

國立高雄大學九十七學年度研究所碩士班招生考試試題

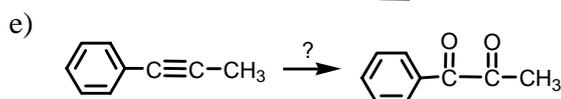
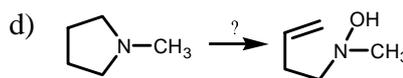
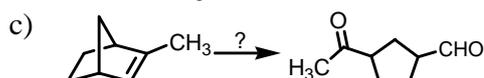
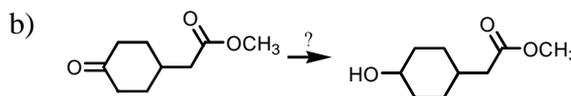
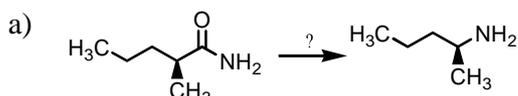
科目：綜合化學(I)
 考試時間：100 分鐘

系所：
 應用化學系碩士班
 本科原始成績：100 分

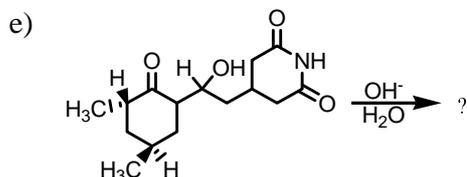
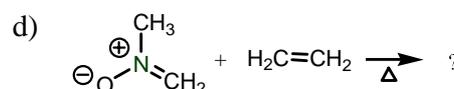
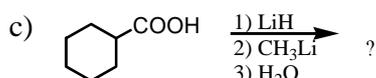
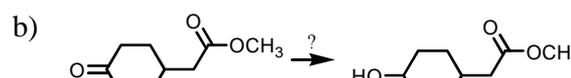
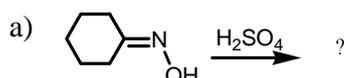
是否使用計算機：是

PART I: Organic Chemistry ; Total = 50 points

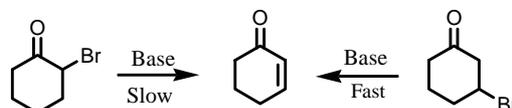
1. Predict the major organic product formed in each following reaction. (10 pts)



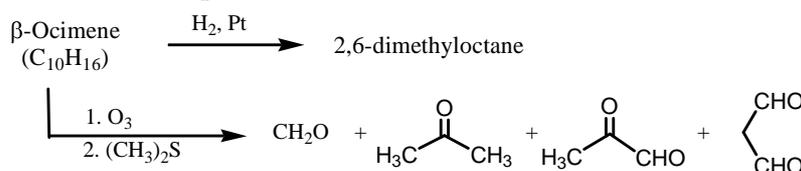
2. Give some proper reagents that bring the following reaction occurrence. (10 pts)



3. Treatment of both α - and β -bromoketones with base results in loss of HBr to form α,β -unsaturated ketones. However, the former react much more slowly and require much stronger bases. Account for this difference in reactivity by providing a complete analysis of both reaction mechanisms. (6 pts)



4. β -Ocimene is a natural product with a pleasant odor. Based on the information below, deduce the structure of β -ocimene. (4 pts)



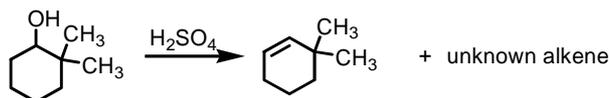
國立高雄大學九十七學年度研究所碩士班招生考試試題

科目：綜合化學(I)
 考試時間：100 分鐘

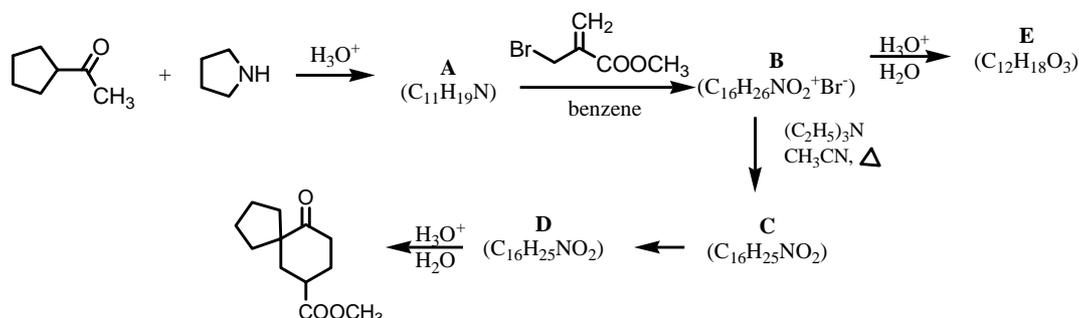
系所：
 應用化學系碩士班
 本科原始成績：100 分

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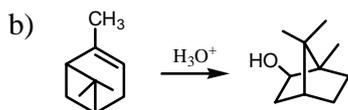
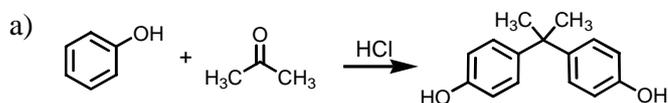
5. Upon treatment with acid, 2,2-dimethylcyclohexanol undergoes dehydration to form 3,3-dimethylcyclohexene and another alkene that exhibits only four unique signals in the ^{13}C NMR spectrum yet has a mass of 110, corresponding to the formula C_8H_{14} . Assign a structure to this product, and account for its formation with a detailed reaction mechanism. (4 pts)



6. provide exact intermediates A-E for the following reactions (10 pts)



7. Suggest a convenient method for carrying out the following syntheses. (6 pts)



PART II: Inorganic Chemistry ; Total = 50 points

1. Provide a concise but thorough explanation of the following (10 points)

- (a) Trans effect (b) Valence bond theory
 (c) n-type semiconductor (d) 18 electrons rule

2. (a) How many spherical nodes dose $4d_{x^2-y^2}$ orbital have? (2 points)
 (b) How many angular nodes dose $4d_{x^2-y^2}$ orbital have? (2 points)

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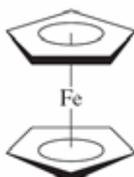
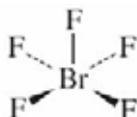
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3. Determine the point groups for (9 points)

(a) Cyclohexane (chair conformation)

(b) BrF_5 (c) $\text{Fe}(\text{C}_5\text{H}_5)_2$ (staggered)



4. The d^2 ions CrO_4^{4-} , MnO_4^{3-} , FeO_4^{2-} , and RuO_4^{2-} have been reported. (9 points)

(a) Which of these has the largest value of Δ_t ? The smallest? Explain briefly.

(b) Of the first three, which ion has the shortest metal-oxygen bond distance? Explain briefly.

(c) The charge-transfer transitions for the first three complexes occur at 43000, 33000, and 21000 cm^{-1} , respectively. Are these more likely to be ligand to metal or metal to ligand charge-transfer transitions? Explain briefly.

5. $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ have D_{4d} symmetry. How many IR-active carbonyl stretching bands would you predict for these compounds? (10 points)

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1	R_z	$x^2 + y^2, z^2$
A_2	1	1	1	1	1	-1	-1		
B_1	1	-1	1	-1	1	1	-1	z	
B_2	1	-1	1	-1	1	-1	1		
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(x, y)	$(x^2 - y^2, xy)$
E_2	2	0	-2	0	2	0	0		
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0	(R_x, R_y)	(xz, yz)

6. Of the donor-acceptor complexes $(\text{CH}_3)_3\text{N-SO}_3$ and $\text{H}_3\text{N-SO}_3$ in the gas phase (8 points)

(a) Which has the longer N-S bond? Explain briefly.

(b) Which has the larger N-S-O angle? Explain briefly.

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科目：綜合化學(II)
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系所：應用化學系碩士班
本科原始成績：100 分

是否使用計算機：是

Part I (physical chemistry)

1. The van der Waals equation is often written as the following: (5%, 複選, 答錯倒扣 1.25%)

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1),$$

where V_m is the molar volume, a and b are called the van der Waals coefficients.

Which terms stated in the kinetic model for ideal gases are corrected as the van der Waals coefficients in equation (1)?

- (a) The gas consists of molecules in ceaseless random motion.
(b) The size of the molecule is much smaller than the average distance traveled between collisions.
(c) The molecules interact only through brief, infrequent, and elastic collisions.
(d) The averaged kinetic energy of the molecules depends only on the Kelvin temperature of the gas.
2. Which of the following statement is correct: (5%, 複選, 答錯倒扣 1%)
- (a) The internal energy of an isolated system is constant.
(b) $\Delta U = q + w$: The change of internal energy, heat transferred to and work done on a system are all state functions.
(c) The maximum work that a system can do to a surrounding is by free expansion.
(d) The Linde refrigerator is operated in a temperature range, where a gas system is cooled on expansion.
(e) A perfect gas expands adiabatically from P_i, V_i, T_i , to P_f, V_f, T_f , its change of the internal energy is $C_v(T_f - T_i) + (P_f V_f - P_i V_i)$
3. The vibrational wavenumbers of CO_2 are 1288 cm^{-1} , 667.4 cm^{-1} , and 2349 cm^{-1} , the second being the doubly degenerate bending mode. The vibrational partition function of CO_2 at 1500 K is about:
(a) 0.0007 (b) 0.07 (c) 7 (d) 700 (e) 70000 (5%, 單選, 答錯倒扣 1%)
4. Fill in the right statement of the following quantum principles from (i) – (v):
- ___ → (a) Born – Oppenheimer approximation
___ → (b) Quantization of energy by Planck
___ → (c) The uncertainty principle by Heisenberg
___ → (d) Hund's multiplicity rule
___ → (e) de Broglie relation. (5%, 答錯倒扣 1%)

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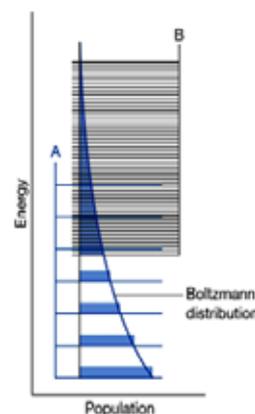
科目：綜合化學(II)
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系所：應用化學系碩士班
 本科原始成績：100 分

是否使用計算機：是

- (i) It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.
- (ii) An atom in its ground state adopts a configuration with the greatest number of unpaired electrons.
- (iii) The energy of each electromagnetic oscillator is limited to discrete values and can not be varied arbitrarily.
- (iv) In the time scale while the electrons move in their field, the nuclei may be treated as stationary.
- (v) Any particle, not only photon, travels with a linear momentum p should have a wavelength given by $\lambda = h/p$.

5. According to the right-hand figure for an $A \rightarrow B$ reaction, which of the following statements are correct? (5%, 複選, 答錯倒扣 1%)



- (a) The reaction is endothermic.
 - (b) The equilibrium compositions always favor the reactant.
 - (c) The equilibrium compositions always favor the product.
 - (d) Changing the reaction Gibbs energy from positive to negative can be possible by heating up the reaction system.
 - (e) The change of entropy is not important in this type of reaction.
6. Which of the following statement are correct? (5%, 複選, 答錯倒扣 1%)
- (a) The FT-IR method can be used to study O_2 vibration.
 - (b) The rotation-vibration spectrum of HCl can be obtained by the FT-IR spectrum.
 - (c) The rotation-vibration FT-IR spectrum of DCl shows P, Q, and R branches, which belong to transitions of $\Delta J = -1, 0,$ and $1,$ respectively.
 - (d) UV-VIS light can be used to electronically excite C_6H_6 .
 - (e) In general, the fluorescence life time is longer than the phosphorescence life time.
7. (a) Construct the orbital energies of Period 2 homonuclear diatomic molecules. (b) Explain why no Be_2 molecule can be formed. (c) Explain why B_2 and O_2 are paramagnetic. (3, 1, 1%)
8. Calculate the mean, root mean square, and most probable velocity of N_2 at $25^\circ C$. (The velocities in an **arbitrary** order are $(2RT/M)^{1/2}, (8RT/\pi M)^{1/2},$ and $(3RT/M)^{1/2};$ $R = 8.314 J K^{-1} mol^{-1};$ and the molar mass of $N_2 = 28 g mol^{-1}.$) (速率定義 3%, 速率值 2%)
9. The rate law of the $2A \rightarrow P$ reaction was determined as the following:

$$\frac{d[P]}{dt} = \frac{a[A]^2}{b + c[A]}$$

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是否使用計算機：是

(a) Proposed the reaction mechanism of the reaction. (b) Derive the rate equation at low-pressure and high-pressure limits. (3, 2%)

10. Calculate the half-life ($t_{1/2}$) of a reaction, $A \rightarrow P$, with an initial reactant concentration of $[A]_0$:

(a) A zeroth-order reaction, rate constant = k^0 .

(b) A second-order reaction, rate constant = k^I .

(c) A second-order reaction, rate constant = k^{II} . (2, 1, 2%)

Part II (analytical chemistry)

- (3 points each) Explain the difference between
 - systematic error and random error
 - sensitivity and detection limit
 - activity and ionic strength
 - Faradaic current and charging current
 - capacity factor (k) and resolution (R) in chromatogram
- Describe how to prepare an aqueous solution with pH 3.76 by mixing acetic acid ($pK_a = 4.76$) with sodium acetate. (5 points)
- A solution containing 0.040 M HA and 0.020 M HB gave chromatogram peak areas of $A_{HA} = 400$ and $A_{HB} = 350$. To analyze an unknown, 10 mL of 0.200 M HB was added to 10.0 mL of unknown, and the mixture was diluted to 25.0 mL in a volumetric flask. This mixture gave the chromatogram with $A_{HA} = 450$ and $A_{HB} = 575$. Find the concentration of HA in the unknown. (5 points)
- Why the pH is not 7.00 at equivalence point in the titration of weak acid with strong base? (5 points)
- Describe the advantage for using three-electrode cell over two-electrode cell on electrolysis. (5 points)
- Describe how to determine the measurement of a spectrometer is absorption or emission on the basis of the alignment among light source, sample cell, and detector. (5 points)
- You have been request to determine the amount of $CH_3CH_2CH_2CH_2Cl$ and $(CH_3)_3CCl$ in a solution by chromatographic method. Describe which method you are going to use, include the detector equipped with the instrument. (5 points)
- Describe three common types of noise in electric instruments. (5 points)

國立高雄大學九十七學年度研究所碩士班招生考試試題

系所：

科目：普通化學
考試時間：100 分鐘

應用化學系碩士班
生物科技研究所碩士班乙組
本科原始成績：100 分

是否使用計算機：是

共二十題選擇題，答對每題五分。

(註：請於考試試卷第一頁依下列格式標示答案，否則不予計分。)

1	2	3	4	5	6	7	8	9	10
11	12	13	14	15	16	17	18	19	20

- In balancing an equation, we change the _____ to make the number of atoms on each side of the equation balance.
 - formulas of compounds in the reactants
 - coefficients of compounds
 - formulas of compounds in the products
 - subscripts of compounds
 - none of these
- The limiting reagent in a reaction
 - has the lowest coefficient in a balanced equation.
 - is the reactant for which you have the fewest number of moles.
 - has the lowest ratio of moles available/ coefficient in the balanced equation.
 - has the lowest ratio of coefficient in the balanced equation/ moles available.
 - none of these
- In the following reaction, which species is oxidized?
$$8\text{NaI} + 5\text{H}_2\text{SO}_4 \rightarrow 4\text{I}_2 + \text{H}_2\text{S} + 4\text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$$
 - sodium
 - iodine
 - sulfur
 - hydrogen
 - oxygen
- The following reaction occurs in aqueous acid solution: $\text{NO}_3^- + \text{I}^- \rightarrow \text{IO}_3^- + \text{NO}_2$. The oxidation state of iodine in IO_3^- is:
 - 0
 - +3
 - 3
 - +5
 - 5

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系所：

科目：普通化學

應用化學系碩士班

是否使用計算機：是

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生物科技研究所碩士班乙組

本科原始成績：100 分

17. For which order reaction is the half life of the reaction proportional to $1/k$ (k is the rate constant)?

- a) zero order b) first order c) second order
d) all of these e) none of these

18. Which of the following statements concerning equilibrium is not true?

- a) A system that is disturbed from an equilibrium condition responds in a manner to restore equilibrium.
b) Equilibrium in molecular systems is dynamic, with two opposing processes balancing one another.
c) The value of the equilibrium constant for a given reaction mixture is the same regardless of the direction from which equilibrium is attained.
d) A system moves spontaneously toward a state of equilibrium.
e) The equilibrium constant is independent of temperature.

19. The hydrogen halides (HF, HCl, HBr, and HI) are all polar molecules. The strength of the acid each forms in water is based on which of the following?

- a) the polarity of the molecule
b) the size of the molecule
c) the strength of the bond
d) two of these
e) none of these

20. The second law of thermodynamics states that

- a) the entropy of a perfect crystal is zero at 0 K.
b) the entropy of the universe is constant.
c) the energy of the universe is increasing.
d) the entropy of the universe is increasing.
e) the energy of the universe is constant.