

國立高雄大學九十八學年度碩士班招生考試試題

科目：綜合化學(I)

系所：

考試時間：100 分鐘

應用化學系

是否使用計算機：是

本科原始成績：100 分

Part I: Inorganic Chemistry; Total = 50 points

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

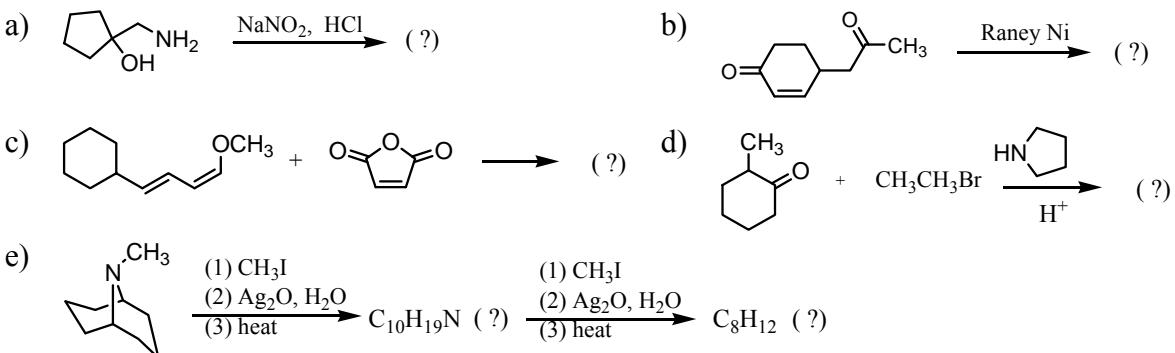
(a) organometallic compound	(b) HOMO
(c) p-type semiconductor	(d) inner-sphere reaction
2. Show that the side of the unit cell for a body-centered cubic crystal is 2.31 times the radius of the atoms in the crystal. (5 points)
3. Draw the Lewis diagram and explanation the point groups for (10 points)
 

(a) $\text{XeF}_4$	(b) diborane
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4. (a) Prepare a molecular orbital energy level diagram for NO, showing clearly how the atomic orbitals interact to form MOs.  
 (b) How does your diagram illustrate the difference in electronegativity between N and O?  
 (c) Predict the bond order and the number of unpaired electrons.  
 (d)  $\text{NO}^+$  and  $\text{NO}^-$  also known. Compare the bond orders of these ions with the bond order of NO. Which of the three would you predict to have the shortest bond? Why? (10 points)
5. Determine the ground terms for the following (including J values): (5 points)
 

(a) O	(b) $\text{V}^{3+}$
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6. Using the angular overlap model, determine the relative energies of d orbitals in a metal complex of formula  $\text{ML}_4$  having tetrahedral geometry. Assume that the ligands are capable of  $\sigma$  interactions only. How does this result for  $\Delta_t$  compare with the value for  $\Delta_o$ ? Explain (10 points)

Part II: Organic Chemistry; Total = 50 points

1. Predict the major organic product formed in each following reaction. (18 pts)



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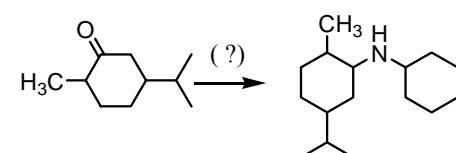
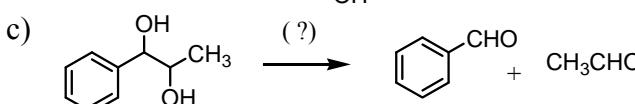
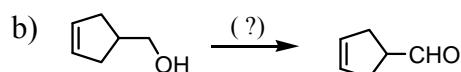
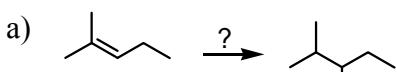
考試時間：100 分鐘

應用化學系

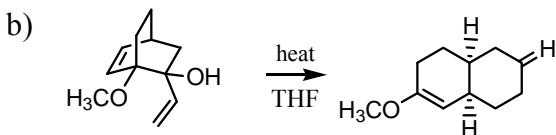
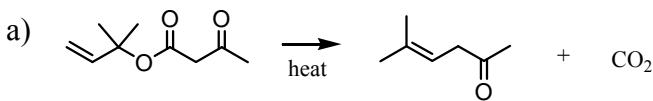
是否使用計算機：是

本科原始成績：100 分

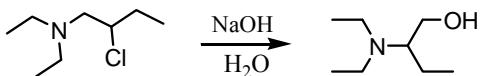
2. Give some proper reagents that bring the following reaction occurrence. (12 points)



3. Propose mechanisms consistent with the following reaction. (8 points)



4. The following nucleophilic substitution occurs with rearrangement. Suggest a mechanism for formation of the observed product. If the start material has the R configuration, what is the configuration of the stereocenter in the product? (6 points)



5. Given here are  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectral data for the unknown compound,  $\text{C}_{10}\text{H}_{12}\text{O}_3$ . It shows strong sharp absorption between  $1700$  and  $1720 \text{ cm}^{-1}$ , and broad absorption over the region  $2500\sim3500 \text{ cm}^{-1}$ . Propose a chemical structure for the unknown compound and account for your choice. (6 points)

$^1\text{H-NMR}$	$^{13}\text{C-NMR}$
2.49 (t, 2H)	173.89
2.80 (t, 2H)	157.57
3.72 (s, 3H)	132.62
6.78 (d, 2H)	128.99
7.11 (d, 2H)	113.55
12.40 (s, 1H)	54.84
	35.75
	29.20

# 國立高雄大學九十八學年度碩士班招生考試試題

科目：綜合化學(II)  
考試時間：100 分鐘

系所：  
應用化學系  
本科原始成績：100 分

是否使用計算機：是

1. Explain the difference between (2 points each)
  - a、determinate error and indeterminate error
  - b、standard addition and internal standard
  - c、capacity factor ( $k$ ) and partition coefficient (K)
  - d、concentration polarization and kinetic polarization
  - e、fluorescence and phosphorescence
2. Between absorption spectrophotometer and emission spectrophotometer which one has better sensitivity? (8 points)
3. The pH at the equivalence point is larger than 7 for a titration between a weak acid and a strong base. Why? (8 points)
4. Describe why FID is insensitive to detect  $\text{NH}_3$  and ECD is insensitive to detect hydrocarbons. (8 points)
5. Why increase the flow rate in chromatography may not increase the plate height? (8 points)
6. What kinds of experimental condition can lead particle to form as precipitation but not colloidal? (8 points)
7. Starting with the van der Waals equation of state, find an expression for the total differential  $dP$  in terms of  $dV$  and  $dT$ . By calculating the mixed partial derivatives
$$\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right)_V \text{ and } \left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T,$$
determine if  $dP$  is an exact differential. (5 points)
8. Using the differential form of  $G$ ,  $dG = VdP - SdT$ , show that if  $\Delta G_{mixing} = nRT \sum_i x_i \ln x_i$ , then  $\Delta H_{mixing} = \Delta V_{mixing} = 0$ . (5 points)

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9. Is the superposition wave function  $\psi(x) = \sqrt{\frac{2}{a}} \left[ \sin\left(\frac{n\pi x}{a}\right) + \sin\left(\frac{m\pi x}{a}\right) \right]$  an eigenfunction of the total energy operator for the particle in the box? (5 points)
10. Derive an equation for the probability that a particle characterized by the quantum number  $n$  is in the first quarter ( $0 \leq x \leq \frac{a}{4}$ ) of an infinite depth box. Show that this probability approaches the classical limit as  $n \rightarrow \infty$ . (5 points)
11. One mole of an ideal gas with  $C_V = 3/2R$  undergoes the transformations described in the following list from an initial state described by  $T = 300$  K and  $P = 1.00$  bar. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for each process. a) The gas is heated to 450 K at a constant external pressure of 1.00 bar. b) The gas is heated to 450 K at a constant volume corresponding to the initial volume. c) The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value. ( $\ln(450) = 6.10925$ ,  $\ln(300) = 5.70378$ ,  $\ln(2) = 0.69315$ ) (10 points)
12. For molecular rotation, the symbol  $J$  rather than  $l$  is used as the quantum number for angular momentum. A  ${}^1\text{H}^{35}\text{Cl}$  molecule whose bond length and force constant are 127 pm and 516 N m $^{-1}$ , respectively, has the rotational quantum number  $J = 10$  and vibrational quantum number  $n = 0$ . a) Calculate the rotational and vibrational energy of the molecule. Compare each of these energies with  $kT$  at 300 K. b) Calculate the period for vibration and rotation. How many times does the molecule rotate during one vibrational period? (10 points)
13. The reaction rate as a function of initial reactant pressures was investigated for the reaction  $2\text{NO}(g) + 2\text{H}_2(g) \longrightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$ , and the following data were obtained

Run	$P_o \text{ H}_2$ (kPa)	$P_o \text{ N}_2$ (kPa)	Rate (kPa s $^{-1}$ )
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

What is the rate law expression for this reaction? (10 points)

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科目：普通化學

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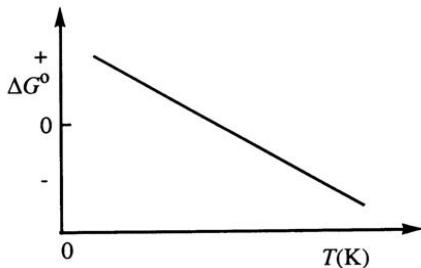
應用化學系

是否使用計算機：是

本科原始成績：100 分

< I > 單一選擇題(共佔 45 分，每題 3 分，答錯不倒扣)

- (1) Potassium chloride, KCl, sodium sulfate, Na<sub>2</sub>SO<sub>4</sub>, glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, carbon dioxide, CO<sub>2</sub> and ammonium phosphate, (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, are soluble in water. Which one produces the largest number of dissolved particles per mole of dissolved solute?
- (A.) KCl      (B.) Na<sub>2</sub>SO<sub>4</sub>      (C.) C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>      (D.) CO<sub>2</sub>      (E.) (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>
- (2) At moderate pressures (~ 200 atm), the measured pressure exerted by CO<sub>2</sub> gas is less than that predicted by the ideal gas equation. This is mainly because
- (A.) such high pressures cannot be accurately measured.  
(B.) CO<sub>2</sub> will condense to a liquid at 200 atm pressure.  
(C.) gas phase collisions prevent CO<sub>2</sub> molecules from colliding with the walls of the container.  
(D.) of attractive intermolecular forces between CO<sub>2</sub> molecules.  
(E.) the volume occupied by the CO<sub>2</sub> molecules themselves becomes significant.
- (3) If M represents a transition element, which of the following oxides should be the least basic?
- (A.) MO      (B.) M<sub>2</sub>O      (C.) M<sub>2</sub>O<sub>3</sub>      (D.) MO<sub>2</sub>      (E.) MO<sub>3</sub>
- (4) How many unpaired electrons will there be in a high-spin octahedral complex of Fe(II)?
- (A.) 0      (B.) 2      (C.) 4      (D.) 6      (E.) None of these choices is correct.
- (5) Consider the figure below which shows ΔG° for a chemical process plotted against absolute temperature.



From this plot, it is reasonable to conclude that:

- (A.) ΔH° > 0, ΔS° > 0      (B.) ΔH° > 0, ΔS° < 0  
(C.) ΔH° < 0, ΔS° > 0      (D.) ΔH° < 0, ΔS° < 0  
(E.) None of these choices is correct.
- (6) When the following redox equation is balanced with smallest whole number coefficients, the coefficient for the hydrogen sulfate ion will be \_\_\_\_\_.  
$$\text{Al}(s) + \text{HSO}_4^-(aq) + \text{OH}^-(aq) \rightarrow \text{Al}_2\text{O}_3(s) + \text{S}^{2-}(aq) + \text{H}_2\text{O}(l)$$

(A.) 1      (B.) 2      (C.) 3      (D.) 4      (E.) None of these choices is correct.

(7) Which of the following has the highest buffer capacity?

(A.) 0.50 M H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/0.50 M HPO<sub>4</sub><sup>2-</sup>      (B.) 0.50 M H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/0.10 M HPO<sub>4</sub><sup>2-</sup>  
(C.) 0.10 M H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/0.10 M HPO<sub>4</sub><sup>2-</sup>      (D.) 0.10 M H<sub>2</sub>PO<sub>4</sub><sup>-</sup>/0.50 M HPO<sub>4</sub><sup>2-</sup>  
(E.) They all have the same buffer capacity.

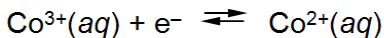
國立高雄大學九十八學年度碩士班招生考試試題

科目：普通化學  
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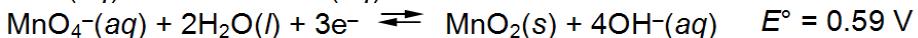
系所：  
應用化學系  
本科原始成績：100 分

是否使用計算機：是

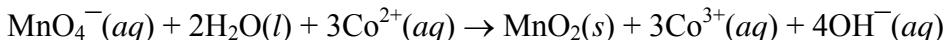
- (8) Calculate  $E^\circ_{\text{cell}}$  and indicate whether the overall reaction shown is spontaneous or nonspontaneous.



$$E^\circ = 1.82 \text{ V}$$



Overall reaction:



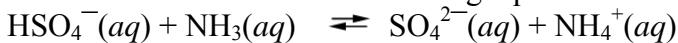
$$(A.) E^\circ_{\text{cell}} = -1.23 \text{ V, spontaneous} \quad (B.) E^\circ_{\text{cell}} = -1.23 \text{ V, nonspontaneous}$$

$$(C.) E^\circ_{\text{cell}} = 1.23 \text{ V, spontaneous} \quad (D.) E^\circ_{\text{cell}} = 1.23 \text{ V, nonspontaneous}$$

(E.) None of these choices is correct.

- (9) The acid dissociation constant  $K_a$  equals  $1.26 \times 10^{-2}$  for  $\text{HSO}_4^-$  and is  $5.6 \times 10^{-10}$  for  $\text{NH}_4^+$ .

Which statement about the following equilibrium is correct?



(A.) The reactants will be favored because ammonia is a stronger base than the sulfate anion.  
(B.) Neither reactants nor products will be favored because all of the species are weak acids or bases.

(C.) The initial concentrations of the hydrogen sulfate ion and ammonia must be known before any prediction can be made.

(D.) This reaction is impossible to predict, since the strong acid and the weak base appear on the same side of the equation.

(E.) None of these choices is correct.

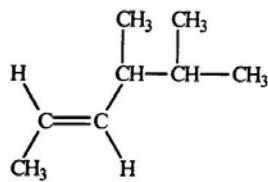
- (10) Sodium hydrogen carbonate decomposes above  $110^\circ\text{C}$  to form sodium carbonate, water, and carbon dioxide.



One thousand grams of sodium hydrogen carbonate are added to a reaction vessel, the temperature is increased to  $200^\circ\text{C}$ , and the system comes to equilibrium. What happens in this system if another 50 g of sodium carbonate are now added?

- (A.) The partial pressure of carbon dioxide will increase.  
(B.) The partial pressure of carbon dioxide will decrease.  
(C.) The amounts of all products will be greater when equilibrium is reestablished.  
(D.) None of these conclusions is justified without knowing the equilibrium constant.  
(E.) None of these choices is correct.

- (11) Select the correct name for the following compound.



(A.) *trans*-4,5-dimethyl-2-hexene (B.) *trans*-2,3-dimethyl-4-hexene

(C.) *cis*-4,5-dimethyl-2-hexene (D.) *cis*-2,3-dimethyl-4-hexene

(E.) None of these choices is correct.

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- (12) The kinetics of the decomposition of dinitrogen pentoxide is studied at 50°C and at 75°C. Which of the following statements concerning the studies is correct?
- (A.) The rate at 75°C will be greater than the rate at 50°C because the activation energy will be lower at 75°C than at 50°C.  
(B.) The rate at 75°C will be greater than the rate at 50°C because the activation energy will be higher at 75°C than at 50°C.  
(C.) The rate at 75°C will be less than the rate at 50°C because the molecules at higher speeds do not interact as well as those at lower speeds.  
(D.) The rate at 75°C will be greater than at 50°C because the concentration of a gas increases with increasing temperature.  
(E.) The rate at 75°C will be greater than the rate at 50°C because the number of molecules with enough energy to react increases with increasing temperature.
- (13) The Clausius-Clapeyron equation is used in calculations of ?
- (A.) melting and freezing points. (B.) vapor pressures of liquids.  
(C.) osmotic pressures of solutions. (D.) crystal structure.  
(E.) None of these choices is correct.
- (14) The nitrosonium ion,  $\text{NO}^+$ , forms a number of interesting complexes with nickel, cobalt, and iron. According to molecular orbital theory, which of the following statements about  $\text{NO}^+$  is correct?
- (A.)  $\text{NO}^+$  has a bond order of 2 and is paramagnetic.  
(B.)  $\text{NO}^+$  has a bond order of 2 and is diamagnetic.  
(C.)  $\text{NO}^+$  has a bond order of 3 and is paramagnetic.  
(D.)  $\text{NO}^+$  has a bond order of 3 and is diamagnetic.  
(E.) None of these choices is correct.
- (15) Which of the following electron configurations represents the ground state of an element?
- (A.)  $[\text{Ne}]3s^13p^1$  (B.)  $[\text{He}]2s^12p^3$  (C.)  $[\text{Ne}]3s^23p^23d^1$  (D.)  $[\text{Ne}]3s^23p^3$   
(E.)  $[\text{Ne}]3s^23p^33d^1$

< II > 計算題(共佔 55 分)

- (1) Mixtures of  $\text{CaCl}_2$  and  $\text{NaCl}$  are used to melt ice on roads. A dissolved 1.9348-g sample of such a mixture was analyzed by using excess  $\text{Na}_2\text{C}_2\text{O}_4$  to precipitate the  $\text{Ca}^{2+}$  as  $\text{CaC}_2\text{O}_4$ . The  $\text{CaC}_2\text{O}_4$  was dissolved in sulfuric acid, and the resulting  $\text{H}_2\text{C}_2\text{O}_4$  was titrated with 37.68 mL of 0.1019 M  $\text{KMnO}_4$  solution.
- (a) Write the balanced net ionic equation for precipitation reaction? (5%)

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- (b) Write the balanced net ionic equation for the titration reaction (unbalance)?



- (c) What is the oxidizing agent? (5%)

- (d) What is the reducing agent? (5%)

- (e) Calculate the mass percent of CaCl<sub>2</sub> in the original sample? (CaCl<sub>2</sub> = 110.98 g/mol) (5%)

- (2) Write the condensed ground-state electron configurations of these transition metal ions, and state which are paramagnetic: (a) Ag<sup>+</sup> and (b) Hg<sup>2+</sup> (10%)

Key:												7A (17)		8A (18)	
												H	He		
1A (1)	2A (2)														
Li	Be	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8) (9) (10)			1B (11)	2B (12)	Al	Si	P	S
Na	Mg	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
K	Ca														Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	112	113	114	115	116
A															
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

- (3) Calculate the pH during the titration of 40.00 mL of 0.100M propanoic acid (CH<sub>3</sub>CH<sub>2</sub>COOH, which we simplify as HPr; K<sub>a</sub>=1.3 × 10<sup>-5</sup>) after adding the following volumes of 0.100M NaOH:

- (a) 30.00mL (b) 40.00mL

(K<sub>w</sub> = 1.0 × 10<sup>-14</sup>, log(2) = 0.301, log(3) = 0.477, log(5)= 0.699, log(11)=1.041) (20%)