Chapter 7
ACIDS AND BASES

Exercises

7.2  (a) A nonpolar solvent because phosphorus pentachloride is a nonpolar covalent compound.
(b) A polar protic solvent because cesium chloride is ionic. Ionic compounds will dissolve only in very polar solvents.
(c) A nonpolar solvent because tin(IV) chloride is a nonpolar covalent molecule (high-oxidation-state metal).

7.4  (a) \( S^{2-}(aq) + 2 H^+(aq) \rightarrow H_2S(g) \)
(b) \( HF(aq) + OH^-(aq) \rightarrow F^-(aq) + H_2O(l) \)
(c) \( HPO_4^{2-}(aq) + H^+(aq) \rightarrow H_2PO_4^-(aq) \)
\( \text{(note: sulfuric acid solution consists largely of the } H^+ + HSO_4^- \text{ ions)} \)

7.6  (a) Specific name for the equilibrium constant for the ionization of an acid. It is equal to the product of the hydronium ion concentration and the conjugate base concentration divided by the acid concentration at equilibrium.
(b) Solvent in which a set of acids or bases completely ionizes.
(c) Acid that contains more than one ionizable hydrogen.

7.8  (a) \( PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq) \)
\( \text{(no reaction for the } Na^+(aq) \text{ ion)} \)
(c) \( HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq) \)
\( \text{(no reaction for the } Na^+(aq) \text{ ion)} \)
(b) \( (CH_3)_3NH^+(aq) + H_2O(l) \rightleftharpoons (CH_3)_3N(aq) + H_3O^+(aq) \)
\( \text{(no reaction for the } Cl^- (aq) \text{ ion)} \)

7.10 \( HSO_3F(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_3F^-(aq) \)
7.12 (a) $H_2Se$ and $S^{2-}$
(b) $PH_4^+$ and $PH_2^-$
(c) $H_2PO_4^-$ and $PO_4^{3-}$

7.14 $HF(NH_3) + NH_3(l) \rightleftharpoons NH_4^+(NH_3) + F^-(NH_3)$

7.16 $HSeO_4^-$ (acid), $SeO_4^{2-}$ (conjugate base); $H_2O$ (base), $H_3O^+$ (conjugate acid).

7.18 Sulfuric acid. The acid with the greater number of oxygen atoms will withdraw electrons from the O–H bond more readily and hence that acid will be stronger.

7.20 The hydrogen phosphate ion is in equilibrium with the phosphate ion:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

The more highly charged phosphate ion would have a higher lattice energy in a compound with copper(II) ion than the lower charged hydrogen phosphate ion:

$$Cu^{2+}(aq) + PO_4^{3-}(aq) \rightarrow Cu_3(PO_4)_2(s)$$

As the phosphate ion is consumed, the acid-base equilibrium would shift right, replenishing the supply of phosphate ion for additional precipitate formation.

7.22 The cyanide ion will act as a hydrogen ion acceptor:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

If the cyanide ion is a strong base, hydrocyanic acid will be a weak acid.

7.24 (a) Basic, because the potassium ion will stay unchanged but the fluoride ion is the conjugate base of a weak acid, hence the following equilibrium will occur:

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

(b) Acidic, because the chloride ion (conjugate base of a strong acid) will stay unchanged but the ammonium ion is the conjugate acid of a weak base, hence the following equilibrium will occur:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$
7.26 Y\(^-\) must be the stronger base, because the solution of NaY has a higher pH than that of NaX. Following from this, HY must be the weaker acid. Thus HX is the stronger acid.

7.28 \(\text{H}_2\text{SO}_4(CH_3\text{COOH}) + \text{CH}_3\text{COOH}(l) \rightleftharpoons \text{H}_3\text{SO}_4^+(CH_3\text{COOH}) + \text{CH}_3\text{COO}^-(CH_3\text{COOH})\)

Acetic acid will act as a differentiating solvent because it is itself a weak acid.

7.30 \(\text{S}^2-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HS}^-(aq) + \text{OH}^-(aq)\)
\(\text{HS}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{S}(g) + \text{OH}^-(aq)\)

Though the equilibria in a closed system lie far to the left, in an open environment the hydrogen sulfide can escape, “driving” the equilibria to the right.

7.32 (a) K\(_2\)O, (b) Cr\(_2\)O\(_3\).

7.34 (a) PCl\(_5\) (acid), ICl (base); (b) POCl\(_3\) (acid), Cl\(^-\) (base);
(c) Li\(_3\)N (acid), NH\(_3\) (base).

7.36 (a) Increasing pH (very large change)
\(\text{O}^2-(aq) + \text{H}_2\text{O}(l) \rightarrow 2 \text{OH}^-(aq)\)
(b) Decreasing pH (very small change)
\([\text{Mg(OH}_2]_6^2+aq) + \text{H}_2\text{O}(l) \rightleftharpoons [\text{Mg(OH}_2]_5(\text{OH})]^+(aq) + \text{H}_3\text{O}^+(aq)\)
(c) Increasing pH (moderately significant change)
\(\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)\)

7.38 (a) Neutral; (b) moderately basic; (c) weakly basic.

7.40 \(\text{H}_3\text{O}^+ > \text{H}_3\text{PO}_4 > \text{HN}_3 > \text{H}_2\text{O} > \text{PH}_3\)

7.42 The chemical reaction is
\(\text{CaO}(s) + \text{SiO}_2(s) \rightarrow \text{CaSiO}_3(s)\)
\(\Delta G^\circ = [1(-1499) - 1(-603) - 1(-856)] \text{kJ mol}^{-1}\)
\(= -40 \text{kJ mol}^{-1}\)
Compared with the series in the text, silicon dioxide will be a weaker acid than carbon dioxide ($\Delta G^o = -134 \text{ kJ} \cdot \text{mol}^{-1}$).

7.44 $\text{BrF}_3(l) + \text{BrF}_3(l) \Leftrightarrow \text{BrF}_2^+(\text{BrF}_3) + \text{BrF}_4^-(\text{BrF}_3)$

7.46 (a) $\text{CN}^-(HF) + \text{HF}(l) \Leftrightarrow \text{HCN}(HF) + \text{F}^-(HF)$
(b) $\text{HClO}_4(HF) + \text{HF}(l) \Leftrightarrow \text{H}_2\text{F}^+(HF) + \text{ClO}_4^-(HF)$

Equation (a) will be further to the right because hydrogen fluoride (acting as a proton donor) is a stronger acid than water, while (b) will be further to the left because hydrogen fluoride (acting as a proton acceptor) is a stronger acid than water.

7.48 (a) Yes. The reactants have the combinations borderline-soft and soft-hard, while the products have combinations borderline-hard and soft-soft. The latter combinations would be preferred.
(b) No. The reactants have the combinations borderline-hard and soft-borderline, while the products have combinations borderline-borderline and soft-hard.

7.50 (a) Products. The reactants are soft-hard and hard-soft, while the products are soft-soft and hard-hard.
(b) Reactants. The reactants are hard-hard and borderline-soft, while the products are hard-soft and borderline-hard.

7.52 (a) $\text{ThO}_2$; (b) $\text{PtAs}_2$; (c) $\text{CaF}_2$.

7.54 Aluminum hydroxide (because one mole of antacid will neutralize three moles of acid). No; one should consider the possible health implications of the accompanying cation.

**Beyond the Basics**

7.56 To precipitate tin(II) sulfide, $[\text{Sn}^{2+}] [\text{S}^{2-}] > K_{sp} = 1.0 \times 10^{-25}$

$1.0 \times 10^{-25} = (0.010) [\text{S}^{2-}]$

$[\text{S}^{2-}] = 5.0 \times 10^{-23} \text{ mol} \cdot \text{L}^{-1}$

Using the formula from 7.43,
[H$_3$O$^+$]$^2 = (8.9 \times 10^{-8})(1.2 \times 10^{-13}) \left( \frac{(0.010)}{(5.0 \times 10^{-23})} \right) = 2.1$

[H$_3$O$^+$] = 1.5 mol·L$^{-1}$, pH = 0.16

7.58 The highest oxidation state acids/bases of the Group 15 elements are HNO$_3$, H$_3$PO$_4$, and H$_3$AsO$_4$; the oxyspecies of antimony are not well characterized, and Bi(OH)$_3$ is the best-established compound for bismuth. Nitric acid is a strong acid, while both phosphoric and arsenic acids are weak acids with very similar K$_a$ values. Bi(OH)$_3$ is basic. Oxyanions in the +5 state are known for both antimony and bismuth, suggesting weak acid behavior.

7.60 NaOH($aq$) + B(OH)$_3$($aq$) $\rightarrow$ Na$^+$($aq$) + [B(OH)$_4$]$^-$($aq$)

7.62 Nitrogen is a harder element than phosphorus. Thus the softer BH$_3$ will bond to phosphorus, while the harder BF$_3$ will bond to nitrogen.

7.64 Silicon in both silicon dioxide and the silicate ion has a theoretical oxidation number of 4+. This would make it a hard acid and would favor bonding to an oxide ion, a hard base.