12.1 \(\text{Cr}^{2+}\) is a \(d^4\) configuration, and with \(\text{H}_2\text{O}\) 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, \([\text{Cr(H}_2\text{O})_6]^{2+}\) is labile, making substitution very favorable. With \(\text{CN}^-\) ligands, \(\text{Cr}^{2+}\) is low spin, with a \(3T_{1g}\) term and less significant Jahn-Teller distortion. Also, \(\text{CN}^-\) forms strong bonds with \(\text{Cr}^{2+}\). All these factors make \([\text{Cr(CN)}_6]^{4-}\) 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 \([\text{Fe(CN)}_6]^{4-}\) is a low-spin \(d^6\) configuration (\(^1A_g\)), with the maximum CFSE of \(-2.4\Delta_o\) (ignoring the \(3P\) pairing energy). The low-spin, strong FeCN bonds, and absence of Jahn-Teller distortion make this a stable and inert complex. Thus, there is no danger of dissociation of toxic \(\text{CN}^-\).

12.16 a. \([\text{Pt(CO)}\text{Cl}_3]^– + \text{NH}_3 \rightarrow trans-[\text{Pt(CO)}(\text{NH}_3)\text{Cl}_2]\) CO is the stronger trans director.

b. \([\text{Pt(NH}_3\text{)}\text{Br}_3]^– + \text{NH}_3 \rightarrow cis-[\text{Pt(NH}_3\text{)}_2\text{Br}_2]\) Br is the stronger trans director.

c. \([\text{Pt(C}_2\text{H}_4\text{)}\text{Cl}_3]^– + \text{NH}_3 \rightarrow trans-[\text{Pt(C}_2\text{H}_4\text{)}(\text{NH}_3)\text{Cl}_2]\) \(\text{C}_2\text{H}_4\) is the stronger trans director.

12.20 Neither \(\text{H}_2\text{O}\) nor \(\text{NH}_3\) is a potential bridging ligand, so the mechanism cannot be inner sphere. Therefore, it is outer sphere.

8.1 a. \(\text{H}_2 \quad 74.2\ \text{pm} \quad 436\ \text{kJ/mol}\)
\(\text{H}_2^+ \quad 106\ \text{pm} \quad 255\ \text{kJ/mol}\)
These data are consistent with the MO descriptions \(\sigma^2\) for \(\text{H}_2\) and \(\sigma^1\) for \(\text{H}_2^+\), corresponding to bond orders of 1 and \(\frac{1}{2}\), respectively.

b. As shown in problem 5.20, the \(D_{3h}\) structure of \(\text{H}_3^+\) has an MO scheme consisting of three MOs, \(a_1'\) and \(e'\). The two electrons of \(\text{H}_3^+\) occupy the \(a_1'\) MO, resulting in a \(3c-2e\) bond for the molecule.
8.2 \( \text{He}_2^+ \) has two electrons in the bonding \( \sigma \) MO and one in the antibonding \( \sigma^* \) MO, resulting in a bond order of \( \frac{1}{2} \). \( \text{HeH}^+ \) has two electrons in the bonding \( \sigma \) MO, resulting in a bond order of 1, but the energies of the 1\( s \) are very mismatched. The electron pair in the bonding MO is localized more on the He.

\[
\begin{array}{ccc}
\text{He} & \text{He}_2^+ & \text{He} \\
\sigma^* \\
\sigma
\end{array}
\]

8.3 Being isoelectronic with IF\(_4^-\) and XeF\(_4\), CsF\(_4^+\) would presumably have a square planar structure with two \textit{trans} lone pairs (VSEPR type AX\(_4\)E\(_2\)). 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 \( D_{4h} \) that could be formed from two \( p_z \) orbitals on separate F atoms would have \( \Sigma_{e}^+ \) and \( \Sigma_{u}^+ \) symmetry. On the central Be atom, the 2\( s \) orbital has \( \Sigma_{e}^+ \) symmetry and the 2\( p_z \) orbital has \( \Sigma_{u}^+ \) symmetry. The \( p_z \) and \( p_y \) orbitals are degenerate as \( \Pi_u \) and are nonbonding. The resulting MO scheme, omitting the nonbonding \( \Pi_u \) level, is shown below.
The combination of orbitals in Al₃(CH₃)₆ is similar to diborane, B₂H₆, except that the CH₃ group can be considered to contribute an sp³ hybrid orbital (rather than a 1s orbital) to overlap with an sp³ hybrid orbital from each Al, resulting an a 3e-2e bond for each bridge.

1. Balanced equations:

   a. NaH + CH₃OH → NaOCH₃ + H₂
   b. Ca₃P₂ + 6H₂O → 3Ca(OH)₂ + 2PH₃
   c. 2Na + 2NH₃(l) $\xrightarrow{\text{Fe}^{3+}, \text{NH}_3(l)}$ 2NaNH₂ + H₂
   d. 2LiNH₂ $\xrightarrow{\Delta}$ Li₂NH + NH₃
   e. Ca(OH)₂(aq) + CO₂(g) → CaCO₃(s) + H₂O(l)
   f. CaO + 3C $\xrightarrow{\Delta}$ CaC₂ + CO
   g. 2NaBH₄ + I₂ $\xrightarrow{\text{diglyme}}$ B₂H₆ + 2NaI + H₂
   h. BCl₃ + 3H₂O → B(OH)₃ + 3HCl
2. a. The "water-gas shift reaction"

\[ \text{C} + \text{H}_2\text{O} \xrightarrow{\Delta} \text{CO} + \text{H}_2 \]

\[ \text{H}_2 + \text{CO} + \text{H}_2\text{O} \xrightarrow{\Delta} \text{CO}_2 + 2\text{H}_2 \]

b. Cracking of methane to produce hydrogen

\[ \text{CH}_4 + \text{H}_2\text{O} \xrightarrow{800^\circ \text{C}} \text{Ni} \text{CO} + 3\text{H}_2 \]

c. Synthesis of LiAlH₄

In ether: \(8\text{LiH} + \text{Al}_2\text{Cl}_6 \rightarrow 2\text{LiAlH}_4 + 6\text{LiCl}\)

d. Mg burning in a CO₂ atmosphere

\[ 2\text{Mg} + \text{CO}_2 \rightarrow 2\text{MgO} + \text{C} \]

e. Slaking of lime

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]

f. Setting of Plaster of Paris

\[ 2\text{CaSO}_4\cdot\frac{1}{2}\text{H}_2\text{O} + 3\text{H}_2\text{O} \leftrightarrow 2\text{CaSO}_4\cdot2\text{H}_2\text{O} \]

g. Cyanamide reaction

\[ \text{CaC}_2 + \text{N}_2 \xrightarrow{1000^\circ \text{C}} \text{CaCN}_2 + \text{C} \]

h. Hall process

\[ 2\text{Al}_2\text{O}_3 \xrightarrow{1000^\circ \text{C}} \text{K}_3\text{AlF}_6/\text{elect.} \rightarrow 4\text{Al} + 3\text{O}_2 \]

i. Goldschmidt or thermite reaction

\[ \text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe} \]

j. Synthesis of B-trichloroborazine

\[ 3\text{NH}_4\text{Cl} + 3\text{BCl}_3 \xrightarrow{140-150^\circ \text{C}} \text{C}_6\text{H}_5\text{Cl} \rightarrow (\text{BCl})_3(\text{NH})_3 + 9\text{HCl} \]
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
      \[
      \begin{array}{c}
      H \\
      N \quad B \quad N \\
      B \quad H \\
      H \\
      \end{array}
      \]
      \[D_{3h}\] Analogue of benzene, with hindered pi delocalization.

   b. solid LiCH₃
      \[
      \begin{array}{c}
      \text{Li} \\
      \text{Li} \\
      \text{Li} \quad \text{CH}_3 \\
      \text{Li} \\
      \text{CH}_3 \\
      \end{array}
      \]
      \[T_d\] Tetrahedral tetramer

   c. solid BeH₂
      \[
      \begin{array}{c}
      H \\
      \text{Be} \quad \text{Be} \\
      \text{Be} \quad \text{H} \\
      \text{Be} \\
      \end{array}
      \]
      \[D_{2h}\] \(3c-2e\) bridge bonds

   d. aluminum trichloride
      \[
      \begin{array}{c}
      \text{Cl} \\
      \text{Al} \\
      \text{Al} \\
      \text{Cl} \\
      \end{array}
      \]
      \[D_{2h}\] Dimer with \(2c-2e\) bridge bonds
e. boric acid

\[ C_3H \quad \text{Planar molecule} \]