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 J mol^{-1} K^{-1}= 0.08206 atm L mol^{-1} 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 $0 \le x \le L$. Which of the following are correct? (複選題，全對才給分) (5 分) (Planck's constant $h = 6.626\times10^{-34}$ J s)

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

(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 $\langle\hat{p}_x^2\rangle = \frac{n^2h^2}{4L^2}$

(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 $\hbar = 1.054\times10^{-34}$ J s)

(A) $E_v = \hbar\omega(v+\frac{1}{2})$, v= 0, 1, 2, …, $\omega = \sqrt{\frac{k}{\mu}}$, 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: $[He]2s^2 2p^4$. 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 Otho-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 CO_2.

(a) Carbonated beverages are typically made by using gaseous CO_2. The Henry's law constant K_i for CO_2 in water is 1.6×10^8 Pa at room temperature. If the pressure of CO_2 in equilibrium with water is 4.8×10^5 Pa, estimate the molarity of CO_2 in the solution? (4%)

(b) The slopes of the lines between the solid and liquid phases in the P-T phase diagrams of H_2O and CO_2 are very different. Comment on this based on the Clapeyron equation. (4%)

(c) If CO_2 (1 mole) can be described by $V = (\frac{RT}{P}) + b - (\frac{a}{RT^2})$, 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 CO_2 that undergoes an isothermal expansion from P_1 to P_2 atm. (5%)

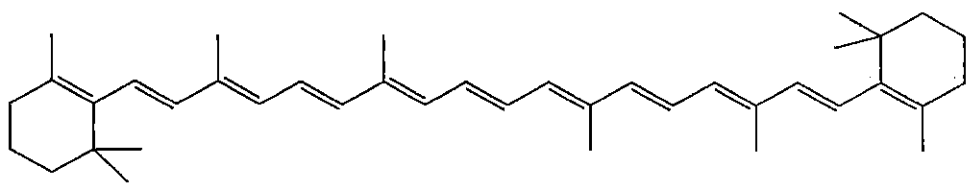
2. Instead of x = 0 to *a* for the particle in the 1-D box, the limits are now set to be $x = -\frac{a}{2}$ to $+\frac{a}{2}$. The general form of the wavefunction is:

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

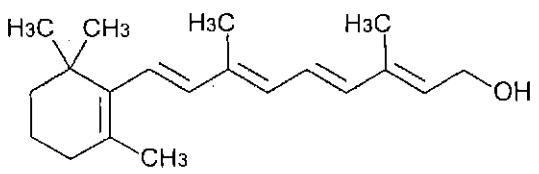
(a) Derive acceptable wavefunctions with corresponding quantum numbers. (4%)

(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:

$$\text{cis- retinal} \xrightarrow{h\nu} \text{trans-retinal (similar to vitamin A)}$$

The activation energy for the isomerization reaction is 160 kJ/mol and the rate constant at 37 °C is 4×10^{11} 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 J/mol·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:

$$\hat{H}_{total} = \hat{H}_{box} + \hat{H}_{rotor} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2ma^2}\frac{\partial^2}{\partial \phi^2}$$ (*m*: 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 mol/L). (5%)

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