國立中山大學115學年度
碩士班考試入學招生考試試題

科目名稱：物理化學及分析化學【化學系碩士班】

—作答注意事項—

考試時間：100分鐘

- **考試開始鈴響前不得翻閱試題，並不得書寫、劃記、作答。**請先檢查答案卷（卡）之應考證號碼、桌角號碼、應試科目是否正確，如有不同立即請監試人員處理。
- **答案卷限用藍、黑色筆(含鉛筆)書寫、繪圖或標示**，可攜帶橡皮擦、無色透明無文字墊板、尺規、修正液（帶）、手錶(未附計算器者)。每人每節限使用一份答案卷，請衡酌作答。
- 答案卡請以2B鉛筆劃記，不可使用修正液（帶）塗改，未使用2B鉛筆、劃記太輕或污損致光學閱讀機無法辨識答案者，後果由考生自負。
- 答案卷（卡）應保持清潔完整，不得折疊、破壞或塗改應考證號碼及條碼，亦不得書寫考生姓名、應考證號碼或與答案無關之任何文字或符號。
- 可否使用計算機請依試題資訊內標註為準，如「可以」使用，廠牌、功能不拘，唯不得攜帶書籍、紙張（應考證不得做計算紙書寫）、具有通訊、記憶、傳輸或收發等功能之相關電子產品或其他有礙試場安寧、考試公平之各類器材入場。
- **試題及答案卷（卡）請務必繳回，未繳回者該科成績以零分計算。**
- **試題採雙面列印，考生應注意試題頁數確實作答。**
- **違規者依本校招生考試試場規則及違規處理辦法處理。**

國立中山大學 115 學年度碩士班考試入學招生考試試題

科目名稱：物理化學及分析化學【化學系碩士班】 **題號：422002**

※本科目依簡章規定「可以」使用計算機（廠牌、功能不拘）(選擇題) 共 9 頁第 1 頁

物理化學部分

(一)選擇題，共五十分 (單選題，不可於試題紙上作答)
第 1-14 題，每題 3 分，第 15-16 題 4 分。答錯一題倒扣 1 分。

R = 8.314 J mol^{-1} K^{-1}, $k_B = 1.381\times10^{-23}$ J K^{-1}, $h = 6.626 \times 10^{-34}$ J s, $\hbar = h/2\pi$

1. If the reaction $2HI \rightarrow H_2 + I_2$ is second order in HI, which plot is linear?
   (A) [HI] vs t
   (B) ln[HI] vs t
   (C) 1/[HI] vs t
   (D) 1/ln[HI] vs t
   (E) [HI]^2 vs t

2. For a reaction at constant pressure, the standard Gibbs energies at two temperatures are: $\Delta_r G^\circ(298\text{K}) = -12.0$ kJ mol^{-1}, $\Delta_r G^\circ(348\text{K}) = -5.0$ kJ mol^{-1}. Using the Gibbs–Helmholtz equation:
   $$\left(\frac{\partial(\Delta_r G^\circ/T)}{\partial T}\right)_P = -\frac{\Delta_r H^\circ}{T^2}$$
   what can be concluded about the sign of $\Delta_r H^\circ$? (assuming that $\Delta_r H^\circ$ does not depend on T)
   (A) $\Delta_r H^\circ = 0$
   (B) $\Delta_r H^\circ > 0$ (endothermic) and $\Delta_r H^\circ$ is around +54 kJ mol^{-1}
   (C) $\Delta_r H^\circ < 0$ (exothermic)
   (D) Cannot be inferred from $\Delta_r G^\circ(T)$
   (E) $\Delta_r H^\circ > 0$ (endothermic) and $\Delta_r H^\circ$ is around +5.4 kJ mol^{-1}

3. An enzyme follows Michaelis–Menten kinetics with $V_{max} = 120$ μM min^{-1} and $K_m = 30$ μM. What is the initial rate v_0 when the substrate concentration is $[S] = 30$ μM?
   A. 15 μM min^{-1}
   B. 30 μM min^{-1}
   C. 60 μM min^{-1}
   D. 90 μM min^{-1}
   E. 120 μM min^{-1}

4. A reaction proceeds by the mechanism:
   $A + B \overset{k_1}{\rightarrow} I$ (fast); $I + B \overset{k_2}{\rightarrow} P$ (slow); $I \overset{k_3}{\rightarrow} A$ (fast)
   Assuming the steady-state approximation for the intermediate I (i.e., $d[I]/dt \approx 0$), what is the rate law for product formation $r = \frac{d[P]}{dt}$ in terms of $[A]$ and $[B]$?
   (A) $r = k_2[A][B]$
   (B) $r = \frac{k_1 k_2 [A][B]^2}{k_2[B]+k_3}$
   (C) $r = \frac{k_1 k_2 [A][B]}{k_2[B]+k_3}$
   (D) $r = k_1[A][B]$
   (E) $r = k_2[I][B]$

5. At the same temperature, the ratio of root-mean-square speeds (u_{rms}) of helium ($M = 4.0$ g mol^{-1}) to nitrogen ($M = 28.0$ g mol^{-1}), i.e., u_{rms}(He) / u_{rms}(N_2), is closest to:
   (A) 0.38
   (B) 0.53
   (C) 1.0
   (D) 2.6
   (E) 7.0

6. For a reversible adiabatic expansion of an ideal gas:
   (A) $q = 0$ and $\Delta S_{sys} > 0$.
   (B) $q = 0$ and $\Delta S_{sys} = 0$.
   (C) $q < 0$ and $\Delta U = 0$.
   (D) $q = 0$ and $\Delta H = 0$.
   (E) $w = 0$ and $\Delta U < 0$.

7. The vapor pressure of a pure liquid is $P_1 = 20.0$ kPa at $T_1 = 300$ K. Its enthalpy of vaporization is approximately constant at $\Delta H_{vap} = 40.0$ kJ mol^{-1}. Using the Clausius–Clapeyron equation, what is the vapor pressure P_2 at $T_2 = 330$ K (closest value)?
   (A) 25 kPa
   (B) 33 kPa
   (C) 45 kPa
   (D) 60 kPa
   (E) 90 kPa

8. For an one-dimensional harmonic oscillator with force constant k and mass m, which statement is wrong?
   (A) $\omega = \sqrt{k/m}$.
   (B) Energy levels are equally spaced.
   (C) Zero-point energy is $\frac{1}{2}\hbar\omega$.
   (D) $\langle x \rangle = 0$ for every stationary state.
   (E) Each vibrational energy level is doubly degenerate.

9. Which function is not acceptable as an one quantum-mechanical wavefunction on $(-\infty, \infty)$?
   (A) $\psi(x) = Ae^{-|x|}$
   (B) $\psi(x) = A\sin(\pi x)\, e^{-x^2}$
   (C) $\psi(x) = A\frac{1}{1+x^2}$
   (D) $\psi(x) = Ae^{+x^2}$
   (E) $\psi(x) = A\, e^{-x^2/2}$

10. A vibrational mode can be approximated as a harmonic oscillator with energy spacing $\Delta E = h\nu$. At $T = 300$ K, for $\Delta E = 6.0$ kJ mol^{-1} and equal degeneracies, what is the ratio $N_{v=1}/N_{v=0}$?
    (A) 0.02
    (B) 0.06
    (C) 0.09
    (D) 0.22
    (E) 0.55

11. For a particle in an one-dimension box of width L with two infinite potential wells, which statement is incorrect?
(A) The energy eigenvalues scale as n^2
(B) The ground state has nonzero energy
(C) The wavefunction has $n-1$ interior nodes for level n
(D) If $L \to \infty$, the energy spectrum becomes continuous
(E) Shifting the box in space changes the energy eigenvalues

12. In the Born–Oppenheimer approximation as used in quantum chemistry, which statement is most accurate?
(A) Nuclear and electronic motions are treated with the same Hamiltonian and solved simultaneously.
(B) Nuclear motion is neglected entirely; only electrons are considered to exist.
(C) The total molecular wavefunction is approximated as a product of an electronic part and a nuclear part because nuclei move much more slowly than electrons.
(D) Electron–nuclear Coulomb interactions are ignored so that electrons move in a field of non-interacting nuclei.
(E) The approximation is only valid for atoms but not for molecules.

13. Which of the following ground-state electron configurations is incorrect according to the Aufbau principle, Hund's rule, and the Pauli exclusion principle?
(A) O: $1s^2\ 2s^2\ 2p^4$
(B) Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$
(C) Cl: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
(D) Fe: [Ar] $4s^2\ 3d^6$
(E) Cu: [Ar] $4s^2\ 3d^9$

14. Which Maxwell relation is correct?
(A) $\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$
(B) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
(C) $\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial P}{\partial T}\right)_S$
(D) $\left(\frac{\partial G}{\partial V}\right)_T = -T$
(E) $\left(\frac{\partial A}{\partial P}\right)_T = V$

15. A rate constant k_1 increases from 1.2×10^{-3} s^{-1} at 300 K to 4.8×10^{-3} s^{-1} at 330 K. Assuming Arrhenius behavior, the activation energy E_a is closest to:
(A) 9.5 kJ mol^{-1}
(B) 19 kJ mol^{-1}
(C) 38 kJ mol^{-1}
(D) 76 kJ mol^{-1}
(E) 150 kJ mol^{-1}

16. For the reaction $A \rightleftharpoons B$, the equilibrium constant is $K_1 = 2.0$ at $T_1 = 300$ K and $K_2 = 8.0$ at $T_2 = 330$ K. Assume $\Delta H°$ is temperature-independent over this range. Using the Van't Hoff equation, what is $\Delta H°$(closest value)?
(A) -20 kJ mol^{-1}

(B) -10 kJ mol^{-1}
(C) $+10$ kJ mol^{-1}
(D) $+20$ kJ mol^{-1}
(E) $+40$ kJ mol^{-1}

分析化學部分

(二)選擇題：(單選題，不可於試題紙上作答)
第 17-41 題，每題 2 分、共 50 分

17. Which of the following statements concerning laboratory safety is ***INCORRECT***?
(A) Safety goggles should be worn at all times in the laboratory.
(B) Chemical waste should be disposed of according to laboratory regulations.
(C) Concentrated acids should be diluted by adding water to acid.
(D) Safety data sheets (SDS) provide important information about chemical hazards.
(E) Spilled chemicals should be cleaned up immediately following proper procedures.

18. Which of the following statements is ***INCORRECT***?
(A) The number 1200 has two significant figures.
(B) The Q test is used to determine whether a suspected data point is an outlier in a small data set.
(C) Assuming a solution density of approximately 1.0 g/mL, 200 ppb Hg^{2+} is equivalent to 1.0 μM Hg^{2+}.
(D) The F test is used to compare the variances of two data sets to determine whether they are significantly different.
(E) $0.4\ (\pm\ 0.01) + 0.2\ (\pm\ 0.02) + 0.1\ (\pm\ 0.01) = 0.7\ (\pm\ 0.04)$

19. Which of the following statements concerning the operation of laboratory glassware in analytical experiments is ***INCORRECT***?
(A) An effective desiccant maintains a low humidity environment inside the desiccator.
(B) The volume of an Eppendorf pipet is set before aspirating the liquid.
(C) In water, the bottom of the meniscus should be read at eye level.
(D) Volumetric glassware is calibrated at a specific temperature.
(E) A buret should be rinsed only with distilled water before titration.

20. Which of the following statements concerning systematic errors and random errors is ***INCORRECT***?
(A) Random errors can be reduced by increasing the number of replicate measurements.
(B) Systematic errors cause measurement results to be consistently biased in one direction.
(C) Systematic errors can be detected and corrected by comparing with an reliable analytical technique.
(D) Carbonate formation in standardized NaOH solutions affects only the equilibrium speciation of basic species and therefore does not result in a true systematic error in acid–base titrations.
(E) The balance offset is a systematic error, and taring is the calibration step used to remove it.

21. The calibration curve for the determination of nitrate (NO_3^-) in agricultural runoff water using UV–visible spectrophotometry was found to be

$$A = 0.025 \times [NO_3^-] + 0.080$$

where A is the absorbance measured at 220 nm and the nitrate concentration is expressed in μM. The reagent blank produced an absorbance of 0.060 ± 0.010. Which of the following statements is ***INCORRECT***?

(A) According to the Beer–Lambert law, increasing the optical path length of the cuvette enhances absorbance sensitivity for a given analyte concentration.
(B) 0.080 represents the background absorbance arising from the reagent blank and the sample matrix.
(C) The coefficient of determination (R^2) can be greater than 1 when the calibration data show excellent linearity.
(D) The relative standard deviation of the reagent blank measurement is 16.7%.
(E) The limit of detection (LOD; signal to noise = 3) estimated from the blank standard deviation is 1.2 μM.

22. Which of the following statements concerning titration is ***INCORRECT***?
(A) During the titration of a weak acid with a strong base, the pH at the half-equivalence point is equal to the pK_a of the acid.
(B) In complexometric titrations, the conditional formation constant of the metal–EDTA complex depends on the solution pH.
(C) Iodine acts as a strong oxidizing agent in acidic, neutral, and basic media and is commonly used as a primary standard without further purification.
(D) In the Mohr method, potassium chromate is used as an indicator, and the titration must be carried out under slightly alkaline conditions.
(E) The addition of ammonia in the EDTA titration of Zn^{2+} is to prevent the precipitation of $Zn(OH)_2$.

23. Which of the following statements concerning amperometry and voltammetry is ***INCORRECT***?
(A) All working electrodes share the same oxidation and reduction potential window, which is determined solely by the electrolyte.
(B) In amperometric measurements, maintaining a constant applied potential allows selective monitoring of a specific redox reaction over time.
(C) Under diffusion-controlled conditions, the peak current in cyclic voltammetry is proportional to the square root of the scan rate.
(D) Pulse and differential pulse voltammetric techniques are designed to minimize charging current while enhancing faradaic current.
(E) Faradaic current in voltammetry is limited by mass transport via diffusion, migration, and convection.

24. Which of the following statements concerning potentiometry is ***INCORRECT***?
(A) In a pH meter, the pH is determined by measuring the absolute electrical potential of an indicator electrode
(B) The pH electrode uses a thin glass membrane that allows H^+ ions to pass through
(C) Potentiometric measurements are based on a two-electrode configuration consisting of an indicator electrode and a reference electrode.
(D) A high-impedance voltmeter is required to avoid drawing current during potentiometric measurements.
(E) The reference electrode provides a stable and reproducible potential.

25. Which of the following statements concerning X-ray radiation is ***INCORRECT***?
(A) X-ray photoelectron spectroscopy (XPS) determines the chemical states of elements.
(B) X-ray diffraction (XRD) is based on the constructive interference of monochromatic X-rays.
(C) Auger Electron Spectroscopy (AES) is extremely surface sensitive, typically probing the top 1–3 nm of a material.

(D) Chemical shifts observed in XPS spectra arise primarily from differences in lattice spacing and long-range crystal order.
(E) In the Auger effect, an electron fills an inner-shell vacancy and the released energy ejects a second electron.

26. Mass spectrometry plays a central role in diverse areas of chemistry for the characterization of chemical species. Which of the following statements is ***INCORRECT***?
(A) Mass spectrometry measures the mass-to-charge ratio (m/z) of ions rather than their absolute mass.
(B) High-resolution mass spectrometry allows the determination of elemental composition.
(C) Soft ionization techniques often produce intact molecular with minimal fragmentation.
(D) Isotopic patterns in mass spectra can be used to confirm molecular formulas.
(E) Electrospray ionization produces only singly charged ions regardless of molecular size.

27. Which of the following statements related to atomic spectroscopy is ***INCORRECT***?
(A) Atomic spectroscopy relies on electronic transitions of free atoms or atomic ions in the gas phase.
(B) X-ray fluorescence provides better detection limits than inductively coupled plasma mass spectrometry (ICP-MS) for trace elements.
(C) At higher plasma temperatures, a larger fraction of atoms occupies higher-energy excited states according to the Boltzmann distribution.
(D) Collision/reaction cell technology is used in ICP-MS to reduce spectral interferences.
(E) Graphite furnace atomic absorption spectroscopy provides higher sensitivity than flame AAS due to the longer residence time of atoms in the optical path.

28. Which of the following statements concerning matrix-assisted laser desorption ionization-time of flight-mass spectrometry (MALDI-TOF-MS) is ***INCORRECT***?
(A) MALDI-TOF-MS commonly detects analytes as protonated, such as $[M+H]^+$, rather than as bare molecular ions.
(B) Delayed extraction in MALDI-TOF-MS improves mass resolution by compensating for initial kinetic energy dispersion of the ions.
(C) MALDI-TOF-MS is well suited for the analysis of high-molecular-weight biomolecules.
(D) The matrix in MALDI serves only as an inert support and does not participate in the ionization process.
(E) In MALDI-TOF-MS, time-of-flight analysis separates ions based on their mass-to-charge ratio by measuring their flight times under a fixed accelerating potential.

29. Which of the following ***factors*** can enhance separation efficiency in chromatographic separations?
(i) Use of uniform stationary phase particle sizes
(ii) Operation at a flow rate close to the Van Deemter optimum
(iii) Thin stationary-phase film thickness
(iv) Slow diffusion coefficient of analytes in the stationary phase
(v) Use of a narrow internal-diameter column
(vi) Use of small packing particle sizes
(vii) Creation of a large detector cell (detection window)
(viii) Injection of a large sample volume
(A) (i), (ii), (iii), (iv)
(B) (i), (ii), (v), (vi)
(C) (iii), (iv), (vii), (viii)

(D) (ii), (v), (vi), (vii)
(E) (i), (iii), (vi), (viii)

30. Which of the following ***methods*** can be used for the separation of a mixture of Li^+, Na^+, and K^+, and NH_4^+ in real-world samples?
(i) Ion-exchange chromatography
(ii) Ion-pair chromatography
(iii) Ion-exclusion chromatography
(iv) Reversed-phase high-performance liquid chromatography
(v) Normal-phase high-performance liquid chromatography
(vi) Size-exclusion chromatography
(vii) Capillary zone electrophoresis
(A) i, ii, vii
(B) i, iii, iv
(C) ii, iv, v
(D) iii, vi, vii
(E) iv, v, vi

31. Which of the following statements concerning fluorescence is ***INCORRECT***?
(A) The fluorescence lifetime of small molecules is typically on the order of nanoseconds.
(B) The fluorescence quantum yield is dependent of excitation power under normal experimental conditions.
(C) Fluorescence occurs from the relaxation of an excited singlet state to the ground singlet state.
(D) Fluorescence emission generally occurs at a longer wavelength than the excitation light due to the Stokes shift.
(E) Fluorescence quenching can occur via dynamic or static mechanisms.

32. Which of the following statements concerning Raman is ***INCORRECT***?
(A) Raman scattering arises from changes in molecular polarizability during vibrational motion.
(B) The Stokes signal arises from inelastic photon scattering, producing a lower-energy shift relative to the excitation light.
(C) A bandpass filter is used to reject the intense Rayleigh-scattered light at the laser wavelength, allowing Raman-shifted signals to be detected.
(D) Raman scattering from Raman-active analytes increases with decreasing excitation wavelength.
(E) Raman scattering from Raman-active analytes is enhanced in the presence of silver nanoparticles due to surface-enhanced Raman scattering.

33. Which of the following statements concerning the ***advantages*** of Fourier transform infrared spectroscopy (FT-IR)?
(i) High signal-to-noise ratio due to the multiplex (Fellgett) advantage.
(ii) FT-IR provides higher spectral resolution solely by using narrower slits.
(iii) High wavenumber accuracy provided by an internal laser reference.
(iv) Photomultiplier tube detectors are commonly used in FT-IR spectroscopy.
(v) A sodium chloride window is commonly used in FT-IR spectroscopy
(A) (i), (iii), (v)
(B) (i), (ii), (iii)
(C) (ii), (iv)
(D) (i), (iv), (v)

(E) (iii), (iv)

34. An unknown volatile organic compound is analyzed by gas chromatography and is found to produce clear signals when detected using a thermal conductivity detector (TCD), an electron capture detector (ECD), and a nitrogen–phosphorus detector (NPD). Based on this information, which of the following elemental compositions is most likely present in the compound?
(A) Carbon, Chlorine, Hydrogen
(B) Carbon, Nitrogen, Bromine
(C) Carbon, Chlorine, Boron
(D) Carbon, Nitrogen, Chlorine
(E) Carbon, Oxygen, Sulfur

35. Which of the following statements concerning activity is ***INCORRECT***?
(A) With increasing ionic strength, the activity coefficient becomes smaller.
(B) An increase in the hydrodynamic radius of ions leads to a higher activity coefficient.
(C) In the absence of dissolved CO_2, the pH of water in 0.1 M NaCl is slightly higher than 7.0.
(D) The activity is defined as the product of the molar concentration and the activity coefficient.
(E) AgCl becomes more soluble in 0.1 M $NaNO_3$.

36. Which of the following statements concerning precipitation is ***INCORRECT***?
(A) The precipitation involves two steps, including nucleation and particle growth.
(B) In homogeneous precipitation, the precipitating species is produced gradually and uniformly within the bulk solution.
(C) The electrical double layer is composed of a charged surface and an oppositely charged ionic layer in the surrounding solution.
(D) The surface charge of the formed AgCl becomes negative when an excess amount of NaCl is added to a solution of $AgNO_3$.
(E) Large, well-formed crystals are obtained by maintaining high supersaturation.

37. Which of the following ***gradient*** techniques are most appropriately used in the respective chromatographic methods:
(i) gas chromatography (GC),
(ii) high-performance liquid chromatography (HPLC), and
(iii) supercritical fluid chromatography (SFC)?
(A) (i) Solvent composition gradient, (ii) Temperature gradient, and (iii) pH gradient
(B) (i) Temperature gradient, (ii) Solvent composition gradient, and (iii) Pressure gradient
(C) (i) Pressure gradient, (ii) pH gradient, and (iii) Temperature gradient
(D) (i) Flow-rate gradient, (ii) Temperature gradient, and (iii) Solvent composition gradient
(E) (i) Temperature gradient, (ii) Flow-rate gradient, and (iii) pH gradient

38. Which of the following statements concerning phosphorescence is ***INCORRECT***?
(A) Phosphorescence is the emission of light resulting from the spin-forbidden transition from an excited triplet state to the singlet ground state.
(B) The phosphorescence quantum yield depends on the efficiency of intersystem crossing.
(C) Heavy atoms enhance phosphorescence by increasing spin–orbit coupling and promoting intersystem crossing.
(D) Phosphorescence emission disappears immediately when the excitation source is removed.
(E) Intersystem crossing from an excited singlet state to a triplet state precedes phosphorescence.

39. Which of the following statements concerning microelectrode is ***INCORRECT***?
(A) Microelectrodes can provide high sensitivity because they have a large double-layer capacitance at the electrode–solution interface.
(B) Microelectrodes have at least one dimension in the micrometer range, resulting in enhanced mass transport by radial diffusion.
(C) Microelectrodes are well suited for fast cyclic voltammetry.
(D) Microelectrodes allow electrochemical measurements in solutions with high resistance and minimal supporting electrolyte.
(E) Microelectrodes exhibit reduced charging currents compared with conventional electrodes.

40. Which of the following statements concerning optical components is ***INCORRECT***?
(A) Lenses made of quartz are suitable for ultraviolet (UV) spectroscopy
(B) The resolution of a monochromator increases with narrower slits, higher grating groove density, longer focal length, and higher diffraction order.
(C) Laser operation does not require population inversion.
(D) An interference filter selectively transmits a narrow wavelength band using thin-film interference.
(E) Microelectrodes exhibit reduced charging currents compared with conventional electrodes.

41. Which of the following statements concerning extraction is ***INCORRECT***?
(A) The recovery of the extraction is defined as the ratio of the instrument signal after extraction to the signal before extraction.
(B) Extraction can effectively alleviate matrix effects.
(C) Methanol is added in supercritical fluid extraction (SFE) to facilitate the extraction of polar compounds such as ibuprofen.
(D) The suitable stationary phase of a solid-phase extraction cartridge for extracting tertiary amine drugs (e.g., lidocaine) is a strong cation-exchange sorbent.
(E) Lowering the pH of the solution enhances the extraction of propionic acid ($pK_a = 4.0$).

國立中山大學115學年度
碩士班考試入學招生考試試題

科目名稱：有機化學及無機化學【化學系碩士班】

—作答注意事項—

考試時間：100分鐘

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- 可否使用計算機請依試題資訊內標註為準，如「可以」使用，廠牌、功能不拘，唯不得攜帶書籍、紙張（應考證不得做計算紙書寫）、具有通訊、記憶、傳輸或收發等功能之相關電子產品或其他有礙試場安寧、考試公平之各類器材入場。
- **試題及答案卷（卡）請務必繳回，未繳回者該科成績以零分計算。**
- **試題採雙面列印，考生應注意試題頁數確實作答。**
- **違規者依本校招生考試試場規則及違規處理辦法處理。**

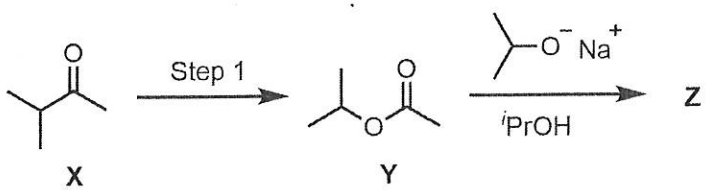
國立中山大學 115 學年度碩士班考試入學招生考試試題

科目名稱：有機化學及無機化學【化學系碩士班】　　題號：422001

※本科目依簡章規定「不可以」使用計算機(混合題)　　

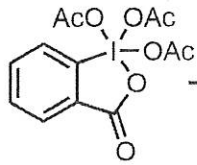
(一) 單選選擇題 (2% × 30 = 60%)

Consider the following scheme and answer questions 1 to 5:



1. Which of the following methods is NOT suitable for the synthesis of Compound **X**?

(A) 3-methylbut-1-yne $\xrightarrow[H_2SO_4]{HgSO_4,\ H_2O}$

(B) 3-methylbutan-2-ol + 

$\longrightarrow$

(C) methyl 2-methylpropanoate $\xrightarrow[2.\ H_3O^+]{1.\ CH_3MgBr}$

(D) acetonitrile $\xrightarrow[2.\ H_3O^+]{1.\ {}^iPrMgBr}$

(E) acetyl chloride $\xrightarrow[2.\ H_3O^+]{1.\ {}^iPr_2CuLi}$

2. How many peaks do you expect to see in the ^{1}H NMR of Compound **X** (assuming the peaks do not overlap with each other)?

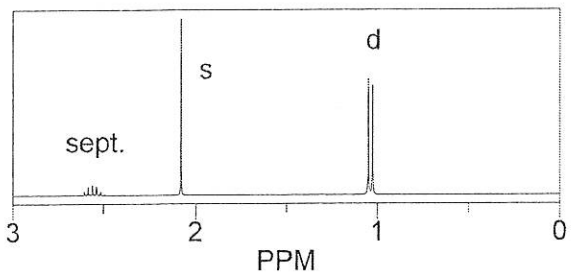
(A) 2 **(B)** 3 **(C)** 4 **(D)** 5 **(E)** 6

3. Which of the following would be suitable reagents in Step 1?

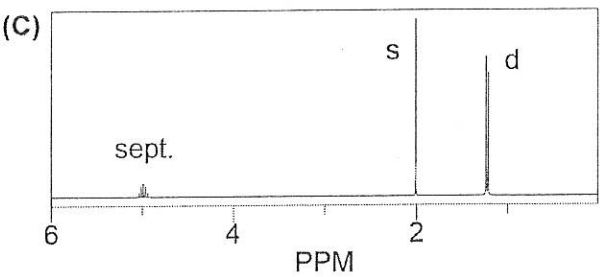
(A) i) $KMnO_4$, ii) isopropanol, concentrated HCl **(B)** i) $NaBH_4$, ii) CH_3COCl
(C) isopropanol, NaH **(D)** *m*-chloroperbenzoic acid **(E)** isopropanol, HCl

4. Which of the following would be the correct ^{1}H NMR of Compound **Y**?

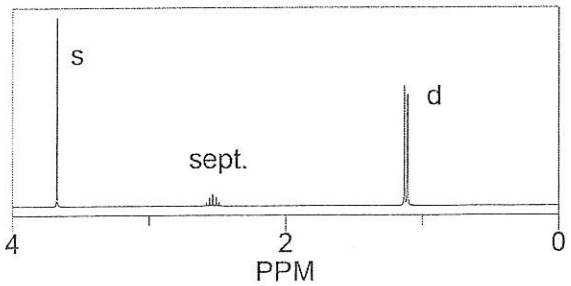
(A)



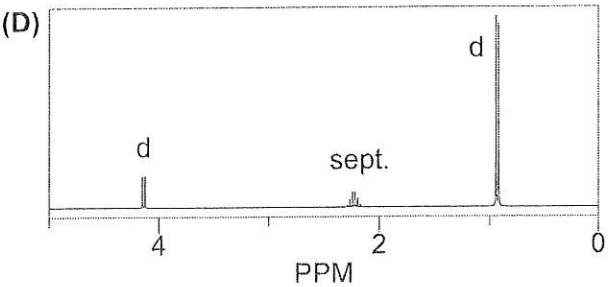
(C)



(B)

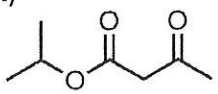
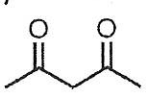
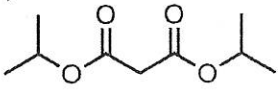
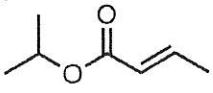
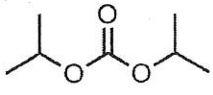


(D)

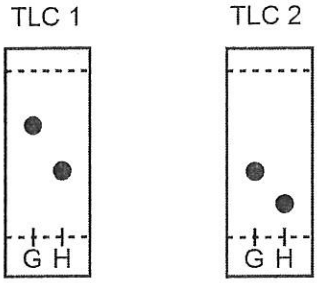


(E) None of the above is correct

5. What is the most likely structure of product **Z**?

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

6. Which of the following descriptions about the TLC analysis of Compound **G** and **H** (shown below) is incorrect?



(A) If "TLC 1" is a normal phase silica TLC plate, Compound **H** is more polar than Compound **G**.

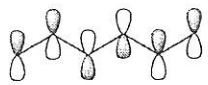
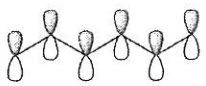
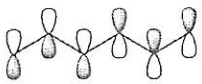
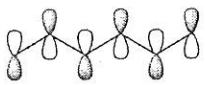
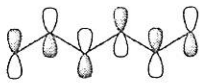
(B) If Compound **G** and **H** are analyzed again with a reverse phase silica TLC plate in EtOAc:*n*-hexane (3:2) then "TLC 2" could be the result.

(C) "TLC 2" could be the result of running a normal phase silica TLC plate with EtOAc:*n*-hexane (2:3).

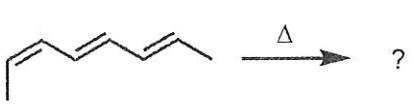
(D) The R_f values of both compounds would change if the TLC is run with different ratios of EtOAc and *n*-hexane.

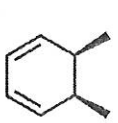
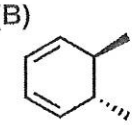
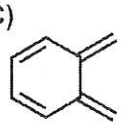
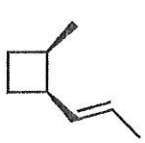
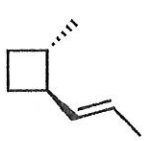
(E) All of the above are incorrect

7. The highest occupied molecular orbital (HOMO) of 1,3,5-hexatriene is:

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

8. What would be the major product of the following reaction?

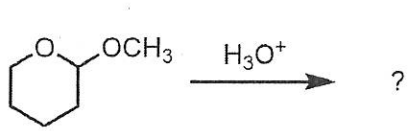


(A) 
(B) 
(C) 
(D) 
(E) 

9. The reaction in question 8 is classified as a …

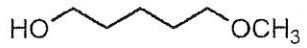
(A) [3,3] sigmatropic rearrangement **(B)** [6π] electrocyclization
(C) [4+2] cycloaddition **(D)** [2+2] cycloaddition **(E)** [3+3] cycloaddition

10. What would be the major product of the following reaction?

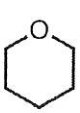


(A) 

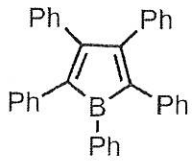
(B) 

(C) 

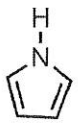
(D) 

(E) 

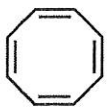
11. Which of the following is/are nonaromatic?

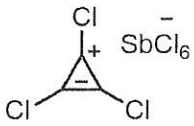


(1)



(2)


(3)

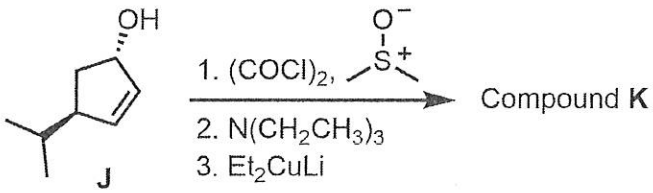


(4)


(5)

A) 1 and 2 **B)** 3 and 5 **C)** 3 **D)** 4 **E)** 4 and 5

Consider the following reaction scheme and answer questions 12 and 13:

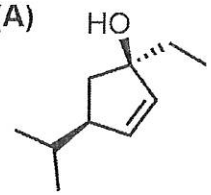


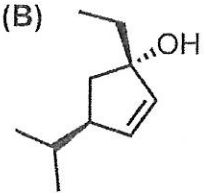
J

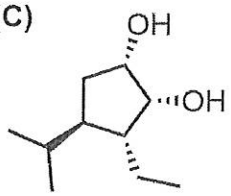
12. What is the complete systematic IUPAC name for Compound **J**?

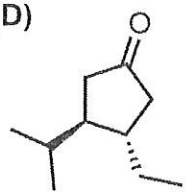
(A) (*1S,4R*)-1-hydroxy-4-isopropylcyclopent-2-ene
(B) (*1R,4S*)-1-hydroxy-4-isopropylcyclopent-2-ene
(C) (*1S,4R*)-4-isopropylcyclopent-2-en-1-ol
(D) (*1R,4R*)-4-isopropylcyclopent-2-en-1-ol
(E) (*1S,4R*)-1-isopropylcyclopent-2-en-4-ol

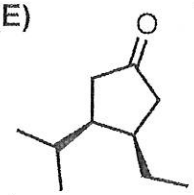
13. What is the most likely structure of Compound **K**?

(A) 

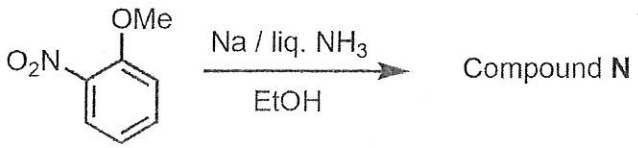
(B) 

(C) 

(D) 

(E) 

Consider the following reaction scheme and answer questions 14 and 15:



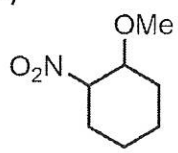
M

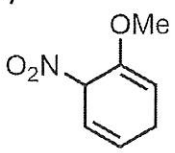
14. How would you use the following sets of reagents to synthesize Compound **M** from benzene (providing that ortho and para products can be separated)?

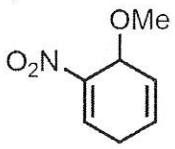
1) NaOMe, MeOH, heat　2) HNO_3, H_2SO_4　3) Cl_2, $FeCl_3$　4) $NaNO_2$, HCl

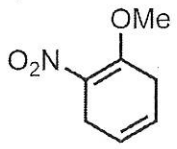
(A) 3 then 1 then 2　**(B)** 2 then 3 then 1　**(C)** 3 then 2 then 1
(D) 4 then 3 then 1　**(E)** 3 then 4 then 1

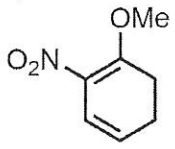
15. What is the most likely structure of Compound **N**?

(A) 

(B) 

(C) 

(D) 

(E) 

16. 18 electrons can generally be the most stable configuration for most organometallic compounds due to:

(A) electrons filling in antibonding orbitals in the molecular orbitals
(B) no electron filling in antibonding orbitals in the molecular orbitals
(C) electrons filling in non-bonding orbitals in the molecular orbitals
(D) no electrons filling in non-bonding orbitals in the molecular orbitals
(E) None of the above

17. What is the point group of a water molecule?

(A) C_{2v} **(B)** C_2 **(C)** C_{3v} **(D)** σ_d **(E)** None of the above

18. X-rays have a shorter wavelength than visible light?

(A) True **(B)** NOT True **(C)** No such thing called X-ray
(D) No such thing called visible light **(E)** None of the above

19. In a two-dimensional crystal lattice, which one of the following indices corresponds to the smallest density of lattice points?

(A) (10) **(B)** (13) **(C)** (21) **(D)** (11) **(E)** (41)

20. AgCl has a higher solubility than AgI, can be most likely explained by:

(A) dipole interaction **(B)** redox chemistry **(C)** Hard and Soft Acids and Bases
(D) corrosion chemistry **(E)** None of the above

21. The first time you are going to operate an unfamiliar high-temperature tube furnace (or a high-pressure autoclave), what would you do?

(甲) Just follow what senior lab members told me—after doing it once, I'll know how.
(乙) Read the SOP/manual first and confirm the safety limits (temperature, heating/cooling rate, atmosphere, pressure).

(丙) Perform a dummy run (blank run) to check that the temperature control and gas flow are functioning properly.
(丁) Set all parameters to the maximum to test the limits.
(戊) Verify ventilation, exhaust/effluent handling, emergency shutoff, and required personal protective equipment (PPE) in advance

(A) 乙丙戊 **(B)** 丙丁 **(C)** 甲丁戊
(D) 乙丁 **(E)** 甲乙丙丁戊

22. For a low-spin d^4 case, it is expected to show a stronger Jahn-Teller effect than that of high-spin one.

(A) True **(B)** NOT True **(C)** the same
(D) No such thing called Jahn-Teller effect **(E)** None of the above

23. Which of the following statements is **correct**?

(A) The concepts of labile/inert are thermodynamic concepts
(B) In octahedral complexes, weak field ligands in the spectrochemical series increase the Δ_o of the complexes.
(C) A metal with six d electrons in an octahedral configuration will be diamagnetic if high-spin.
(D) In the selection rules, transition between different spin multiplicities is forbidden
(E) All of the above

24. What is the formal name for $[Cu(NH_3)_4]SO_4$?

(A) tetraamminecopper(II) sulfide **(B)** tetraamminecopper sulfide
(C) fouramminecopper (II) sulfide **(D)** tetraamminecopper(II) sulfate
(E) None of the above

25. Which of the following theory models can explain that there are two lone pairs in a water molecule?

(A) Hard and Soft Acids and Bases
(B) Lewis structure model
(C) molecular orbital
(D) Le Chatelier's principle
(E) Ligand field theory

26. In a group meeting, you are asked a question that you do not know how to answer. What would you do?

(A) Talk your way out through bad chemicals.
(B) Be silent and wait until the meeting ends
(C) Change the subject
(D) Blame the instrument
(E) Admit that you do not know, explain how you would verify it or what additional experiments you would do, and report back next time with a careful data analysis.

27. As a new graduate student, you are about to begin a research project. Which of the following practices should you follow to get started?

(甲) Search and read the literature for one time
(乙) Keep searching and reading the literature all the time
(丙) The results and theory from the literature are always correct. I should not argue with them.
(丁) Always questioning the results published in scientific papers and in the literature
(戊) Before starting any experiment, form a logical expectation (hypothesis) for the outcome.

(A) 甲丁 **(B)** 乙丁戊 **(C)** 乙丁 **(D)** 丙戊 **(E)** None of the above

28. If a reaction suddenly cannot be repeated under your operation, what is your first step?

(A) Do other reactions or experiments, so my Professor will forget to ask me about it later
(B) Report to my professor, and he/she will tell me what to do next.
(C) Make a variable checklist (e.g., temperature, concentrations, solvent, reagent purity, atmosphere, stirring, equipment, and batch-to-batch differences), and then carefully check all the variables one after one until knowing what the problem is.
(D) Increase the temperature first to see whether it improves.
(E) None of the above

29. Which of the following statements regarding zeolite materials is **incorrect**?

(A) mainly octahedral frameworks
(B) mainly tetrahedral frameworks
(C) doping transition metals in the framework is possible
(D) selective catalysts for industry
(E) All of the above

30. What information is **not** provided by XPS (X-ray Photoelectron Spectroscopy) data?

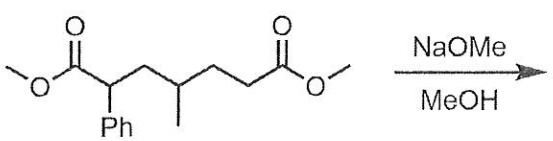
(A) oxidation states **(B)** binding energy **(C)** chemical environments
(D) crystallinity **(E)** All of the above

(二) 非選擇題 (共 40%)

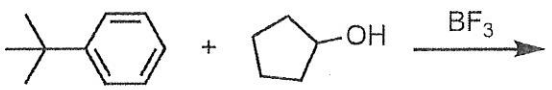
1. Explain why deuterated solvents are used in the sample preparation for measuring ^{1}H NMR? (2%)

2. Draw the major organic product for the following reactions. (12%)

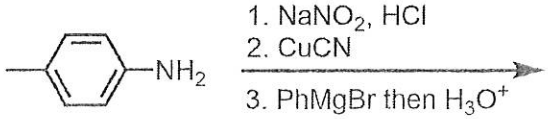
a)



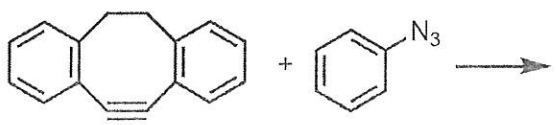
b)



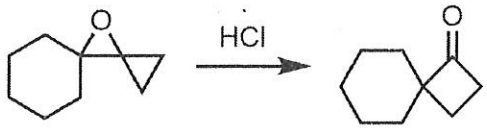
c)



d)



3. Draw a reasonable mechanism for the following transformation. (3%)



4. Provide a stepwise synthesis (give reagents) for the following transformation. (3%)

5. Cubic close packing (ccp) and hexagonal close packing (hcp) are two common closest-packed structures. Explain the key differences between ccp and hcp. (4%)

6. An unknown metal sample **X** (single phase, with no obvious segregation) was measured by powder XRD using Cu Kα radiation (λ=1.5406 Å). The observed peaks are listed below (background-subtracted). Detection limit: reflections with a relative intensity < 0.5% are considered not observable. (10%)

Peak	2θ	*d* spacing (Å)	d^2 (Å^2)	(*hkl*)
1	38.48	2.338	5.466	*x*
2	44.73	2.025	4.101	200
3	65.11	1.432	2.051	*y*
4	78.24	1.221	1.491	*z*

Here are the equations/information you may need below:

$2d\sin\theta = n\lambda$

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$

Simple cubic: all (*hkl*) reflections are allowed.
Body-centered cubic (bcc): reflections are allowed only when h+k+l is even.
Face-centered cubic (fcc): reflections are allowed only when h,k,l are all odd or all even.

Answer the following questions:

a) Please determine whether the unknown crystalline sample is simple cubic, face-centered cubic (fcc), or body-centered cubic (bcc). Explain your reasons.

b) Please give the possible (*hkl*) of *x*, *y*, and *z*.

c) If a very weak peak appears at 2θ=30.5° (relative intensity 1%), how would you determine whether it arises from a second/impure phase, or it still corresponds to a single phase, but the structure distortion from the ideal lattice? Please propose one additional check you would perform (e.g., adjust the scan conditions, perform XPS, use a different X-ray wavelength, etc.) to support your answer.

7. A molecular orbital diagram of a ML_6 octahedral complex with sigma-donor and pi-acceptor interaction is shown below. Please fill out all the square blank fields (**i - xx**) with the proper irreducible representation. You may need a character table below to complete this work. (6%) Please give your answer with the corresponding label of the empty field.

Note: sigma-donor symmetry representation: A_{1g}, T_{1u}, E_g
pi-acceptor symmetry representation: T_{1g}, T_{2g}, T_{1u}, T_{2u}

The figure credit: adapted from 5th Ed. "*Inorganic Chemistry*" by Gary L. Miessler

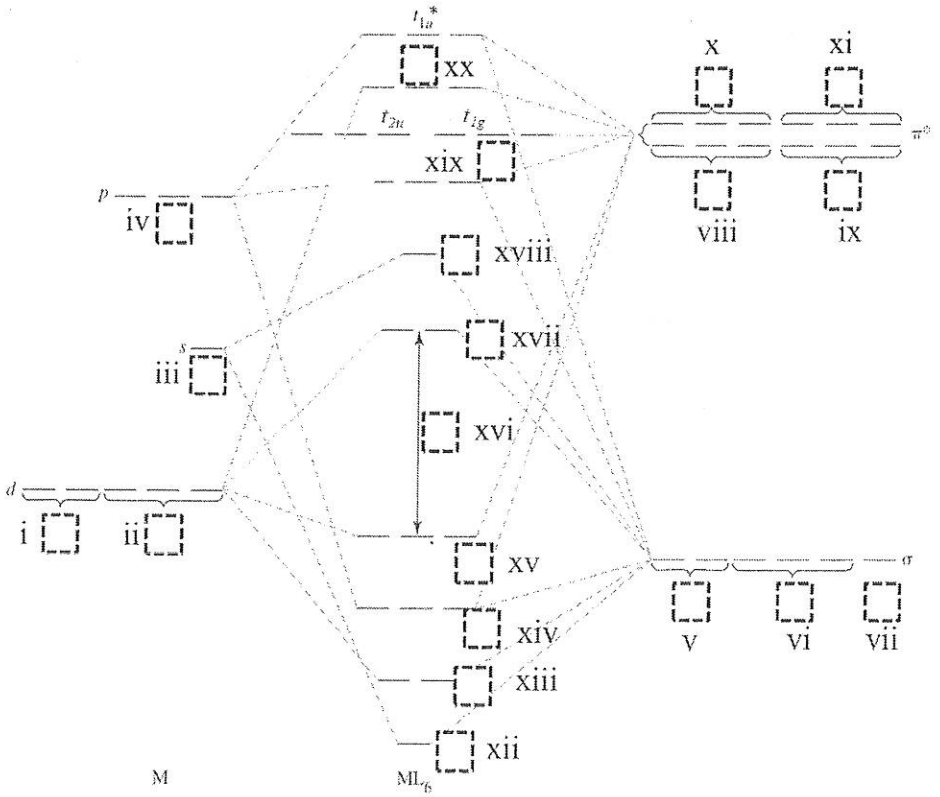


TABLE 10.4 Character Table for O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		