國立臺灣大學95學年度碩士班招生考試試題

一、單選題：共25題，每題2分，答錯不倒扣。請於試卷上「選擇題作答區」依序作答。

1. Which of the following quantities can be used as the criteria of spontaneity and equilibrium at constant volume and temperature?
   (A) $\delta S \geq 0$ (B) $\delta U \leq 0$ (C) $\delta G \leq 0$
   (D) $\delta H \leq 0$ (E) $\delta A \leq 0$

2. Which of the following represents the equation of standing waves for a particle confined in a one dimensional box with potential $V(x) = 0, 0 < x < L$ and ∞ outside the box?
   (A) $\psi(x) = A\sin(n\pi x/L), n = 1, 2, 3, \ldots$
   (B) $\psi(x) = A\cos(n\pi x/L), n = 0, 1, 2, \ldots$
   (C) $\psi(x) = A\sin(n\pi x/L), n = 0, 1, 2, 3, \ldots$
   (D) $\psi(x) = A\cos(2n\pi x/L), n = 1, 2, 3, \ldots$
   (E) $\psi(x) = A\sin(2n\pi x/L), n = 1, 2, 3, \ldots$

3. The activation energy of a reaction can be determined from the slope of which of the following graphs? (k is rate constant)
   (A) ln k vs T (B) ln k/T vs T (C) ln k vs 1/T
   (D) T/ln k vs 1/T (E) ln k/T vs 1/T

4. The rate data for the net reaction X+Y→ Z was obtained at 25°C.

[X]	[Y]	rate
1.0	1.0	0.01
1.0	2.0	0.02
3.0	1.0	0.09

   The initial rate of increase in [Z] is
   (A) second order in both X and Y
   (B) first order in X and second in Y
   (C) second order in X and zero order in Y
   (D) second order in X and first order in Y
   (E) first order in both X and Y

5. Compared to the harmonic oscillator, an oscillator described by a Morse potential function
   (A) has more closed spaced vibrational energy levels.
   (B) accounts for the dissociation of molecules.
   (C) has deeper potential well.
   (D) predicts different equilibrium internuclear distance.
   (E) has larger vibrational frequency.

6. The Hamiltonian for the electronic and nuclear repulsion energies of H_2^+ could be represented by which of the following?
   (A) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} + \frac{1}{R}$
   (B) $H = \frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} + \frac{1}{r_{B1}} + \frac{1}{R}$
   (C) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} + \frac{1}{r_{B1}} + \frac{1}{R}$
   (D) $H = \frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{R}$
   (E) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{r_{A1}} - \frac{1}{r_{B1}} - \frac{1}{R}$

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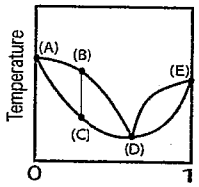
7. Based on the third law of thermodynamics we know that all perfect crystals at absolute zero have
   (A) the same enthalpy.
   (B) differing ΔA values.
   (C) the same entropy.
   (D) the same crystal structures.
   (E) the same Gibbs energy.

8. In this low boiling azetrope diagram, select the point where the azetrope occurs.



9. All of the following equations are Maxwell' relations, with one exception. Indicate the letter of the equation that does not designate a correct Maxwell relation.
   (A) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$　(B) $\left(\frac{\partial S}{\partial P}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_P$　(C) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$
   (D) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$　(E) $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

10. According to the IUPAC convention, the expression for work w, if negative for a system in adiabatic enclosure, implies all of the following, except:
    (A) work has been done by the system.
    (B) the internal energy of the universe is the same.
    (C) the system has lost the internal energy.
    (D) a negative amount of work has been done on the system.
    (E) the entropy change of the system is zero.

11. Which of following statement is true for a free electron moving in a ring with radius R?
    (A) All energy levels of this system are nondegenerate.
    (B) The angular momentum of the lowest level is $\hbar$.
    (C) There is no zero point energy for this system.
    (D) The wavelength of the lowest level is R.
    (E) The energy levels are equally spaced.

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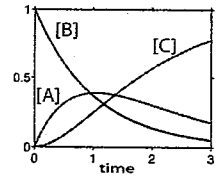
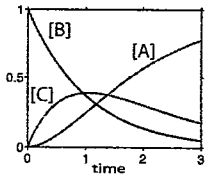
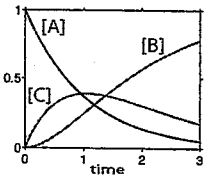
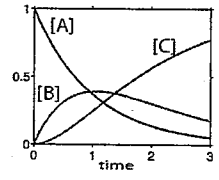
12. Which of the following graphs can represent the kinetics of consecutive first-order reactions?

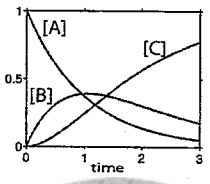
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

(A) 

(B) 

(C) 

(D) 

(E) 

13. Which of following method can be used to measure ionization potential of a molecule?
(A) UV-Visible spectroscopy
(B) Photoelectron spectroscopy
(C) NMR spectroscopy
(D) Microwave spectroscopy
(E) ESR spectroscopy

14. If the ionization energy for an electron in the first quantum state of a hydrogen atom is 13.6eV, what is the ionization energy for an electron in the second quantum state?
(A) 13.6 eV (B) 2*13.6 eV (C) 4*13.6 eV
(D) 13.6/2 eV (E) 13.6/4 eV

15. The vibrational degrees of freedom for a linear and nonlinear polyatomic molecule of four atoms each, are respectively:
(A) 7 and 6 (B) 12 and 11 (C) 8 and 9
(D) 5 and 6 (E) 11 and 12

16. What is the number of degrees of freedom to specify the intensive state of a one-phase, nonreactive system with 4 chemical species?
(A) 2 (B) 3 (C) 4
(D) 5 (E) 6

17. Which formula below could be used to calculate the wavelength (λ) of an electron given its velocity (v), its mass (m) and Planck constant (h)?
(A) $\lambda = hmv$ (B) $\lambda = \frac{h}{mv}$ (C) $\lambda = \frac{hv}{m}$
(D) $\lambda = \frac{mv^2}{h}$ (E) $\frac{1}{2}mv^2h$

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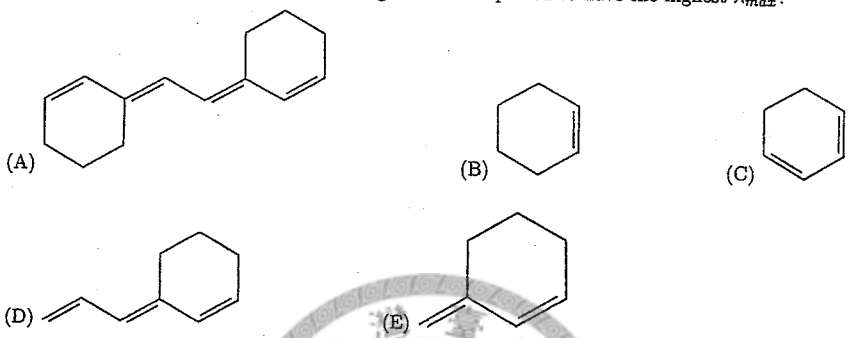
18. According to kinetic theory of gases, which of following statement is correct?
    (A) The mean free path increases when temperature is increased.
    (B) The mean free path decreases when temperature is increased.
    (C) The effusion rate is proportional to the molecular mass.
    (D) The mean speed is proportional to the molecular mass.
    (E) The mean speed is less than the root-mean-square speed.

19. In the UV spectrum, which of the following would be expected to have the highest λ_{max}?



20. Consider a tricarboxylic acid $R(COOH)_3$, where the three $-CO_2H$ groups are far apart. The acid dissociation constants K_1, and K_2 are the equilibrium constants for the reactions

$$R(CO_2H)_3 \rightleftarrows R(CO_2H)_2CO_2^- + H^+$$

and

$$R(CO_2H)_2CO_2^- \rightleftarrows R(CO_2H)(CO_2^-)_2 + H^+$$

respectively. What will be the ratio of the acid dissociation constants K_1/K_2 based on statistical method?
(A) 9 (B) 4 (C) 3 (D) 2 (E) 1

21. Which of following statements about the Hückel molecular orbitals of π-electrons in the square cyclobutadiene is correct?
    (A) There are two degenerate pairs of molecular orbitals.
    (B) The molecular orbitals can be determined completely according to the symmetry.
    (C) There are four possible dipole-allowed transitions between HOMOs and LUMOs.
    (D) The highest occupied molecular orbitals have two nodes.
    (E) This is a closed-shell system.

22. The Joule-Thomson experiment is a constant-enthalpy process as gases undergo:
    (A) an isothermal compression
    (B) an isentropic expansion
    (C) an adiabatic compression
    (D) an isochoric expansion
    (E) a throttled adiabatic expansion

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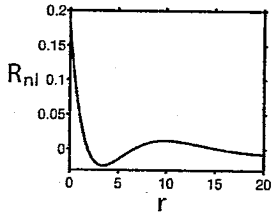
23. The plot below is the radial wavefunction vs radius for an electron in a particular orbital of hydrogen atom.



What is this wave function corresponding to?

(A) 3s (B) 4s (C) 3p (D) 4p (E) 3d

24. The Schrödinger equation when solved for a molecular system cannot give

(A) the polarizability (B) the molecular geometry (C) the mean free path (D) the dipole moment (E) the excitation energy

25. According to molecular orbital theory, which of the following could not be a viable molecule?

(A) He_2^{2+} (B) He_2^{+} (C) H_2^{-} (D) H_2^{2-} (E) H_2^{+}

Analytical Chemistry

二、 Briefly answer the following questions

1. A 25ml class A pipet delivers 25.00 ± 0.03 ml. Calculate the uncertainty if you use the pipet to deliver 100ml solution. 3%

2. List one of the two assumptions in the construction of a calibration curve. 3%

3. List the major reason that a buffer solution is not prepared by calculation what to mix. 3%

4. Convert $[H^+]= 1.0* 10^{-5}$ to a pH value. 2 %

5. State the reason that indicator color changes often occur at pKind ± 1. 4%

6. Based on Nernst equation, state the reason that in aqueous solution, AgCl has a smaller standard reduction potential than AgNO3. 4%

7. State the reason of using an auxiliary electrode in an electrochemical cell. 4%

8. In atomic absorption spectrometry, list one method for background correction. 3%

9. Draw a signal with S/N ratio of 3 (noise is the root mean square noise) 3%

10. In mass spectrometry, state the reason that selected reaction monitoring has higher selectivity than selected ion monitoring. 4%

11. State the operation and its usefulness of solvent traping in GC sample injection. 4%

12. In HPLC , state the reasons that small particles give high efficiency. 4%

13. State one occasion of using ANOVA(analysis of variance) in analytical chemistry. 3%

14. State the major reason that the invention of FT-NMR is critical to the development of ^{13}C NMR 3%

15. List one technique using energy dispersive as a detection method. 3%