

類組：化學類 科目：物理化學(1004)

※選擇題請在答案卡內作答，非選擇題請在答案卷內作答

1. For one mole of ideal gas, which of the following are correct? (複選題，全對才給分) (5 分) (Gas constant $R = 8.31447 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1}$)

(A) Kinetic energy is $\frac{3}{2}RT$, where T is the absolute temperature.

(B) Heat capacity under constant pressure $C_p = \frac{3}{2}R$

(C) Heat capacity under constant volume $C_v = \frac{5}{2}R$

(D) For an isothermal expansion from (4 atm, 2 L) to (2 atm, 4 L), the change of entropy $\Delta S = R \ln 2$.

(E) The volume at 273 K is 22.4 L.

2. One mole of ideal gas goes through an adiabatic expansion from (4 atm, 2 L) to 2 atm. Which of the following are correct? (複選題，全對才給分) (5 分)

(A) At 2 atm, the volume is larger than 4 L.

(B) At 2 atm, the volume is smaller than 4 L.

(C) During the expansion, there is no heat exchange.

(D) The work is $\frac{3}{2}R\Delta T$

(E) The change of internal energy $\Delta U = \frac{5}{2}R\Delta T$

3. For a particle (mass m) in a one-dimensional box (length = L) in quantum mechanics, the potential energy $V = \infty$ for $x > L$ and $x < 0$, and $V = 0$ for $0 \leq x \leq L$. Which of the following are correct? (複選題，全對才給分) (5 分)

(Planck's constant $h = 6.626 \times 10^{-34} \text{ J s}$)

(A) $E_n = \frac{n^2 h^2}{8mL^2}$, $n = 1, 2, 3, \dots$

(B) There are three nodes at $n = 3$.

(C) Expectation value of momentum $\langle \hat{p}_x \rangle = 0$

(D) Expectation value of momentum squared $\langle \hat{p}_x^2 \rangle = \frac{n^2 h^2}{4L^2}$

(E) Expectation value of position $\langle \hat{x} \rangle = 0.5L$

4. For a quantized harmonic oscillator in quantum mechanics, which of the following are correct? (複選題，全對才給分) (5 分) (Planck's constant $\hbar = 1.054 \times 10^{-34} \text{ J s}$)

(A) $E_v = \hbar\omega(v + \frac{1}{2})$, $v = 0, 1, 2, \dots$, $\omega = \sqrt{\frac{k}{\mu}}$, k : force constant, μ : reduced mass

(B) There are three nodes for $v = 3$.

(C) The potential energy is zero for $v = 0$

(D) Expectation value of momentum $\langle \hat{p}_x \rangle = 0$

(E) The zero-point energy is zero.

注意：背面有試題

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5. The ground state oxygen atom has the electronic configuration: $[He]2s^22p^4$. With respect to the atomic term symbols for this electronic configuration, which of the following are correct? (複選題，全對才給分) (5 分)
- (A) The atomic term symbols includes 3D_2
 (B) The atomic term symbols includes 1D_2
 (C) The atomic term symbols includes 1P_1
 (D) The atomic term symbols includes 1S_0
 (E) The atomic term symbol 3P_2 corresponds to the lowest energy.
6. Water (H_2O) molecule belongs to the C_{2v} point group symmetry. If we define the z-axis coincides with the C_2 rotational axis, while the x-axis is perpendicular to the plane containing the three atoms and the y-axis lies in the plane, which of the following are correct? (複選題，全對才給分) (5 分)

 C_{2v} Point Group Character Table

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	R_y, x, xz
B_2	1	-1	-1	1	R_x, y, yz

- (A) The lone pairs of oxygen have A_1+B_1 symmetry representations
 (B) The σ bonds have A_1+B_2 symmetry representations
 (C) The vibrations have $2A_1+B_2$ symmetry representations
 (D) Electronic transition from molecular orbital a_1 to molecular orbital b_1 is allowed.
 (E) Electronic transition from molecular orbital b_1 to molecular orbital b_2 is allowed.
7. With respect to hydrogen molecule (H_2), which of the following are correct? (複選題，全對才給分) (5 分)
- (A) H_2 can be observed by IR spectroscopy.
 (B) H_2 can be observed by Raman spectroscopy.
 (C) Para- H_2 refers to the paired nuclear spins.
 (D) Ortho- H_2 refers to the parallel nuclear spins.
 (E) The statistical weight between Para- H_2 and Ortho- H_2 for a given J rotational level is 3:1.
8. With respect to the relaxation times (T_1 and T_2) in pulsed NMR spectroscopy, which of the following are correct? (複選題，全對才給分) (5 分)
- (A) T_1 denotes the spin-lattice relaxation and is related to Zeeman energy exchange.
 (B) T_2 denotes the spin-spin relaxation and is not related to Zeeman energy exchange.
 (C) T_1 can be measured by spin echo technique.
 (D) T_2 can be measured by inversion recovery technique.
 (E) $T_1 \leq T_2$

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非選擇題 (60%)

1. Answer the following questions with regard to CO₂.

(a) Carbonated beverages are typically made by using gaseous CO₂. The Henry's law constant K_H for CO₂ in water is 1.6×10^8 Pa at room temperature. If the pressure of CO₂ in equilibrium with water is 4.8×10^5 Pa, estimate the molarity of CO₂ in the solution? (4%)

(b) The slopes of the lines between the solid and liquid phases in the P-T phase diagrams of H₂O and CO₂ are very different. Comment on this based on the Clapeyron equation. (4%)

(c) If CO₂ (1 mole) can be described by $V = \left(\frac{RT}{P}\right) + b - \left(\frac{a}{RT^2}\right)$, find the expression for the Boyle temperature in terms of a , b and R (a and b are constants). (6%). Also write the expression of ΔG for CO₂ that undergoes an isothermal expansion from P_1 to P_2 atm. (5%)

2. Instead of $x = 0$ to a for the particle in the 1-D box, the limits are now set to be

$x = -\frac{a}{2}$ to $+\frac{a}{2}$. The general form of the wavefunction is:

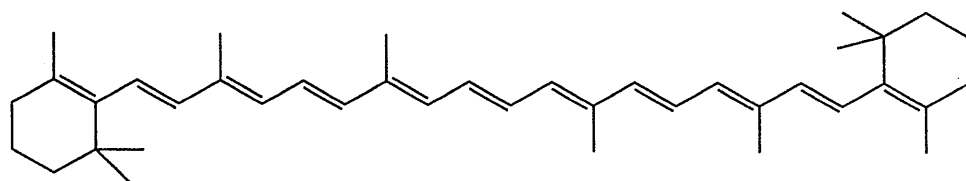
$$\psi = A \sin(Kx) + B \cos(Kx) \quad -\frac{a}{2} \leq x \leq \frac{a}{2} \quad \text{where} \quad K = \frac{\sqrt{2mE}}{\hbar}$$

(a) Derive acceptable wavefunctions with corresponding quantum numbers. (4%)

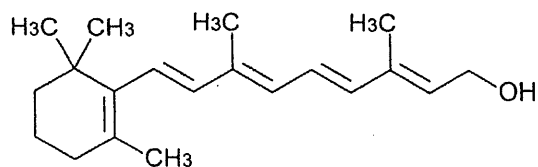
(b) Without calculations, explain why $\int_{-a/2}^{+a/2} \psi_{n+1}^* \psi_n dx = 0$ and $\int_{-a/2}^{+a/2} \psi_{n+1}^* \cdot x \cdot \psi_n dx \neq 0$

based on the results in (a). (4%)

3. β -Carotene plays important roles in the chemistry of human vision because it can be converted into two vitamin A molecules (structures shown below). The electronic spectrum of β -Carotene can be approximated using the particle in a 1-D box if one assumes that the conjugated double bonds consist of the entire system.



β -Carotene



Vitamin A

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(a) If each box level can only have two π electrons and the π electronic transition has a maximum absorption band at 480 nm for β -Carotene, what you expect the absorption wavelength for vitamin A if the molecular length of vitamin A is half of that of β -Carotene? (5%)

(b) The vision process begins when the cis-retinal absorbs a photon and is isomerized to be trans-retinal:

$$h\nu$$

cis-retinal \rightarrow trans-retinal (similar to vitamin A)

The activation energy for the isomerization reaction is 160 kJ/mol and the rate constant at 37 °C is $4 \times 10^{11} \text{ s}^{-1}$. Assuming that an icefish lives in water at -3 °C, what is the rate constant if the same chemical process occurs in icefish eyes. (note: $R = 8.0 \text{ J/mol}\cdot\text{K}$; $e^{-9.56} = 7 \times 10^{-5}$) (5%)

4. Single-walled carbon nanotubes can be approximately by a particle-on-a-cylindrical-surface model. Suppose the cylinder has length l and radius a , with the z -axis along the cylinder. Combining ideas from the particle-in-a-box and 2D rigid rotor models, the Hamiltonian operator for this system is:

$$\hat{H}_{total} = \hat{H}_{box} + \hat{H}_{rotor} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2ma^2} \frac{\partial^2}{\partial \phi^2} \quad (m: \text{mass of electron})$$

(a) Write an expression for the energy. (3%)

(b) The wavefunction of this system can be written as $\psi(z, \phi) = N \cdot R(nz) \cdot Y(m\phi)$, where $R(nz)$ and $Y(m\phi)$ are the wavefunctions obtained from the particle-in-a-box and 2-D rigid rotor, respectively, and N is the normalization constant. Write down the mathematical functions for $R(nz)$ and $Y(m\phi)$. What are the allowed values of the quantum numbers n and m ? (8%) Determine the normalization constant N . (3%)

5. An interesting example of consecutive reaction involves the absorption of ethyl alcohol by the body, which is a first-order process, and the consequent oxidation of alcohol to acetaldehyde by liver alcohol dehydrogenase (LADH), which is a zeroth-order process. The differential changes in the three states of ethanol can therefore be described as

$$-\frac{d[A]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2$$

$$\frac{d[C]}{dt} = k_2$$

(a) Determine an integrated form for [B] over time. (4%)

(b) Derive the expression for the time at which the concentration of the intermediate B reaches the maximum value. ($[A]_0 = 1.0 \text{ mol/L}$). (5%)

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