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)

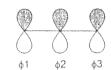
For questions 1 and 2

In a one-dimensional particle-in-a-box, for a wavefuction 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 Ma₃bcd (M is the center atom while a, b, c, and d are ligands), how many stereo isomers can be found?
- (A) 2 (B) 3 (C) 4 (D) 5 (E) 6
- 8. What is the ground state term of Mn^{2+} ?
- (A) $^{5}D (B)$ $^{4}F (C)$ $^{3}F (D)$ $^{4}G (E)$ ^{6}S
- 9. For $Mn(OH_2)_6^{3+}$, 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 CaF₂ (fluorite structure):

- 10. What are the coordination numbers of the ions in CaF₂?
- (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 g.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) η^{5} -Cp₂Co (B) Ph(MeO)C=Cr(CO)₅ (C) η^{5} -CpFe(CO)₂Cl (D) HCo(CO)₄ (E) Mn(CO)₅Cl
- 15. Consider the following compounds. Which one has the largest affinity towards H⁺ in gas phase?
- (A) NF₃ (B) NH₃ (C) NMeH₂ (D) NMe₂H (E) NMe₃
- 16. Which one of the following molecules has the highest M-C bond enthalpy? (M is the center atom)
- (A) CMe₄ (B) SiMe₄ (C) GeMe₄ (D) SnMe₄ (E) PbMe₄

注:背面有試題

H-Gr-O-

MoO.

台灣聯合大學系統98學年度碩士班考試命題紙

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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. Mo₂(O₂CMe)₄ has a Mo-Mo quadruple bond. Rh₂(O₂CMe)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) Na₂O (B) B₂O₃ (C) Al₂O₃ (D) P₂O₅ (E) SO₃
- 23. Using the information below:

$$VO_3^+ \xrightarrow{1.000} VO^{2+} \xrightarrow{0.337} V^{3+} \xrightarrow{-0.255} V^{2+} \xrightarrow{-1.13} V$$
 acid solution

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) CaF₂ (E) Si

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:

_				
	'H 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		

- 1. Used the data to draw a structure for A. Discuss why you propose this structure. (6%)
- 2. Count the number of valence electrons for A. (2%)
- 3. Discuss the bonding between the hydrocarbon fragment and the metal center in A. (4%)
- 4. Is the C3-C4 bond length in A longer or shorter than a $C \equiv C$ bond? Why? (4%)
- 5. 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;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 $(Ph_4As)^+[Ir(CO)_2I_2]^-(A)$ and MeI generated $(Ph_4As)^+[cis,fac-Ir(CO)_2I_3Me]^-(B)$. 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.

¹H NMR	¹³ C NMR	ν(CO)	Elemental
	(C formed from B with ¹³ C enriched methyl)	and the second s	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 $\nu(CO)$ absorptions at 2094 and 2041 cm⁻¹. Then, D reacted with CO quickly and underwent migratory insertion to form E. E showed $\nu(CO)$ 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

hydrogen 1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 1.0079				Kay:														He
Sthium 3	beryllium 4				men nemele Imun olmo								baren 5	carbon 6	nitrogen 7	axygen 8	Bucrine 9	neon 10
Li	Вe				ymb								В	C	N	Ŏ	F	Ne
6.941 sodum	9 0122 magnesium			stomic wa	ight (mean rel	stive mass)							10 811 Warning	12,011 silicon	14 007 phosphorus	15,969 Nullur	18.998 chlorine	20 190 argon
11	12												13	14	15	16	17	18
Na	Mg												Al	Si	Р	S	CI	Ar
22,990 potássium	24.305 calcium		scandium	Blantum	vanadium	chron-lum	manganese	kon	coball	l nickel	COPPET	zinc	26.962 galliyan	28 086 germanium	30 974 #198THS	32.065 26/909200	25.452 bromme	39 948 Anypton
19	20		21	22	23	24	25	26	27	28	29	30	31	32	33	3.4	35	36
K	Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39 098 rubidium	40.078 strentlum		44.956 yttrium	47 967 zirconium	30 942 nioblum	51.996 molybdenum	54,938 lachnellum	55.845 ruthersium	58.933 rhodeum	58 693 cañadum	53 540 80vm/	85.38 cadmium	69.723 Indiaen	72.61	74.622	78.96	79.904	83.80
37	38		39	40	41	42	43	44	45	46	47	48	49	tn 50	antimony 51	tellurlum 52	todine 53	54
Rb	Sr		Υ	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	No.	Xe
85.468 CN441UM	87.52 backum		88,906 (utetium	91.224 næfnium	92 906 tantakun	95.96 tungsten	(96)	101.07 0smium	102.91 #KSum	106.42 platinum	107 87 gold	112.41	\$14.92 thattion	118 71	121.76	127.50	126.60	131.29
55	56	57-70	71	72	73	74	75	76	77	78	79	80 maidray	8.1	tead 82	barnuth 83	potorkum. 84	astatine 85	radon 86
Cs	Ва	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
francium	137 33 (adkum		174.97 lawtencium	178.49 rutherfordium	189.95	183 84	186.21	190.23	192.22	195.08	196 97	200.58	204.38	207.2	208.98	[208]	[210]	E221
87	88	89-102	103	104	dubnium 105	seaborghum 106	torrium 107	hassium 108	melinerium 109	darmstadhum 110	igenigenium 111	umunbium 112	ununinum 113	tzhunguadium 114	unungenkum 115	ununhexium 116	ununsephum 117	ununochum 118
Fr	Ra	**	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds		Uub					f 1878.	Uuo
12331	[226]		(252)	1267)	(268)	18211	(272)	(279)	(276)	1281)	[280]	12851	[284]	[289]	[288]	(593)	~~	[294]

	Cabanum 57	58	presentymeur 59	neodymium 68	promethium 61	samarium 62	#urcolum 63	gadolinium 64	terbium 65	dysprosium 66	holmlum 87	erbium 68	thuilum 69	ytterbium 70
*lanthanoids	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Ĕr	Tim	Υb
	138.91	140.12	140.91	144 24	[145]	150.36	151.96	157 25	158.93	162.50	184.93	167,26	168.93	173.08
	actinium	Bhorlum	prefactionum	te entre	neptunium	plutonium	americium	curture	berkesum	callfornium	#insteaken	fermium	merale evans	
	8.9	90	91	92	93	94	95	96	97	98	99	100	101	102
**actinoids	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
	[327]	232.04	231.04	238.03	13371	[244]	12431	[247]	[247]	12511	1252)	[257]	(758)	12591