

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

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

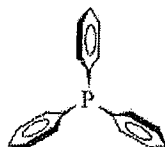
共 5 頁第 1 頁

I. 無機單選題 (3% x 10 = 30%)

1. How does the absorption band in the electronic spectra of complexes shift when the ligands I^- is replaced by Cl^- and CN^- respectively?
 (A) both blue shift (B) both red shift (C) no shift for both
 (D) blue shift for Cl^- and red shift for CN^- (E) red shift for Cl^- and blue shift for CN^-

2. How many species below (i~vi) may be chiral?

- (i) $[Ru(bipy)_3]^{2+}$ (ii) $CuCl_2(NH_3)_4$ (iii) O_2F_2
 (iv) Dichlorospiroheptane (v) PPh_3 (vi) $[PtHBrFI]^{2-}$



- (A) 1 (B) 2 (C) 3 (D) 4 (E) 5

3. Based on the D_{4h} character table below, please choose the correct statement:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(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	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x, y)	

- (A) The order for this point group is 12.
 (B) Orbital d_{yz} is antisymmetric upon C_2 rotation operation.
 (C) Irreducible representation E_u can be both IR and Raman active.
 (D) There are sixteen classes in this point group.
 (E) The dimension for E_g irreducible representation is 4.

4. Which trend is correct?

- (A) Acid strength: $BF_3 > BCl_3 > BBr_3$ (B) pK_a : $H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$
 (C) Hardness: $Cu^+ > Zn^{2+} > Fe^{3+}$ (D) Acidity: $HClO_4 > HClO_3 > HClO_2 > HClO$
 (E) N-B bond length: $Me_2NH \cdot BF_3 > MeNH_2 \cdot BF_3 > NH_3 \cdot BF_3$

5. Which of the following ion does not show inert pair effect?

- (A) Sn^{+2} (B) Bi^{+3} (C) Tl^{+1} (D) Ga^{+3} (E) Pb^{+2}

6. The predicted magnetic moment for $[NH_4]_2[CoF_4]$ is

- (A) 0 BM (B) 1.9 BM (C) 2.9 BM (D) 3.9 BM (E) 1.0 BM

7. Which of the following is not a suitable method to generate hydrogen gas?

- (A) cracking of petroleum hydrocarbons (B) reacting metals with acid
 (C) reacting hydrides with water (D) steam reforming of methane
 (E) electrolysis of pure water

背面有題

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

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

共 5 頁 第 2 頁

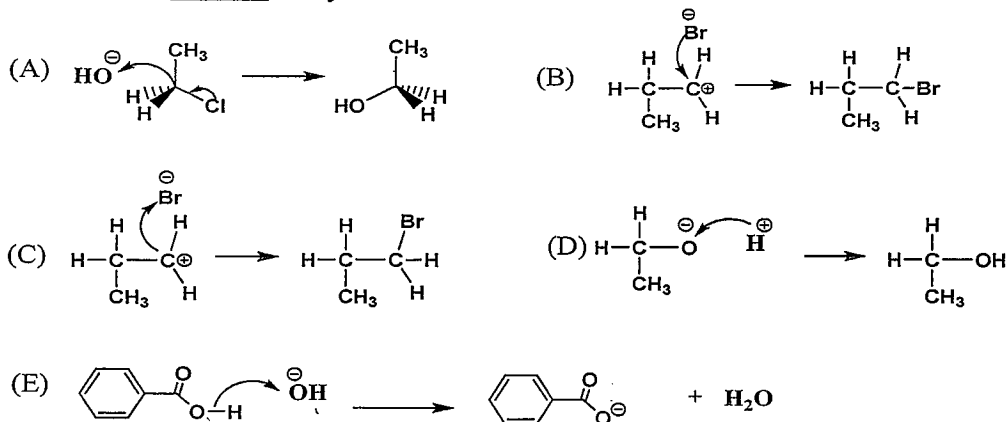
8. Which of the following has the shortest N-O bond length?
 (A) NO_3^- (B) NO^+ (C) NO_2^- (D) NO^- (E) NO
9. Choose the false statement below (Organometallic Chemistry):
 (A) The C=C stretching frequency in $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)\text{Cl}_3]^-$ is lower than that in free ethylene
 (B) $\text{Cr}(\text{NO})_4$ is isoelectronic with $\text{Ni}(\text{CO})_4$
 (C) The CO stretching frequency of terminal metal-CO is lower than that of the bridging CO
 (D) Among metallocenes of Fe, Co and Ni, ferrocene has the shortest M-C distance
 (E) The CO stretching frequency in $\text{Cr}(\text{CO})_6$ is higher than that of the $[\text{V}(\text{CO})_6]^-$
10. Choose the correct statement below (Solid State Chemistry):
 (A) Smaller quantum dots has larger band gap
 (B) Forward bias p-n junction has positive potential applied to the n-type side of the junction
 (C) Meissner effect exists above the critical temperature of the superconducting material
 (D) Fermi level is above the conduction band but lower than the valence band
 (E) Light emitting diode (LED) contains reverse bias junction

II. 無機問答題 (5% x 4 = 20%)

1. Please draw the three-dimensional structure for the following species:
 (A) $\mu\text{-amido-}\mu\text{-hydroxobis}(\text{tetraaminecobalt})(4+)$
 (B) $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$
2. Explain the difference in structure for BCl_3 and ICl_3 .
3. Write down the term symbols (with J specified) for d^8 ion and specify the ground state term. Explain briefly how you get your answer.
4. Even though the trend of covalent radii is $\text{N} > \text{O} > \text{F}$, the bonding distances in the corresponding diatomic molecules increase ($\text{N}_2 < \text{O}_2 < \text{F}_2$). Explain it in MO terms.

III. 有機單選題 (3% x 15 = 45%)

11. Which is the correct curly arrows for the reaction below?



12. Which of the following alkyl halides would undergo $\text{S}_{\text{N}}2$ reaction fastest?

- (A) $\text{CH}_3\text{CH}_2\text{-Br}$ (B) $\text{CH}_3\text{CH}_2\text{-Cl}$ (C) $(\text{CH}_3)_3\text{C-I}$ (D) $\text{CH}_3\text{CH}_2\text{-F}$ (E)

背面有題

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

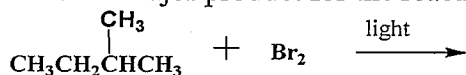
科目名稱：有機化學及無機化學【化學系碩士班】

題號：422001

※本科目依簡章規定「不可以」使用計算機

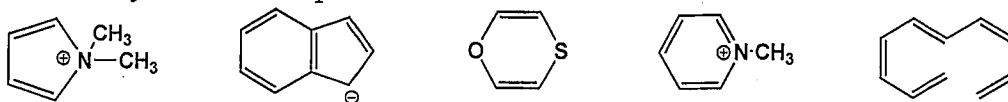
共 5 頁第 3 頁

13. What is the major product for the reaction below?



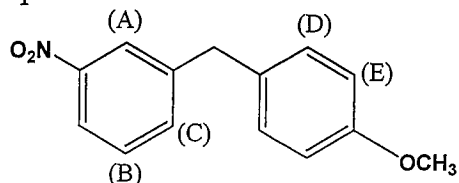
- (A) $\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{Br}$ (B) $\text{CH}_3\text{CH}_2\overset{\text{CH}_2\text{Br}}{\text{CH}}\text{CH}_2\text{Br}$ (C) $\text{CH}_3\text{CH}_2\overset{\text{CH}_3}{\underset{\text{Br}}{\text{C}}}\text{CH}_3$
- (D) $\text{BrCH}_2\text{CH}_2\overset{\text{CH}_3}{\text{CH}}\text{CH}_3$ (E) $\text{CH}_3\overset{\text{Br}}{\text{C}}\overset{\text{CH}_3}{\text{CH}}\text{CH}_3$

14. How many of these compounds are aromatic?



- (A) 1 (B) 2 (C) 3 (D) 4 (E) 5

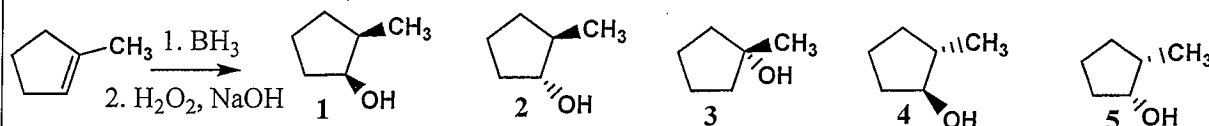
15. Which position is the most reactive towards electrophilic aromatic substitution?



16. Which compound below has chiral center?

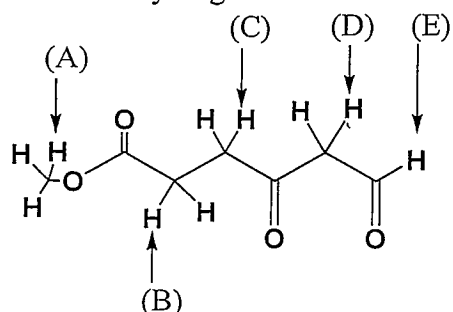
- (A) 2-methylpentane (B) 3-methylpentane (C) 2-methylhexane
(D) 3-methylhexane (E) methylcyclohexane

17. Choose the product(s) for the hydroboration of 1-methylcyclopentene



- (A) Equal mixture of 1 and 5 (B) Compound 3 (C) Equal mixture of 2 and 4
(D) Equal mixture of 4 and 5 (E) Equal mixture of 1 and 2

18. Which hydrogen in the molecule is most acidic?



國立中山大學 103 學年度碩士暨碩士專班招生考試試題

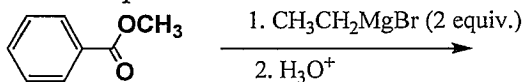
科目名稱：有機化學及無機化學【化學系碩士班】

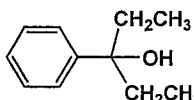
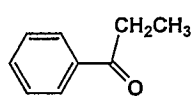
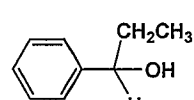
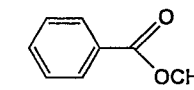
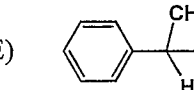
題號：422001

※本科目依簡章規定「不可以」使用計算機

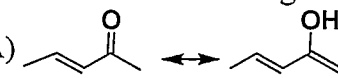
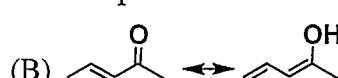

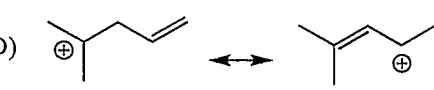
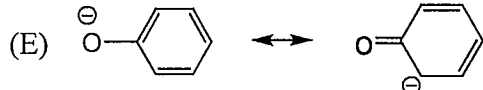
共 5 頁第 4 頁

19. What is the correct product for the reaction below:

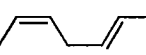
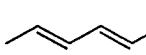
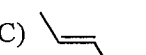




- (A)  (B)  (C) 
 (D)  (E) 

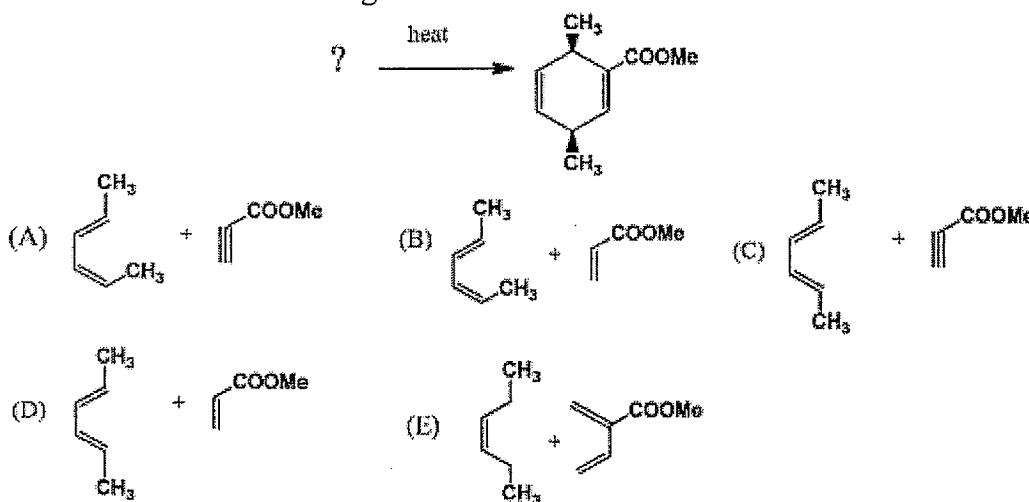
20. Which of the following can be consider a pair of resonance structure

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






21. Which structure below is (2Z,4E)-2,4-heptadiene

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

22. Which of the reactants will give the Diels-Alder reaction with the correct stereochemistry?



23. Which compound below is expected to contain a singlet peak at the proton NMR?

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

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

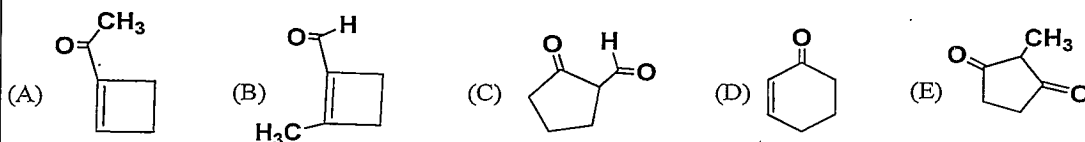
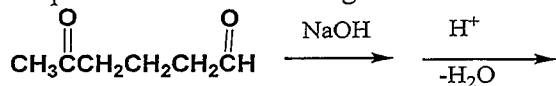
科目名稱：有機化學及無機化學【化學系碩士班】

題號：422001

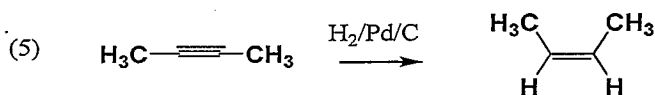
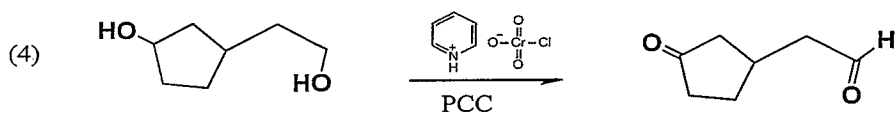
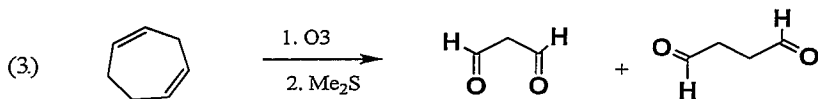
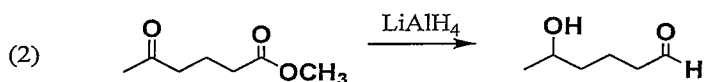
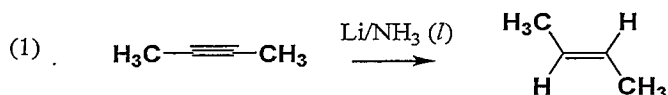
※本科目依簡章規定「不可以」使用計算機

共 5 頁第 5 頁

24. What is the product for the following aldol reaction followed by dehydration?

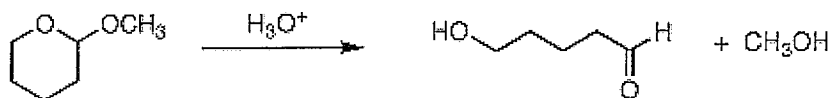


25. Which of the following reactions below give the correct major product(s).



(A) 1,5 (B) 2 (C) 1,5,2 (D) 1,3,4 (E) All the reactions

IV. 有機問答題 (5%) Give a clear mechanism for the reaction (use curved arrows)



-END-

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

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「不可以」使用計算機

共 5 頁第 1 頁

物理化學部分

(一) 選擇題，每題四分，共三十六分 (不可於試題紙上作答)

1. Which of the following is the smallest hole in a closest-packed lattice of spheres?
 - a. Trigonal
 - b. Tetrahedral
 - c. Cubic
 - d. Octahedral
 - e. None of these

2. Aluminum metal crystallizes in a face-centered cubic structure. The relationship between the radius of an Al atom (r) and the length of an edge of the unit cell (E) is :
 - a. $r = E/2$
 - b. $r = (\sqrt{2}/4) E$
 - c. $r = (\sqrt{3}/4) E$
 - d. $r = 2 E$
 - e. $r = 4 E$

3. Pure rubidium crystallizes in a body-centered cubic lattice; the edge length of the unit cell is 562 pm. The density of rubidium in g/cm^3 is
 - a. $2 \times 85.5 \times 6.02 \times (5.62)^3 \times 10^{-1}$
 - b. $\frac{4 \times 6.02}{10 \times (5.62)^3}$
 - c. $\frac{2 \times 85.5 \times 10}{6.02 \times (5.62)^3}$
 - d. $\frac{4 \times 85.5 \times 10}{6.02 \times (5.62)^3}$
 - e. $\frac{5 \times 85.5 \times 10}{6.02 \times (5.62)^3}$

4. If the reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ is second order, which of the following will yield a linear plot?
 - a. $\log [\text{HI}]$ vs time
 - b. $1/[\text{HI}]$ vs time
 - c. $[\text{HI}]$ vs time
 - d. $\ln[\text{HI}]$ vs time

5. What is the rate law for the following reaction, given the data below?
 $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$

Experiment	Initial [NO] (mol/L)	Initial [H ₂] (mol/L)	Initial Rate of Disappearance of NO (mol/L · s)
1	6.4×10^{-3}	2.2×10^{-3}	2.6×10^{-5}
2	12.8×10^{-3}	2.2×10^{-3}	1.0×10^{-4}
3	6.4×10^{-3}	4.5×10^{-3}	5.1×10^{-5}

a. Rate = $k[\text{NO}]$

背面有題

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

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「不可以」使用計算機

共 5 頁第 2 頁

- b. $\text{Rate} = k[\text{NO}]^2$
- c. $\text{Rate} = k[\text{NO}]^2[\text{H}_2]$
- d. $\text{Rate} = k[\text{NO}][\text{H}_2]$
- e. $\text{Rate} = k[\text{N}_2\text{O}][\text{H}_2\text{O}]$

6. The reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{O}_2(\text{g}) + 4\text{NO}_2(\text{g})$ is first order in N_2O_5 . For this reaction at 45°C , the rate constant $k = 1.0 \times 10^{-5} \text{s}^{-1}$, where the rate law is defined as

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]$$

For a particular experiment ($[\text{N}_2\text{O}_5]_0 = 1.0 \times 10^{-3} \text{M}$), calculate $[\text{N}_2\text{O}_5]$ after 1.0×10^5 seconds

- a. $5.0 \times 10^{-4} \text{M}$
 - b. $1.0 \times 10^{-3} \text{M}$
 - c. $3.7 \times 10^{-4} \text{M}$
 - d. 0
 - e. None of these
7. Which statement regarding water is true?
- a. Energy must be given off in order to break down the crystal lattice of ice to a liquid.
 - b. Hydrogen bonds are stronger than covalent bonds.
 - c. Liquid water is less dense than solid water.
 - d. Only covalent bonds are broken when ice melts.
 - e. All of the statements (a-d) are false.
8. Which is true about the vapor pressure of methane (CH_4) and ammonia (NH_3)?
- a. The vapor pressure of ammonia is greater than the vapor pressure of methane because ammonia is polar and methane is nonpolar.
 - b. The vapor pressure of ammonia is less than the vapor pressure of methane because ammonia is nonpolar and the methane is polar.
 - c. The vapor pressure of methane is greater than the vapor pressure of ammonia because methane has more hydrogen bonding than ammonia.
 - d. The vapor pressure of ammonia is equal to the vapor pressure of methane.
 - e. None of the above statements are true.
9. The density of the solid phase of a substance is 0.9 g/cm^3 and the density of the liquid phase is 1.0 g/cm^3 . A large increase in pressure will
- a. Lower the freezing point.
 - b. Raise the freezing point.
 - c. Lower the boiling point.
 - d. Raise the triple point.
 - e. Lower the triple point.

(二)計算題，共十四分(不可於試題紙上作答)

10. 2.50 mol of an ideal gas with $C_{v,m} = 12.47 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ is expanded adiabatically against a constant external pressure of 1.00 bar. The initial temperature and pressure of the gas are 325 K and 2.50 bar, respectively. The final pressure is 1.25 bar. Calculate the final temperature, q , w , ΔU , and ΔH . (五分)

11. The average bond enthalpy of the O-H bond in water is defined as one-half of the enthalpy change for the reaction $\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$. the formation enthalpies, ΔH_f° for $\text{H}(\text{g})$ and $\text{O}(\text{g})$ are 218.0 and

背面有題

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

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「不可以」使用計算機

共 5 頁第 3 頁

$249.2 \text{ kJ mol}^{-1}$, respectively, at 298.15 K , and ΔH_f° for $\text{H}_2\text{O}(\text{g})$ is $-241.8 \text{ kJ mol}^{-1}$ at the same temperature. (五分)

- Use this information to determine the average bond enthalpy of the O-H bond in water at 298.15 K .
- Determine the average bond energy, ΔU , of the O-H bond in water at 298.15 K . Assume ideal gas behavior.

12. What is the enthalpy of 1 mol of an ideal monatomic gas? (四分)

分析化學部分

(三)單擇題，每題兩分，共三十分(不可於試題紙上作答)

13. Which of the following statements are INCORRECT?

- $2 \text{ ppb Hg}^{2+} = 100 \text{ nM Hg}^{2+}$ (Atomic mass of Hg is 200 amu).
- $1 \text{ fM Hg}^{2+} = 1 \times 10^{-15} \text{ M Hg}^{2+}$.
- 20% w/v sugar solution = 20 g of sugar per 100 mL of solution.
- $1 \text{ ppt} = 1 \text{ nanogram per kilogram}$

14. To determine whether two standard deviations are significantly different from each other, which of the following tests should be conducted?

- t test
- F test
- Q test
- Y test

15. The diprotic acid H_2A has $\text{pK}_1 = 5.00$ and $\text{pK}_2 = 9.00$. Which of the following statements concerning 0.05 M NaHA are INCORRECT?

- The pH of 0.05 M NaHA is 7.0.
- $[\text{H}_2\text{A}] = 5 \times 10^{-4} \text{ M}$.
- $[\text{HA}^-] = 0.05 \text{ M}$.
- $[\text{A}^{2-}] = 5 \times 10^{-3} \text{ M}$.

16. The calibration curve equation for Cu standard was $I = 0.50 \times [\text{Cu}] + 4.00$, where I is the intensity and the Cu concentration is in micromole/L. The reagent blank gave value of 8.40 ± 1.18 . What is the detection limit for Cu based on a signal-to-noise ratio of 3?

- $7.08 \mu\text{M}$.
- $6.08 \mu\text{M}$.
- $5.08 \mu\text{M}$.
- $4.08 \mu\text{M}$.

17. Which of the following statements concerning titration are INCORRECT?

- EDTA titrations are best performed at low pH.
- When a weak base is titrated with a strong acid, the pH at the equivalence point is always smaller than 7.0.
- In iodimetry, starch can be added at the beginning of the titration.
- In iodometry, starch should not be added until immediately before the equivalence point.

背面有題

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

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「不可以」使用計算機

共 5 頁第 4 頁

18. Which of the following statements concerning voltammetry are INCORRECT?
- Current is measured while voltage between working electrode and reference electrode is varied.
 - A dropping mercury electrode is usually used to oxidize analyte.
 - Compared to linear scan voltammetry, square wave voltammetry offers the advantages of great speed and high sensitivity
 - Faradaic current arises from reduction or oxidation of analyte at the working electrode
19. Which of the following statements concerning capillary zone electrophoresis are INCORRECT?
- Peak broadening under ideal conditions is due to longitudinal diffusion.
 - Capillary zone electrophoresis allows uncharged analytes to be separated.
 - Electroosmotic flow is relatively small at low pH as compared to high pH.
 - Electroosmotic flow remains constant with increasing electric field strength.
20. Which of the following statements concerning surface spectroscopic methods are INCORRECT?
- X-Ray photoelectron spectroscopy provides information about oxidation state of analyte.
 - Auger electron spectroscopy uses either monochromatic Aluminum $K\alpha$ or nonmonochromatic Magnesium $K\alpha$ to eject a photoelectron from an atom at the sample's surface.
 - X-Ray photoelectron spectroscopy is a more qualitative than quantitative technique.
 - 10^{-8} to 10^{-9} Torr is the best when performing an Auger electron spectroscopy measurement.
21. You would like to resolve to mass signals at $m/z = 400.0$ and $m/z = 400.1$ in mass spectrometry. The minimum required resolution is
- 4000.
 - 5000.
 - 6000.
 - 7000.
22. The activity coefficients of H^+ and OH^- are 0.86 and 0.805 when the ionic strength is 0.05. The pH of water containing 0.05 M KCl at $25^\circ C$ is
- 7.00.
 - 7.02.
 - 6.98.
 - 4.00
23. Which of the following detector are the best for fixed gas analysis (O_2 , N_2 , CO , CO_2 , H_2S , NO , etc.) in gas chromatography?
- Flame ionization detector
 - Electron capture detector
 - UV-Visible absorbance detector
 - Thermal conductivity detector
24. Which of the following methods are the best for the separation of proteins ranging in molecular

背面有題

國立中山大學 103 學年度碩士暨碩士專班招生考試試題

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「不可以」使用計算機

共 5 頁第 5 頁

mass from 10000 to 60000?

- a. Ion-exchange chromatography
- b. Ion-pair chromatography
- c. Ion-exclusion chromatography
- d. Size exclusion chromatography

25. An increase in which of the following would decrease the resolution between two analytes?

- a. Particle size
- b. Column length
- c. Selectivity factor
- d. Retention factor

26. Which of the following statements concerning fluorescence are INCORRECT?

- a. A fluorescence emission spectrum is a plot of the fluorescence intensity versus wavelength (nanometers).
- b. A typical fluorescence lifetime is near 10 ns.
- c. The emission spectrum is typically a mirror image of the absorption spectrum of the $S_0 \rightarrow S_1$ transition.
- d. Emission spectra are typically dependent on the excitation wavelength.

27. Which of the following would increase Raman scattering signal of analytes?

- a. A decrease in the intensity of the source
- b. Analytes are adsorbed on the surface of colloidal metal particles.
- c. An increase in the wavelength of the source
- d. A decrease in the concentration of analytes.

(四)定義下列各項，每題四分，共二十分(不可於試題紙上作答)

- 28. Matrix-assisted laser desorption/ionization mass spectrometry.
- 29. Inductively coupled plasma atomic emission spectroscopy.
- 30. pH meter
- 31. Supercritical fluid extraction
- 32. Flow injection analysis