Attention: For some calculations, you might need the following physical constants:

h = 6.626 × 10^{-34} J·s (Planck constant); $\hbar = \frac{h}{2\pi}$; c = 3.0 × 10^{8} m/s (speed of light),

m = 9.11× 10^{-31} kg (mass of electron); $\sqrt{5} = 2.24$

一、單選題（一題 4 分，答錯不倒扣） 共80分

01. Define the operators $\hat{a} = \frac{1}{\sqrt{2}}(\hat{x} + i\hat{p}_x)$ and $\hat{a}^{+} = \frac{1}{\sqrt{2}}(\hat{x} - i\hat{p}_x)$, where $\hat{x}$ and $\hat{p}_x$ are the position and momentum operators. What is the value of the commutator $[\hat{a}, \hat{a}^{+}]$? (hint: $\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}$ and $[\hat{x}, \hat{p}_x] = i\hbar$)

(A) 0
(B) 1
(C) $i\hbar$
(D) $\hbar$
(E) $2\hbar$

02. What is the $(\frac{\partial U}{\partial V})_T$ for a non-ideal gas whose state can be expressed as the virial equation:

$Z = \frac{PV}{RT} = 1 + \frac{B}{V}$ (V = molar volume)?

(A) $\frac{R}{V} + \frac{BR}{V^2}$

(B) $\frac{C_V T}{V} + \frac{RT}{V^2}(\frac{\partial B}{\partial T})_V$

(C) $\frac{BR}{TV^2} - P$

(D) $\frac{C_V T}{V} + \frac{BR}{V^2}$

(E) $\frac{RT^2}{V^2}(\frac{\partial B}{\partial T})_V$

注意：背面有試題

03. Which valence bond wavefunction for He is not a proper wavefunction because it violates the Pauli exclusion principle? (**Please note**: the numbers 1 and 2 represent the two electrons of He, *N* is the normalization constant, $1s_A$ and $1s_B$ represent the atomic orbitals, and α and β are spin wavefunctions.)

(A) $\psi(1,2) = N[1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$
(B) $\psi(1,2) = N[1s_A(1)1s_B(2) + 1s_A(2)1s_B(1)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$

(C) $\psi(1,2) = N[1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)]$
(D) $\psi(1,2) = N[1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)][\alpha(1)\alpha(2)]$
(E) $\psi(1,2) = N[1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)][\beta(1)\beta(2)]$

04. We can construct three sp^2 hybrid orbitals (i.e., $\psi_n, n = 1,2,3$) as follows:

$$\psi_1 = a_1(2s) + b_1(2p_z)$$
$$\psi_2 = a_2(2s) + b_2(2p_z) + c_2(2p_x)$$
$$\psi_3 = a_3(2s) + b_3(2p_z) + c_3(2p_x)$$

where $2s, 2p_x$ and $2p_z$ are normalized atomic orbitals and a_n, b_n and c_n are constants. Assume these hybrid orbitals are normalized and orthogonal to each other, then which of the following is **incorrect.**

(A) $a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$

(B) $b_1 = \sqrt{\frac{2}{3}}$

(C) $b_2 = b_3 = -\frac{1}{\sqrt{6}}$

(D) $c_2 = c_3 = \frac{1}{\sqrt{2}}$

(E) $a_2^2 + b_2^2 + c_2^2 = 1$

05. According to the selection rules in the atomic spectra, which of the following transition is **NOT** allowed.

(A) $^2P_{3/2} \rightarrow {}^2S_{1/2}$
(B) $^2D_{3/2} \rightarrow {}^2P_{1/2}$
(C) $^2D_{5/2} \rightarrow {}^2P_{1/2}$
(D) $^2P_{1/2} \rightarrow {}^2S_{1/2}$
(E) $^2D_{5/2} \rightarrow {}^2P_{3/2}$

06. Two metal blocks with the same mass at different temperatures (T$_1$ and T$_2$) are contacting each other the reach the same temperature. What is ΔS assuming no heat loss during heat transfer.

(A) $\ln\frac{C_P(T_1+T_2)}{4T_1T_2}$

(B) $C_P \ln\frac{(T_1+T_2)}{T_1^2T_2^2}$

(C) $C_P \ln\frac{(T_1+T_2)^2}{4T_1T_2}$

(D) $\ln\frac{(T_1+T_2)^2}{C_P T_1 T_2}$

(E) $\ln\frac{(T_1+T_2)}{C_P T_1 T_2}$

07. The first few spherical harmonics $Y_l^m(\theta,\phi)$ responsible for the angular parts of the hydrogen wavefunctions are listed below.

$$Y_1^1(\theta,\phi) = -\sqrt{\frac{3}{8\pi}}sin\theta e^{i\phi} \;; \quad Y_1^{-1}(\theta,\phi) = \sqrt{\frac{3}{8\pi}}sin\theta e^{-i\phi}$$

$$Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}cos\theta \quad ; \quad Y_2^0(\theta,\phi) = \sqrt{\frac{5}{16\pi}}(3cos^2\theta - 1)$$

$$Y_2^1(\theta,\phi) = -\sqrt{\frac{15}{8\pi}}sin\theta cos\theta e^{i\phi} \;; \quad Y_2^{-1}(\theta,\phi) = -\sqrt{\frac{15}{8\pi}}sin\theta cos\theta e^{-i\phi} \;;$$

$$Y_2^2(\theta,\phi) = \sqrt{\frac{15}{32\pi}}sin^2\theta e^{2i\phi} \;; \quad Y_2^{-2}(\theta,\phi) = \sqrt{\frac{15}{32\pi}}sin^2\theta e^{-2i\phi}$$

Which combination of spherical harmonics $Y_l^m(\theta,\phi)$ can give you the p_y orbital?
hint: Euler formula $e^{\pm in\phi} = \cos(n\phi) \pm isin(n\phi)$

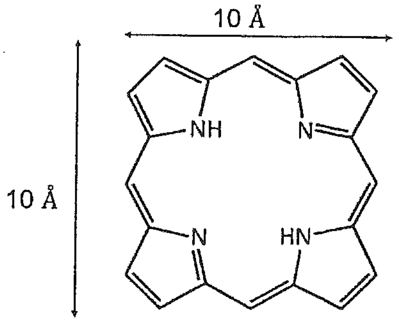
(A) $Y_2^2 + Y_2^{-2}$
(B) $Y_1^1 + Y_1^{-1}$
(C) $Y_2^2 - Y_2^{-2}$
(D) $Y_1^1 - Y_1^{-1}$
(E) $Y_2^1 - Y_2^{-1}$

08. An unnormalized wavefunction of the hydrogen atom is given by $r^2 e^{-\frac{r}{3}}(3\cos^2\theta - 1)$. What are the three quantum numbers (n, l, m) associated with this orbital?

(A) (2, 2, 0)
(B) (2, 1, 1)
(C) (3, 2, 0)
(D) (3, 1, 1)
(E) none of the above.

注意：背面有試題

09. The general structure of the porphyrin molecule is shown on the right side. This molecule is planar and so we can approximate the π electrons as being confined in a square with the length $a = 10$ Å. The porphyrin molecule has "22" π electrons. According to the particle in a two-dimensional (2D) box, the energy states are given by



$$E(n_x, n_y) = \frac{h^2}{8ma^2}(n_x^2 + n_y^2)$$

where n_x and n_y are quantum numbers. Assume that each energy level in the box is capable of holding no more than two electrons. What is the electronic transition responsible for the promotion of an electron from the highest filled energy level to the lowest empty energy level?

(A) $E(3,3) \rightarrow E(4,2)$

(B) $E(3,2) \rightarrow E(4,1)$

(C) $E(2,3) \rightarrow E(2,4)$

(D) $E(3,3) \rightarrow E(4,3)$

(E) $E(3,4) \rightarrow E(4,4)$

10. Following the question 09, what is the transition energy for an electron from the highest filled level to the lowest empty level?

(A) 8091 cm^{-1}

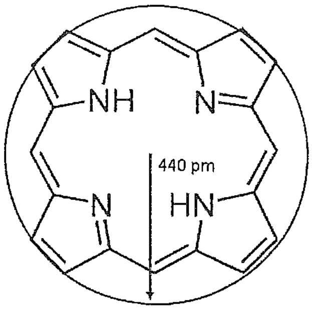
(B) 11006 cm^{-1}

(C) 7240 cm^{-1}

(D) 9230 cm^{-1}

(E) 6061 cm^{-1}

11. Following the questions 09 and 10, alternately, we can approximate the 22 π electrons of the porphyrin molecule on a circular ring with radius of 440 pm (i.e, $r = 440$ pm), as shown on the right side. For the particle on a ring model, the Schrodinger equation is



$$\hat{H}\psi = -\frac{\hbar^2}{2mr^2}\frac{d^2}{d\phi^2}\psi = E\psi$$

What is the predicted lowest transition energy?

(A) 5.2×10^{-14} Hz

(B) 6.8×10^{-14} Hz

(C) 2.4×10^{-14} Hz

(D) 9.0×10^{-15} Hz

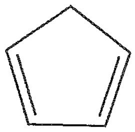
(E) 1.2×10^{-14} Hz

注意：背面有試題

12. According to the Hückel Molecular Orbital (MO) Theory for π bonding, the secular determinant for MO energies for cyclopentadiene can be set up as

$$f(x) = \begin{vmatrix} x & 1 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

where $x = \dfrac{\alpha - E}{\beta}$



cyclopentadiene

The polynomial $f(x)$ can be factored into

$$f(x) = x^5 - 5x^3 + 5x + 2 = (x+2)(x^2 + ax + b)^2$$

What are "a" and "b" values?

(A) $a = 0;\ \ b = 1$

(B) $a = 1;\ \ b = 1$

(C) $a = -1;\ \ b = 1$

(D) $a = 1;\ \ b = -1$

(E) $a = -1;\ \ b = -1$

13. Following the question 12, what is the total energy value (in terms of α and β) of the ground state for cyclopentadienyl anion which has 6 π electrons?

Hint: $\sqrt{5} = 2.24$

(A) $6\alpha + 6\beta$

(B) $6\alpha + 6.48\beta$

(C) $6\alpha + 7.24\beta$

(D) $6\alpha + 2.04\beta$

(E) $6\alpha + 10.48\beta$

14. Which of the following statement is **correct**?

(A) CO_2 is a linear molecule and therefore there is no bending vibration.

(B) CO_2 has 4 vibrational modes and all of them are IR-active.

(C) The frequency of the symmetric stretching vibration mode is lower than that of the antisymmetric stretching mode for CO_2.

(D) The point group of CO_2 is $C_{\infty v}$.

(E) CO_2 is a well-known greenhouse gas, but N_2 is not because it has no vibration.

15. CO_2 can be hydrogenated into methanol through flowing a gas mixture (molar ratio between H_2 and CO_2 = 3) into a catalyst bed at 1 bar. It is an exothermic reaction whose equation is shown below. Choose the **incorrect** statement.

$$\mathbf{CO_{2(g)} + 3H_{2(g)} \longrightarrow CH_3OH_{(g)} + H_2O_{(g)}}$$

(A) The yield of methanol cannot reach 100% given any reaction condition.
(B) The extent of reaction (ξ) at equilibrium can be increased by pressurizing the reactor.
(C) Adding an inert gas into the mixture at fixed pressure will reduce ξ at equilibrium.
(D) Decreasing reaction temperature increases ξ at equilibrium.
(E) The equilibrium conversion can be calculated by solving $K_{eq} = \xi^2(4-2\xi)^2/(3-3\xi)^3$.

16. Benzene is mixed with toluene to form an ideal solution. At 100 °C, the vapor pressures of pure benzene and toluene are 1.80 bar and 0.74 bar, respectively. Choose the **incorrect** description.
(A) In the boiling point diagram of this mixture, points above the dew point line are in the vapor phase.
(B) The bubble point line can be derived from Raoult's law.
(C) The enthalpy of mixing is equal to zero.
(D) If this mixture boils at 100 °C, the mole fraction of benzene in the mixture is higher than that of toluene.
(E) The final volume (V_{total}) is equal to $V_{benzene} + V_{toluene}$.

17. Consider a gaseous unimolecular isomerization reaction (which contains two consecutive reactions and the mechanism is shown below), where A and P represent the reactant and product, respectively. S is a non-reactive substrate for activating A. Answer question 17-20.

$$A_{(g)} + S_{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^*_{(g)} + S_{(g)}$$

$$A^*_{(g)} \xrightarrow{k_2} P_{(g)}$$

What is the partial pressure $[A^*]$ by applying steady state approximation?

(A) $\frac{k_1[A][S]}{k_{-1}[S]+k_2}$

(B) $\frac{k_1[S]^2}{k_{-1}[S]+k_2}$

(C) $\frac{k_1[A]^2}{k_{-1}[S]+k_2}$

注意：背面有試題

(D) $\frac{k_1k_2[A][S]}{k_{-1}[S]+[P]}$

(E) $\frac{k_1[A][S]}{k_{-1}[S]+[P]}$

18. What is the formation rate of the product [P]?

(A) $\frac{k_1^2[A][S]}{k_{-1}[S]+k_2}$

(B) $\frac{k_1k_2[A][S]}{k_{-1}[S]+k_2}$

(C) $\frac{k_1^2[A][S]}{k_{-1}[S]}$

(D) $\frac{k_1k_2[A][S]}{k_{-1}[S]+[P]}$

(E) $\frac{k_1k_2[A][S]}{k_{-1}[S]}$

19. The formation rates of product are measured under different reaction conditions, choose the **incorrect** statement.

(A) If the second reaction is extremely slow, the reaction is first order with respect to the partial pressure of A.

(B) If the second reaction is extremely slow, the reaction rate can be increased by increasing the equilibrium constant of the first reaction.

(C) If the second reaction is extremely fast, the reaction rate is independent of the partial pressure of S.

(D) Holding the initial partial pressure of A constant, the reaction approaches zero order in high pressure regime.

(E) Holding the initial partial pressure of A constant, the reaction approaches first order with respect to the partial pressure of S in low pressure regime.

20. What is the apparent activation energy in high pressure regime (by only varying the partial pressure of S)?

(A) $E_1 - E_2 - E_{-1}$.

(B) $E_1 - E_2 + E_{-1}$.

(C) $E_1 + 2E_2 + E_{-1}$.

(D) $2E_1 - E_2 - 2E_{-1}$.

(E) $E_1 + E_2 - E_{-1}$.

每題每一選項(ABCDE)單獨計分

二、多選題，每題 5 分，共 20 分。每答對一選項可得 1 分，答錯一選項倒扣 1 分，倒扣至本大題 0 分為止。未作答該題以 0 分計算。

21. For an isothermal and irreversible expansion process (V_1 to V_2) of an ideal gas, which following statement is **correct**?

(A) $\Delta S = q/T$

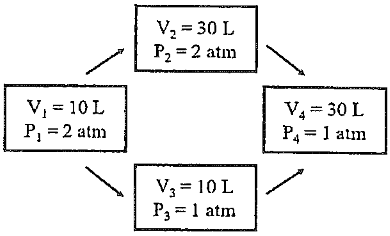
(B) $\Delta S = nR\ln(V_2/V_1)$

(C) $w = -nRT\ln(V_2/V_1)$

(D) $\Delta S_{sys} + \Delta S_{surr} > 0$

(E) $q = nRT\ln(V_2/V_1)$

22. $He_{(g)}$ (n mole) is taken from state 1 (P_1, V_1) to state 4 (P_4, V_4) through state 2 (P_2, V_2) or state 3 (P_3, V_3). Assuming $He_{(g)}$ obeys ideal gas law, choose the **correct** statement.



(A) $w = 0$ from state 2 to state 4.

(B) $q = n(\frac{3}{2}R)(\frac{P_1(V_2-V_1)}{nR})$ from state 1 to state 2.

(C) $\Delta H = n(\frac{5}{2}R)(\frac{V(P_3-P_1)}{nR})$ from state 1 to state 3.

(D) $\Delta H = q$ from state 3 to state 4.

(E) Pathway A (through state 2) and pathway B (through state 3) have the same ΔH.

23. Given a sequential reaction below, choose the **correct** statement assuming $k_1 < k_2$.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

(A) At the same conversion, the selectivity of B can be improved by increasing the reaction temperature.

(B) The $|m|$ (m = slope) of the curve of the first reaction is smaller than that of the second reaction in the Arrhenius plot.

(C) With the same reaction time, adding a catalyst to catalyze the second reaction can improve the yield of C.

(D) The apparent activation energy of the whole sequential reaction is closer to the activation energy of the second reaction.

(E) The second reaction has a lower activation energy.

注意：背面有試題

24. Considering parallel reactions forming P_1 and P_2 from A, choose the **correct** statement given the potential energy diagram on the right side.

(A) There is an intermediate from A to P_2.

(B) P_2 is the kinetically controlled product.

(C) With a catalyst significantly increasing the rate from B to P_2, the selectivity towards P_2 can be improved by lowering reaction temperature.

(D) There are three transition states in this potential energy diagram.

(E) P_2 is the thermodynamically controlled product.