※注意：請於試卷上「非選擇題作答區」標明題號並依序作答。

R=8.314 J/mol-K;
m_e=9.109 x 10^{-31} kg;
h=6.626x 10^{-34} J-s;
1 J=1 kg m^2/s^2
F=96500 C

I. 單選題 (Pick **one** best answer, 60 pts)

1. The rate constant for a second-order 2A → B reaction is 2.5x10^{-3} L/mol-s. If the initial concentration of reactant is 3.5 mol/L, what is the molar concentration (M) of the reactant after 2.5 minutes?
(A) 0.97 　　(B) 1.5 　　(C) 3.35 　　(D) 2.33 　　(E) None of the above

2. Which of the following statements is true for crystal field theory of an octahedral complex?
(A) The d_{xy}, d_{yz}, d_{xz} orbitals are lower in energy than the d_z^2, and the $d_{x^2-y^2}$ because they are unaffected by the ligand field.
(B) The d_{xy}, d_{yz}, d_{xz} orbitals are lower in energy than the d_z^2, and the $d_{x^2-y^2}$ because their energy is increased less than the d_z^2, and the $d_{x^2-y^2}$.
(C) In low spin complexes, the d_z^2, and the $d_{x^2-y^2}$ are lower in energy than the d_{xy}, d_{yz}, d_{xz} orbitals.
(D) Both A & C
(E) A, B and C are all correct.

3. Why is there an energetic barrier to rotate the C=C bond in ethane (C_2H_4)?
(A) The trans isomer is more stable than the cis isomer.
(B) Rotation breaks the σ C-C bond.
(C) Rotation breaks the π C-C bond.
(D) Steric repulsion between the hydrogen atoms.
(E) There is no energy barrier to rotation of this bond.

4. The energy for one-dimensional particle-in-a-box is $E_n = \dfrac{n^2 h^2}{8mL^2}$. For a particle in a three-dimensional cubic box (L_x=L_y=L_z), if an energy level has twice the energy of the ground state, what is the degeneracy of this energy level?
(A) 0 　　(B) 1 　　(C) 2 　　(D) 3 　　(E) 4

5. The vapor pressure of methanol (CH_3OH) at 25°C is 93.3 Torr. If 5 g of methanol is placed into an evacuated 10 L container at a constant temperature of 25°C, what is the final pressure in the container (1 atm = 760 torr)?
(A) 58.1 Torr 　　(B) 93.3 Torr 　　(C) 376 Torr 　　(D) 760 torr

6. Arrange the following compound in order of increasing CN bond strength.
(A) $NHCH_2$ < NH_2CH_3 < HCN 　　(B) NH_2CH_3 < HCN < $NHCH_2$
(C) NH_2CH_3 < $NHCH_2$ < HCN 　　(D) HCN < $NHCH_2$ < NH_2CH_3

7. Arrange the following ions in order of increasing ionic radius.
(A) S^{2-} < Cl^- < P^{3-} 　　(B) Cl^- < S^{2-} < P^{3-}
(C) P^{3-} < S^{2-} < Cl^- 　　(D) S^{2-} < P^{3-} < Cl^-

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8. The K_f for the complex ion $Ag(NH_3)_2^+$ is 1.7×10^7, and K_{sp} for AgI is 1.5×10^{-16}. What is the molar solubility of AgI in a solution that is 2.0 M in NH_3?
(A) 1.5×10^{-9} (B) 1.3×10^{-3} (C) 1.0×10^{-4} (D) 5.8×10^{-12} (E) 8.4×10^{-5}

9. Which of the following will not produce a buffered solution?
(A) 100 mL of 0.1 M Na_2CO_3 and 50 mL of 0.1 M HCl
(B) 100 mL of 0.1 M $NaHCO_3$ and 25 mL of 0.2 M HCl
(C) 50 mL of 0.2 M Na_2CO_3 and 5 mL of 1.0 M HCl
(D) 100 mL of 0.1 M Na_2CO_3 and 50 mL of 0.1 M NaOH

10. What is the root-mean-square speed of carbon dioxide molecules at 25°C?
(A) 153 m/s   (B) 413 m/s   (C) 45.6 m/s   (D) 874 m/s

11. In the homonuclear N_2 molecules, the $E(\sigma_{2p})$ is higher than $E(\pi_{2p})$, while the two energies reverse in O_2 molecules. All the following molecules are paramagnetic except
(A) O_2^+ (B) O_2^- (C) N_2^{2+} (D) N_2^{2-}

12. Sodium crystallizes in a body-centered cubic structure (as drawn here) with a density of 0.97 g/cm³. Estimate its atomic radius.
(A) 95 pm   (B) 320 pm   (C) 370 pm   (D) 190 pm
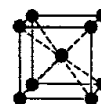
13. Which of the following statements regarding the comparisons of boiling point is true?
(A) *trans*- CHCl=CHCl has a higher boiling point than *cis*- CHCl=CHCl.
(B) CH_4 has a higher boiling point than CCl_4.
(C) CO_2 has a higher boiling point than SO_2.
(D) NH_3 has a higher boiling point than PH_3.

14. Which of the atomic orbitals drawn below has the highest energy?
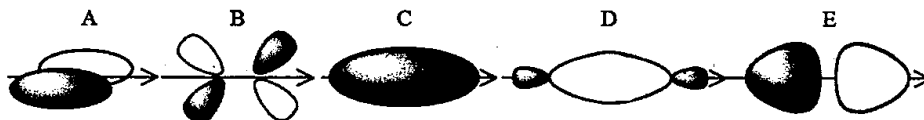
15. A system undergoes a two-step process. In step 1, it absorbs 50 J of heat at a constant volume. In step 2, it releases 20 J of heat at 2.00 atm as it is returned to its original internal energy. Find the change in the volume of the system during the second step.
(A) expansion 15 L   (B) expansion 0.15 L   (C) compression 15 L   (D) compression 0.15 L

16. Consider the following potential energy profile for the A→C reaction, which statement is wrong?
(A) The overall reaction is exothermic.
(B) There is one intermediate state.
(C) The B→C step is the rate-determining step.
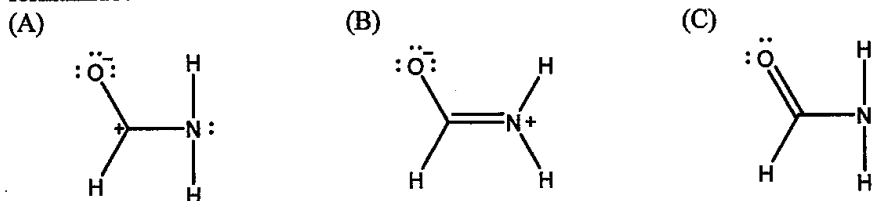(D) There are two elementary steps.
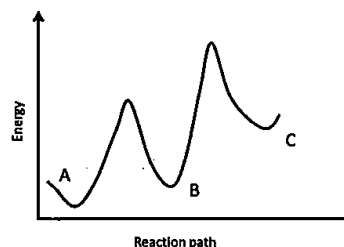
17. Which of the following acid strength (from strong to weak) is true?
(A) $H_2O > H_2S > H_2Se$ (B) $H_2SeO_4 > H_2SO_4$
(C) 1-hexanol($C_6H_{13}OH$)>Phenol(C_6H_5OH)   (D) $PH_3 > NH_3$
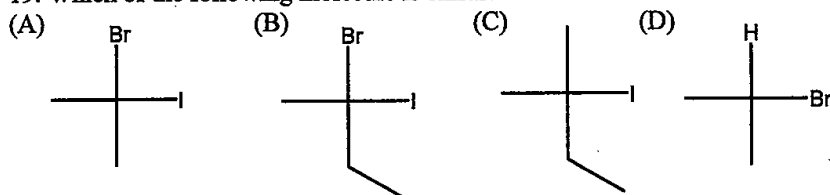
18. Which of the following structure would contribute most to the resonance hybrid structure of formamide?

(A)

(B)

(C)

19. Which of the following molecule is chiral?

(A)   (B)   (C)   (D)

20. Tollen's reagent is a widely used reagent composed of $[Ag(NH_3)_2]^+$. What is true?
(A) Tollen's reagent is used to identify aldehydes only.
(B) Tollen's reagent's reaction is a redox reaction, aldehydes are reduced to carboxylic acids.
(C) Adding silver chloride crystals to ammonia solution gives water-soluble $[Ag(NH_3)_2]^+$.
(D) Tollen's reagent can be used to coat silver on mirrors.

II. Calculation and description questions (40 pts)

21. Ψ is wavefunction and $P(r)$ is radial probability function. Draw the (A) Ψ vs. r; and (B) $P(r)$ vs. r for the $3p$ atomic orbital of hydrogen.

22. Construct the molecular orbital (MO) diagram of carbon monoxide (CO) step-by-step: (A) put atomic orbitals (AO) of C atom on the left side and those of O atom on the right (including only 2s and 2p electrons, and note the relative energy of AOs of C and O atoms), (B) put up the MO of CO molecule in the middle, and connect the MOs with the contributing AOs. (C) Fill up the electrons of AOs and MOs. Note that when combining the p orbitals, the π_b molecular orbital has a lower energy than the σ_b molecular orbital.

23. For the reaction of $Br_2(g) \rightleftharpoons 2Br(g)$, the equilibrium constant is determined to be 0.048 at 1100 K and 2×10^{-4} at 900 K under standard state. Calculate the (A)ΔG^o, (B) ΔH^o, and (C) ΔS^o at 900 K, assuming that ΔH^o, and ΔS^o are constants.

24. (A) Draw the schematic titration curve on using NaOH to titrate triprotic phosphoric acid (H_3PO_4), where the x-axis is the relative amount of NaOH added, and y-axis is the pH. (B) Mark the points (①, ②, ③) where pH=pK_{a1}(2.12), pK_{a2}(7.21), and pK_{a3}(12.68). (C) Identify the major species when pH=4.00.

25. The standard emf (E^o) of a galvanic cell of $Zn(s)|Zn^{2+} \parallel H^+|H_2$(1 bar)$|Pt$ is 0.76 V at 25°C.
(A) Begin with a relation between ΔG and Q, derive the Nernst equation

$$E_{cell} = E^o_{cell} - \frac{RT}{nF} \ln Q$$

(B) When the concentration of $ZnSO_4$ (aq) is 1.00×10^{-4} M, the cell emf is determined to 0.54 V at 25°C. Calculate the $[H^+]$.

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