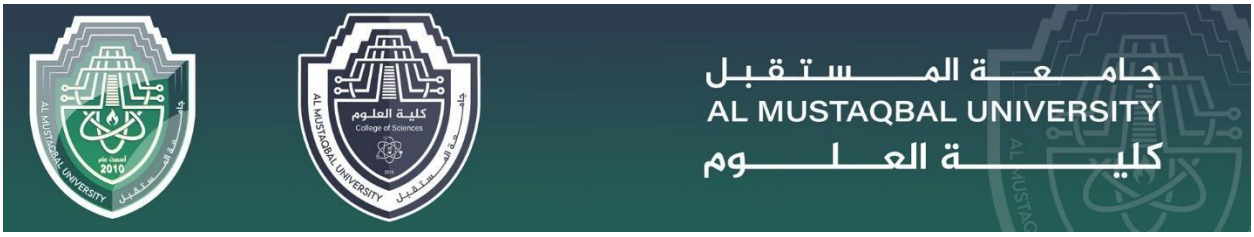
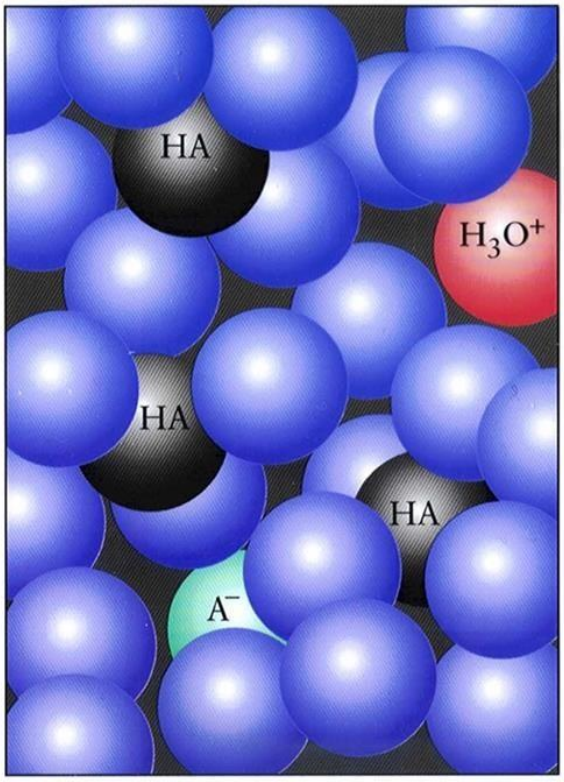
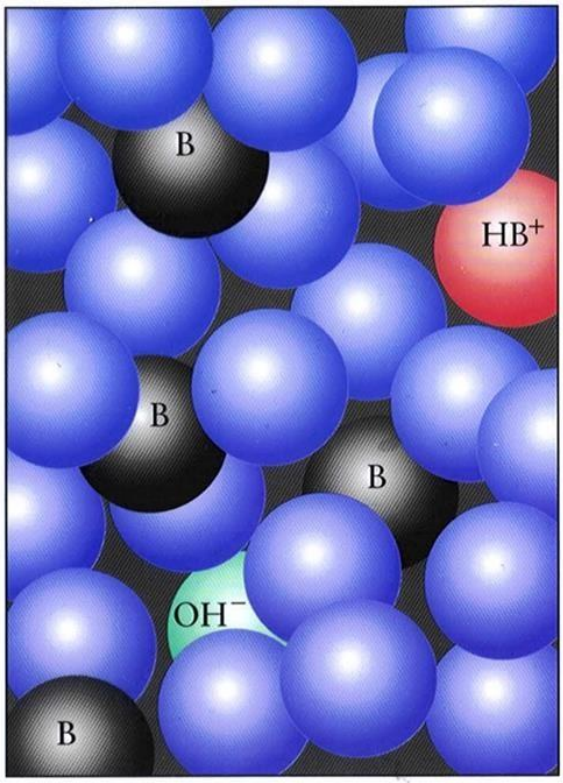


Acid/base equilibria.

Buffer solution





Figures 3 and 4.14, page 520
Atkins/Jones: *Chemistry: Molecules, Matter, and Change*, **3e**

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Bronsted-Lowry Acids and Bases

- These two chemists pointed out that acids and bases can be seen as proton transfer reactions.

- According to the Bronsted-Lowry concept:
  - An acid is the species donating a proton in a proton-transfer reaction
  - A base is the species accepting the proton in a proton-transfer reaction.

Table 6.2 Acidity constants (K_a) and values of pK_a for some common acids at 298 K

Acid		K_a / mol dm^{-3}	pK_a	
Hydriodic acid	HI	1×10^{10}	−10	Strongest acid
Perchloric acid [chloric(VII) acid]	$HClO_4$	1×10^{10}	−10	
Hydrobromic acid	HBr	1×10^{9}	−9	Strong acids
Hydrochloric acid	HCl	1×10^{7}	−7	
Sulfuric acid [sulfuric(VI) acid]	H_2SO_4	1×10^{3}	−3	
Nitric acid [nitric(V) acid]	HNO_3	25	−1.4	
Trichloroethanoic acid	CCl_3CO_2H	2.2×10^{-1}	0.66	
Chlorous acid [chloric(III) acid]	$HClO_2$	1.1×10^{-2}	1.94	
Hydrofluoric acid	HF	6.3×10^{-4}	3.20	
Nitrous acid [nitric(III) acid]	HNO_2	5.6×10^{-4}	3.25	
Methanoic acid	HCO_2H	1.8×10^{-4}	3.75	
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	Weak acids
Ethanoic acid	CH_3CO_2H	1.7×10^{-5}	4.76	
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	4.87	
Carbonic acid	H_2CO_3	4.5×10^{-7}	6.35	
Hypochlorous acid [chloric(I) acid]	HOCl	4.0×10^{-8}	7.40	
Hydrocyanic acid	HCN	6.2×10^{-10}	9.21	Weakest acid
Phenol	C_6H_5OH	1.0×10^{-10}	9.99	

Strong Acids	Strong Bases
perchloric acid ($HClO_4$)	lithium hydroxide ($LiOH$)
hydrochloric acid (HCl)	sodium hydroxide ($NaOH$)
hydrobromic acid (HBr)	potassium hydroxide (KOH)
hydroiodic acid (HI)	calcium hydroxide ($Ca(OH)_2$)
nitric acid (HNO_3)	strontium hydroxide ($Sr(OH)_2$)
sulfuric acid (H_2SO_4)	barium hydroxide ($Ba(OH)_2$)

TABLE 9-2

Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	$K_a = \dfrac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
		$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_b = \dfrac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \dfrac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \dfrac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \dfrac{[I_2]_{org}}{[I_2]_{aq}}$

FEATURE 9-1

Stepwise and Overall Formation Constants for Complex Ions

The formation of $Ni(CN)_4^{2-}$ (Table 9-2) is typical in that it occurs in steps as shown. Note that **stepwise formation constants** are symbolized by K_1, K_2, and so forth.

$$Ni^{2+} + CN^- \rightleftharpoons Ni(CN)^+ \qquad K_1 = \frac{[Ni(CN)^+]}{[Ni^{2+}][CN^-]}$$

$$Ni(CN)^+ + CN^- \rightleftharpoons Ni(CN)_2 \qquad K_2 = \frac{[Ni(CN)_2]}{[Ni(CN)^+][CN^-]}$$

$$Ni(CN)_2 + CN^- \rightleftharpoons Ni(CN)_3^- \qquad K_3 = \frac{[Ni(CN)_3^-]}{[Ni(CN)_2][CN^-]}$$

$$Ni(CN)_3^- + CN^- \rightleftharpoons Ni(CN)_4^{2-} \qquad K_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni(CN)_3^-][CN^-]}$$

Overall constants are designated by the symbol β_n. Thus,

$$Ni^{2+} + 2CN^- \rightleftharpoons Ni(CN)_2 \qquad \beta_2 = K_1K_2 = \frac{[Ni(CN)_2]}{[Ni^{2+}][CN^-]^2}$$

$$Ni^{2+} + 3CN \rightleftharpoons Ni(CN)_3^- \qquad \beta_3 = K_1K_2K_3 = \frac{[Ni(CN)_3^-]}{[Ni^{2+}][CN^-]^3}$$

$$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-} \qquad \beta_4 = K_1K_2K_3K_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$$

9B-4 Applying the Ion-Product Constant for Water

Aqueous solutions contain small concentrations of hydronium and hydroxide ions as a result of the dissociation reaction

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad (9\text{-}9)$$

An equilibrium constant for this reaction can be written as shown in Equation 9-7:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad (9\text{-}10)$$

The concentration of water in dilute aqueous solutions is enormous, however, when compared with the concentration of hydronium and hydroxide ions. As a result, $[H_2O]^2$ in Equation 9-10 can be taken as constant, and we write

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-] \qquad (9\text{-}11)$$

where the new constant K_w is given a special name, the **ion-product constant for water.**

If we take the negative logarithm of Equation 9-11, we discover a very useful relationship.

$$-\log K_w = -\log[H_3O^+] - \log[OH^-]$$

By the definition of p-function, (see Section 4B-1)

$$pK_w = pH + pOH \qquad (9\text{-}12)$$

At 25°C, $pK_w = 14.00$.

EXAMPLE 9-1

Calculate the hydronium and hydroxide ion concentrations of pure water at 25°C and 100°C.

Solution

Because OH^- and H_3O^+ are formed only from the dissociation of water, their concentrations must be equal:

$$[H_3O^+] = [OH^-]$$

We substitute this equality into Equation 9-11 to give

$$[H_3O^+]^2 = [OH^-]^2 = K_w$$
$$[H_3O^+] = [OH^-] = \sqrt{K_w}$$

At 25°C,

$$[H_3O^+] = [OH^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\ M$$

At 100°C, from Table 9-3,

$$[H_3O^+] = [OH^-] = \sqrt{49 \times 10^{-14}} = 7.0 \times 10^{-7}\ M$$

9B-6 Using Acid/Base Dissociation Constants

When a weak acid or a weak base is dissolved in water, partial dissociation occurs. Thus, for nitrous acid, we can write

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^- \qquad K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

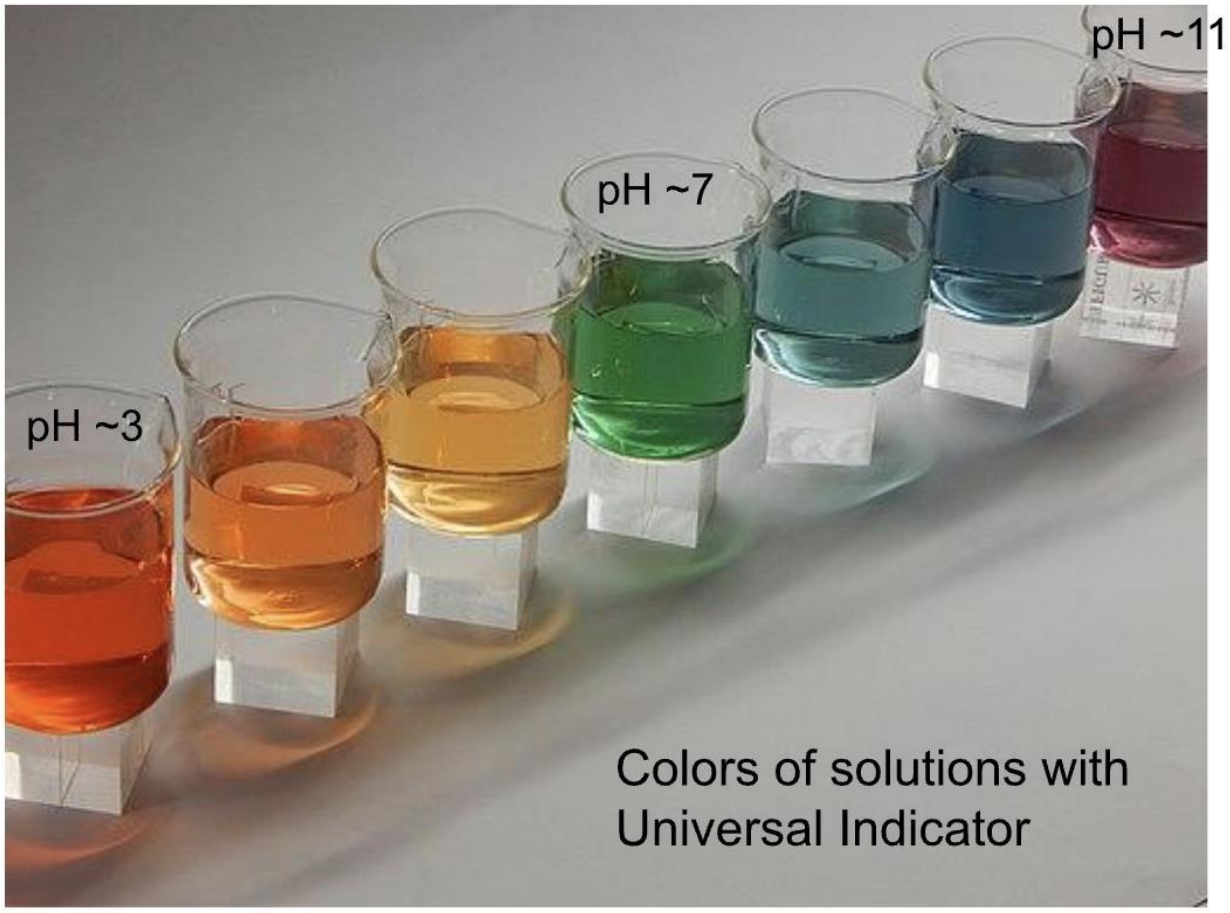
where K_a is the **acid dissociation constant** for nitrous acid. In an analogous way, the **base dissociation constant** for ammonia is

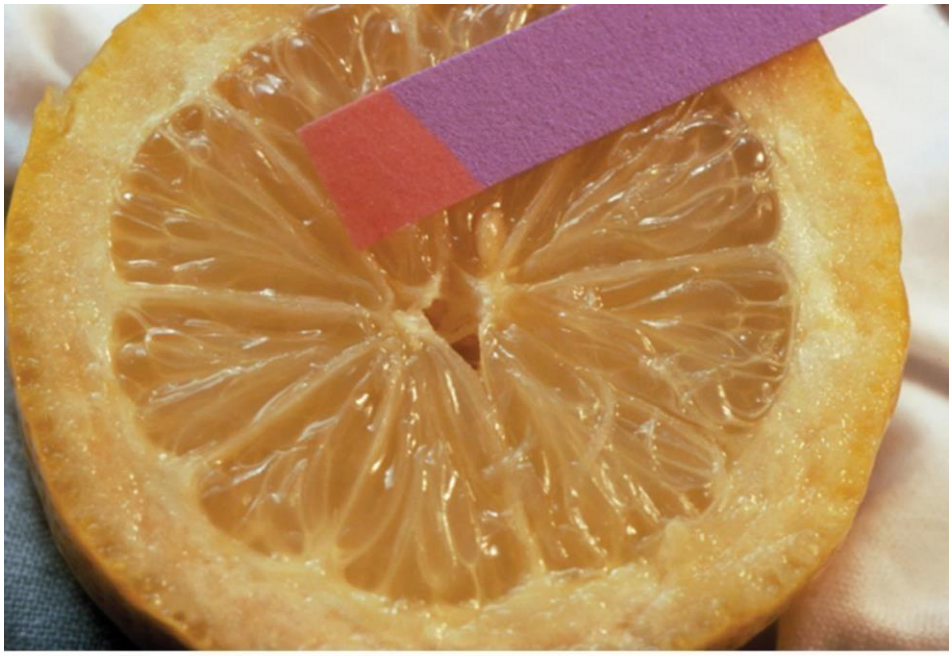
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Notice that $[H_2O]$ does not appear in the denominator of either equation because the concentration of water is so large relative to the concentration of the weak acid or base that the dissociation does not alter $[H_2O]$ appreciably (see Feature 9-2). Just as in the derivation of the ion-product constant for water, $[H_2O]$ is incorporated into the equilibrium constants K_a and K_b. Dissociation constants for weak acids are found in Appendix 3.

$$K_w = K_a K_b$$

Buffer Solution





Buffer Solution Definition

A buffer solution is a solution that resists changes in pH when small amounts of an acid or a base are added. It is usually composed of a weak acid and its conjugate base or a weak base and its conjugate acid.

How Buffer Solutions Work

Buffer solutions work by neutralizing added acids or bases. When an acid (H^+) is added, the conjugate base reacts with it, and when a base (OH^-) is added, the weak acid reacts with it, maintaining a stable pH.

Key Equations

The pH of a buffer solution can be calculated using the Henderson-Hasselbalch equation:

For acidic buffer:

$pH = pKa + \log ([A^-] / [HA])$ For

basic buffer:

$pOH = pKb + \log ([B^+] / [BOH])$

Solved Examples Example 1: Calculating the pH of an Acidic Buffer

A buffer solution is prepared by mixing 0.2 M acetic acid (CH_3COOH) and 0.1 M sodium acetate (CH_3COONa). The pKa of acetic acid is 4.76. Calculate the pH of the buffer solution.

Solution:

Using the Henderson-Hasselbalch equation:

$pH = 4.76 + \log (0.1 / 0.2)$

$pH = 4.76 + \log (0.5)$ pH

$= 4.76 - 0.30$ pH = 4.46

Example 2: Effect of Adding Acid to a Buffer

Consider the same buffer solution from Example 1. If 0.01 moles of HCl are added to 1 liter of the buffer, what will be the new pH? Assume no volume change.

Solution:

HCl dissociates completely, increasing H^+ concentration. The reaction:

$CH_3COO^- + H^+ \rightarrow CH_3COOH$

New concentrations:

$CH_3COOH = 0.2 + 0.01 = 0.21$ M

$CH_3COO^- = 0.1 - 0.01 = 0.09$ M

Using the equation again: pH =

4.76 + log (0.09 / 0.21) pH = 4.76

+ log (0.4286) pH = 4.76 - 0.37

pH ≈ 4.39 (slight decrease in pH)