

科目：物理化學(1004)

校系所組：中央大學化學學系

交通大學應用化學系 (甲組)

清華大學化學系

清華大學材料科學工程學系 (丙組)

單選題，共 25 題，每題 4 分

參考用

- Calculate the Gibbs energy for the following dissociation at a temperature of 298 K (= T)  

$$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$$

(A)  $pK_a$   
 (B)  $-RT \ln pK_a$   
 (C)  $e^{-pK_a}$   
 (D)  $pK_a / (RT \ln 10)$   
 (E)  $pK_a \times RT \ln 10$
- Two cylinders, one containing 1 mole of  $\text{C}_3\text{H}_8$  gas at 1 atm and the other containing 1 mole of  $\text{CH}_4$  gas at 1 atm, are at 288 K. If each gas absorbs 20 J of heat under conditions of constant volume, which of the following is true?  
 (A) The temperature of the  $\text{CH}_4$  increases less than the temperature of the  $\text{C}_3\text{H}_8$ .  
 (B) The internal energy of both the  $\text{CH}_4$  and the  $\text{C}_3\text{H}_8$  decreases.  
 (C) The heat capacity of the  $\text{C}_3\text{H}_8$  is larger than the heat capacity of the  $\text{CH}_4$ .  
 (D) The entropy of both the  $\text{CH}_4$  and the  $\text{C}_3\text{H}_8$  decreases.  
 (E) The heat transferred to the  $\text{C}_3\text{H}_8$  is greater than the heat transferred to the  $\text{CH}_4$ .
- Determine the change of molar Gibbs energy ( $\Delta G_m$ ) and molar entropy ( $\Delta S_m$ ) of mixing for the formation of an equimolar mixture of two perfect gases at a temperature of  $T^\circ \text{K}$ .  
 (A)  $\Delta G_m = RT \ln 0.5$ ;  $\Delta S_m = -R \ln 0.5$   
 (B)  $\Delta G_m = -RT \ln 0.5$ ;  $\Delta S_m = R \ln 0.5$   
 (C)  $\Delta G_m = 0.0$ ;  $\Delta S_m = -R \ln 0.5$   
 (D)  $\Delta G_m = 0.5RT \ln 0.5$ ;  $\Delta S_m = -0.5R \ln 0.5$   
 (E)  $\Delta G_m = 0.0$ ;  $\Delta S_m = 0.0$
- Sodium acetate spontaneously crystallizes out of a supersaturated solution on standing or on the addition of a seed crystal. Which of the following is true for the thermodynamic quantities of this system for this process?  
 (A)  $\Delta G < 0$  and  $\Delta H > 0$   
 (B)  $\Delta S < 0$  and  $\Delta G > 0$   
 (C)  $\Delta S > 0$  and  $\Delta H > 0$   
 (D)  $\Delta S > 0$  and  $\Delta G < 0$   
 (E)  $\Delta S < 0$  and  $\Delta H < 0$
- When 2.0 kJ of heat is added to 5.0 L of an ideal gas, the gas expands against a constant external pressure of 1.0 bar to a final volume of 8.0 L. What is the change in internal energy,  $\Delta U$ , for the gas? (1.0 L-bar = 0.10 kJ)  
 (A) 1.30 kJ  
 (B) 1.70 kJ  
 (C) 2.0 kJ  
 (D) 2.3 kJ  
 (E) 2.8 kJ

注意：背面有試題

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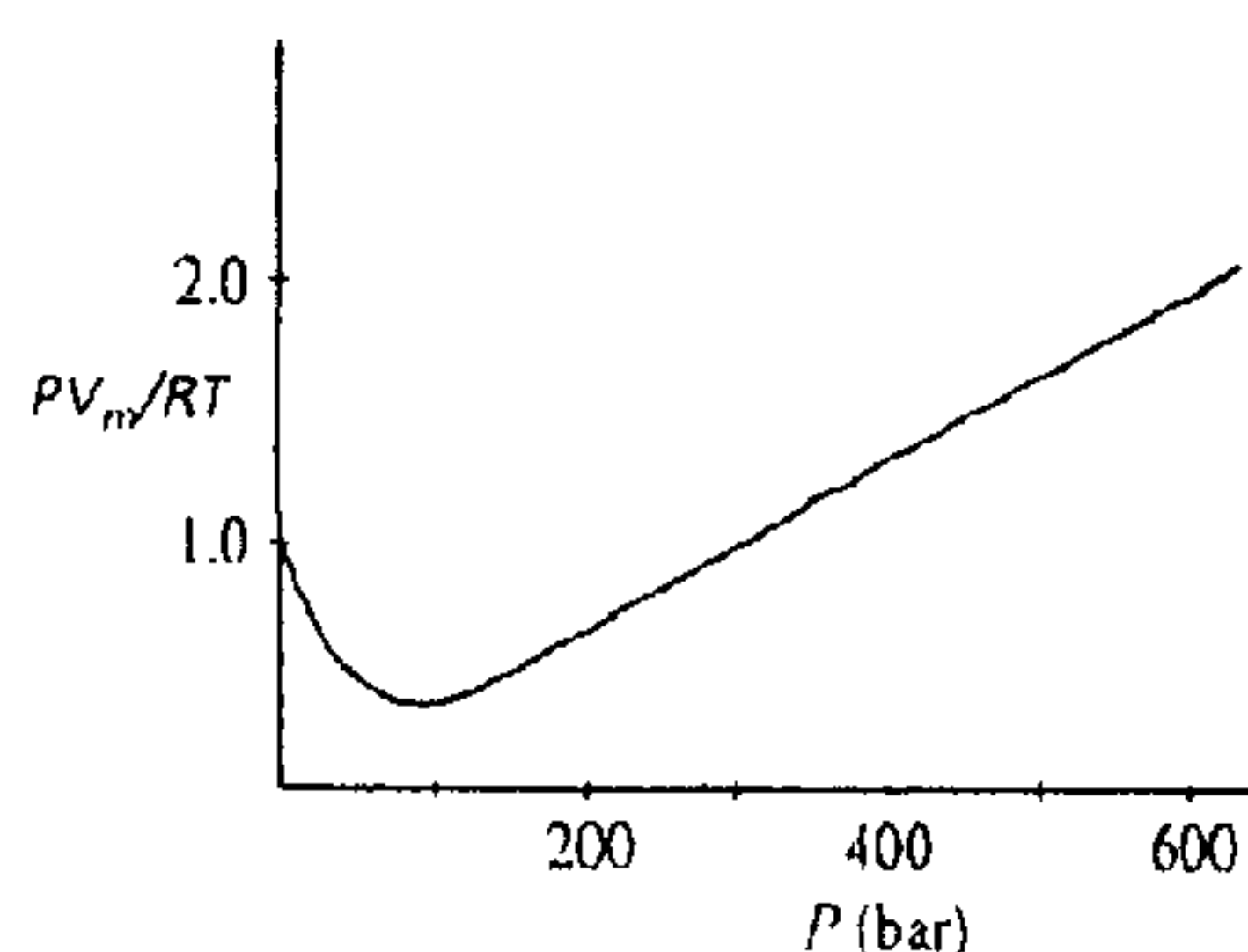
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參考用



6. The curve shown above illustrates the  $PV_m$  behavior of a real gas, where  $V_m$  is the molar volume. According to the van der Waals model for nonideal gas behavior, the values of  $PV_m/RT$  greater than 1.0 at high pressures are due to
- the effects of increased rate of collision of the molecules with the walls of the container
  - the effects of dissociation of individual gas molecules
  - the effects of the volume occupied by the molecules themselves
  - the effects of forces of attraction between molecules
  - ideal gas behavior in this pressure region
7. Find the value of  $(\frac{\partial P}{\partial S})_{V,n}$  for 1.000 mol of helium at  $P$  atm and  $T^\circ$  K. Assume that the helium is an ideal gas.
- 0.0
  - $-\frac{2P}{3R}$
  - $\frac{2R}{3P}$
  - $\frac{T}{V}$
  - $-\frac{5V}{3T}$
8. Supercooled (metastable) water vapor commonly occurs in the atmosphere if dust particles are not present. Sometimes small particles, such as tiny crystals of silver iodide (AgI), are released from airplanes in an attempt to begin condensation. This process is called "cloud seeding." At a certain location, water vapor at  $25^\circ\text{C}$  has a metastable partial pressure of 30.0 torr. The equilibrium value at this temperature is 23.756 torr. Consider the air that is present to be the surroundings, and assume it to remain at equilibrium at  $25^\circ\text{C}$ . A tiny particle is added to begin condensation. Calculate  $\Delta S_{\text{univ}}$  per mole of water that condenses. Assume the gas is ideal.  $\Delta_f H^\circ(\text{H}_2\text{O}(g)) = -241.826 \text{ kJ/mol}$  and  $\Delta_f H^\circ(\text{H}_2\text{O}(l)) = -285.83 \text{ kJ/mol}$ .
- $\Delta S_{\text{univ}} = 1.94 \text{ J K}^{-1}$
  - $\Delta S_{\text{univ}} = 0.0 \text{ J K}^{-1}$
  - $\Delta S_{\text{univ}} = -2.48 \text{ J K}^{-1}$
  - $\Delta S_{\text{univ}} = 147.59 \text{ J K}^{-1}$
  - $\Delta S_{\text{univ}} = 4.96 \text{ J K}^{-1}$

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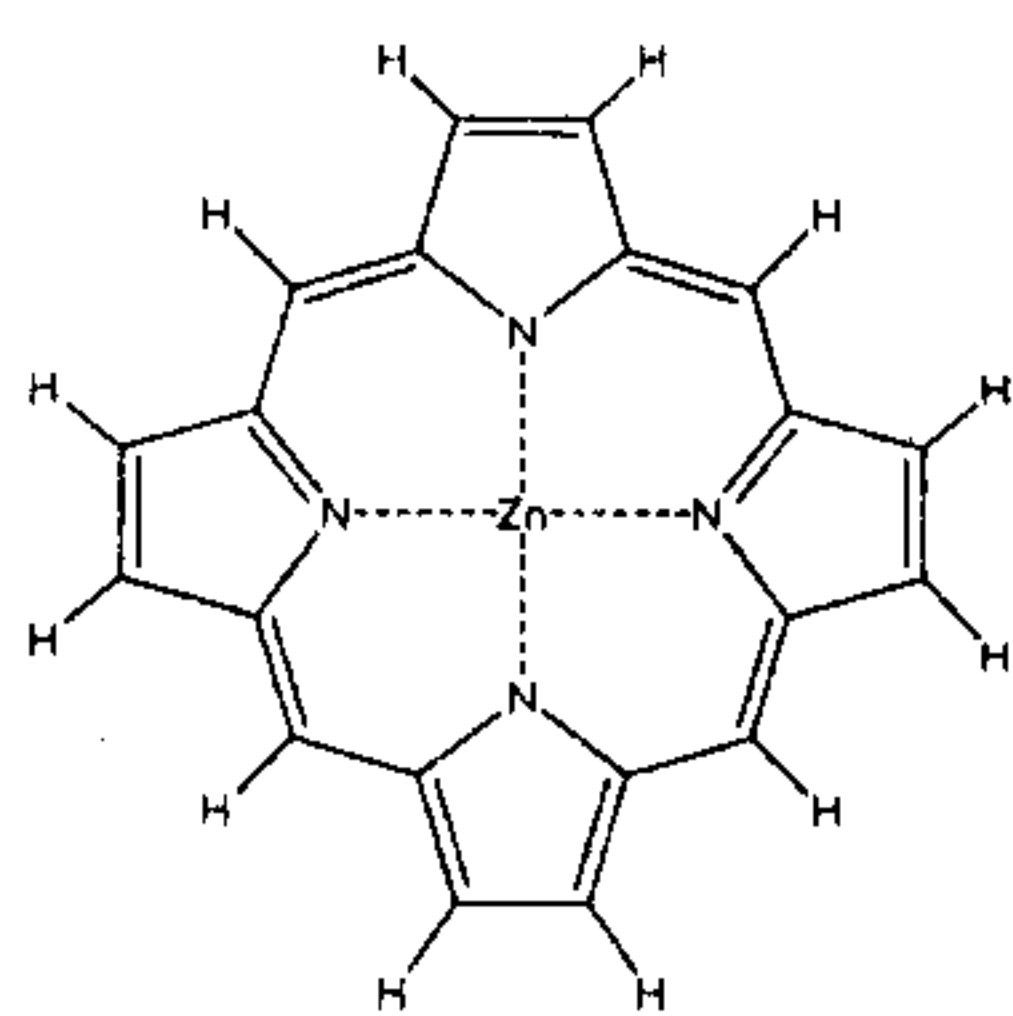
9. The effective length of the  $\pi$  system in the conjugated linear hydrocarbon 1,3,5-hexatriene,  $C_6H_8$ , is  $7.4 \text{ \AA}$  ( $= L$ ). By treating the  $\pi$  electrons as particles in a one-dimensional box, the energy of the lowest energy absorption in the electronic spectrum of 1,3,5-hexatriene is

- (A)  $\frac{h^2}{8mL^2}$   
 (B)  $\frac{3h^2}{8mL^2}$   
 (C)  $\frac{5h^2}{8mL^2}$   
 (D)  $\frac{7h^2}{8mL^2}$   
 (E)  $\frac{9h^2}{8mL^2}$

參考用

10. Which of the following function is a wavefunction,  $\Psi(r, \theta, \phi)$ , for an  $s$  electron?

- (A)  $N(2 - \frac{Zr}{a})e^{-\frac{Zr}{2a}}$   
 (B)  $Nre^{-\frac{Zr}{2a}} \sin \theta \cos \phi$   
 (C)  $Nre^{-\frac{Zr}{2a}} \cos \theta$   
 (D)  $Nre^{-\frac{Zr}{2a}} \sin \theta \sin \phi$   
 (E)  $Nr^2 e^{-\frac{Zr}{3a}} (3 \cos^2 \theta - 1)$



11. The chemical structure shown above is Zn-porphine, which is a planar and aromatic molecule. Determine its point group.

- (A)  $C_{4v}$   
 (B)  $C_{4h}$   
 (C)  $D_{4d}$   
 (D)  $D_{4h}$   
 (E)  $D_{6h}$

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12. The moment of inertia of a heteronuclear diatomic molecule measured from its microwave spectrum provides information about the
- force constant  $k$  of the bond
  - vibrational frequency
  - $\sigma \rightarrow \sigma^*$  transition energy
  - bond length
  - Maxwell-Boltzmann distribution of molecular velocity
13. According to quantum mechanics, an electron that is incident on a barrier of energy height  $V_0$  (where the energy of the electron is less than  $V_0$ ) shows which of the following statement?
- There is 100% transition through the barrier.
  - There is both transmission and reflection.
  - The particle is 100% trapped by the barrier.
  - The particle does not interact with the barrier.
  - There is 100% reflection from the barrier.
14. Use molecular orbital theory to determine whether the  $\text{Ne}_2^+$  ion is likely to be bound, and if so, to predict its bond order.
- Not bound, bond order = 0
  - Bound, bond order = 0.5
  - Bound, bond order = 1
  - Bound, bond order = 2
  - Not Bound, bond order = 0.25
15. In the photoelectron spectrum of carbon disulfide,  $\text{CS}_2$ , ionization from the highest occupied,  $1\pi_g$ , molecular orbital results in little vibrational structure. In contrast, ionization from the next lowest occupied  $1\pi_u$  molecular orbital results in a long vibrational progression in the  $\nu_1$  symmetric stretching mode of the  $\text{CS}_2^+$  ion. Which of the following descriptions of the bonding in neutral  $\text{CS}_2$  best explains these observations?
- Both the  $1\pi_g$  and  $1\pi_u$  molecular orbitals of  $\text{CS}_2$  are non-bonding in character.
  - The  $1\pi_g$  molecular orbital of  $\text{CS}_2$  is antibonding in character and the  $1\pi_u$  orbital is nonbonding in character.
  - The  $1\pi_g$  molecular orbital of  $\text{CS}_2$  is nonbonding in character and the  $1\pi_u$  orbital is bonding in character.
  - Both the  $1\pi_g$  and  $1\pi_u$  molecular orbitals of  $\text{CS}_2$  are antibonding in character.
  - All of the above statements are incorrect.
16. The vibrational transition from the  $\nu = 1$  to  $\nu = 2$  in  $\text{HCl}$  gives rise a line that is much less intense than the line from the  $\nu = 0$  to  $\nu = 1$  transition at  $20^\circ\text{C}$ . The main reason for this is that the
- $\nu = 1$  to  $\nu = 2$  transition is forbidden
  - $\nu = 1$  state has a smaller dipole moment
  - $\nu = 1$  state has more rotational state than the  $\nu = 0$  state
  - $\nu = 1$  to  $\nu = 2$  transition requires more energy
  - $\nu = 0$  state is more populated than the  $\nu = 1$  state

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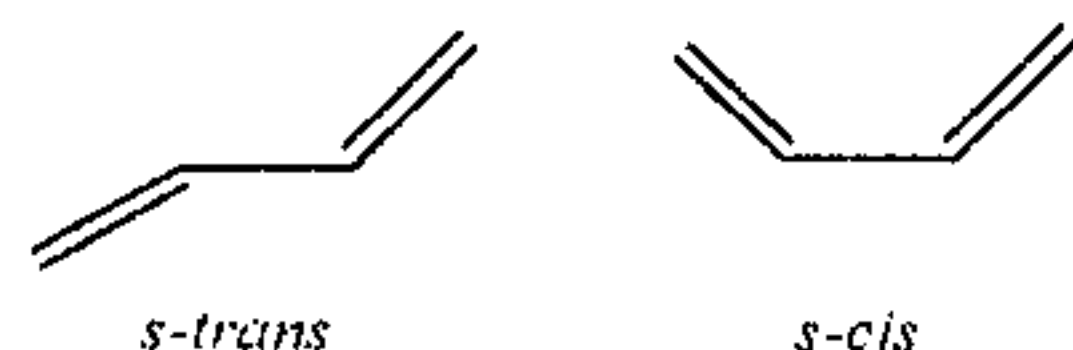
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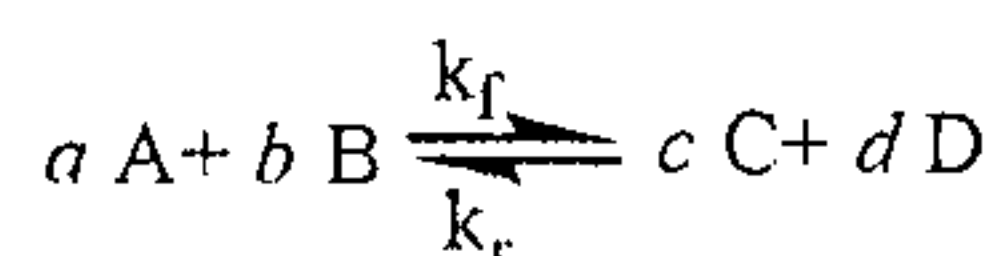
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17. The chemical structures shown above illustrate the two conformers of butadiene. Based on the  $E_\pi$  energy calculated from the Hückel theory, which of the following statement is true?

- (A) The *s-trans* form is more stable than the *s-cis* form.  
 (B) The *s-cis* form is more stable than the *s-trans* form.  
 (C) The *s-cis* and *s-trans* forms have identical  $E_\pi$  energy.  
 (D) The *s-trans* form has resonance energy and the *s-cis* form does not have resonance energy.  
 (E) The *s-cis* form has resonance energy and the *s-trans* form does not have resonance energy.

參考用



18. For the reaction shown above, assume that the order with respect to each substance is equal to its stoichiometric coefficient. Determine its equilibrium constant.

- (A)  $\frac{k_f}{k_r}$   
 (B)  $\frac{k_r}{k_f}$   
 (C)  $\frac{k_f^{(a+b)}}{k_r^{(c+d)}}$   
 (D)  $k_r + k_f$   
 (E)  $k_r - k_f$

19. For the gas-phase oxidation of nitric oxide:  $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ . The proposed mechanism is as below:

- (a).  $\text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2$       rate constant =  $k_a$   
 (b).  $\text{N}_2\text{O}_2 \rightarrow \text{NO} + \text{NO}$       rate constant =  $k_b$   
 (c).  $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow \text{NO}_2 + \text{NO}_2$       rate constant =  $k_c$

Derive the rate law for the formation of  $\text{NO}_2$  in the presence of excess oxygen.

- (A)  $\frac{2k_a k_c}{k_b + k_c} [\text{NO}]^2 [\text{O}_2]$   
 (B)  $(2k_a k_c / k_b) [\text{NO}]^2 [\text{O}_2]$   
 (C)  $2k_a [\text{NO}]^{1/2} [\text{O}_2]$   
 (D)  $2k_a [\text{NO}]^2$   
 (E)  $k_a [\text{NO}]^{3/2}$

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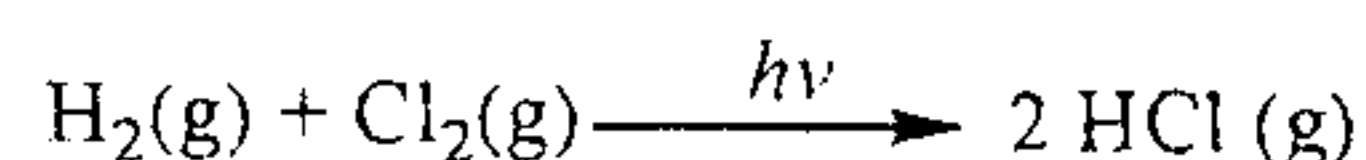
20. Which of the following statement is true? If a statement is true only under special circumstances, consider it as false.

- I. The mean value of a velocity component is equal to the mean speed of the molecules of a dilute gas.
- II. The mean molecular kinetic energy of a gas is independent of the molecular mass.
- III. The ratio of the most probable speed to the mean speed has the same value for all gases at all temperatures.

- (A) I only
- (B) II only
- (C) III only
- (D) I and II
- (E) II and III

21. The reaction  $\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5$  is an important step in the mechanism for the pyrolysis of ethane:  $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ . What is the best description of this step in the chain reaction?

- (A) Initiation
- (B) Propagation
- (C) Retardation
- (D) Termination
- (E) Inhibition



22. The yield of HCl from the photochemical reaction shown above is found to be  $3.0 \times 10^{-3}$  mol when  $7.5 \times 10^{16}$  photons are absorbed. Which of the following statement explain this observation?

- (A) The process requires multiphoton absorption.
- (B) The process violates the Frank-Condon principle.
- (C) The fluorescence quantum yield is 1.00.
- (D) The reaction is an oscillating reaction.
- (E) The reaction is a chain reaction.

23. Which of the following parameter is used in the Marcus theory to provide a formula for the activation energy of electron transfer?

- I. reorganization energy
  - II. standard reaction Gibbs free energy
  - III. entropy
- (A) I only
  - (B) II only
  - (C) III only
  - (D) I and II
  - (E) I, II and III

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24. The ground-state electronic configuration of the NO radical has a term symbol of  ${}^2\Pi$ , which comprises  ${}^2\Pi_{1/2}$  and  ${}^2\Pi_{3/2}$  levels.

The  ${}^2\Pi_{1/2}$  level lies lowest in energy and has a degeneracy of 2; the  ${}^2\Pi_{3/2}$  level lies the equivalent of  $109\text{ cm}^{-1}$  ( $\bar{\nu}$ ) higher in energy and has a degeneracy of 4. Assuming that all other levels lie too high in energy to be significantly populated, the electronic partition function of the NO radical at 298 K ( $= T$ ) is given by

(A) one

(B)  $2 + 4e^{-\frac{hc\bar{\nu}}{kT}}$

(C)  $2e^{-\frac{hc\bar{\nu}}{kT}}$

(D)  $4e^{-\frac{hc\bar{\nu}}{kT}}$

(E)  $6e^{-\frac{hc\bar{\nu}}{kT}}$

參考用

25. The translation partition function of He gas at 300K depends on which of the following property?

- I. Mass of He atom
  - II. Collision frequency
  - III. Mean free path
- (A) I only  
(B) II only  
(C) III only  
(D) I and II  
(E) I, II and III