一、單選題，每題3分，共60分。答錯不倒扣。

1. In the darn of quantum theory, Max Planck explained the blackbody radiation. From his theoretical work, one can derived the maximum wavelength $\lambda_{max} T = \frac{hc}{4.965 k_B}$, which can justify the empirical Wien displacement law. Which of the following is true? Max Planck introduced (A) the idea of energy quanta (B) the quantization of angular momentum (C) photoelectric effect (D) Uncertainty principle.

2. The mean temperature of the earth's surface is 288 K, what is the maximum wavelength of the earth's black body radiation? (Planck constant $h = 6.626 \times 10^{-34} J \cdot s$, speed of light $c = 3 \times 10^{8}\, m \cdot s^{-1}$, Boltzmann constant $k_B = 1.38 \times 10^{-23} J \cdot K^{-1}$.)
(A) 10^{-7} m, in the UV-visible region (B) 10^{-5} m, in the IR region (C) 10^{-3} m, in the microwave region.
(D) 10^{-1} m, in the microwave region.

3. Which of the following is correct according to the Franck-Condon principle?
(A) During the electronic transition, the nuclear distance can simultaneously rearrange.
(B) Under the Born-Oppenheimer approximation, the Franck-Condon factor is the overlap integral of vibrational wave functions of the initial and final states.
(C) The UV-Vis. absorption of molecule is the electronic transition from the ground state to the energy minimum of the excited state.
(D) The emission spectra of molecule represent the transition from the electronic excited state to the energy minimum of the ground state.

4. Of the following sets of four quantum numbers $\{n, l, m_l, m_s\}$, identify the one that is allowed for an electron in an atom.
(A) {2, 2, 0, +1/2}　(B) {3, 1, -1, 0}　(C) {4, 0, 1, +1/2}　(D) {4, 2, -2, -1/2}

5. What is the molecular term symbol of N_2^+ in its ground state?
(A) $^3\Sigma_u^+$　(B) $^2\Pi_g$　(C) $^3\Sigma_g^-$　(D) $^2\Pi_u$

6. The Schrödinger equation of particle in a box (length from 0 to a) with boundary conditions $\psi(0) = \psi(a) = 0$ and normalization condition.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

Which of the following statements is NOT correct?
(A) The lowest possible energy > 0. (B) for $n = 1$, the wavelength is equal to the length of the box. (C) As the mass of the particle becomes heavier, the lowest possible energy decreases. (D) The probability of finding the particle in a region is proportional to the square of wavefunction.

7. The electronic energy levels of benzene are well-approximated using the particle in a two-dimensional square box, containing 6 π electrons. The $HOMO \rightarrow LUMO$ transition of a π electron absorbs the light having wavelength of 176 nm. What is the wavelength of light (in nm) required for the $(HOMO-1) \rightarrow (LUMO+1)$ transition of the π electron in benzene?
(A) 132 nm　(B) 88 nm　(C) 66 nm　(D) 44 nm

注意:背面有試題

8. Assume the vibrational energy with anharmonicity is $E_v = \left(v+\frac{1}{2}\right)h\nu_e - \left(v+\frac{1}{2}\right)^2 h\nu_e\chi_e$, where χ_e is anharmonicity constant. What is the maximum vibrational quantum number?

(A) $\frac{1}{2\chi_e} - 1$　(B) $\frac{1}{2\chi_e} - \frac{1}{2}$　(C) $2\chi_e - \frac{1}{2}$　(D) $2\chi_e - 1$

Answer the question 9. – 11. using the reaction schemes shown below:

A parallel reaction is that a reactant can occurs by more than one pathway.

$$A \xrightarrow{k_1} B \quad ; A \xrightarrow{k_2} C$$

9. The rate equations of species A is (A) $[A] = [A]_0\, e^{-(k_1+k_2)t}$; (B) $[A] = [A]_0\, e^{-(k_1)t}$; (C) $[A] = [A]_0\, e^{-(k_2)t}$; (D) $[A] = [A]_0\left[1 - e^{-(k_1+k_2)t}\right]$

10. The rate equations of species B is (A) $[B] = \frac{k_1}{k_1+k_2}[B]_0\, e^{-(k_1+k_2)t}$; (B) $[B] = [B]_0\, e^{-(k_1)t}$; (C) $[B] = \frac{k_1}{k_1+k_2}[B]_0\, e^{-(k_1)t}$; (D) $[B] = \frac{k_1}{k_1+k_2}[A]_0\left[1 - e^{-(k_1+k_2)t}\right]$

11. The branching ratio, [B]/[C] is (A) $\frac{k_1}{k_1+k_2}$; (B) $\frac{k_2}{k_1+k_2}$; (C) $\frac{k_1}{k_2}$; (D) $\frac{k_2}{k_1}$

Answer the question 12. – 13. using the reaction schemes shown below:

When iodine atoms excited to electronic excited state, fluorescence occurs.

$$I^* \xrightarrow{k_{rad}} I + h\nu$$

Someone uses NO ($v = 0$) gas to quench the fluorescence.

$$I^* + NO(v=0) \xrightarrow{k} I + NO(v>0)$$

12. Consider the concentration of NO is much larger than I^*, the reaction rate of fluorescence quenching is

(A) k　(B) k[NO]　(C) k_{rad}　(D) k_{rad} + k

13. From experimental data, the reaction rate of fluorescence quenching is 4×10^3 s^{-1} $torr^{-1}$. In addition to fluorescence rate k_{rad} (= 8 s^{-1}), what are the overall reaction rate of the above reactions with 2 torr NO gas? (A) 4×10^3 s^{-1}　(B) 8 s^{-1}　(C) 8008 s^{-1}　(D) 1000 s^{-1}

14. Which of the following statement about the molar heat capacity at constant pressure ($\bar{C}_P$) of the ideal gas is correct? (Include all of the vibrational contribution in your calculation, if any. R is the gas constant)

(A) $\bar{C}_P$ of $CCl_{4(g)}$ is $13R$ (B) $\bar{C}_P$ of $H_2O_{(g)}$ is $4R$ (C) $\bar{C}_P$ of $Ar_{(g)}$ is $1.5R$ (D) $\bar{C}_P$ of $CO_{2(g)}$ is $6.5R$

15. Which of the following reaction has a positive standard entropy change?

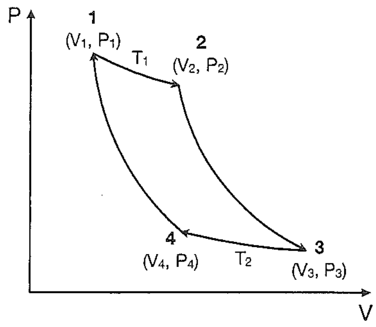
(A) $2Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$　(B) $2O_{(g)} \rightarrow O_{2(g)}$　(C) $NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$

(D) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

注意:背面有試題

16. What is the ionic strength of 0.1M K_3PO_4 (in molar)?
(A) 0.7　(B) 0.6　(C) 0.5　(D) 0.1

17. The right figure depicts a Carnot Cycle of an ideal gas, starting from 1. Which of the following statement is NOT correct?



(A) $T_1 > T_2$
(B) $\Delta U_{sys}(cycle) = \Delta S_{sys}(cycle) = 0$
(C) $q(3 \rightarrow 4) = -nRT_2 \ln \frac{V_4}{V_3}$　(D) The efficiency $\eta = \frac{T_1 - T_2}{T_1}$

Answer the question 18. – 20. using the equation of states for real gases shown below:

The van der Waals equation: $P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$, where $\bar{V} = V/n$ is molar volume

The virial equation: $Z = \frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \cdots$

18. The virial coefficients B, C and D can be expressed using the van der Waals constants a and b. Which of the following statement is NOT correct? (Hint: $\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots$ for $|x| < 1$)

(A) $B = b - \frac{a}{RT}$　(B) $C = b^2$　(C) $D = b^3$　(D) The Boyle temperature $T_{Boyle} = \frac{b}{Ra}$

19. What is the work (w) done by the system for the isothermal reversible expansion at temperature T from V_1 to V_2 of 1 mole of a real gas, which obeys van der Waals equation of state?

(A) $RT \ln \frac{V_1-b}{V_2-b} - a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$　(B) $RT \ln \frac{V_2-b}{V_1-b} + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$　(C) $RT \ln \frac{V_1-b}{V_2-b} + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

(D) $RT \ln \frac{V_1-b}{V_2-b} + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

20. What is the expression of ΔG for the isothermal reversible expansion at temperature T from V_1 to V_2 of 1 mole of a real gas, which obeys van der Waals equation of state?

(A) $-RT\left[b\left(\frac{1}{V_1-b} - \frac{1}{V_2-b}\right) + \ln \frac{V_2-b}{V_1-b}\right] + 2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

(B) $-RT\left[b\left(\frac{1}{V_1-b} - \frac{1}{V_2-b}\right) - \ln \frac{V_2-b}{V_1-b}\right] + 2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

(C) $RT\left[b\left(\frac{1}{V_1-b} - \frac{1}{V_2-b}\right) - \ln \frac{V_2-b}{V_1-b}\right] + 2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

(D) $-RT\left[b\left(\frac{1}{V_1-b} + \frac{1}{V_2-b}\right) + \ln \frac{V_2-b}{V_1-b}\right] + 2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

二、多選題，每題 5 分，共 40 分。每題有五個選項，每答對一個選項可得 1 分；每答錯一個選項倒扣 1 分，倒扣至本大題（即多選題）0 分為止。未作答者，該題以 0 分計算。

Answer the question 21. – 22. using the equations shown below:

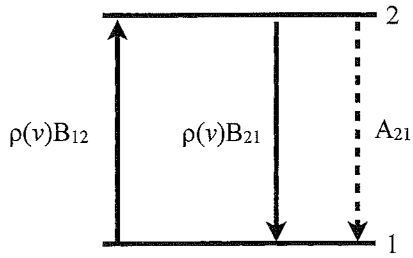
Photochemistry involves the absorption of light. It can be described as simple kinetic equations.

$$\frac{dN_1}{dt} = -N_1 B_{12}\,\rho(v) + N_2[B_{21}\,\rho(v) + A_{21}]$$

where A_{21} : spontaneous emission from state 2 to 1

B_{21} : stimulated emission from state 2 to 1

B_{12} : absorption from state 1 to 2



From black body radiation:

$$\rho(v) = \frac{8\pi h v^3}{c^3}\frac{1}{e^{hv/kT} - 1}$$

From Boltzmann distribution:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1}e^{-hv/kT}$$

where, g_1 and g_2 are the degeneracies of level 1 and 2, respectively.

21. When the system is at equilibrium, which of the following statement(s) are TRUE?

(A) $A_{21} = \frac{8\pi h v^3}{c^3}B_{21}$　(B) $A_{21} = B_{21}$　(C) $B_{12} = \frac{g_2}{g_1}B_{21}$　(D) $\frac{N_2}{N_1} = \frac{B_{12}\,\rho(v)}{B_{21}\,\rho(v) + A_{21}}$

(E) $A_{21} = \frac{8\pi h v^3}{c^3}B_{12}$

22. From Beer-Lambert law:

$$-dI(v) = I(v)\,\sigma(v) N_1 dl$$

where dl is differential absorption length, $I(v)$ is light intensity per unit frequency, $\sigma(v)$ is the absorption cross section.

It is known that $\rho(v)c = I(v)$, which of the following statement(s) are true?

(A) $B_{21} = A_{21}\,I(v)$　(B) $B_{12} = \frac{c\,\sigma(v)dv}{hv}$　(C) $B_{12}\,\rho(v) = B_{21}\,\rho(v) + A_{21}$

(D) $B_{21} = B_{12}\,I(v) - A_{21}$　(E) $B_{12} = \frac{c\,I(v)dv}{hv}$

23. The fluorescence quantum yield ($\emptyset_f$) of benzene is 25 %, and the fluorescence lifetime is 125 ns. k_r is the radiative rate constant, and k_{nr} is the non-radiative rate constant. Which of the following are TRUE?
(A) $k_r = 2 \times 10^6\ sec^{-1}$ (B) $k_r = 8 \times 10^6\ sec^{-1}$ (C) $k_{nr} = 8 \times 10^6\ sec^{-1}$
(D) $k_{nr} = 6 \times 10^6\ sec^{-1}$ (E) $k_{nr} = 3k_r$

24. Which of the following statement(s) are TURE in the transition state theory (or activated complex theory)?
(A) From the infrared emission spectra of the activated complex, one can directly determine the molecular structure of the transition state. (B) The activated complex can only become the product, never returning to the reactant. (C) The energy is fully localized on the specific vibrational mode, which will dissociate into the product. (D) The equilibrium between the activated complex and the reactant is assumed. (E) The rate of the activated complex decomposition is considered equal to the vibrational frequency of the activated complex along the path of the reaction coordinate to the product.

25. Based on the selection rule of quantum mechanics, which of the following transition(s) between the electronic energy levels are allowed?
(A) $1s \rightarrow 3s$ (B) $5p \rightarrow 1s$ (C) $1s \rightarrow 3d$ (D) $5d \rightarrow 6f$ (E) $4d \rightarrow 3s$

26. Which of the following candidate(s) for wavefunctions are normalizable over the indicated intervals?
(A) $e^{-x^2/2}$, $(-\infty, \infty)$ (B) e^{-x}, $(-\infty, \infty)$ (C) $e^{i\theta}$, $(0, 2\pi)$ (D) $\cosh x$, $(0, \infty)$
(E) xe^{-x}, $(0, \infty)$

27. Which of the following statement(s) are TRUE?
(A) For an adiabatic process in a closed system, $\Delta T = 0$. (B) In a spontaneous process, the entropy of a closed system can decrease significantly. (C) For a one-component system, the maximum number of phases that can coexist in equilibrium is three. (D) The work done by a closed system cannot exceed the decrease in the internal energy of system. (E) $\Delta S_{sytem} + \Delta S_{surroundings} < 0$ for every irreversible process.

28. In a binary ideal solution, x_1 and x_2 are mole fractions of the two components having P_1° and P_2° vapor pressures in their pure state. Which of the following statement(s) are TRUE?
(A) The solution must obey Raoult's law and Henry's law over the entire composition range. (B) The total pressure above the solution is $P_2^\circ + (P_1^\circ - P_2^\circ)x_1$ (C) The enthalpy of mixing is zero. (D) The entropy of mixing is $x_1 \ln x_1 + x_2 \ln x_2$ (E) The Gibbs free energy of mixing is zero.