注意：請依序作答

1. (20%)Provide explanation for the following:
(a)Although both the Br_3^- and I_3^- ions are known, the F_3^- does not exist。Explain.
(b)The stabilization of a half-filled d subshell is even more pronounced than that of the p subshell。Why?
(c)Protonation of piperidine is slightly more favorable than protonation of pyridine。Explain.
(d)Ionic compoumds, such as $KMnO_4$, can be dissolved in nonpolar solvents by adding crown ethers. Suggest how crown ethers make $KMnO_4$ soluble in nonpolar solvents。
(e)Oxygen is more electronegative than nitrogen; fluorine is more electronegative than the other halogens. Fluoride is a stronger field ligand than the other halides, but ammonia is a stronger field ligand than water.Why?

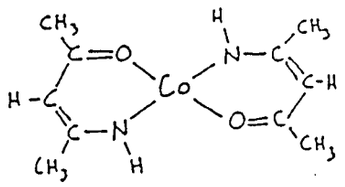
2.(8%) Among the homonuclear diatomic molecules in the second period, which are paramagnetic based on MO theory and why the extent of s-p mixing decreases across this period?

3.(6%) The first band in photoelectron spectrum of molecule oxygen shows a progression with an interval of 1774 cm^{-1}. What does this suggest about the nature of the highest occupied MO? The vibration frequency of molecular oxygen is 1568cm^{-1}.

4.(6%) The ion $TeBr_6^{2-}$ has been show to have a regular octahedral structure whereas XeF_6 exhibits a non-octahedral structure. Are these results in agreement with the predictions of the

Valence Shell Electron Pair Repulsion theory? If not, how can the discrepancy be explained?

5.(8%) The Co(II) complex, show below, exhibits a magnetic moment of 2.88 B.M. in $CHCl_3$ solution at room temperature, which is independent of concentration. As the temperature is decreased the value of u_{eff} decreases also. Suggest an explanation for these observations.



Co(II)=$3d^7$

6.(6%) There are two CO stretching frequencies observed in IR spectroscopy of $Fe(CO)_5$, but only one carbon-13 NMR resonance signal is found. Explain these observations.

7.(6%) Describe the Laporte selection rule and explain why the d-d transitions (or ligand-field transitions) in octahedral metal complexes may occur.

8.(6%) For a d^4, octahedral complex,
(a) determine the ground terms for high-spin and low-spin configurations respectively;
(b) compare the Jahn-Teller effect for the two cases;
(c) calculate LFSE and CFSE for the high-spin configuration.

9.(8%) Consider σ-bonding in XeF_4, a molecule of D_{4h} symmetry,

(a) derive the possible hybrids for the Xe atom;

(b) Show that the d_{xy} orbital is of B_{2g} symmetry.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

10.(6%) $[IrBr_6]^{2-}$ exhibits two sets of charge transfer absorptions one of lower intensity in the visible region of the spectrum and one of higher intensity in the ultraviolet. $[IrBr_6]^{3-}$ however, shows only the high-intensity charge transfer in the ultraviolet. Explain.

11.(10%) Which compound is more stable in air (答錯倒扣)

(a) $RhCp_2$ or $RuCp_2$

(b) $Mo(CO)_6$ or $Mo(Co)_7$

(c) $Mo(CO)_3(PMe_3)_3$ Or $Mo(CO)_3(PPh_3)_3$

(d) $CpMo(CO)_3H$ or $CpMo(CO)_3Cl$

(e) $Na_2Fe(CO)_4$ or $NaCo(CO)_4$

12. Propose a synthesis for

(a) $HMn(CO)_5$ from $Mn_2(CO)_{10}$ (4%)

(b) $BrW(CO)_4Ph$ from $W(CO)_6$ (4%)

(C) $NaV(CO)_6$ from $V(CO)_6$ (2%)