

I Choose the best answer and one answer only (75%; 3% each)

1. Triethylamine $[(CH_3CH_2)_3N]$ is a molecule in which the nitrogen atom is _____ hybridized and the CNC bond angle is _____.

- A. sp^2 , $>109.5^\circ$ B. sp^2 , $<109.5^\circ$ C. sp^3 , $>109.5^\circ$ D. sp^3 , $<109.5^\circ$ E. sp , 109.5°

2. Which of the following ketones below will give a positive iodoform test?

- A. 4-heptanone B. 3-hexanone C. 2-hexanone D. cyclohexanone E. 2-methyl-3-pentanone

3. The reasonable route to prepare butanal from butanoic acid:

- A. 1. $LiAlH_4$ 2. PCC B. 1. $LiAlH_4$ 2. $KMnO_4$ C. 1. $MeOH/H^+$ 2. $LiAlH_4$ D. 1. $NaBH_4$ 2. MnO_2
E. 1. PCC 2. $NaBH_4$






4. What reagent can be used for the conversion of cyclohexanone to cyclohexane?

- A. $LiAlH_4$ B. Zn/HCl C. NH_2NH_2/H^+ D. Li/NH_3 E. $NH_2NH_2/NaOH$






5. Orbitals which are equal in energy are referred to as :

- A. filled B. symmetrical C. nodes D. nonpolar E. degenerate






6. Which of the following compound is expected to show intense IR absorption at 1680 cm^{-1} ?

- A.  B.  C.  D.  E. 






7. Which of this compounds will have the most downfield chemical shift in the 1H NMR spectrum?

- A.  B.  C.  D.  E. 

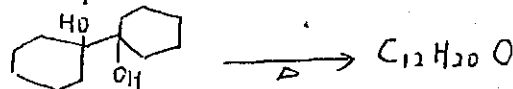
8. Which of this compounds has the most acidic proton?






- A.  B.  C.  D.  E. 

9. Which of these compounds is a bridged bicyclic alkane?

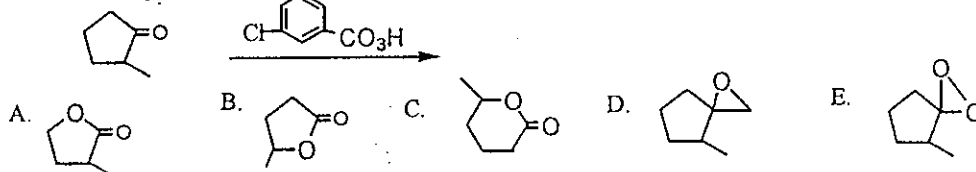
- A.  B.  C.  D.  E. 






10. What is the product for the reaction below:



- A.  B.  C.  D.  E. 

11. What is the product for this reaction?



- A.  B.  C.  D.  E. 

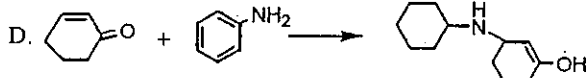
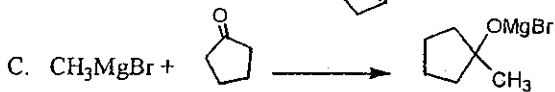
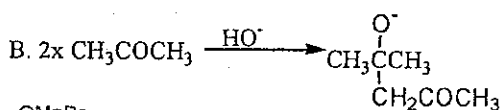
國立中山大學八十九學年度碩博士班招生考試試題

科目：有機化學

化學系碩士班

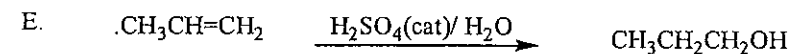
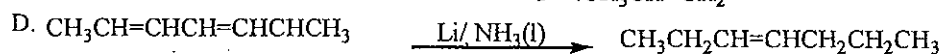
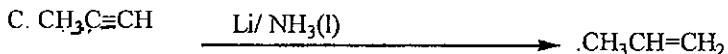
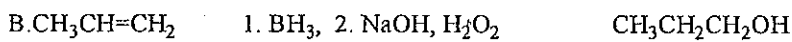
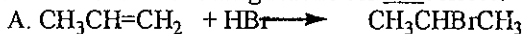
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12. Which of the reaction below is irreversible:

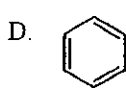
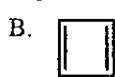
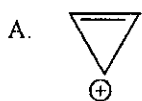


E. Non of the above

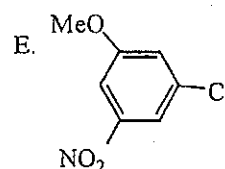
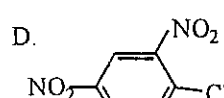
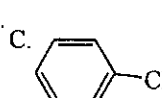
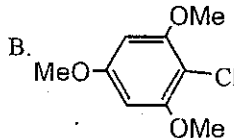
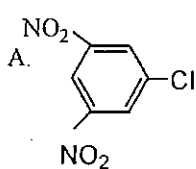
13. Which of the following reaction is not correct?



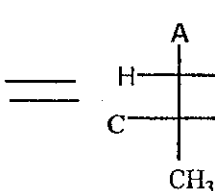
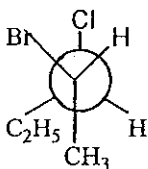
14. Which of this compound is not aromatic



15. Which of this compound will readily undergo nucleophilic displacement of the chloride?



16. Which is the correct correlation for A, B, C below?



A. A = C₂H₅, B = Cl, C = Br

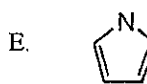
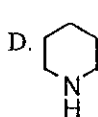
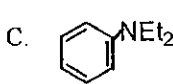
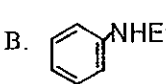
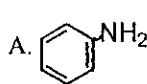
B. A = Cl, B = C₂H₅, C = Br

C. A = Br, B = Cl, C = C₂H₅

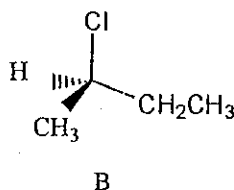
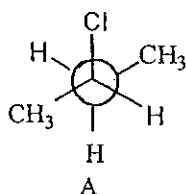
D. A = C₂H₅, B = Br, C = Cl

E. A = Cl, B = Br, C = C₂H₅

17. Which of this amine is the most basic?



18. What best describe the relationship between compound A and B?

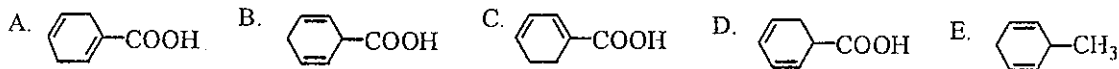


A. Same compound B. Achiral
C. Enantiomer D. Diastereomer
E. Meso compound

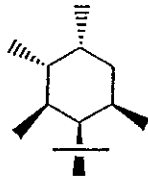
19. Which is the HOMO (highest occupied molecular orbital) for butadiene?



20. Which is the correct product for the Birch reduction of benzoic acid?

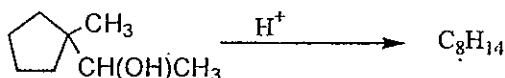


21. For the most stable conformation of A, how many methyl groups are in the equatorial positions?



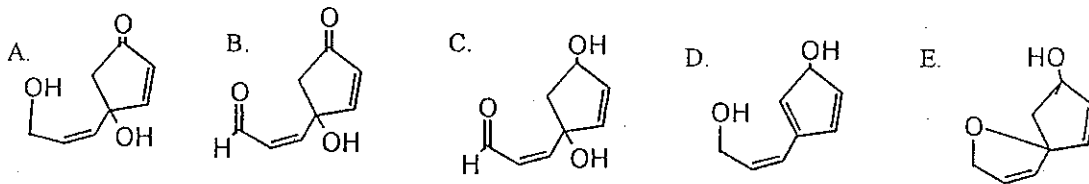
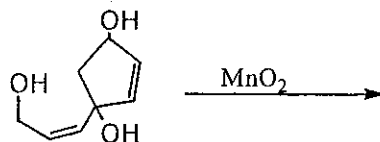
A. 0 B. 1 C. 2 D. 3 E. 4

22. The reaction below yields a product (C_8H_{14}). What is this product?

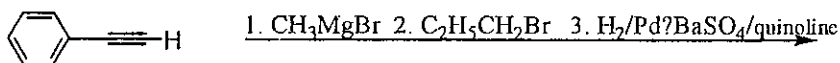


A. cyclooctene B. 1,2-dimethylcyclohexene C. 3,3-dimethylcyclohexene D. 1,2,3-trimethylpentane
E. 1,2-dimethyl hexane

23. What is the product for the reaction:



24. Give the product for the following reaction sequence:

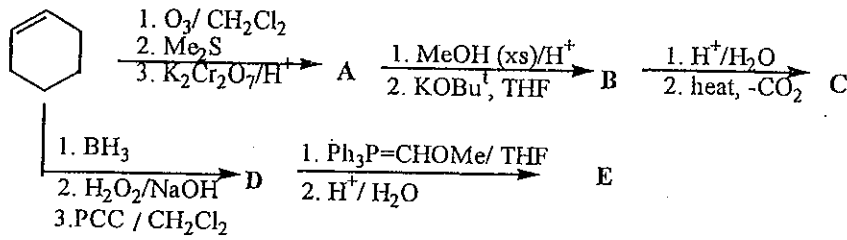


A. trans-1-phenyl-1-butene B. 1-phenylbutane C. trans-2-phenyl-2-pentene
D. cis-1-phenyl-1-butene E. 2-phenylpentane

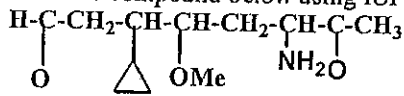
25. Which of the following constitutes the best synthesis of 2-bromo-4-nitrobenzoic acid from benzene?

A. 1. $CH_3Cl/AlCl_3$ 2. HNO_3/H_2SO_4 3. $K_2Cr_2O_7/H^+$ 4. $Br_2/FeBr_3$
B. 1. $CH_3Cl/AlCl_3$ 2. HNO_3/H_2SO_4 3. $Br_2/FeBr_3$ 4. $K_2Cr_2O_7/H^+$
C. 1. $Br_2/FeBr_3$ 2. HNO_3/H_2SO_4 3. $CH_3Cl/AlCl_3$ 4. $K_2Cr_2O_7/H^+$
D. 1. HNO_3/H_2SO_4 2. $Br_2/FeBr_3$ 3. $CHCl_3/AlCl_3$ 4. $K_2Cr_2O_7/H^+$
E. 1. HNO_3/H_2SO_4 2. H_2SO_4 (fuming) 3. $CHCl_3$ 4. Br_2

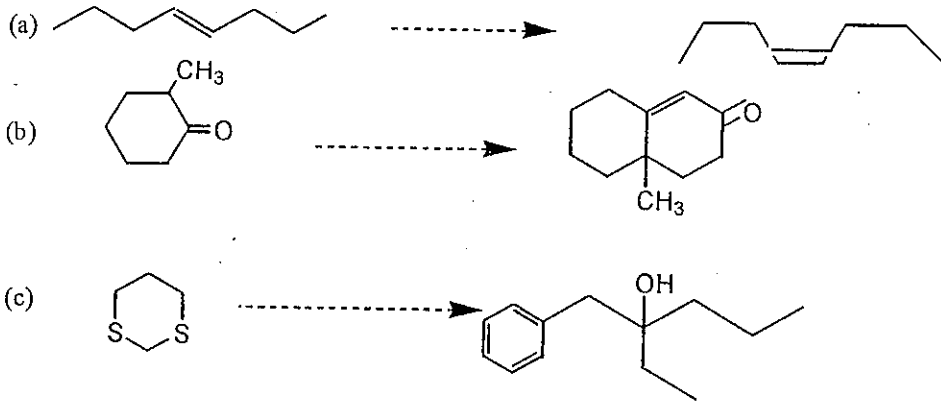
II. Provide the structure A to E for the reaction scheme below (10%, 2% each)



III. Name the compound below using IUPAC nomenclature. (3%)



IV. Show how you will accomplish the following syntheses (more than one step may be required). Show clearly the reagent used for this transformation. (12%, 4% each)



1. (10%) To ionize Mg to Mg^{+2} costs three times as much energy as to form Mg^+ . The formation of O^{2-} is endothermic rather than exothermic as for O^- . Nevertheless, magnesium oxide is always formulated as $Mg^{+2}O^{2-}$ rather than Mo^+O^- .
 - (a) What theoretical reason can be given for the $Mg^{+2}O^{2-}$ formulation.
 - (b) What simple experiment could be performed to prove that magnesium oxide is not Mo^+O^- .

2. (10%) List the following acids in order of their strength when reacting with NH_3 :
 $B(CH_3)_3$ $B(C_6H_2(CH_3)_3)_3$ BF_3 $B(C_2H_5)_3$
 Where $C_6H_2(CH_3)_3$ is 2,4,6-trimethylphenyl. Explain your answer.

3. (10%) The **leveling effect** is the compression of a range of acid or base strengths to the strengths of the solvent acid or base. Use an example to explain this.

4. (10%) Alkali metal ions generally do not form stable complexes with Lewis bases, which readily dissociate in polar solvents. However, **crown ethers** and **cryptands** can bind alkali metal ions strongly. Show the general structures for crown ethers and cryptands and explain why they can form stable complexes with the alkali metal ions.

5. (10%) Gas-phase BeF_2 is monomeric and linear. Prepare a molecular orbital description of the bonding in BeF_2 .

6. (15%) For the isoelectronic series $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$.
 - (a) show the ligand-field splitting for the d orbitals of these compounds.
 - (b) Do these compounds exhibit the **Jahn-Teller effect**?
 - (c) Would you expect the energy of metal to ligand charge transfer bands to increase or decrease with increasing charge on the complex? Why?
 - (d) Would you expect the energy for the CO stretching vibrations to increase or decrease with increasing charge on the complex? Why?

7. (15%) Rationalize the following observations:
 - (a) $Cu(NH_3)_4^+$ is a completely colorless complex in contrast to $Cu(NH_3)_4^{2+}$, which is intense blue.
 - (b) Aqueous Na^+ is colorless. However, it shows yellow color while burning in flame (the flame tests).
 - (c) $Co(H_2O)_6^+$ is very pale pink, although $CoCl_4^{2-}$ is deep blue.
 - (d) The complex $[Ni(CN)_4]^{2-}$ is diamagnetic but $[NiCl_4]^{2-}$ is paramagnetic with two unpaired electrons.
 - (e) $Pb^{2+}(aq)$ and $SO_4^{2-}(aq)$ are both colorless, while they form white precipitate in combination.

8. (10%) Giving the trans-effect ordering:
 $OH^- < NH_3 < Cl^- < Br^- < NO_2^- < PPh_3 < CN^-$
 Design two-step syntheses of cis- and trans- $[PtCl_2(NO_2)(NH_3)]^-$ from $[PtCl_4]^{2-}$.

9. (10%) Inorganic materials have been well developed in the following two areas. Describe each of them.
 - (a) nonlinear optics
 - (b) chemical vapor deposition

國立中山大學八十九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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Physical Chemistry

選擇題（每題 5 分，單選及複選都有，複選必須全對才得分，答錯不倒扣。）

$$\text{Molar gas constant } R = 8.314 \text{ Joule K}^{-1} \text{ mole}^{-1}$$

$$\text{Planck constant } h = 6.626 \times 10^{-34} \text{ Joule sec}$$

$$\text{Speed of light } c = 2.998 \times 10^8 \text{ m sec}^{-1}$$

- The third law of thermodynamics states that
 - energy is conserved in spontaneous processes.
 - the entropy of the universe increases during a spontaneous process.
 - matter and energy are inter-convertible, but matter and energy together are conserved.
 - the entropy of every element is zero at absolute zero temperature.
 - none of these.
- For which of the following thermodynamic quantities can an absolute value be calculated in principle?
 - U (internal energy)
 - H (enthalpy)
 - S (entropy)
 - G (Gibbs free energy)
 - μ (chemical potential)
- Consider the process whereby 1.00 mole of $\text{H}_2\text{O}_{(s)}$ is melted to $\text{H}_2\text{O}_{(l)}$ at 273.15K and 1 atm. Which of the following is true?
 - $\Delta H > 0$
 - $\Delta G = 0$
 - $\Delta S < 0$
 - $\Delta H = T\Delta S$
 - None of these is true.
- Element A is found in two allotropic forms, with allotrope A_1 being thermodynamically more stable than A_2 under normal conditions. Which of the following statement is valid?
 - Allotrope A_2 should rapidly converted to A_1 .
 - The conversion of A_2 to A_1 is favorable but may or may not occur at an appreciable rate.
 - Allotrope A_2 cannot occur naturally but must be made in the laboratory
 - Diamond would be a good example for A_1 .
 - None of these is valid.
- Which of the following statements is/are true?
 - At phase equilibrium, a substance that occurs in two phases will have the same chemical potential in both phases.
 - The Clausius-Clapeyron equation can be used for a phase transition involving a vapor phase.
 - Every sample of a pure element, regardless of its physical state, is assigned a free energy of formation, ΔG_f° , equal to 0.
 - An exothermic reaction producing more moles of gases than are consumed has a negative standard reaction of free energy.
 - None of these.
- In the van der Waals equation for a real gas, $P = [nRT/(V-nb)] - a(n^2/V^2)$, the term " $a(n^2/V^2)$ " corrects for the fact that molecules
 - have a finite volume.
 - are in constant motion.
 - are less dense than an ideal gas.
 - are attracted to each other.
 - None of these is correct.

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7. The quantity k in a rate law expression
- is called the equilibrium constant.
 - is independent of concentration.
 - is dimensionless.
 - is independent of the temperature.
8. The powers in the rate law are determined by
- the coefficients in the balanced chemical equation.
 - the physical states of the reactants and products.
 - the principle of detailed balance
 - experiment.
 - molecular simulations.
9. The gaseous isomerization reaction, $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$, displays first-order kinetics in the presence of excess argon: rate = $k[\text{CH}_3\text{NC}]$. Measurements at 500K show that the concentration of the reactant has declined to 75% of its initial value after 440 s. How much additional time will be required for the concentration of CH_3NC to drop to 25% of its initial value?
- 440 s
 - 880 s
 - 1320 s
 - 1680 s
 - 2120 s
10. The decomposition of gaseous dinitrogen oxide in the presence of Cl_2 at high temperature is thought to follow the mechanism,
- $$\text{Cl}_2(\text{g}) \rightarrow 2 \text{Cl}(\text{g})$$
- $$\text{N}_2\text{O}(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{ClO}(\text{g})$$
- $$2 \text{ClO}(\text{g}) \rightarrow \text{Cl}_2(\text{g}) + \text{O}_2(\text{g})$$
- In the net overall reaction, the second step occurs twice for each occurrence of the first and third steps. In this mechanism, the catalysts are _____, and the intermediates are _____.
- catalysts— Cl_2 ; intermediates— Cl
 - catalysts— Cl_2 and Cl ; intermediates— ClO
 - catalysts— Cl_2 ; intermediates— Cl and ClO
 - catalysts— Cl and ClO ; intermediates— Cl_2
11. According to the Arrhenius concept and collision theory,
- collisions that occur with an energy less than E_a (activation energy) do not result in product formation.
 - the smaller the value of E_a , the greater the number of successful collisions per unit time.
 - the larger the value of E_a , the slower the reaction at a given temperature.
 - the larger the value of E_a , the more sensitive to temperature for the reaction rate.
 - None of these.
12. According to the Conventional Transition State Theory (CTST),
- there is an equilibrium between reactants and activated complexes.
 - the derivation of rate constants in CTST involves using the partition functions for different types of motion of molecules.
 - its derivation of rate constants treats the motion through the transition state as a very loose vibration.
 - its alternative derivation treats the motion through the transition state as a translational motion.
 - none of the above is correct.
13. In the photoelectric effect, light directed onto the surface of metal in a vacuum causes electrons to be ejected. As the intensity of the light increases,
- the kinetic energy of the ejected electrons increases.

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- b. the kinetic energy of the ejected electrons decreases.
c. the number of ejected electrons increases.
d. the number of ejected electrons decreases.
e. None of these.
14. Which of the following instruments is/are based upon the result demonstrated by the Davisson-Germer experiment?
a. Low Energy Electron Diffraction
b. Photoelectron Spectroscopy
c. Electron Energy Loss Spectroscopy
d. Small-Angle Neutron Scattering
e. Synchrotron Radiation
15. The energy of a one-electron atom depends on
a. principal quantum number
b. angular momentum quantum number
c. magnetic quantum number
d. spin quantum number
e. none of these
16. In a one-electron atom, _____ of light corresponds to a decrease in the principal quantum number, while _____ of light corresponds to an increase in the principal quantum number.
a. diffraction, interference
b. interference, diffraction
c. emission, absorption
d. excitation, relaxation
e. pumping, probing
17. Spectroscopic experiments in the visible spectral region involve excitation of the _____.
a. core electrons. b. valence electrons.
c. vibrational levels. d. nuclear spins.
18. Which of the following statements about the quantum harmonic oscillator is/are incorrect?
a. The wave functions of a harmonic oscillator are orthogonal to each other.
b. According to this model, diatomic molecules vibrate even at 0 K.
c. For a harmonic oscillator at its first excited state, the maximum probability occurs at its equilibrium position.
d. The larger the force constant, the larger the absorption frequency.
e. This model can exactly describe the vibration of a diatomic molecule.
19. Given a particle in a box, which of the following quantum statements is/are not true?
a. Shifting the box in space will change the wave function of the particle.
b. The exact position of the particle is unpredictable.
c. If the size of the box is infinite, the energy states of the particle are no more quantized.
d. Shifting the box in space will change the energy of the particle.
e. The energy of the particle depends on the shape of the box.
20. The longest wavelength of light capable of exciting electrons across the band-gap in a certain semiconductor is 512 nm. The band-gap energy is
a. 2.43 eV b. 1.43 eV c. 0.04 eV d. 5.31 eV e. None of the above.

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Note: Be sure to use the correct number of significant figures in the answers of all your calculations!

(10%) 1. If 0.350 L of aqueous solution with a density of 1.00 g/mL contains 13.7 μ g of pesticide A, express the concentration of pesticide A in (a) M and (b) ppm, respectively. (Given: molecular weight of pesticide A = 120.0)

(10%) 2. (a) Define and calculate α_2 for a solution of oxalic acid (H_2Ox) that is buffered to pH 4.00. ($K_1 = 5.36 \times 10^{-2}$; $K_2 = 5.42 \times 10^{-5}$)
(b) Calculate the molar solubility of calcium oxalate in a solution that has been buffered to a constant pH of 4.00. (for $CaOx$, $K_{sp} = 2.30 \times 10^{-9}$)

(10%) 3. (a) What is buffer solution?
(b) What is buffer capacity?
(c) Malonic acid (H_2A) is a weak acid ($K_1 = 1.42 \times 10^{-3}$, $K_2 = 2.01 \times 10^{-6}$). If you are asked to prepare a buffer solution of pH 4.3, will you use malonic acid to prepare this buffer solution? Why or why not?

(10%) 4. For the titration of 50.00 mL of 0.100 M H_2CO_3 with 0.200 M NaOH, calculate the pH after the addition of (a) 20.00 and (b) 40.00 mL of 0.200 M NaOH, respectively. (for H_2CO_3 , $K_1 = 4.45 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$)

(10%) 5. The majority of commercially available FT-IR instruments are based on the Michelson interferometer.

(a) Briefly define "Fourier Transform".
(b) In comparison with the conventional dispersive IR instrument, what advantages does FT-IR appear to have?
(c) Briefly describe the principle of Michelson interferometer.

(10%) 6. (a) What is cyclic voltammetry?
(b) The three-electrode system is normally used in voltammetry. Name these three electrodes.
(c) Show the schematic diagram of a pH glass-electrode. Please include the necessary components and solutions.

(10%) 7. The following data were obtained by gas chromatography on a 40-cm packed column:

Compound	Retention Time, min	W, min
nonretained	3.1	-
toluene	5.4	0.41
cyclohexene	7.3	1.07

Calculate:

(a) the number of plates from toluene. (b) the plate height for the column.
(c) the resolution for toluene and cyclohexene. (d) the capacity factor for toluene.

(30%) 8. Define the following terms in detail:

(a) quadrupole mass spectrometer (b) an ESCA electron
(c) determinate error (d) fluorescence
(e) PMT (f) monochromator