Note: Always use the correct significant figures in your calculations!!

(10%)1. Name the following devices / symbols in English (2 points) or in Chinese (1 point):

(a) —⋁⋁—   (b)   (c)   (d)

(e)
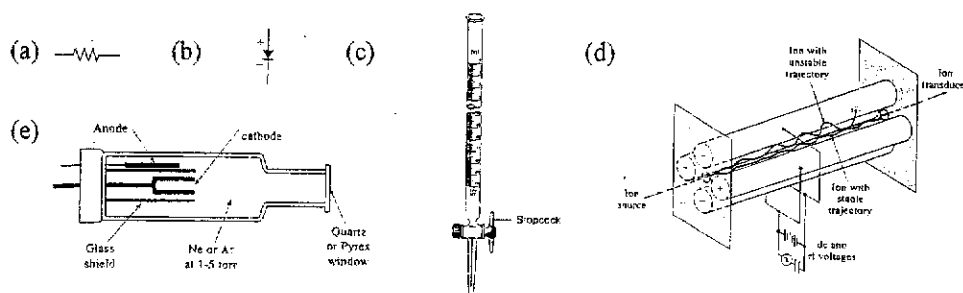
(30%)2. Define and explain the following terms:

(a) precision   (b) confidence interval   (c) ionic strength
(d) Nernst equation   (e) Beer's law   (f) EDTA (name and structure)

(12%)3. The diprotic acid H_2A has $pK_1 = 4.00$ and $pK_2 = 8.00$.

(a) Calculate the pH of 0.100 M H_2A.
(b) At what pH is $[HA^-] = [A^{2-}]$? Why?
(c) Define $\alpha_A{}^{2-}$ and give the equation to calculate $\alpha_A{}^{2-}$.

(10%)4. The schematic diagram of a three-electrode potentiostat to perform linear-scan voltammetry is given in Fig 1.

(a)   Name the three marked (1, 2, 3) electrodes in the cell and explain the role each electrode plays in the system.
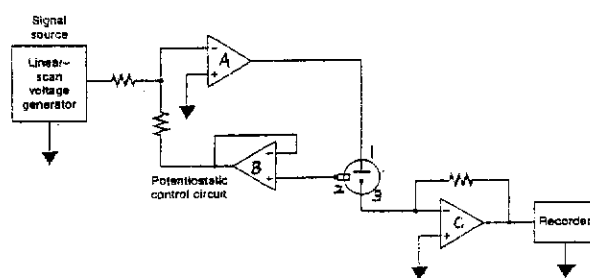(b)   What is the name and function of the circuit that consists of Op Amp C?

Fig. 1

(10%)5. ESCA is one of the important spectroscopic methods for analysis of surfaces.

    (a) What does ESCA stand for?

    (b) Describe the mechanism of the production of an ESCA electron. Also, give the equation for E_k in the mechanism.

    (c) What information can be obtained from the ESCA spectrum?

(10%)6. (a) Show the schematic diagram of a capillary zone electrophoresis (CZE) system.

    (b) What is electrophoresis? How does it occur?

    (c) Predict the migration order of Na^+, ClO_4^-, and CH_3OH in CZE. Why?

(08%)7. (a) What does PMT stand for?

    (b) What is the advantage to use PMT? Describe the basic principle about how it works.

(10%)8. (a) The spectra of IR, NMR, and Mass are very important for identification of organic compounds. What information can be obtained from each of them?

    (b) What is the molecular ion? Which ionization method (EI or CI) is better in order to obtain the molecular ion mass? Why?

Symbols and constants:

m_e: mass of electron = 9.1×10^{-31} Kg

h: Plank constant = 6.62×10^{-34} Jsec

ev: electron volt = 1.6×10^{-19} J

c: speed of light in vacuum = 3×10^{8} msec^{-1}

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1. (10%) The wavefunction amplitude decays in the barrier according to $\Psi = A\exp(-(2m(V_0-E)h^2)^{1/2}x)$. Assuming that the tunneling current through a barrier between the tip of a scanning tunneling microscope and a metal surface is proportional to $|\Psi|^2$. How much larger would the tunneling current be for the distance between the tip of a scanning tunneling microscope and a metal surface decrease from 0.5nm to 0.4nm when V_0-E is 1ev?

2. (10%) Base on the uncertainty principle, estimating the width of a spectral line originating from a decay of a exciting state with lifetime of 10^{-12} second.

3. (10%) Ammonia is usually produced from hydrogen and nitrogen in the Haber-Bosch process. Calculate the reaction enthalpy, entropy and Gibbs energy for this reaction under standard conditions. What is the mole fraction of ammonia that would form theorectically under standard conditions? Assuming that all the gases behave like ideal gases and that the reactants are added in the stoichiometric ratio

Chemical substance	$\Delta_f H^\circ$ (KJmol^{-1})	S° (Jmol^{-1}K^{-1})
$N_2(g)$	0.0	191.6
$H_2(g)$	0.0	130.7
$NH_3(g)$	-45.9	192.8

4. (10%) The temperature dependence of a reaction rate constant k is given in the following table. What is the activation energy and Arrhenius preexponential factor for this reaction?

Temp.($^\circ$C)	$k(s^{-1})$
22.2	7.0×10^{-4}
27.2	9.8×10^{-4}
33.7	1.6×10^{-3}
38.0	2.0×10^{-3}

5. (60%) Please give a detailed description/definition and explanation of the following terms:

(a) Antisymmetrical wavefunction, (b) Born-Oppenheimer approximation, (c) LCAO, (d) Aufbau principle,

(e) Zero point energy, (f) Azeotrope, (g) Complete set, (h) Bohr radius. (i) Canonical ensember.

(j) Orthogonality, (k) Central field approximation, (l) Helmholtz energy. (m) Steady-state approximation

(n) Frank-Condon principle, (o) Ideal dilute solution.
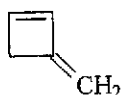
(A) Multiple choice (choose one correct answer for the following questions) (60 pts)
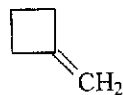
1. Which is the correct structure for vinylcyclobutane?

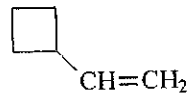a)   b)   c)   d)
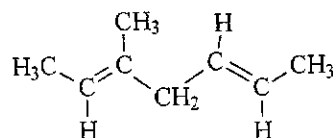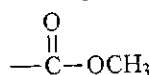
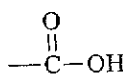2. Which is the correct name for the following compound?

a) 2E, 5E-5-methyl-2,5-heptadiene   b) 2E, 5E-3-methyl-2,5-heptadiene
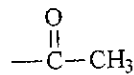c) 2Z, 5E-3-methyl-2,5-heptadiene   d) 2E, 5Z-5-methyl-2,5-heptadiene

3. Arrange the following groups in the order of increasing priority (lowest first).
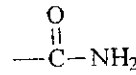
$$-\overset{\overset{O}{\|}}{C}-OCH_3 \qquad -\overset{\overset{O}{\|}}{C}-OH \qquad -\overset{\overset{O}{\|}}{C}-CH_3 \qquad -\overset{\overset{O}{\|}}{C}-NH_2$$

   I   II   III   IV
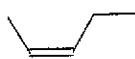
a) II, I, IV, III   b) II, III, I, IV   c) I, II, IV, III   d) III, IV, II, I
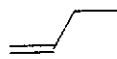
4. Which reagents react with an alkene by anti addition?

   I. Cl_2 II. Br_2 III. H_2/Pt IV. $OsO_4/ROOH$

a) I, II   b) III, IV   c) II, III   d) I, IV

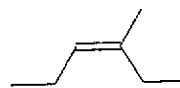5. Which compound has the lowest (least negative) heat of hydrogenation?

a)   b)   c)   d)

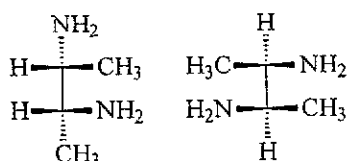6. How many stereoisomers are possible for 1,2-dichlorocyclopentane?

a) 1   b) 2   c) 3   d) 4

7. What is the relationship between these two structures?

a) Identical structures　　b) Enantiomers　　c) Diastereomers　　d)　Constitutional isomers

8. Which statement about enantiomers is false?

a)　enantiomers have the same boiling and melting points.

b)　enantiomers have the same chemical properties.

c)　enantiomers have the same atom connectivity.

d)　enantiomers have the same three dimensional orientation.

9. Which statements about stereoisomers are true?

I) enantiomers and diastereomers have the same physical properties.

II) 50/50 mixtures of R and S enantiomers are called racemic mixtures.

III) meso isomers rotate the plane of plane polarized light.

IV) dextrorotatory compounds rotate plane polarized light to the right.

a)　I, II　　b)　II, III　　c)　II, IV　　d)　III, IV

10. Arrange the nucleophiles in order of increasing reactivity (least first).

NH_3　　　　　　H_2O　　　　$^\ominus OH$　　　　　　$CH_3O^\ominus$
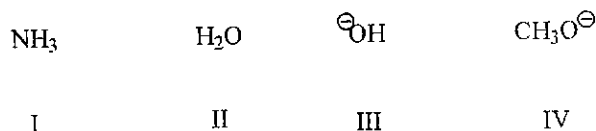
I　　　　　　　　　II　　　　　III　　　　　　　IV

a)　I, IV, II, III　　b)　IV, II, I, III　　c)　II, I, III, IV　　d)　IV, III, I, II

11. Arrange the leaving groups in order of increasing leaving group ability (least first).

$Cl^\ominus$　　　　　$I^\ominus$　　　$Br^\ominus$　　　　$F^\ominus$

I　　　　　　　II　　　III　　　　　IV

a)　IV, I, III, II　　b)　III, I, IV, II　　c)　III, I, IV, II　　d)　II, III, I, IV

12. Which solvents are polar aprotic?

    I) DMSO   II) H_2O III) Acetone   IV) Formic acid

  a) II, III b) III, IV c) I, III d) II, IV

13. Which statements apply to an S_N1 reaction?

    I) The rate limiting step of the reaction involves the alkyl halide and the nucleophile.

    II) The order of reactivity is methyl > 1°>2°>3°.

    III) The rate limiting step of the reaction involves only the alkyl halide.

    IV) There is an intermediate carbocation.

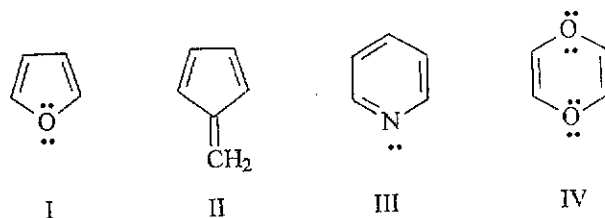 a) I, II b) III, IV c) I, IV d) III

14. What is the major product from an elimination reaction starting with 2-bromopentane?

  a) 1-pentene b) cis-2-pentene c) trans-2-pentene d) a mixture of cis and trans-2-pentene

15. Treatment of cyclopentene with dilute sulfuric acid, followed by reaction with chromic acid gives which of the following compounds as the major product?
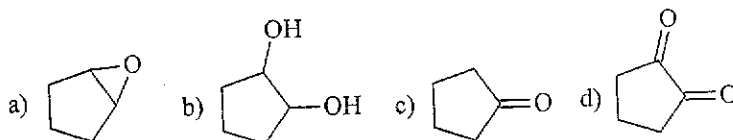
16. Which structures are aromatic?

  a) II, III b) III, IV c) I, III d) II, IV

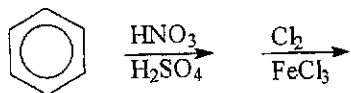17. Which is the electrophile in the nitration of benzene?

  a) HNO_3 b) $\overset{\oplus}{NO_2}$ c) $\overset{\oplus}{NO_3}$ d) $\overset{\oplus}{NO}$

18. Which is the major product of the following reaction?

$$\text{benzene} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \xrightarrow[\text{FeCl}_3]{\text{Cl}_2}$$

a) 1-chloro-4-nitrobenzene　　b) 1-chloro-3-nitrobenzene　　c) 1-chloro-2-nitrobenzene

d) a mixture of 1-chloro-4-nitrobenzene and 1-chloro-2-nitrobenzene

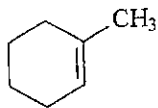19. Arrange the amines in order of increasing basicity (weakest first).
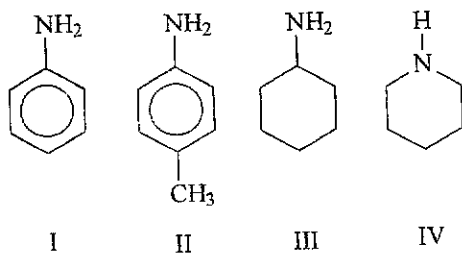
I　　　　II　　　　III　　　　IV

a)　IV, II, III, I　　b)　II, I, III, IV　　c)　I, II, III, IV　　d)　II, I, IV, III

20. Which compound has a sharp IR absorption at 1710 cm^{-1} and a broad band at 3300 cm^{-1}?

a) $CH_3\overset{O}{\overset{\|}{C}}OH$　　b) CH_3CH_2OH　　c) $CH_3\overset{O}{\overset{\|}{C}}CH_3$　　d) CH_3OCH_3
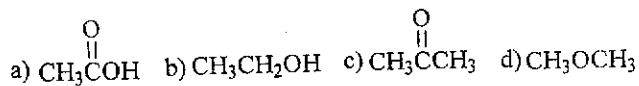
21. How many sets of equivalent hydrogen atoms are there for the following compound?

a)　3　　b)　4　　c)　5　　d)　6

22. A compound has three signals in the ^{13}C NMR spectrum and two signals in the ^{1}H-NMR spectrum.
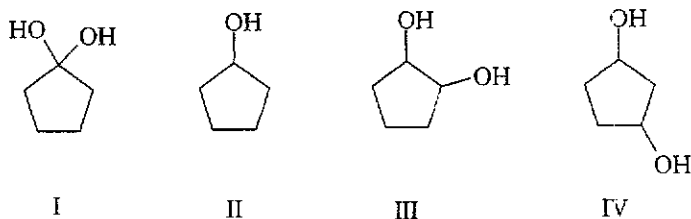Which is most likely the compound?

a) bromobenzene　　b) para-dibromobenzene　　c) ortho-dibromobenzene

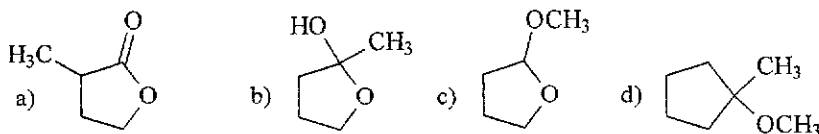d) meta-dibromobenzene

23. Which compounds have 3 signals in the ^{13}C NMR spectrum?

    I   II   III   IV
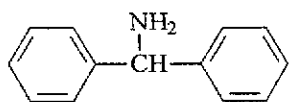
    a) I, II   b) I, II, III   c) I, III   d) I, II, III, IV

24. Which compound reacts with aqueous acid to give an aldehyde?
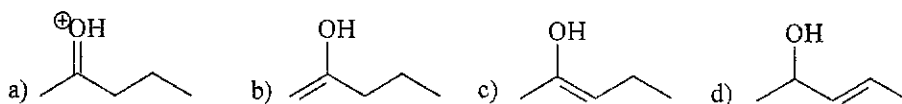

    a)   b)   c)   d)

25. The following product can be made from the reductive amination of which combination of compounds?

    a) benzaldehyde and benzylamine   b) benzaldehyde and aniline

    c) benzophenone and ammonia   d) acetophenone and ammonia

26. Which structure is the major tautomer of 2-pentanone in aqueous acid?

    a)   b)   c)   d)

27. Which conditions will convert pentanoic acid to pentanoyl chloride?

    a) HCl   b) NaCl   c) $SOCl_2$ d) $LiAlH_4$ followed by HCl

28. Which conditions are best for the transformation?

a) LiAlH₄ b) NaBH₄ c) Ag(NH₃)₂OH / NH₄OH d) Pyridine · Cr₃O₄

29. Which is the product of the reaction of ethyl benzoate with 2 equivalents of methyl grignard followed by aqueous acid?
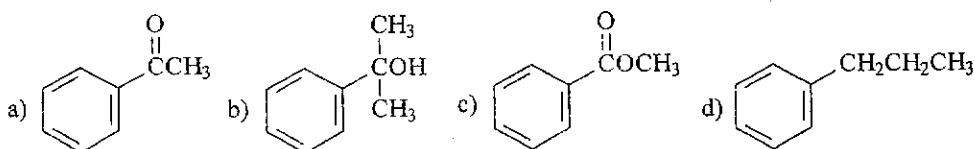
30. Which ester is likely to undergo a Claisen condensation to give this product?
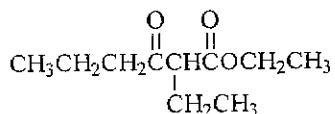
a) ethyl 2-methylpropanoate b) ethyl butanoate c) butyl ethanoate

d) 2-methylpropyl ethanoate

(B) The following road-map problem centers on the structure and properties of 1, a key intermediate in these reactions. Give structures for compounds 1 through 10. (20 pts)
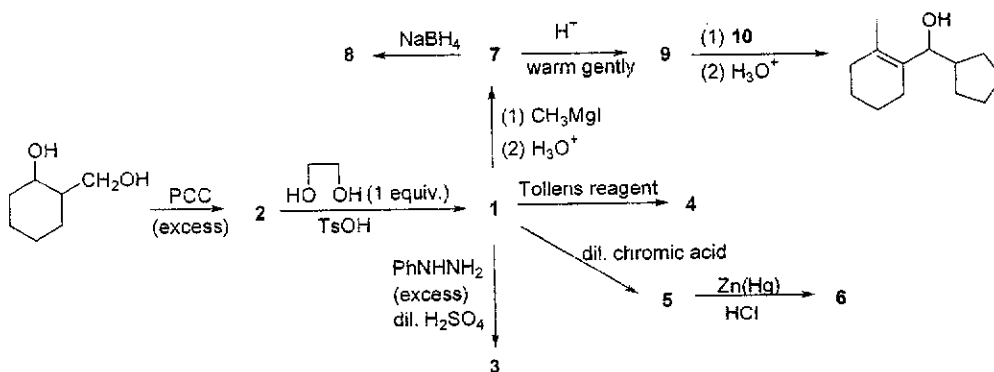
(C) Accomplish the following transformations. (you may use any necessary reagents) (10 pts)

1.

2.

(D) Give reasonable mechanism for each of the following reactions. (10 pts)

1.

2.

簡答題：請簡單回答或解釋下列問題

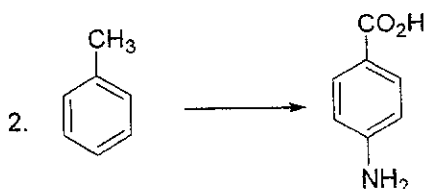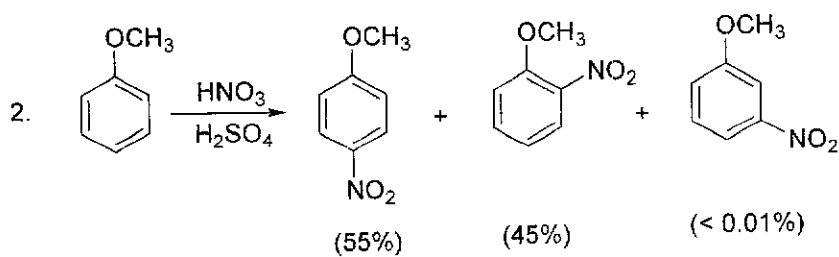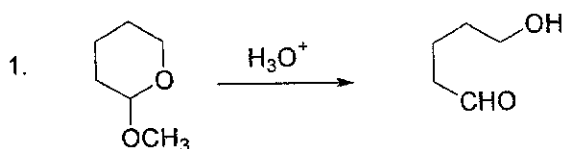**1. 鍵結理論** (每小題五分；共二十分)

(a) Determine the point group for S_8 (puckered ring).

(b) Predict the geometry for I_3^-.

(c) Show the bond dipole and molecular dipole for IF_5.

(d) On the basis of molecular orbital theory, predict the bond order for the NO^- ion.

2. 酸鹼及固態化學 (每小題五分；共二十分)

(a) List the order of acid strength of CO_2, $HClO_4$, HCl, and Na_2CO_3 in aqueous solution.

(b) Nickel crystallizes in a face-centered cubic lattice with a unit cell length of 3.52 Å. Calculate the density of nickel in g/cm^3. (Ni 原子量 58.7)

(c) Predict the order of solubility in water of $PbBr_2$, $PbCl_2$, PbS, and PbI_2.

(d) Which of the following ions has the smallest radius: Ti^{2+}, Pt^{2+}, Zr^{2+}, Ni^{2+}, Cd^{2+}.

3. 主群元素化學 (每小題五分；共二十分)

(a) Draw the structure of cryptand [2,2,2].

(b) Draw the structure of borazine.

(c) Draw the structure of diborane.

(d) Draw the structure of white phosphorous.

4. 配位化學 (每小題五分；共二十分)

(a) Draw the structure of $[Co(en)_3]Cl_2$

(b) Draw the structure of trans-dichlorobis(trimethylphosphine)palladium(II)

(c) Predict the spin state and magnetism for $[Fe(H_2O)_6]^{2+}$.

(d) Using the angular overlap method, determine the relative energies of d orbitals in a metal complex of formula ML_6 having octahedral geometry. Assume that the ligands are capable of σ interactions only.

5. 有機金屬 (每小題五分；共二十分)

(a) Predict the metal-containing product for the reaction: $V(CO)_6 + NO \rightarrow$

(b) Predict the metal-containing product for the reaction: $2 C_5H_5Li + FeCl_2 \rightarrow$

(c) Draw the structure of $Os_3(CO)_{12}$.

(d) Identify the most likely second row transition metal for $MCl(PPh_3)_3$ (square-planar complex).

1	H 1																	He 2
2	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
3	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
6	Cs 55	Ba 56	*	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
7	Fr 87	Ra 88	**	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Uun 110	Uuu 111	Uub 112						