallic elements is FALSE?

(a) These elements form ions larger in size than the neutral atoms.
(b) These elements have relatively low ionization energies.
(c) These elements have few outer shell electrons.
(d) These elements have relatively low electronegativities.
(e) These elements have relatively high densities.

14. Of the five ΔH values needed to calculate a lattice energy using the Born–Haber cycle, the one that is most difficult to measure is
(a) The heat of sublimation of the metal.
(b) The heat of formation of gaseous atoms of the nonmetal.
(c) The ionization energy of the metal.
(d) The electron affinity of the nonmetal.
(e) The standard heat of formation of the crystal.

15. Which of the following statements is TRUE?
(a) Endothermic reactions have higher activation energies than exothermic reactions.
(b) The rate law for a reaction depends on the concentrations of all reactants that appear in the stoichiometric equation.
(c) The rate of a catalyzed reaction is independent of the concentration of the catalyst.
(d) The specific rate constant for a reaction is independent of the concentrations of the reacting species.
(e) In all reaction mechanisms, there is a single rate-determining step.

16. The first-order rate constant for the decomposition of N_2O_5 in CCl_4 solution is 6.2×10^{-4} at 45 °C and 2.1×10^{-3} at 55 °C. What is the value of the activation energy for this reaction in kilojoules per mole?
(a) 46 (b) 1.1×10^2 (c) 2.5×10^3 (d) 2.5×10^4 (e) 1.1×10^5

17. For the reaction $A + 2B \rightarrow 2C$, the rate law for formation of C is
(a) rate $= k[A][B]^2$ (b) rate $= k[A][B]$ (c) rate $= [C]^2/[A][B]^2$
(d) rate $= k[A]^2[B]$ (e) impossible to state from the data given

18. The rate law for the dimerization of NO_2 is $-d[NO_2]/dt = k[NO_2]^2$.
Which of the following changes will change the value of the specific rate constant, k?
(a) Doubling the total pressure on the system.
(b) Doubling the volume of the container in which the reaction is occurring.
(c) Adding more O_2 to the reaction mixture.
(d) Adding more NO_2 to the reaction mixture.
(e) Running the reaction in CCl_4 solution rather than in the gas phase.

19. For a reaction for which the activation energies of the forward and reverse directions are equal in value,
(a) the stoichiometry is the mechanism (b) $\Delta H = 0$ (c) $\Delta S = 0$
(d) the order is 0 (e) there is no catalyst

Ⅲ. For the following reaction:

$$A \xrightarrow{k_0} X \xrightarrow{k_1} \text{Product}$$

where A is reactant; X is intermediate and k_0, k_1 are the first order rate constants for the above reaction. At time $t = 0$, $[A] = [A]_0$ and $[X] = 0$. Prove the following two equations that at time = t,

(1) $[A] = [A]_0 e^{-k_0 t}$ (5%)

(2) $[X] = \frac{k_0}{k_1 - k_0} (e^{-k_0 t} - e^{-k_1 t}) [A]_0$ (7%)