

Chem 370 - Spring, 2019
Assignment 9 - Solutions

- 11.11 a. $d^8 (O_h)$ is $t_{2g}^6 e_g^2$. There is only one configuration for this, so it is ${}^3A_{2g}$, as the Tanabe-Sugano or Orgel diagram shows.
- b. d^5 high spin is $t_{2g}^3 e_g^2$, for which there is only one configuration, so it is ${}^6A_{1g}$.
 d^5 low spin is $t_{2g}^5 e_g^0$. The unpaired electron can be in any of the three t_{2g} orbitals, making this a triply degenerate T terms. This is ${}^2T_{2g}$.
- c. $d^4 (T_d)$ is $e^2 t_2^2$. Recall that all T_d ML_4 complexes are high spin. Here, the hole can be in any one of the three t_2 orbitals, so this is a triply degenerate state. The $d^4 T_d$ Orgel diagram is the same as the $d^1, d^6 O_h$ diagram, so this is a 5T_2 state (no subscript g).
- d. d^9 square planar (D_{4h}). The highest orbital, $b_{1g} (d_{x^2-y^2})$, has one electron in it, so this is a non-degenerate state. In D_{4h} this would be ${}^2B_{1g}$.
- 11.13 $[Ni(H_2O)_6]^{2+}$ is $d^8 O_h$. This case is covered by the left side of the second Orgel diagram, the diagram for $d^2, d^7 O_h$ and related cases. For $d^8 O_h$, the lowest energy transition, ${}^3A_{2g} \rightarrow {}^3T_{2g}$, is equivalent to Δ_o , so from Figure 11-8 for $[Ni(H_2O)_6]^{2+}$ Δ_o is $\sim 8,700 \text{ cm}^{-1}$. The other two bands arise from the transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The splitting of the bands is a result of Jahn-Teller distortion of the triply degenerate excited states in each case. Note that the ground state (${}^3A_{1g}$) is immune from Jahn-Teller distortion.
- 11.14 a. $[Cr(C_2O_4)_3]^{3-}$ has $Cr^{3+} d^3$. Either from the Orgel diagram or the Tanabe-Sugano diagram, we expect the following transitions: $\nu_1 [{}^4A_{2g} \rightarrow {}^4T_{2g}]$, $\nu_2 [{}^4A_{2g} \rightarrow {}^4T_{1g}(F)]$, $\nu_3 [{}^4A_{2g} \rightarrow {}^4T_{1g}(P)]$. In $d^3 O_h$ cases, Δ_o corresponds to the energy of the first transition, ν_1 . For this complex, $\nu_1 = 17,400 \text{ cm}^{-1} = \Delta_o$.
- b. $[Ti(NCS)_6]^{3-}$ has $Ti^{3+} d^1$. The single band arises from the transition ${}^2T_{2g} \rightarrow {}^2E_g$, as predicted from the right side of the first Orgel diagram. Thus, $\Delta_o = 18,400 \text{ cm}^{-1}$. Both the ground state and the excited state are subject to Jahn-Teller distortions, but only the 2E_g state will have appreciable splitting, because it arises from an imbalance in e_g orbitals directed at ligands. This is the probable cause of the band splitting.
- c. $[Ni(en)_3]^{2+}$ has $Ni^{2+} d^8$. The Orgel diagram for d^8 is the same as d^3 (see above), so we expect three bands: $\nu_1 [{}^3A_{2g} \rightarrow {}^3T_{2g}]$, $\nu_2 [{}^3A_{2g} \rightarrow {}^3T_{1g}(F)]$, $\nu_3 [{}^3A_{2g} \rightarrow {}^3T_{1g}(P)]$. As with the $d^3 O_h$ case, for $d^8 O_h$ Δ_o is the energy of the first band, here $\nu_1 = 11,200 \text{ cm}^{-1} = \Delta_o$.
- 11.16 a. $t_{2g}^4 e_g^2 - T$ The pair in t_{2g} orbitals can be in any of the three.
 b. $t_{2g}^6 - A$ There is only one way of assigning the electrons.
 c. $t_{2g}^3 e_g^3 - E$ An excited state; the pair in e_g (or the unpaired electron) can be in either orbital.
 d. $t_{2g}^5 - T$ The unpaired electron can be in any of the three t_{2g} orbitals.

e. $e_g^1 - E$ An excited state; the electron can be in either orbital.

11.17 Configurations corresponding to nondegenerate states will not have distortions. Those that are e_g^1 and e_g^3 , which lead to E states, will have large distortions, because e_g orbitals are directed at ligands. Configurations that correspond to triply degenerate states arise from an imbalance among t_{2g} orbitals, which lie between ligands. These have only small distortions.

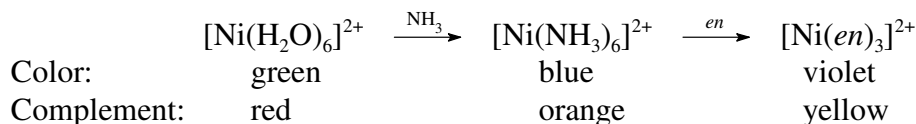
d^n	$t_{2g}^x e_g^y$	State	Distortion	$t_{2g}^x e_g^y$	State	Distortion
1	t_{2g}^1	${}^2T_{2g}$	small			
2	t_{2g}^2	${}^3T_{2g}$	small			
3	t_{2g}^3	${}^4A_{2g}$	none			
4	$t_{2g}^3 e_g^1$	5E_g	large	t_{2g}^4	${}^3T_{1g}$	small
5	$t_{2g}^3 e_g^2$	${}^6A_{1g}$	none	t_{2g}^5	${}^2T_{2g}$	small
6	$t_{2g}^4 e_g^2$	${}^5T_{2g}$	small	t_{2g}^6	${}^1A_{1g}$	none
7	$t_{2g}^5 e_g^2$	${}^4T_{1g}$	small	$t_{2g}^6 e_g^1$	2E_g	large
8	$t_{2g}^6 e_g^2$	${}^3A_{2g}$	none			
9	$t_{2g}^6 e_g^3$	2E_g	large			

11.23 a. At 80 K, $\mu_s = 0.65 = \sqrt{n(n+2)}$, from which $n = 0.19 \approx 0$.

At 300 K, $\mu_s = 5.2 = \sqrt{n(n+2)}$, from which $n = 4.3 \approx 4$.

b. The complex appears to be d^6 low-spin at 80K and d^6 high spin at 300 K. Looking at the Tanabe-Sugano diagram, we would expect as many as five bands arising from the ${}^1A_{1g}$ ground state of the low-spin complex at 80 K. More realistically, there are probably only two or three bands, because the upper 1E_g and ${}^1T_{2g}$ states are nearly degenerate, and the transition to the highest state (${}^1A_{2g}$) probably falls in the uv. The transition to the accidentally degenerate 1E_g and ${}^1T_{2g}$ states may also fall in the uv. By contrast, the d^6 high-spin complex should have only one band, ${}^5T_{2g} \rightarrow {}^5E_g$. This band may show some spitting, owing to strong Jahn-Teller distortion in the excited state.

- 11.27 Adding NH_3 causes replacement of the H_2O ligands, and adding ethylenediamine (*en*) causes replacement of NH_3 ligands with *en*.



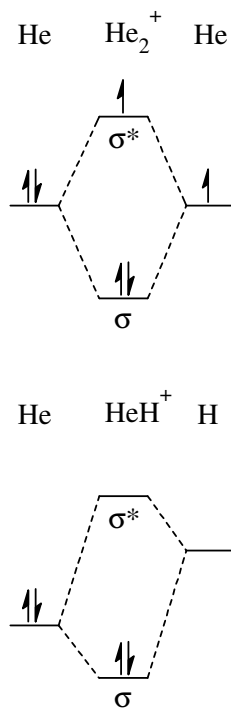
In the spectrochemical series, H_2O is weaker than NH_3 , which is weaker than *en*. Thus, through the series of substitutions, the value of Δ_o increases. Treating all of these as octahedral (the *en* complex is actually D_3), from the d^8 Orgel diagram we predict three absorption bands, arising from the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. As Δ_o increases, the frequencies of all of these transitions increase, which means the absorbed region of the visible spectrum shifts toward the blue end of the visible spectrum. The absorbed regions are the complements of the colors we perceive. These complements change from red to orange to yellow, a shift toward higher frequencies, consistent with increasing Δ_o .

- 12.1 Cr^{2+} is a d^4 configuration, and with H_2O ligands it is high spin, with one electron in the e_g^* level. Moreover, its ground state term is 5E_g , which is subject to significant Jahn-Teller distortion. Therefore, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is labile, making substitution very favorable. With CN^- ligands, Cr^{2+} is low spin, with a ${}^3T_{1g}$ term and less significant Jahn-Teller distortion. Also, CN^- forms strong bonds with Cr^{2+} . All these factors make $[\text{Cr}(\text{CN})_6]^{4-}$ inert.
- 12.2 The rate law expressions for I_a and I_d are too similar (often first order) to form a basis for distinguishing between them. However, if the rate constants for different entering ligands are quite different, that suggests that the formation of an associative complex (effectively increasing the coordination number) is a rate determining step, and the mechanism is I_a . If dissociation is more important, then the rates with different leaving groups should be quite different, and the mechanism is I_d .
- 12.4 $[\text{Fe}(\text{CN})_6]^{4-}$ is a low-spin d^6 configuration (${}^1A_{1g}$), with the maximum CFSE of $-2.4\Delta_o$ (ignoring the $3P$ pairing energy). The low-spin, strong Fe–CN bonds, and absence of Jahn-Teller distortion make this a stable and inert complex. Thus, there is no danger of dissociation of toxic CN^- .
- 12.16 a. $[\text{Pt}(\text{CO})\text{Cl}_3]^- + \text{NH}_3 \rightarrow \textit{trans}\text{-}[\text{Pt}(\text{CO})(\text{NH}_3)\text{Cl}_2]$ CO is the stronger *trans* director.
- b. $[\text{Pt}(\text{NH}_3)\text{Br}_3]^- + \text{NH}_3 \rightarrow \textit{cis}\text{-}[\text{Pt}(\text{NH}_3)_2\text{Br}_2]$ Br is the stronger *trans* director.
- c. $[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]^- + \text{NH}_3 \rightarrow \textit{trans}\text{-}[\text{Pt}(\text{C}_2\text{H}_4)(\text{NH}_3)\text{Cl}_2]$
 C_2H_4 is the stronger *trans* director.
- 12.20 Neither H_2O nor NH_3 is a potential bridging ligand, so the mechanism cannot be inner sphere. Therefore, it is outer sphere.

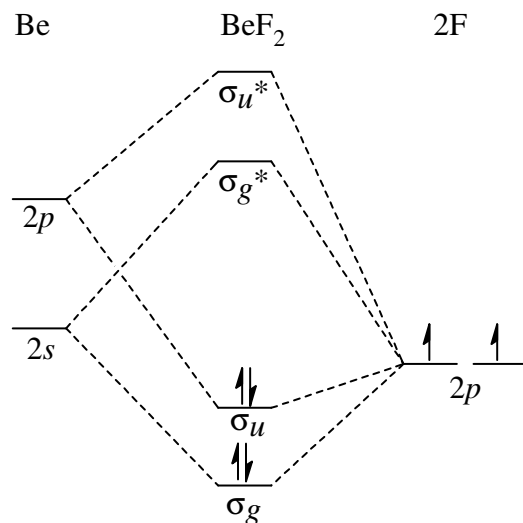
- 8.1 a. H_2 74.2 pm 436 kJ/mol
 H_2^+ 106 pm 255 kJ/mol
 These data are consistent with the MO descriptions σ^2 for H_2 and σ^1 for H_2^+ , corresponding to bond orders of 1 and $1/2$, respectively.

b. As shown in problem 5.20, the D_{3h} structure of H_3^+ has an MO scheme consisting of three MOs, a_1' and e' . The two electrons of H_3^+ occupy the a_1' MO, resulting in a $3c-2e$ bond for the molecule.

- 8.2 He_2^+ has two electrons in the bonding σ MO and one in the antibonding σ^* MO, resulting in a bond order of $1/2$. HeH^+ has two electrons in the bonding σ MO, resulting in a bond order of 1, but the energies of the $1s$ are very mismatched. The electron pair in the bonding MO is localized more on the He.

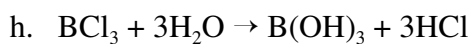
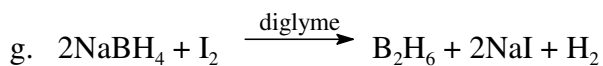
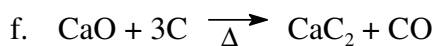
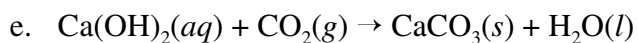
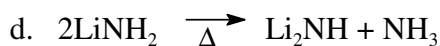
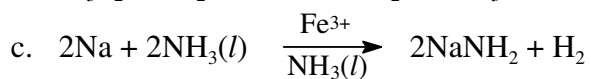


- 8.3 Being isoelectronic with IF_4^- and XeF_4 , CsF_4^+ would presumably have a square planar structure with two *trans* lone pairs (VSEPR type AX_4E_2). However, in CsF_4^+ the cesium would be in the previously unknown oxidation state of +5. This would be such a potent oxidizing agent that it would likely have an instantaneous redox with fluoride to yield F_2 and CsF . It is unlikely that this species will ever be synthesized, let alone isolated.
- 8.5 As we have seen in numerous previous examples, the SALCs in $D_{\infty h}$ that could be formed from two p_z orbitals on separate F atoms would have Σ_g^+ and Σ_u^+ symmetry. On the central Be atom, the $2s$ orbital has Σ_g^+ symmetry and the $2p_z$ orbital has Σ_u^+ symmetry. The p_x and p_y orbitals are degenerate as Π_u and are nonbonding. The resulting MO scheme, omitting the nonbonding Π_u level, is shown below.

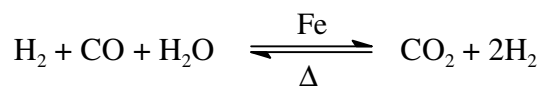


8.9 The combination of orbitals in $\text{Al}_2(\text{CH}_3)_6$ is similar to diborane, B_2H_6 , except that the CH_3 group can be considered to contribute an sp^3 hybrid orbital (rather than a $1s$ orbital) to overlap with an sp^3 hybrid orbital from each Al, resulting in a $3c-2e$ bond for each bridge.

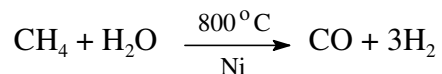
1. Balanced equations:



2. a. The "water-gas shift reaction"



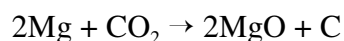
- b. Cracking of methane to produce hydrogen



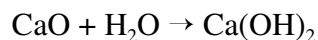
- c. Synthesis of LiAlH_4



- d. Mg burning in a CO_2 atmosphere



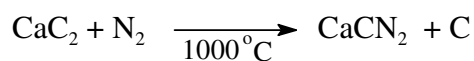
- e. slaking of lime



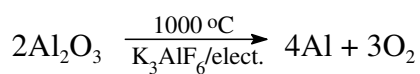
- f. setting of Plaster of Paris



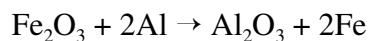
- g. cyanamide reaction



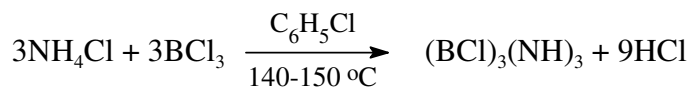
- h. Hall process



- i. Goldschmidt or thermite reaction

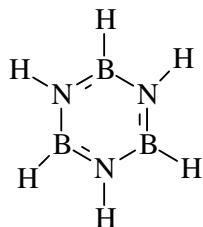


- j. synthesis of B-trichloroborazine



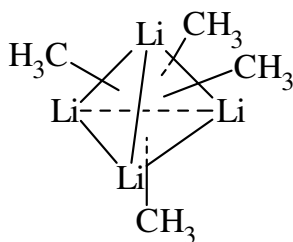
3. Draw structures for the following molecules. Give the point group of the molecule, and note any peculiar bonding features (type of bridge bond, Lewis-base active lone pair, etc.)

a. borazine



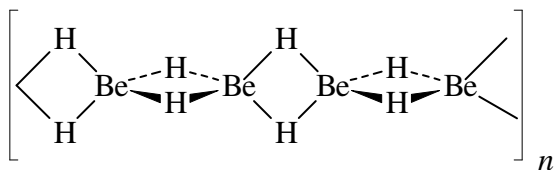
D_{3h} Analogue of benzene, with hindered pi delocalization.

b. solid LiCH_3



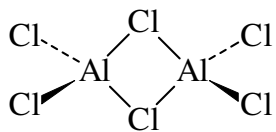
T_d Tetrahedral tetramer

c. solid BeH_2



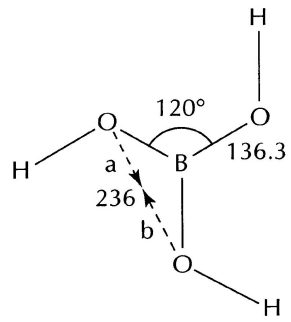
D_{2h} $3c-2e$ bridge bonds

d. aluminum trichloride



D_{2h} Dimer with $2c-2e$ bridge bonds

e. boric acid



C_{3h}

Planar molecule