

Chapter 7

ACIDS AND BASES

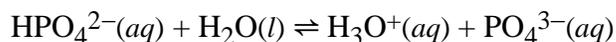
Exercises

- 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) $\text{S}^{2-}(aq) + 2 \text{H}^+(aq) \rightarrow \text{H}_2\text{S}(g)$
(b) $\text{HF}(aq) + \text{OH}^-(aq) \rightarrow \text{F}^-(aq) + \text{H}_2\text{O}(l)$
(c) $\text{HPO}_4^{2-}(aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{PO}_4^-(aq)$
(note: sulfuric acid solution consists largely of the $\text{H}^+ + \text{HSO}_4^-$ 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) $\text{PO}_4^{3-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{OH}^-(aq)$
(no reaction for the $\text{Na}^+(aq)$ ion)
(c) $\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq)$
(no reaction for the $\text{Na}^+(aq)$ ion)
(b) $(\text{CH}_3)_3\text{NH}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons (\text{CH}_3)_3\text{N}(aq) + \text{H}_3\text{O}^+(aq)$
(no reaction for the $\text{Cl}^-(aq)$ ion)
- 7.10 $\text{HSO}_3\text{F}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{SO}_3\text{F}^-(aq)$

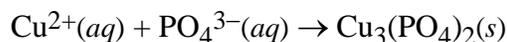
7.12 (a) H_2Se and S^{2-} (b) PH_4^+ and PH_2^- (c) H_2PO_4^- and PO_4^{3-} 7.14 $\text{HF}(\text{NH}_3) + \text{NH}_3(l) \rightleftharpoons \text{NH}_4^+(\text{NH}_3) + \text{F}^-(\text{NH}_3)$ 7.16 HSeO_4^- (acid), SeO_4^{2-} (conjugate base); H_2O (base), H_3O^+ (conjugate acid).

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:

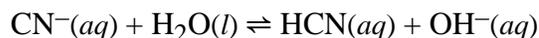


The more highly charged phosphate ion would have a higher lattice energy in a compound with copper(II) ion than the lower charged hydrogen phosphate ion:



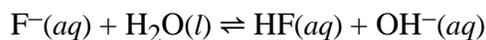
As the phosphate ion is consumed, the acid-base equilibrium would shift right, replenishing the supply of phosphate ion for additional precipitate formation.

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

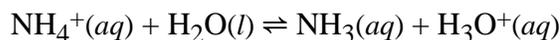


If the cyanide ion is a strong base, hydrocyanic acid will be a weak acid.

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:



(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:



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 $H_2SO_4(CH_3COOH) + CH_3COOH(l) \rightleftharpoons H_3SO_4^+(CH_3COOH) + CH_3COO^-(CH_3COOH)$
Acetic acid will act as a differentiating solvent because it is itself a weak acid.

7.30 $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$
 $HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(g) + OH^-(aq)$
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_2O , (b) Cr_2O_3 .

7.34 (a) PCl_5 (acid), ICl (base); (b) $POCl_3$ (acid), Cl^- (base);
(c) Li_3N (acid), NH_3 (base).

7.36 (a) Increasing pH (very large change)
 $O^{2-}(aq) + H_2O(l) \rightarrow 2 OH^-(aq)$
(b) Decreasing pH (very small change)
 $[Mg(OH_2)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(OH_2)_5(OH)]^+(aq) + H_3O^+(aq)$
(c) Increasing pH (moderately significant change)
 $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

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

7.40 $H_3O^+ > H_3PO_4 > HN_3 > H_2O > PH_3$

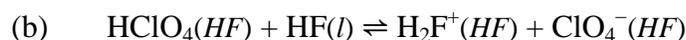
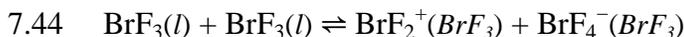
7.42 The chemical reaction is

$$CaO(s) + SiO_2(s) \rightarrow CaSiO_3(s)$$

$$\Delta G^\circ = [1(-1499) - 1(-603) - 1(-856)] \text{ kJ}\cdot\text{mol}^{-1}$$

$$= -40 \text{ kJ}\cdot\text{mol}^{-1}$$

Compared with the series in the text, silicon dioxide will be a weaker acid than carbon dioxide ($\Delta G^\circ = -134 \text{ kJ}\cdot\text{mol}^{-1}$).



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) ThO_2 ; (b) PtAs_2 ; (c) 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, $[\text{Sn}^{2+}][\text{S}^{2-}] > K_{\text{sp}} = 1.0 \times 10^{-25}$

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

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

Using the formula from 7.43,

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

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

- 7.58 The highest oxidation state acids/bases of the Group 15 elements are HNO_3 , H_3PO_4 , and H_3AsO_4 ; the oxyspecies of antimony are not well characterized, and $\text{Bi}(\text{OH})_3$ 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. $\text{Bi}(\text{OH})_3$ is basic. Oxyanions in the +5 state are known for both antimony and bismuth, suggesting weak acid behavior.
- 7.60 $\text{NaOH}(aq) + \text{B}(\text{OH})_3(aq) \rightarrow \text{Na}^+(aq) + [\text{B}(\text{OH})_4^-](aq)$
- 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.

