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

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

$$CH_3COOH(aq) + H_2O(aq) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

(A) pK_a
(B) $-RT\ln pK_a$
(C) e^{-pKa}
(D) $pK_a / (RT \ln 10)$
(E) $pK_a \times RT \ln 10$

2. Two cylinders, one containing 1 mole of C_3H_8 gas at 1 atm and the other containing 1 mole of 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 CH_4 increases less than the temperature of the C_3H_8.
(B) The internal energy of both the CH_4 and the C_3H_8 decreases.
(C) The heat capacity of the C_3H_8 is larger than the heat capacity of the CH_4.
(D) The entropy of both the CH_4 and the C_3H_8 decreases.
(E) The heat transferred to the C_3H_8 is greater than the heat transferred to the CH_4.

3. Determine the change of molar Gibbs energy (ΔG_m) and molar entropy (ΔS_m) of mixing for the formation of an equimolar mixture of two perfect gases at a temperature of T° 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) $\Delta G_m = 0.0$; $\Delta S_m = 0.0$

4. 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) $\Delta S >$ and $\Delta H > 0$
(D) $\Delta S > 0$ and $\Delta G < 0$
(E) $\Delta S < 0$ and $\Delta H < 0$

5. 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, ΔU, 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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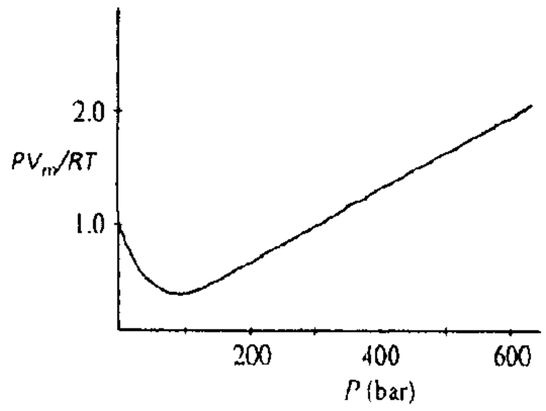

6. The curve shown above illustrates the PV_m behavior of a real gas, where V_m is the molar volume. According to the van der Waals model for nonideal gas behavior, the values of PV_m/RT greater than 1.0 at high pressures are due to
(A) the effects of increased rate of collision of the molecules with the walls of the container
(B) the effects of dissociation of individual gas molecules
(C) the effects of the volume occupied by the molecules themselves
(D) the effects of forces of attraction between molecules
(E) 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° K. Assume that the helium is an ideal gas.
(A) 0.0
(B) $-\frac{2}{3}\frac{P}{R}$
(C) $\frac{2}{3}\frac{R}{P}$
(D) $\frac{T}{V}$
(E) $-\frac{5}{3}\frac{V}{T}$

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°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°C. A tiny particle is added to begin condensation. Calculate ΔS_{univ} per mole of water that condenses. Assume the gas is ideal. $\Delta_f H°(H_2O(g)) = -241.826$ kJ/mol and $\Delta_f H°(H_2O(l)) = -285.83$ kJ/mol.
(A) $\Delta S_{univ} = 1.94\ J\ K^{-1}$
(B) $\Delta S_{univ} = 0.0\ J\ K^{-1}$
(C) $\Delta S_{univ} = -2.48\ J\ K^{-1}$
(D) $\Delta S_{univ} = 147.59\ J\ K^{-1}$
(E) $\Delta S_{univ} = 4.96\ J\ K^{-1}$

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9. The effective length of the π system in the conjugated linear hydrocarbon 1,3,5-hexatriene, C_6H_8, is 7.4 Å (= L). By treating the π 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?

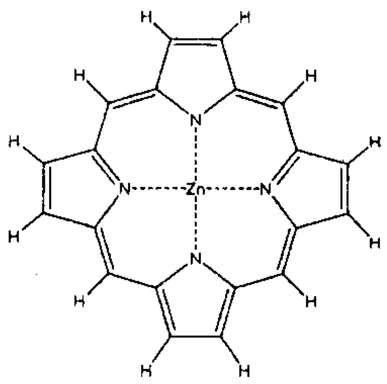
(A) $N(2-\frac{Zr}{a})e^{\frac{-2r}{2a}}$

(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) $Nr^2e^{\frac{-Zr}{3a}}(3\cos^2\theta-1)$



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
(A) force constant k of the bond
(B) vibrational frequency
(C) $\sigma \rightarrow \sigma^*$ transition energy
(D) bond length
(E) Maxwell-Boltzmann distribution of molecular velocity

13. According to quantum mechanics, an electron that is incident on a barrier of energy height V_o (where the energy of the electron is less than V_o) shows which of the following statement?
(A) There is 100% transition through the barrier.
(B) There is both transmission and reflection.
(C) The particle is 100% trapped by the barrier.
(D) The particle does not interact with the barrier.
(E) There is 100% reflection from the barrier.

14. Use molecular orbital theory to determine whether the Ne_2^+ ion is likely to be bound, and if so, to predict its bond order.
(A) Not bound, bond order = 0
(B) Bound, bond order = 0.5
(C) Bound, bond order = 1
(D) Bound, bond order = 2
(E) Not Bound, bond order = 0.25

15. In the photoelectron spectrum of carbon disulfide, 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 ν_1 symmetric stretching mode of the CS_2^+ ion. Which of the following descriptions of the bonding in neutral CS_2 best explains these observations?
(A) Both the $1\pi_g$ and $1\pi_u$ molecular orbitals of CS_2 are non-bonding in character.
(B) The $1\pi_g$ molecular orbital of CS_2 is antibonding in character and the $1\pi_u$ orbital is nonbonding in character.
(C) The $1\pi_g$ molecular orbital of CS_2 is nonbonding in character and the $1\pi_u$ orbital is bonding in character.
(D) Both the $1\pi_g$ and $1\pi_u$ molecular orbitals of CS_2 are antibonding in character.
(E) All of the above statements are incorrect.

16. The vibrational transition from the $v = 1$ to $v = 2$ in HCl gives rise a line that is much less intense than the line from the $v = 0$ to $v = 1$ transition at 20°C. The main reason for this is that the
(A) $v = 1$ to $v = 2$ transition is forbidden
(B) $v = 1$ state has a smaller dipole moment
(C) $v = 1$ state has more rotational state than the $v = 0$ state
(D) $v = 1$ to $v = 2$ transition requires more energy
(E) $v = 0$ state is more populated than the $v = 1$ state

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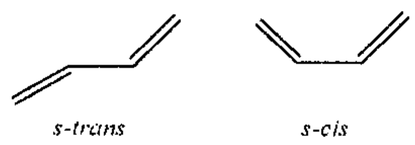

17. The chemical structures shown above illustrate the two conformers of butadiene. Based on the E_π energy calculated from the Hückel theory, which of the following statement is true?
(A) The *s-trans* form is more stable than the *s-cis* form.
(B) The *s-cis* form is more stable than the *s-trans* form.
(C) The *s-cis* and *s-trans* forms have identical E_π 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

$$a\,A + b\,B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} c\,C + d\,D$$

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: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$. The proposed mechanism is as below:
(a). $NO + NO \rightarrow N_2O_2$ rate constant = k_a
(b). $N_2O_2 \rightarrow NO + NO$ rate constant = k_b
(c). $N_2O_2 + O_2 \rightarrow NO_2 + NO_2$ rate constant = k_c
Derive the rate law for the formation of NO_2 in the presence of excess oxygen.
(A) $\frac{2k_ak_c}{k_b + k_c}[NO]^2[O_2]$
(B) $(2k_ak_c / k_b)[NO]^2[O_2]$
(C) $2k_a[NO]^{1/2}[O_2]$
(D) $2k_a[NO]^2$
(E) $k_a[NO]^{3/2}$

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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 $H + C_2H_6 \rightarrow H_2 + C_2H_5$ is an important step in the mechanism for the pyrolysis of ethane: $C_2H_6 \rightarrow C_2H_4 + H_2$. What is the best description of this step in the chain reaction?
(A) Initiation
(B) Propagation
(C) Retardation
(D) Termination
(E) Inhibition

$$H_2(g) + Cl_2(g) \xrightarrow{h\nu} 2\,HCl\,(g)$$

22. The yield of HCl from the photochemical reaction shown above is found to be 3.0×10^{-3} mol when 7.5×10^{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 cm^{-1} ($\tilde{\nu}$) 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) $2+4e^{-\frac{hc\tilde{\nu}}{kT}}$

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

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

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

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