6-1.  a. \[
\begin{array}{cccc}
H_3\text{AsO}_4 & H_2\text{SO}_3 & H_2\text{SO}_4 & \text{HMnO}_4 \text{ (in order of increasing acidity)} \\
pK_a \text{ (9-7n)} & 2 & 2 & -5 & -12 \\
pK_a \text{ (8-5n)} & 3 & 3 & -2 & -7 \\
pK_a \text{ (exptl)} & 9.2 & 2.2 & 1.8 & -11
\end{array}
\]

b. \[
\begin{array}{cccc}
\text{HClO} & \text{HClO}_2 & \text{HClO}_3 & \text{HClO}_4 \text{ (in order of increasing acidity)} \\
pK_a \text{ (9-7n)} & 9 & 2 & -5 & -12 \\
pK_a \text{ (8-5n)} & 8 & 3 & -2 & -7 \\
pK_a \text{ (exptl)} & 7.4 & 2 & -1 & -10
\end{array}
\]

6-2. BF\textsubscript{3} > B(CH\textsubscript{3})\textsubscript{3} > B(C\textsubscript{2}H\textsubscript{5})\textsubscript{3} > B(C\textsubscript{6}H\textsubscript{2}(CH\textsubscript{3})\textsubscript{3}\textsubscript{3}) Alkyl groups are electron-donating and increase the electron density on B and reduce the attraction for the lone pair of NH\textsubscript{3}. The large mesitylene groups reduce the adduct formation because they are too bulky to fold back readily into the required tetrahedral geometry.

6-3. Dimethylamine acts as a weak base in water, with a very small amount of OH\textsuperscript{-} provided by the reaction (CH\textsubscript{3})\textsubscript{2}NH + H\textsubscript{2}O \rightleftharpoons (CH\textsubscript{3})\textsubscript{2}NH\textsuperscript{+} + OH\textsuperscript{-}. Acetic acid is a stronger acid than water, so dimethylamine acts as a stronger base and the reaction (CH\textsubscript{3})\textsubscript{2}NH + HOAc \rightarrow (CH\textsubscript{3})\textsubscript{2}NH\textsuperscript{+} + OAc\textsuperscript{-} goes to completion. 2-Butanone is a neutral solvent; there is no significant acid-base reaction with dimethylamine.

6-5.  a. CaH\textsubscript{2} + 2 H\textsubscript{2}O \rightarrow Ca\textsuperscript{2+} + 2 H\textsubscript{2}↑ + 2 OH\textsuperscript{-} Calcium has a lower electronegativity than hydrogen, so CaH\textsubscript{2} is Ca\textsuperscript{2+}(H\textsuperscript{-})\textsubscript{2} and the hydride ions react with the positive hydrogens of water.

b. HBr + H\textsubscript{2}O \rightarrow H\textsubscript{3}O\textsuperscript{+} + Br\textsuperscript{-} Bromine has a larger electro-negativity than hydrogen, so the hydrogen is strongly positive and is readily lost to the lone pair of water.

c. H\textsubscript{2}S + H\textsubscript{2}O \rightleftharpoons H\textsubscript{3}O\textsuperscript{+} + HS\textsuperscript{-} Sulfur is slightly more electronegative than hydrogen, and the positive hydrogen can dissociate to a small extent.

d. CH\textsubscript{4} + H\textsubscript{2}O \rightarrow no reaction. The C-H bond is almost nonpolar; the hydrogens are not positive enough to be attracted to the water lone pair.
6-9. In general, oxide ion reacts with water to form hydroxide: $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2 \text{OH}^-$ unless other factors prevent it. In $\text{B}_2\text{O}_3$, the small, hard $\text{B}^{3+}$ holds on to the oxide ions strongly. As a result, $\text{B}_2\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 2 \text{B(OH)}_3 \rightleftharpoons \text{H}^+ + \text{H}_2\text{BO}_3^-$, and the solution is very weakly acidic ($pK_a = 9.25$). In $\text{Al}_2\text{O}_3$, the $\text{Al}^{3+}$ ion is larger and softer. It can form either $[\text{Al(OH)}_4]^{-}$ (acting as an acid) or $[\text{Al}($$\text{H}_2\text{O})_6]^{3+}$ (acting as a base), depending on the other species in solution. $\text{Sc}^{3+}$ is still larger and softer, so it combines better with water than with hydroxide ion. As a result, $\text{Sc}_2\text{O}_3 + 15 \text{H}_2\text{O} \rightarrow 2 [\text{Sc}($$\text{H}_2\text{O})_6]^{3+} + 6 \text{OH}^- \text{ is possible.}$

6-10. $\text{Al}^{3+}$ is acidic: $[\text{Al}($$\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Al}($$\text{H}_2\text{O})_3($$\text{OH})]^{2+} + \text{H}_3\text{O}^+$

The hydronium ions react with the basic bicarbonate to form CO$_2$: 

$\text{H}_3\text{O}^+ + \text{HCO}_3^- \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2 \uparrow$ With $pK_a$ values of 5.0 for $[\text{Al}($$\text{H}_2\text{O})_3]^{3+}$, 6.4 for $\text{H}_2\text{CO}_3$ and 2.0 for $\text{HSO}_4^-$, the pH is about 3, low enough to convert the bicarbonate to CO$_2$.

6-14. An increase in conductivity suggests that ions are formed:

$\text{BrF}_3 + \text{AgF} \rightleftharpoons \text{BrF}_4^- + \text{Ag}^+$

$\text{BrF}_3 + \text{SnF}_4 \rightleftharpoons \text{BrF}_2^+ + \text{SnF}_5^-$ or

$2 \text{BrF}_3 + \text{SnF}_4 \rightleftharpoons 2 \text{BrF}_2^+ + \text{SnF}_6^{2-}$

6-23. Soft metal ions do not combine with oxygen as strongly as hard metal ions, so reactions like

$\Delta$ 
$2 \text{HgO} \rightarrow 2 \text{Hg} + \text{O}_2 \uparrow$ $\quad$ $\Delta$ 
$2 \text{CuO} \rightarrow 2 \text{Cu} + \text{O}_2 \uparrow$ $\quad$ $\Delta$ 
$2 \text{Ag}_2\text{O} \rightarrow 4 \text{Ag} + \text{O}_2 \uparrow$

$\Delta$ 
$\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO} \uparrow$ $\quad$ $\Delta$ 
$2\text{CuO} + \text{C} \rightarrow 2\text{Cu} + \text{CO}_2 \uparrow$

are more easily carried out. Reduction of some of the softer metals can be carried out with relatively low temperatures (campfires); some think use of rocks containing ores could lead to accidental reduction to the metals and discovery of the smelting process. Harder metals such as iron require much higher temperatures for the reduction process.