

科目：無機化學(2003)

校系所組：中大化學學系 交大應用化學系甲組 清大化學系

(單選，每題 2 分，答錯不倒扣分數)

一 單選題 答案請填寫於電腦答案卡上 (2% each, 54% total)

For questions 1 and 2

In a one-dimensional particle-in-a-box, for a wavefunction with $n = 8$:

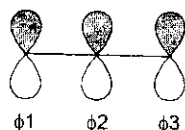
1. How many wavelengths equal the size of the box?

(A) 4 (B) 5 (C) 6 (D) 7 (E) 8

2. How many nodes are there?

(A) 4 (B) 5 (C) 6 (D) 7 (E) 8

For questions 3 and 4

Linear combination $\phi_1 + \phi_2 + \phi_3 =$ 

3. To what type of interaction does the linear combination belong?

(A) σ (B) μ (C) π (D) η (E) δ

4. Which one of the following linear combinations is an allowed antibonding interaction?

(A) $\phi_1 + \phi_2 + \phi_3$ (B) $\phi_1 - \phi_2 + \phi_3$ (C) $\phi_1 - \phi_2 - \phi_3$ (D) $\phi_1 - \phi_2$ (E) $\phi_1 - \phi_3$ 5. What is the shape of SF_4 ?

(A) tetrahedral (B) trigonal bipyramidal (C) seesaw (D) square planar (E) T-shaped

6. Which one of the following diatomic molecules and ions is paramagnetic?

(A) CO (B) N_2 (C) NO^+ (D) O_2^{2-} (E) NO^- 7. For an octahedral complex Ma_3bcd (M is the center atom while a, b, c, and d are ligands), how many stereoisomers can be found?

(A) 2 (B) 3 (C) 4 (D) 5 (E) 6

8. What is the ground state term of Mn^{2+} ?(A) ^5D (B) ^4F (C) ^3F (D) ^4G (E) ^6S 9. For $\text{Mn}(\text{OH}_2)_6^{3+}$, which one of the following magnetic moments (in Bohr magneton) is most likely?

(A) 1.73 (B) 2.83 (C) 3.87 (D) 4.90 (E) 5.92

For questions 10 and 11

Consider CaF_2 (fluorite structure):10. What are the coordination numbers of the ions in CaF_2 ?

(A) Ca: 2, F: 4 (B) Ca: 8, F: 4 (C) Ca: 4, F: 8 (D) Ca: 4, F: 4 (E) Ca: 8, F: 8

11. What are the numbers of the ions per unit cell?

(A) Ca: 2, F: 4 (B) Ca: 8, F: 4 (C) Ca: 4, F: 8 (D) Ca: 4, F: 4 (E) Ca: 8, F: 8

For questions 12 and 13

Consider Pt:

12. The density of Pt is $21.09 \text{ g}\cdot\text{cm}^{-3}$. Pt crystallizes in a cubic close-packed structure. Estimate its atomic radius.

(A) 100 pm (B) 113 pm (C) 126 pm (D) 139 pm (E) 152 pm

13. What is the ratio of the volume occupied by Pt atoms to the volume of the solid?

(A) 0.80 (B) 0.74 (C) 0.68 (D) 0.60 (E) 0.52

14. Which one of the following complexes is not an 18-electron species?

(A) $\eta^5\text{-Cp}_2\text{Co}$ (B) $\text{Ph}(\text{MeO})\text{C}=\text{Cr}(\text{CO})_5$ (C) $\eta^5\text{-CpFe}(\text{CO})_2\text{Cl}$ (D) $\text{HCo}(\text{CO})_4$ (E) $\text{Mn}(\text{CO})_5\text{Cl}$ 15. Consider the following compounds. Which one has the largest affinity towards H^+ in gas phase?(A) NF_3 (B) NH_3 (C) NMe_2 (D) NMe_2H (E) NMe_3

16. Which one of the following molecules has the highest M-C bond enthalpy? (M is the center atom)

(A) CMe_4 (B) SiMe_4 (C) GeMe_4 (D) SnMe_4 (E) PbMe_4

參考用

注意：背面有試題

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17. Which one of the following compounds does not contain three-center two-electron bonds?

(A) B_2H_6 (B) B_4H_{10} (C) Al_2Me_6 (D) $Al_2Me_4Cl_2$ (E) Al_2Ph_6

18. $Mo_2(O_2CMe)_4$ has a Mo-Mo quadruple bond. $Rh_2(O_2CMe)_4$ is isostructural to the Mo complex. What is the Rh-Rh bond order?

(A) 0 (B) 1 (C) 2 (D) 3 (E) 4

19. According to the Frost diagrams of Cr, Mo and W shown on the right, determine their most stable oxidation numbers.

(A) Cr:6, Mo:6, W:0 (B) Cr:0, Mo:0, W:0 (C) Cr:3, Mo:4, W:6 (D) Cr:4, Mo:4, W:4 (E) Cr:3, Mo:5, W:5

20. Which one of the following complexes displays the lowest CO stretching frequency?

(A) $Ti(CO)_6^{2-}$ (B) $V(CO)_6^-$ (C) $Cr(CO)_6$ (D) $Mn(CO)_6^+$ (E) $Fe(CO)_5$

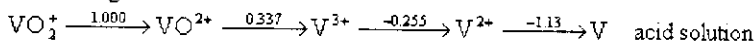
21. Which one of the following molecules possesses an S_4 axis?

(A) allene (B) ethylene (C) hydrazine (D) benzene (E) ferrocene

22. Which one of the following oxides is the most acidic?

(A) Na_2O (B) B_2O_3 (C) Al_2O_3 (D) P_2O_5 (E) SO_3

23. Using the information below:



What is the most stable oxidation number of vanadium in an acid solution?

(A) 1 (B) 2 (C) 3 (D) 4 (E) 5

24. Which one of the following elements has the largest metallic radius?

(A) Ca (B) Co (C) Cr (D) Cs (E) Cu

25. Which one of the following elements has the highest first ionization energy?

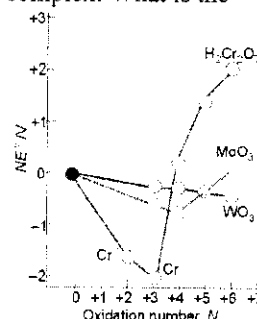
(A) S (B) Sb (C) Si (D) Sn (E) Sr

26. All of the following solids have rock-salt structures. Which one of them has the highest melting point?

(A) CaO (B) MgO (C) LiF (D) NaCl (E) KBr

27. Which one of the following solids is not considered to be a semiconducting material?

(A) GaN (B) CdS (C) SiC (D) CaF_2 (E) Si



參考用

二 閱讀題目內容後，回答各小題答案於答案卷上 (20% total)

From a reaction between 3-hexyne and $AuCl$ in CH_2Cl_2 , a new monomeric compound A is isolated. A displays the following data:

1H NMR	^{13}C NMR	Elemental Analyses
δ 1.23 ppm, triplet, $J = 7.2$ Hz	δ 14.7 ppm	C: 22.91%
δ 2.61 ppm, quartet, $J = 7.2$ Hz	δ 15.2 ppm	H: 3.20%
	δ 86.4 ppm	

- Used the data to draw a structure for A. Discuss why you propose this structure. (6%)
- Count the number of valence electrons for A. (2%)
- Discuss the bonding between the hydrocarbon fragment and the metal center in A. (4%)
- Is the C3-C4 bond length in A longer or shorter than a $C \equiv C$ bond? Why? (4%)
- Predict the angles of $\angle C2-C3-C4$ and $\angle C3-C4-C5$ in A. Explain your reasons. (4%)

Reference: *Inorg. Chem.*, 2009, 48 (2), 423-425

注意：背面有試題

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三 閱讀題目內容後，回答各小題答案於答案卷上 (26% total)

BP Chemicals developed the Cativa process to compete with the Monsanto process for the carbonylation of methanol. The new process used Ir instead of Rh to assist the reaction. During the investigation, it was discovered that the reaction between $(\text{Ph}_4\text{As})^-\text{[Ir}(\text{CO})_2\text{I}_2]^-$ (**A**) and MeI generated $(\text{Ph}_4\text{As})^+\text{[cis, fac-Ir}(\text{CO})_2\text{I}_3\text{Me}]^-$ (**B**). Heating **B** at 150°C produced compound **C**. **C** is a centrosymmetric dimer linked through bridging iodide ligands. The methyl group is at a site trans to the bridging iodide. In addition, **C** displays the following data.

¹ H NMR	¹³ C NMR (C formed from B with ¹³ C enriched methyl)	$\nu(\text{CO})$	Elemental Analyses
δ 2.75 ppm, singlet, 3H	δ -14.3 ppm	2029 cm^{-1}	C: 31.25%
δ 7.6-7.9 ppm, multiplet, 20H			H: 2.32%
			I: 38.1%

C reacted with CO to form **D** first. **D**, an isomer of **B**, showed $\nu(\text{CO})$ absorptions at 2094 and 2041 cm^{-1} . Then, **D** reacted with CO quickly and underwent migratory insertion to form **E**. **E** showed $\nu(\text{CO})$ absorptions at 2064 and 1653 cm^{-1} .

1. Draw structures for the anions in **A** and **B**. (4%)
2. What type of reaction is the reaction between **A** and MeI to produce **B**? (2%)
3. Draw structures for the anions in **C**, **D**, and **E** (6%). Discuss why you propose these structures. (9%)
4. Using ¹³CO to react with **C** and **D** may assist you to identify whether the conversion of **D** to **E** is via methyl migration or CO insertion. Explain how this is done. (5%)

Reference: *Inorg. Chem.*, 2009, 48 (1), pp 28-35

參考用

1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18			
hydrogen 1 H 1.0079		beryllium 4 Be 9.0122																						boron 5 B 10.811		carbon 6 C 12.011		nitrogen 7 N 14.007		oxygen 8 O 15.999		fluorine 9 F 18.998		neon 10 Ne 20.180			
lithium 3 Li 6.941		beryllium 4 Be 9.0122																						aluminum 13 Al 26.982		silicon 14 Si 28.086		phosphorus 15 P 30.974		sulfur 16 S 32.065		chlorine 17 Cl 35.453		argon 18 Ar 39.948			
sodium 11 Na 22.990		magnesium 12 Mg 24.305																						gallium 31 Ga 69.723		germanium 32 Ge 72.61		arsenic 33 As 74.922		selenium 34 Se 78.96		bromine 35 Br 79.904		krypton 36 Kr 83.80			
potassium 19 K 39.098		calcium 20 Ca 40.078		scandium 21 Sc 44.956		titanium 22 Ti 47.867		vanadium 23 V 50.942		chromium 24 Cr 51.996		manganese 25 Mn 54.938		iron 26 Fe 55.845		cobalt 27 Co 58.933		nickel 28 Ni 58.693		copper 29 Cu 63.546		zinc 30 Zn 65.38		gallium 31 Ga 69.723		germanium 32 Ge 72.61		arsenic 33 As 74.922		selenium 34 Se 78.96		bromine 35 Br 79.904		krypton 36 Kr 83.80			
rubidium 37 Rb 85.468		strontium 38 Sr 87.62		yttrium 39 Y 88.906		zirconium 40 Zr 91.224		niobium 41 Nb 92.906		molybdenum 42 Mo 95.94		technetium 43 Tc [98]		ruthenium 44 Ru 101.07		rhodium 45 Rh 102.91		palladium 46 Pd 106.42		silver 47 Ag 107.87		cadmium 48 Cd 112.41		indium 49 In 114.82		tin 50 Sn 118.71		antimony 51 Sb 121.76		tellurium 52 Te 127.60		iodine 53 I 126.90		xenon 54 Xe 131.29			
cesium 55 Cs 132.91		barium 56 Ba 137.33		lanthanum 57-70 La-Lu 138.91		hafnium 72 Hf 178.49		tantalum 73 Ta 180.95		tungsten 74 W 183.84		rhenium 75 Re 186.21		osmium 76 Os 190.23		iridium 77 Ir 192.22		platinum 78 Pt 195.08		gold 79 Au 196.97		mercury 80 Hg 200.59		thallium 81 Tl 204.38		lead 82 Pb 207.2		bismuth 83 Bi 208.98		polonium 84 Po [209]		astatine 85 At [210]		radon 86 Rn [222]			
francium 87 Fr [223]		radium 88 Ra [226]		actinoids 89-102 Ac-Lr [227]		rutherfordium 103 Rf [261]		dubnium 104 Db [262]		seaborgium 105 Sg [263]		bohrium 106 Bh [264]		hassium 107 Hs [265]		meitnerium 108 Mt [266]		darmstadtium 109 Ds [267]		roentgenium 110 Rg [268]		copernicium 111 Cn [269]		nihonium 112 Nh [270]		flerovium 113 Fl [271]		tennessine 114 Ts [272]		oganesson 115 Og [273]		unbinilium 116 Uub [274]		ununtrium 117 Uut [275]		ununquadium 118 Uuq [276]	

lanthanoids		actinoids											
57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.91	140.12	140.91	144.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.06
89	90	91	92	93	94	95	96	97	98	99	100	101	102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
[227]	[232.04]	[231.04]	[238.03]	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[259]	[259]