# Chapter 7

ACIDS AND BASES

Exercises

7.1   Polar protic: solvents with a dielectric constant usually between 50 and 100.

Dipolar aprotic: solvents with dielectric constant usually between 20 and 50.

Nonpolar: solvents with dielectric constant close to zero.

7.3   (a) $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

(b) $2\ HCO_3^-(aq) + Co^{2+}(aq) \rightarrow CoCO_3(s) + H_2O(l) + CO_2(g)$

(c) $OH^-(aq) + CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

7.5   (a) Pairs of species that differ in formula by one ionizable hydrogen.

(b) Solvent that undergoes its own acid-base reaction, for example,

$$HA + HA \rightleftharpoons H_2A^+ + A^-$$

(c) Ability of a substance to act as an acid or a base; for example, water can act as a base to form the hydronium ion or as an acid to form the hydroxide ion.

7.7   (a) $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

(no reaction for the $NO_3^-(aq)$ ion)

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

(no reaction for the $K^+(aq)$ ion)

(c) $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

(no reaction for the $Na^+(aq)$ ion)

7.9 $ClNH_2(aq) + H_2O(l) \rightleftharpoons ClNH_3^+(aq) + OH^-(aq)$

7.11 $H_2SO_4(l) + H_2SO_4(l) \rightleftharpoons H_3SO_4^+(H_2SO_4) + HSO_4^-(H_2SO_4)$

7.13   (a) The ammonium ion, NH_4^+; (b) the amide ion, NH_2^-.
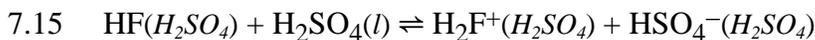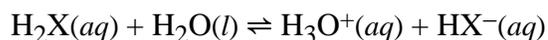
7.15 $HF(H_2SO_4) + H_2SO_4(l) \rightleftharpoons H_2F^+(H_2SO_4) + HSO_4^-(H_2SO_4)$
HF is acting as a base and H_2F^+ is the conjugate acid,
H_2SO_4 is acting as an acid and HSO_4^- is the conjugate base.

7.17 $HSeO_4^-$ (base), H_2SO_4 (conjugate acid); H_2O (acid), OH^- (conjugate base).
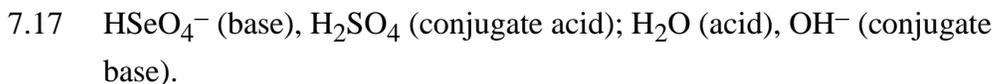
7.19   Because the ionization process depends on the breaking of the bond to hydrogen,
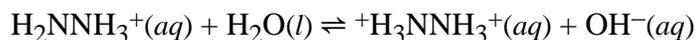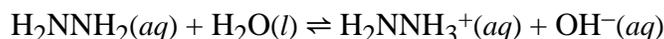$$H_2X(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HX^-(aq)$$
The weaker the H−X bond, the stronger the acid. Bond energies usually decrease down a group (see Bond Energy section in Chapter 6); hence the H−Se bond will be weaker than the H−S bond. Thus hydrogen selenide will be the stronger acid.

7.21   The hydrated ion will lose one hydrogen ion in a similar manner to the hydrated iron(III) and aluminum ions:
$$[Zn(OH_2)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Zn(OH_2)_5(OH)]^+(aq) + H_3O^+(aq)$$
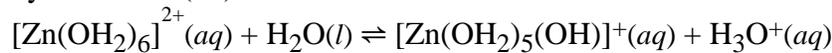
7.23   Because stepwise acid-base equilibria proceed to a lesser and lesser extent, the diprotic acid must be present in the least proportion.
$$H_2NNH_2(aq) + H_2O(l) \rightleftharpoons H_2NNH_3^+(aq) + OH^-(aq)$$
$$H_2NNH_3^+(aq) + H_2O(l) \rightleftharpoons {}^+H_3NNH_3^+(aq) + OH^-(aq)$$

7.25   (a) Acidic, because aluminum is a small high-charge cation that will lose an ionizable hydrogen from one of the surrounding water molecules:
$$[Al(OH_2)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH_2)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$
(b) Neutral, because the sodium ion will stay unchanged, and the iodide ion is the conjugate base of a strong acid, so it, too, will remain unchanged.

7.27   With a smaller pK_b, A^- must be the stronger base. Hence HA must be the weaker acid. Thus HB will be the stronger acid.

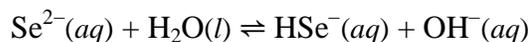7.29 $H_3PO_4(aq) + HPO_4^{2-}(aq) \rightleftharpoons 2\ H_2PO_4^-(aq)$

7.31   (a) N_2O_5; (b) CrO_3; (c) I_2O_7.

7.33   (a) SiO_2 (acid), Na_2O (base); (b) NOF (acid), ClF_3 (base); (c) Al_2Cl_6
        (acid), PF_3 (base).

7.35   (a) No effect.
        (b) Increasing pH (moderately large change)
             $$Se^{2-}(aq) + H_2O(l) \rightleftharpoons HSe^-(aq) + OH^-(aq)$$
        (c) Decreasing pH (large change by analogy with aluminum ion)
             $$[Sc(OH_2)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Sc(OH_2)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$
        (d) Increasing pH (small change)
             $$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$
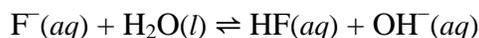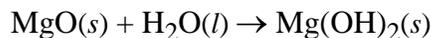

7.37   (a) Weakly basic; (b) neutral; (c) moderately basic; (d) strongly basic.

7.39   (a) Strongly basic; (b) very strongly basic.

7.41   The chemical reaction is
             $$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(s)$$
        $\Delta G° \quad = [1(-834) - 1(-569) - 1(-237)]$ kJ·mol^{-1}
        $\quad\quad\quad = -28$ kJ·mol^{-1}

        Compared with the series in the text, magnesium oxide will be a weaker
        base than calcium oxide ($\Delta G° = -59$ kJ·mol^{-1}).

7.43 NO^+ is a Lewis acid because it is an electron pair acceptor; similarly, Cl^-
        is a Lewis base because it is an electron pair donor (when they combine to
        form NOCl).
        $(NO)(AlCl_4)(NOCl) + [(CH_3)_4N]Cl(NOCl) \rightarrow [(CH_3)_4N](AlCl_4)(NOCl) +$
        $NOCl(l)$

7.45 $NH_3(NH_3) + NH_3(NH_3) \rightleftharpoons NH_4^+(NH_3) + NH_2^-(NH_3)$
        (a) $K = [NH_4^+][NH_2^-] = 1 \times 10^{-33}$ since $[NH_4^+] = [NH_2^-]$
                $[NH_4^+] = 3 \times 10^{-17}$ mol·L^{-1}
        (b)   Let $[NH_4^+] = x$, then $[NH_2^-] = 1.0 + x$
                $K = (x)(1.0 + x) = 1 \times 10^{-33}$
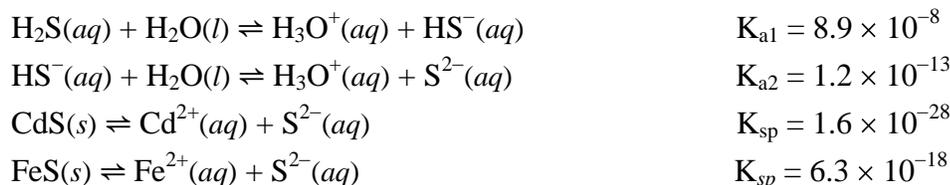
Assume $x \ll 1.0$

$x = 1 \times 10^{-33}$ mol·L^{-1} = [NH$_4^+$]

7.47   (a) No. The reactants have the combinations borderline-borderline and hard-hard, while the products have combinations borderline-hard and hard-borderline. These like combinations are preferred over the mixed combinations that would result in the products.
(b) Yes. For the reactants, hard titanium(IV) ion is combined with soft iodide ion, soft titanium(II) ion with hard fluoride ion. The products will be preferred where hard-hard and soft-soft combinations result.

7.49   (a) Greater than unity, because silver ion is soft, as is cyanide ion, and chloride ion is hard.
(b) Less than unity, because both mercury and iodide ions are soft, and chloride ion is hard.

7.51   (a) Because thallium(I) is a large soft cation, it will probably have an insoluble chloride, TlCl, and precipitate with the other soft cations, silver(I), lead(II), and mercury(I) in analysis group I.
(b) Rubidium ion would behave like the other alkali metals in analysis group V and not give a precipitate (it would give a precipitate with a very large anion, as does potassium).
(c) Radium would probably behave like the other alkaline earth metals (analysis group IV) and give a precipitate of RaCO$_3$ with carbonate ion.
(d) Iron(III) would probably resemble chromium(III) and aluminum(III) and give a precipitate of Fe(OH)$_3$ upon addition of hydroxide ion in the analysis group III.

7.53   (a) MgSO$_4$; (b) CoS.

Beyond the Basics

7.55   We start by writing the relevant equilibria:

$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ $K_{a1} = 8.9 \times 10^{-8}$

$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq)$ $K_{a2} = 1.2 \times 10^{-13}$

$CdS(s) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)$ $K_{sp} = 1.6 \times 10^{-28}$

$FeS(s) \rightleftharpoons Fe^{2+}(aq) + S^{2-}(aq)$ $K_{sp} = 6.3 \times 10^{-18}$

Then combine the acid ionization constants:

$$K_{a1} \times K_{a2} = \left(\frac{[H_3O^+][HS^-]}{[H_2S]} \right)\left(\frac{[H_3O^+][S^{2-}]}{[HS^-]} \right) = \left(\frac{[H_3O^+]^2[S^{2-}]}{[H_2S]} \right)$$

We can solve for sulfide ion concentration:

$$[S^{2-}] = (8.9 \times 10^{-8})(1.2 \times 10^{-13})\left(\frac{(0.010)}{(1.0)^2} \right) = 1.1 \times 10^{-22}$$

For cadmium ion: $[Cd^{2+}][S^{2-}] = (0.010)(1.1 \times 10^{-22}) = 1.1 \times 10^{-24}$.
This is greater than K_{sp}; thus cadmium sulfide will precipitate.

For iron(II) ion: $[Fe^{2+}][S^{2-}] = 1.1 \times 10^{-24}$.
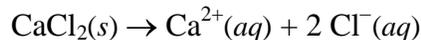This is less than K_{sp}; thus iron(II) sulfide will not precipitate.

7.57   Mercury(II) ion is a soft acid, so it will be found as ores of soft bases, such as sulfide ion. Zinc is a borderline acid, so it can be found as ores of both hard and soft bases.

7.59 $H_2CO_3(aq) + MgSiO_4(s) \rightarrow H_2O(l) + SiO_2(s) + MgCO_3(s)$
Thus, over geological time, the atmospheric concentration of carbon dioxide has decreased, in part due to the formation of magnesium (and calcium) carbonate minerals.

7.61   Dimethylsulfoxide must be a softer base than water, thus favoring the soft acid copper(I) rather than the borderline copper(II) ion.

7.63   In terms of the HSAB concept, the harder calcium ion is likely to form a stronger bond to the water molecules of hydration than the softer barium ion, thus driving the reaction towards solution.
$CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$
In thermodynamic terms, the enthalpy (and free energy) of hydration of the calcium ion compared to the lattice energy of calcium chloride must be greater than the enthalpy of hydration of the barium ion compared to the lattice energy of barium chloride.

7.65   Aluminum oxide would act as an acid while iron(III) oxide would be a base, according to Lux-Flood theory. Thus the product should be $Fe^{3+}(AlO_6)^{3-}$.