

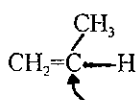
國立中山大學九十學年度碩博士班招生考試試題

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Part I Choose the best answer and one answer only. (35 x 2% = 70%)

1. The arrow in the structure points to a bond that is formed by

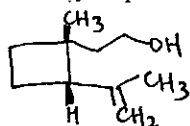


- a. overlap of H-s orbital and C-sp<sup>2</sup> orbital  
 b. overlap of H-s orbital and C-s orbital  
 c. overlap of C-s orbital and H-sp<sup>2</sup> orbital  
 d. overlap of H-s orbital and C-sp<sup>3</sup> orbital

2. The reaction  $\text{CH}_4 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{HCl}$  is an example of

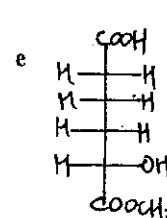
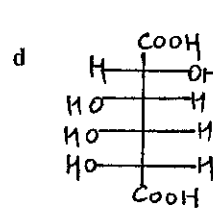
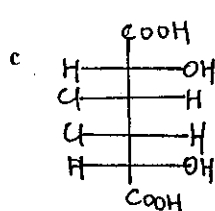
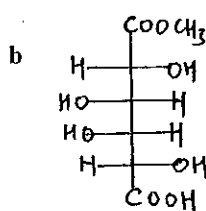
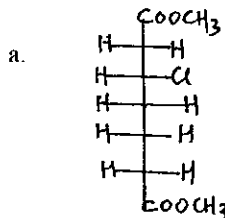
- a. neutralization    b. isomerization    c. radical reaction    d. ionic reaction    e. S<sub>N</sub>1 reaction.

3. How many isoprene unit does grandisol has

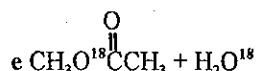
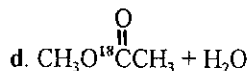
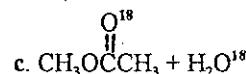
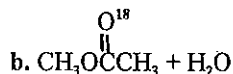
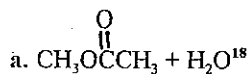


- a. one    b. two    c. three    d. four    e. five

4. Which compound is not optically active



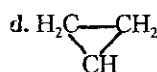
5. The product for the ester formation between  $\text{MeO}^{18}\text{H}$  and  $\text{CH}_3\text{COOH}$  is best illustrated by



6. Which is the best method for preparing the ether  $(\text{CH}_3)_3\text{COCH}_3$

- a.  $\text{CH}_3\text{Br} + (\text{CH}_3)_3\text{CO}^-\text{K}^+$     b.  $(\text{CH}_3)_3\text{COH} + \text{CH}_3\text{MgBr}$     c.  $(\text{CH}_3)_3\text{CMgBr} + \text{CH}_3\text{OH}$     d.  $\text{CH}_3\text{O}^-\text{K}^+ + (\text{CH}_3)_3\text{CBr}$

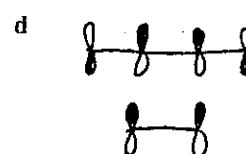
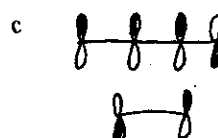
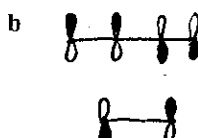
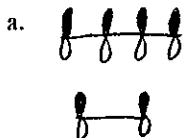
7. One of the following compounds will show a doublet as part of its <sup>1</sup>H NMR spectrum. Which one?



8. Which reaction below will give a different product for the reaction of trans-3-hexene and cis-3-hexene

- a. hydrogenation    b. ozonolysis    c. Br<sub>2</sub> addition    d. none of the above

9. Which diagram below illustrate the HOMO and LOMO interaction of butadiene and ethylene respectively



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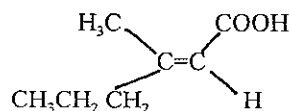
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10. The species that is not aromatic according to Huckel rule is

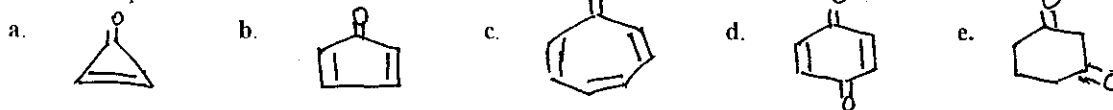


11. What is the IUPAC name of the compound shown

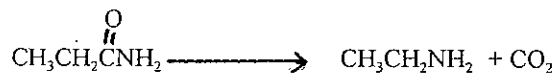


- a. (E)-3-methyl-2-hexanoic acid      b. (E)-3-propyl-2-butenoic acid  
c. (E)-3-methyl-2-hexenoic acid      d. (Z)-3-methyl-2-hexenoic acid

12. Which compound below is most unstable



13. Identify the best conditions for the following transformation



- a.  $\text{H}_2/\text{Pd}/\text{C}$       b. excess  $\text{CH}_3\text{I}, \text{K}_2\text{CO}_3$       c.  $\text{Br}_2, \text{NaOH}, \text{H}_2\text{O}$       d.  $\text{LiAlH}_4$       e.  $\text{NH}_2\text{NH}_2, \text{NaOH}$

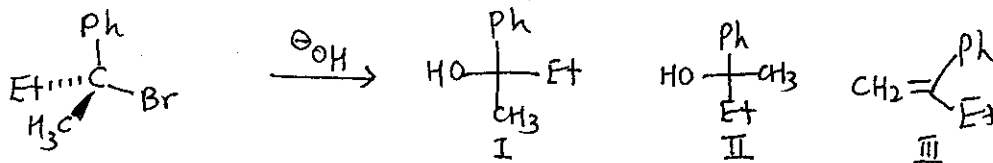
14. Which of the following correctly lists the conformation of cyclohexane in order of increasing energy

- a. chair < boat < twist < half-chair      b. chair < twist < boat < half-chair      c. half chair = boat < twist < chair  
d. chair < twist < half-chair < boat      e. half-chair < chair < boat < twist

15. Which of the following reagent should be used to convert 3-hexyne to (E)-3-hexene

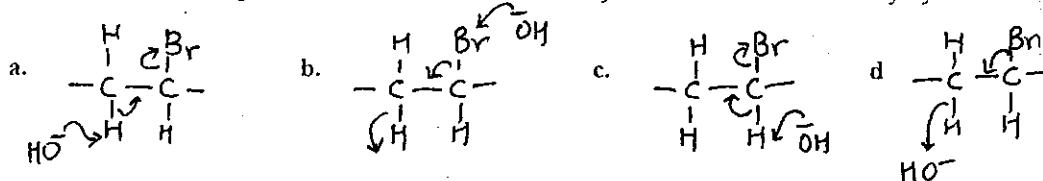
- a.  $\text{NH}_3(\text{l}), \text{Na}$       b.  $\text{H}_2/\text{Pd}/\text{C}$       c.  $\text{H}_2/\text{Pd}/\text{BaSO}_4/\text{quinoline}$       d.  $\text{HgSO}_4/\text{H}_2\text{O}$       e.  $\text{H}_2/\text{Ni}/\text{C}$

16. If the reaction below was  $\text{S}_{\text{N}}2$ , the organic product would be



- a. I only      b. I and II      c. I, II and III      d. II only      e. III only

17. Which of the following mechanism is correct for the dehydrobromination reaction by hydroxide ion

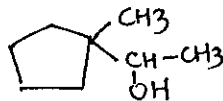


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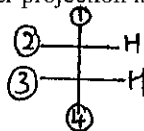
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18. The reaction below yield a product ( $C_8H_{14}$ ) which contain no cyclopentane ring. What is the product?



- a. cyclooctene    b. 1,2-dimethylcyclohexene    c. 1-octyne  
d. 3,3-dimethylcyclohexene    e. 1,2,3,4-tetramethylcyclobutene

19. The Fisher projection is a representation for (2S, 3S)-2,3-dichloropentane. The identity of 1, 2, 3, 4 is



- a. 1 = Cl, 2 = Et, 3 = Cl, 4 = Me    b. 1 = Et, 2 = Cl, 3 = Cl, 4 = Me  
c. 1 = Cl, 2 = Et, 3 = Me, 4 = Cl    d. 1 = Cl, 2 = Me, 3 = Cl, 4 = Et

20. An alkene  $C_{10}H_{20}$  yield a mixture of 2-pentenone and 3-pentenone when treated with ozone ( $O_3$ ) followed by  $Me_2S$ . The alkene  $C_{10}H_{20}$  is

- a. 1-methyl-2-propylcyclopentene    b. 1,2-dimethylcyclopentene    c. 3-pentene  
d. 3-ethyl-4-methyl-3-heptene    e. (E)-3,4-dimethyl-3-hexene

21. Which of these alcohols will reactive with Lucas reagent (conc.  $HCl/ZnCl_2$ )?

- a. 1-propanol    b. ethanol    c. phenol    d. methanol    e. benzyl alcohol

22. Which reagent is can convert cyclobutanone to cyclopentanone

- a.  $CH_2N_2$     b.  $CO/Pd$     c.  $CH_3MgBr$     d.  $CH_3Br$     e.  $HCHO$

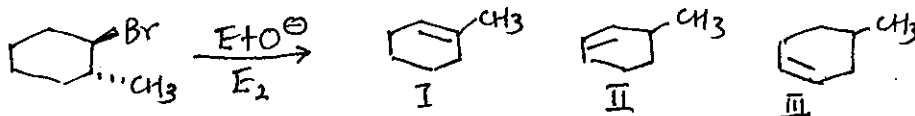
23. How many hydrogen atoms are present in bicyclo[2.2.2]octa-2,3,7-triene?

- a. 6    b. 8    c. 10    d. 12    e. 14

24. Which compound has the most acidic hydrogen atom in the molecule?

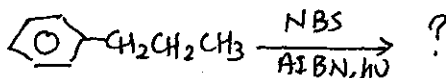
- a. cyclobutane    b. cyclobutene    c. cyclopentadiene    d. cyclopropene    e. benzene

25. Predict the major product for the reaction below



- a. I    b. II    c. III    d. I and II    e. I, II and III.

26. What would be the major for the following reaction



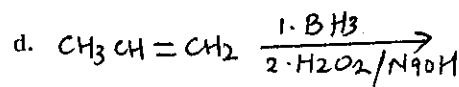
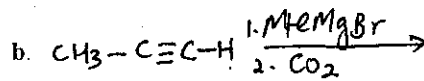
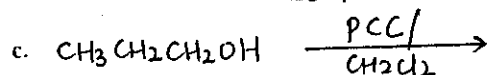
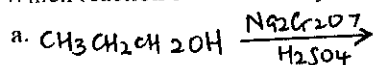
- a.    b.    c.    d.    e.

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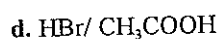
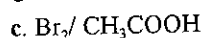
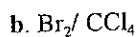
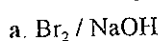
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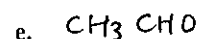
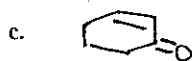
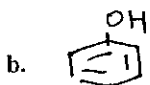
27. Which reaction below would yield propanal



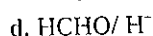
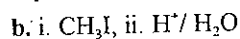
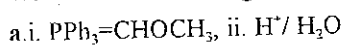
28. Acetone may be monobromination using which reagent below



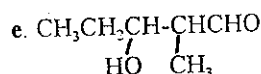
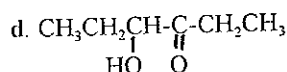
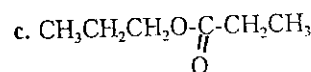
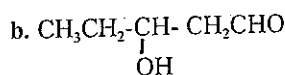
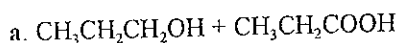
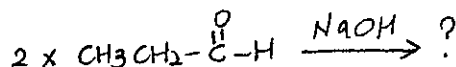
29. Which of the following compound is expected to show intense IR absorption at  $1689\text{cm}^{-1}$



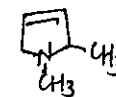
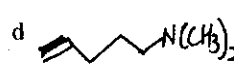
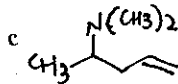
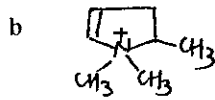
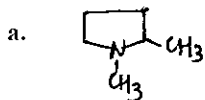
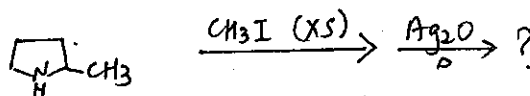
30. Which of the following reagent will give phenylacetaldehyde ( $\text{PhCH}_2\text{CHO}$ ) from benzaldehyde ( $\text{PhCHO}$ )



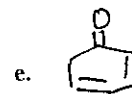
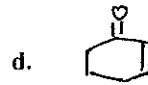
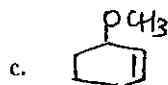
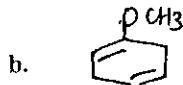
31. What is the major product for the following reaction



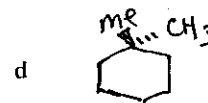
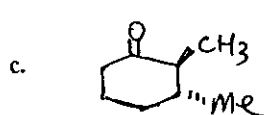
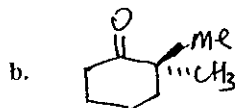
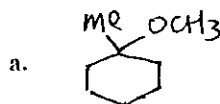
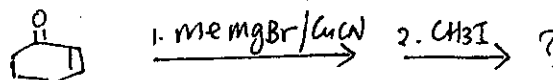
32. What is the major product for the reaction



33. Which is the correct product for the Birch reduction of methoxybenzene ( $\text{CH}_3\text{OC}_6\text{H}_5$ )



34. The major product for this reaction would be



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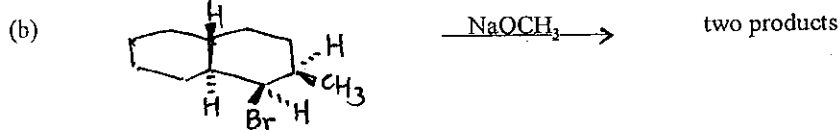
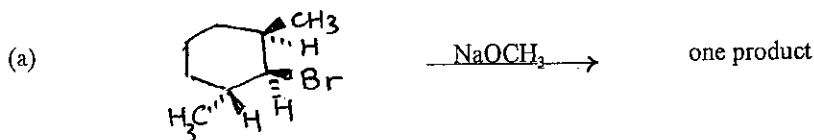
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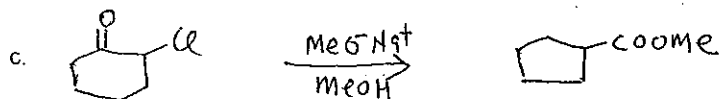
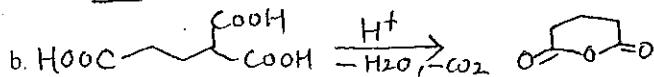
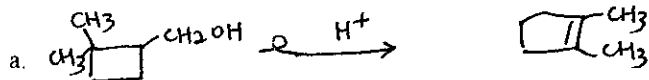
- 35 Which compound below will undergo nitration most rapidly using  $\text{HNO}_3/\text{H}_2\text{SO}_4$   
 a. aniline    b. benzene    c. benzoic acid    d. toluene    e. benzaldehyde

Part II. Answer the following questions below

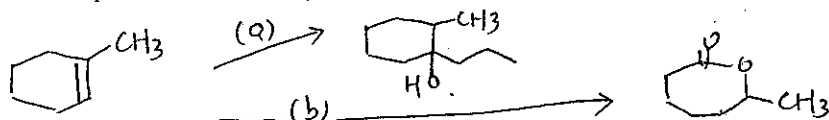
1. Give the expected product(s) for the  $\text{E}_2$  elimination for each reaction and explain your answer. (2 x 3%)



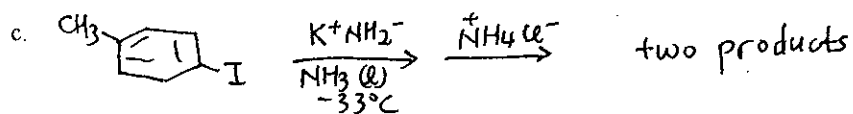
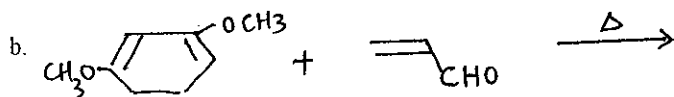
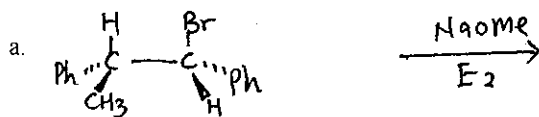
2. Give a mechanism for the following reaction below (3 x 3%)



3. How would you accomplish the following transformation below, showing all the steps and reagents (6%)



4. Complete the following reaction, showing stereochemistry. (3 x 3%)



國立中山大學九十學年度碩博士班招生考試試題

科目：無機化學【化學系碩士班】

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Inorganic Chemistry

- (1) (12%) For the molecule  $\text{PCl}_5$ :
- (a) Determine the possible type(s) of hybrid orbitals that can be used by P in forming  $\sigma$  bonds to the five Cl atoms.
  - (b) What type(s) of hybrids can be used in bonding to the axial chlorines? to the equatorial chlorines?
  - (c) Illustrate the energy splitting of the five d orbitals in  $\text{PCl}_5$ .
  - (d) Considering your answer to part b, explain the experimental observation that the axial P-Cl bonds (219 pm) are longer than the equatorial bonds (204 pm).
- (2) (25%) The CO stretching frequencies for  $\text{V}(\text{CO})_6^-$ ,  $\text{Cr}(\text{CO})_6$ , and  $\text{Mn}(\text{CO})_6^+$  are 1859, 1981, and  $2101 \text{ cm}^{-1}$ , respectively. Draw the MO diagram of CO molecule and illustrate the formation of metal-CO bonding.
- (3) (14%) If  $\pi$  bonding between Si and the lone pairs of N is important, what difference in structure between  $\text{N}(\text{SiH}_3)_3$  and  $\text{N}(\text{CH}_3)_3$  do you expect? Which one is a stronger base?
- (4) (12%) Heating  $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$  with NaH in solution gives A, which has empirical formula  $\text{C}_7\text{H}_6\text{O}_2\text{Fe}$ . A reacts rapidly at room temperature to eliminate a colorless gas B, forming a purple-brown solid C having empirical formula  $\text{C}_7\text{H}_5\text{O}_2\text{Fe}$ . Treatment of C with iodine generates a brown solid D of empirical formula  $\text{C}_7\text{H}_5\text{O}_2\text{FeI}$ , which on treatment with  $\text{TiCl}_4$  gives a solid E of formula  $\text{C}_{12}\text{H}_{10}\text{O}_2\text{Fe}$ . E, on heating, gives off a colorless gas, leaving an orange solid F of formula  $\text{C}_{10}\text{H}_{10}\text{Fe}$ . Propose structural formulas for A through F.
- (5) (12%) Explain and predict the molecular geometry including expected distortions:
- (a)  $[\text{ICl}_4]^-$
  - (b)  $[\text{TeF}_5]^-$
  - (c)  $\text{SOF}_4$
  - (d)  $\text{XeF}_4$
  - (e)  $[\text{NO}_2]^-$
  - (f)  $[\text{NO}_2]^+$
- (6) (25%) Sample of  $\text{Fe}(\text{CO})_5$  has IR spectra consistent with a TBP structure with distinct axial and equatorial CO groups. However, when studied by  $^{13}\text{C}$  NMR a single resonance line is observed, indicating that the five CO groups are identical. Why?

# 國立中山大學九十學年度碩博士班招生考試試題

科目：物理化學【化學系碩士班】

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1. (50 %)

Briefly describe one experiment for each of the following categories. To each experiment, (1) first state the purpose and the principle of the experiment, including the equations involved, (2) then draw a diagram of the experimental apparatus, (3) then draw a diagram of the experimental data collected, and 4) finish by describing how the physical property can be deduced from the data.

- (a) Solutions or phase equilibria
- (b) Chemical kinetics
- (c) Spectra and molecular structure

2. (50 %)

以下任選十題作圖，如超過十題，只批改前十題。未標出座標者以零分計。

Draw diagrams for ten of the followings. To each figure, label the axes, the areas, the points, the lines, etc., when appropriate.

- (a) Blackbody radiation at three temperatures
- (b) Speed distribution function at three temperatures
- (c) Kinetic energy distribution function for three different gases at 300K
- (d) An Arrhenius plot
- (e) A portion of a pure rotational spectrum
- (f) Schematic diagram of a crossed-molecular-beam apparatus
- (g) Contour map of the H + H<sub>2</sub> potential-energy-surface
- (h) Normal vibrational modes of H<sub>2</sub>O
- (i) Radial distribution functions for 1s and 2s H-atom orbitals
- (j) Wave functions for the lowest three particle-in-a-box states
- (k) Isotherms of H<sub>2</sub>O at three temperatures
- (l) Pressure-versus-composition liquid-vapor phase diagram for an ideal solution at fixed T
- (m) Temperature-versus-composition liquid-vapor phase diagram for an ideal solution at fixed pressure
- (n) Triangular coordinate system used in ternary phase diagrams

-----END OF EXAM.-----

國立中山大學九十學年度碩博士班招生考試試題

科目：分析化學【化學系碩士班】

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Analytical Chemistry

1. A student obtained the following percentages of manganese in a steel: 1.01, 0.95, 0.99, 1.05, 1.06, 0.94, 0.85 and 1.05.
  - (a) At the 95% confidence level, could any of the results be discarded?
  - (b) Calculate the mean.
  - (c) Calculate the standard deviation.
  - (d) Calculate the 95% confidence limits of the mean.Please show your calculation. (10%)
2. Describe the preparation of 100 mL of 1.00 M  $\text{HNO}_3$  from a concentrated solution that has a specific gravity of 1.42 and is 70.5% (w/w)  $\text{HNO}_3$  (63.0 g/mol). (8%)
3. How many grams of ammonium chloride and how many milliliters of 3.00 M NaOH should be added to 200 mL of water and diluted to 500 mL to prepare a buffer of pH 9.50 with a salt ( $\text{NH}_4\text{Cl}$ ) concentration of 0.100 M?  $K_{b,\text{NH}_3} = 1.75 \times 10^{-5}$ . (8%)
4. Calculate the theoretical potential for the following cells. Indicate whether the cell, as written, is galvanic or electrolytic.  
 $\text{Pd}/\text{Pd}^{2+} (0.0300 \text{ M}) // \text{Ag}^+ (0.120 \text{ M}) / \text{Ag}$   
 $E_{\text{Pd}^{2+}}^\circ = 0.987 \text{ V}$ ,  $E_{\text{Ag}^+}^\circ = 0.799 \text{ V}$ . (10%)
5. The chelate  $\text{CuA}_2^{2-}$  exhibits maximum absorption at 480 nm. When the chelating reagent is present at least a tenfold excess, the absorbance is dependent only upon the analytical concentration of  $\text{Cu(II)}$  and conforms to Beer's law over a wide range. A solution in which the analytical concentration of  $\text{Cu}^{2+}$  is  $2.30 \times 10^{-4} \text{ M}$  and that for  $\text{A}^{2-}$  is  $8.60 \times 10^{-3} \text{ M}$  has an absorbance of 0.690 when measured in a 1.00-cm cell at 480 nm. A solution in which the analytical concentrations of  $\text{Cu}^{2+}$  and  $\text{A}^{2-}$  are  $2.30 \times 10^{-4} \text{ M}$  and  $5.00 \times 10^{-4} \text{ M}$ , respectively, has an absorbance of 0.580 when measured under the same conditions. Use this information to calculate the formation constant  $K_f$  for the process  
$$\text{Cu}^{2+} + 2\text{A}^{2-} \rightleftharpoons \text{CuA}_2^{2-} \quad (10\%)$$
6.
  - (a) Why is atomic emission more sensitive to flame instability than atomic absorption or fluorescence?
  - (b) Why are ionization interferences less severe in ICP than in flame emission spectrometry? (10%)
7. Explain the difference between a fluorescence emission spectrum and a fluorescence excitation spectrum. Which more closely resembles an absorption spectrum? Explain. (8%)
8.
  - (a) What are the advantages of a Fourier transform infrared spectrometer compared with a dispersive instrument?
  - (b) Many UV-Vis spectrophotometers are single-beam instruments, but it is generally not practical to have single-beam infrared spectrophotometers. Explain why. (12%)
9. Define (a) plate height (b) selectivity factor (c) longitudinal diffusion (d) gradient elution in liquid chromatography. (16%)
10. What is the principle of separation by capillary zone electrophoresis? (8%)



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科目：分析化學【化學系碩士班】

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Critical Values for the Rejection Quotient  $Q^*$

Number of Observations	$Q_{crit}$		
	90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

\*Reproduced from D. B. Rorabacher, *Anal. Chem.*, 1991, 63, 139. By courtesy of the American Chemical Society.

Values of  $t$  for Various Levels of Probability

Degrees of Freedom	Factor for Confidence Interval				
	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.60
5	1.48	2.02	2.57	4.03	6.86
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.40
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59
11	1.36	1.80	2.20	3.11	4.44
12	1.36	1.78	2.18	3.06	4.32
13	1.35	1.77	2.16	3.01	4.22
14	1.34	1.76	2.14	2.98	4.14
$\infty$	1.29	1.64	1.96	2.58	3.29