Lecture 10

Spring 2022

General Chemistry II

Chem 102

Acid-Base Equilibria

pH

Ahmad Alakraa

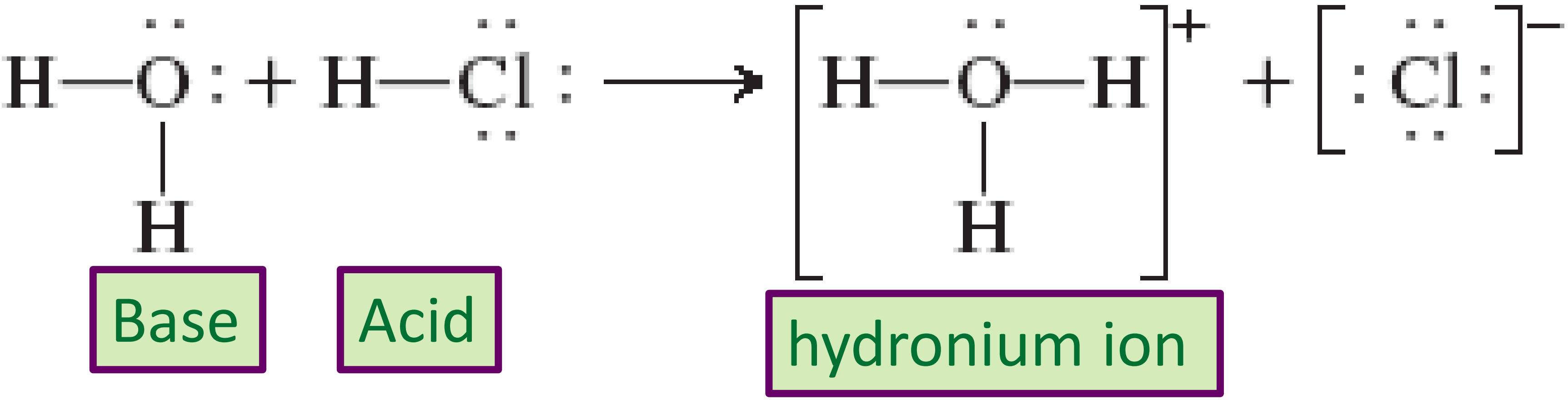
Acids and Bases

Arrhenius

- **acids** produce hydrogen ions in aqueous solutions, e.g., HCl, H_2SO_4
- **bases** produce hydroxide ions in aqueous solutions, e.g., KOH, NaOH

Brønsted–Lowry

- **acids** Proton donors e.g., HCl, H_2SO_4
- **bases** Protons acceptors, e.g., ammonia NH_3

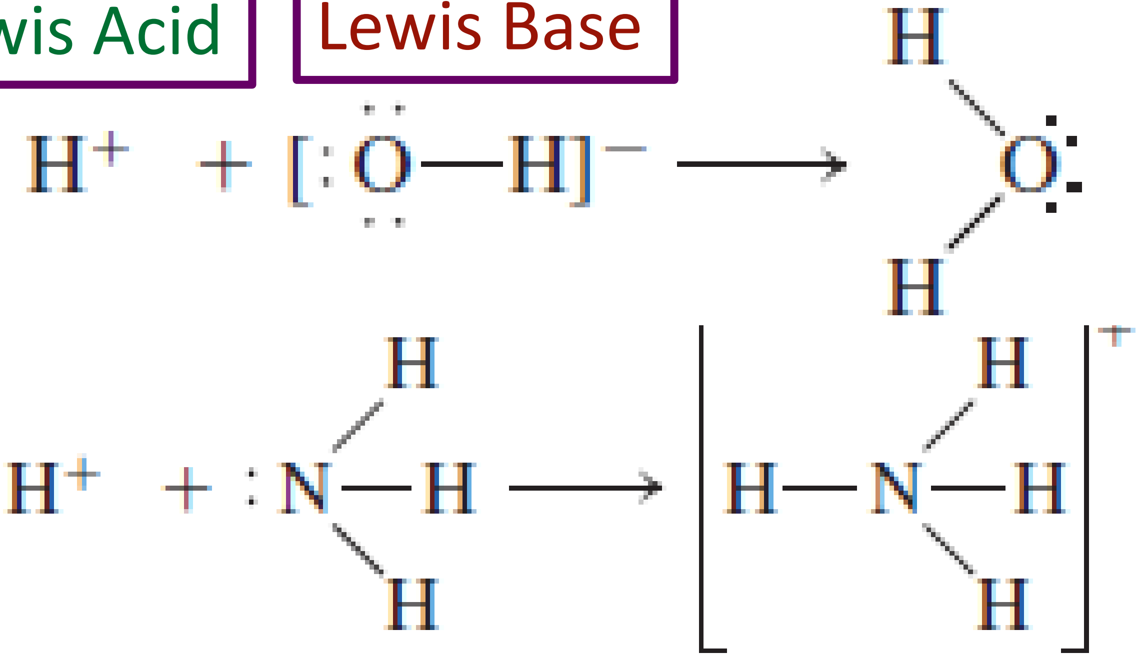


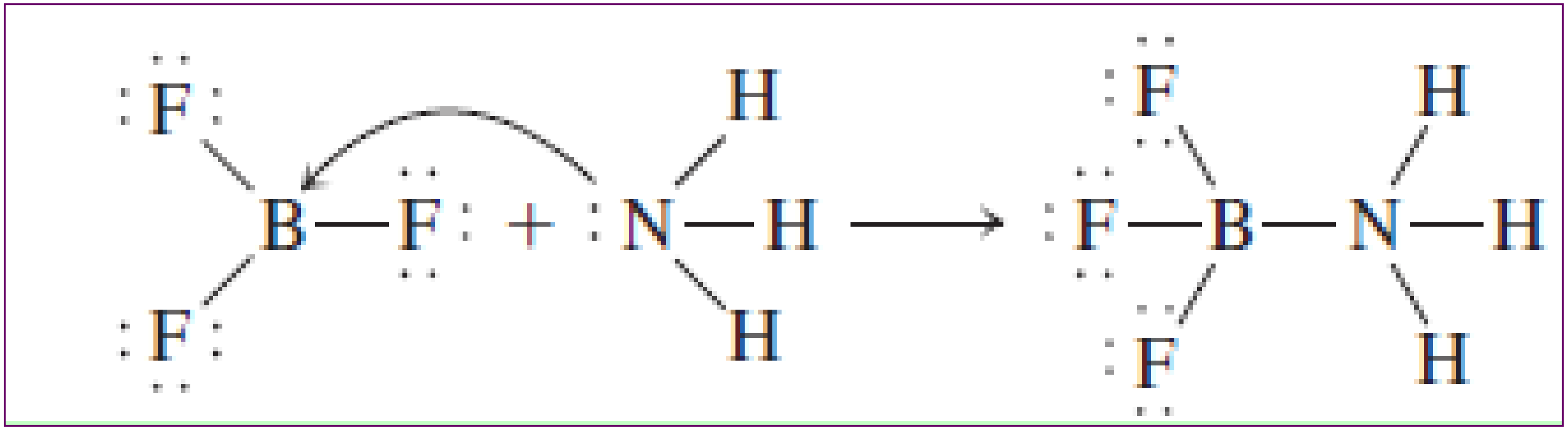
Lewis

- **Acids** electron-pair acceptors, e.g., BF_3
- **bases** electron-pair donors, e.g., NH_3

Lewis Acid

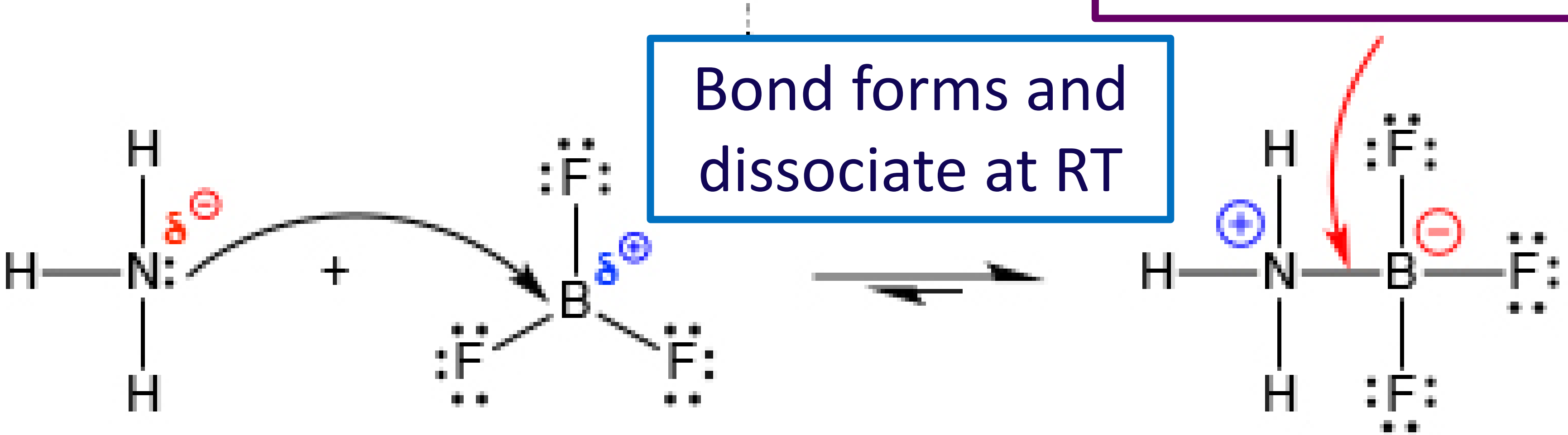
Lewis Base





New coordinate bond

Bond forms and dissociate at RT



Lewis Base

Lewis Acid

B atom has an unfilled valence shell

Lewis Acid-Lewis base Complex

Acids and Bases

Model	Acid	Base
Arrhenius	H^+ produce	OH^- produce
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair donor

Conjugate Acids and Bases

- When acids dissolve in water;

$$\underset{\text{Acid}}{HA\,(aq)} + \underset{\text{Base}}{H_2O\,(l)} \leftrightarrow \underset{\text{Conjugate Acid}}{H_3O^+(aq)} + \underset{\text{Conjugate Base}}{A^-(aq)}$$

- The conjugate base is everything that remains of the acid molecule after a proton is lost.
- The conjugate acid is formed when the proton is transferred to the base.
- A conjugate acid–base pair consists of two substances related to each other by the donating and accepting of a single proton.
- The equation shown above contains two conjugate acid–base pairs: HA and A^- and H_2O and H_3O^+.

$$\underset{\text{Acid}}{HA\ (aq)} + \underset{\text{Base}}{H_2O\ (l)} \leftrightarrow \underset{\text{Conjugate Acid}}{H_3O^+(aq)} + \underset{\text{Conjugate Base}}{A^-(aq)}$$

- Notice the competition for the proton between the two bases H_2O and A^-.

- If H_2O is a much stronger base than A^- (H_2O has a much greater affinity for H^+ than does A^-), the equilibrium position will be far to the right, i.e., most of the acid will dissolve (dissociated) at equilibrium.

- If A^- is a much stronger base than H_2O, the equilibrium position will lie far to the left (most of the acid will remain undissociated as HA at equilibrium).

Acid dissociation constant, K_a

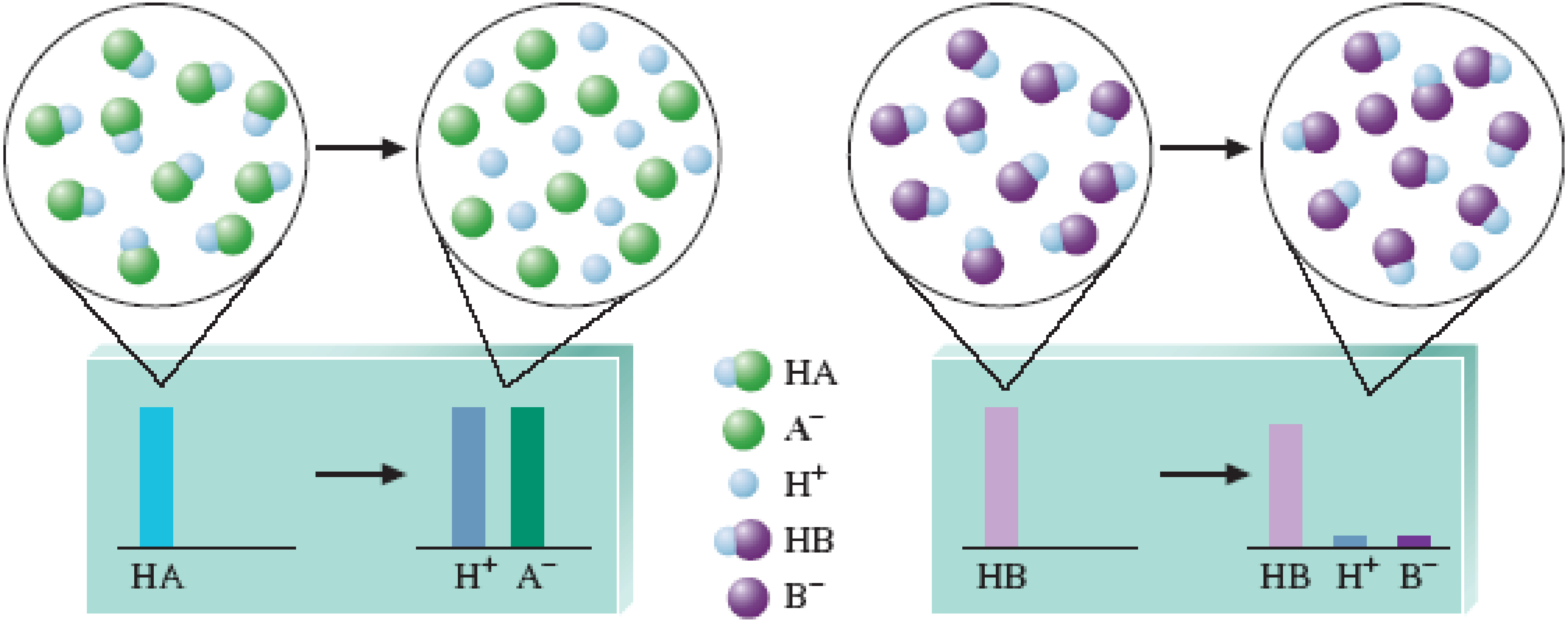
$$\underset{\text{Acid}}{\mathbf{HA\ (aq)}} + \underset{\text{Base}}{\mathbf{H_2O\ (l)}} \leftrightarrow \underset{\text{Conjugate Acid}}{\mathbf{H_3O^+(aq)}} + \underset{\text{Conjugate Base}}{\mathbf{A^-(aq)}}$$

$$\mathbf{K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]}}$$

- In a dilute solution we assume that the concentration of liquid water remains essentially constant when an acid is dissolved. Thus the term $[H_2O]$ is not included

Acid Strength

is measured by the equilibrium position of its dissociation (ionization) reaction



Strong Acid

Weak Acid

The weaker the acid, the stronger its conjugate base

Strong Acids

- The dissociation equilibrium lies far to the right.
- Almost all the original HA is dissociated (ionized) at equilibrium.
- Dissociation produces a weak conjugate base that has a low affinity for protons (much weaker base than water) .

Weak Acids

- The dissociation equilibrium lies far to the left (i.e., very small extent of dissociation).
- Almost all the original HA remains undissociated (not inozied) at equilibrium.
- The dissociation produces a strong conjugate base that is much stronger base than water.

Acid Strength: Examples

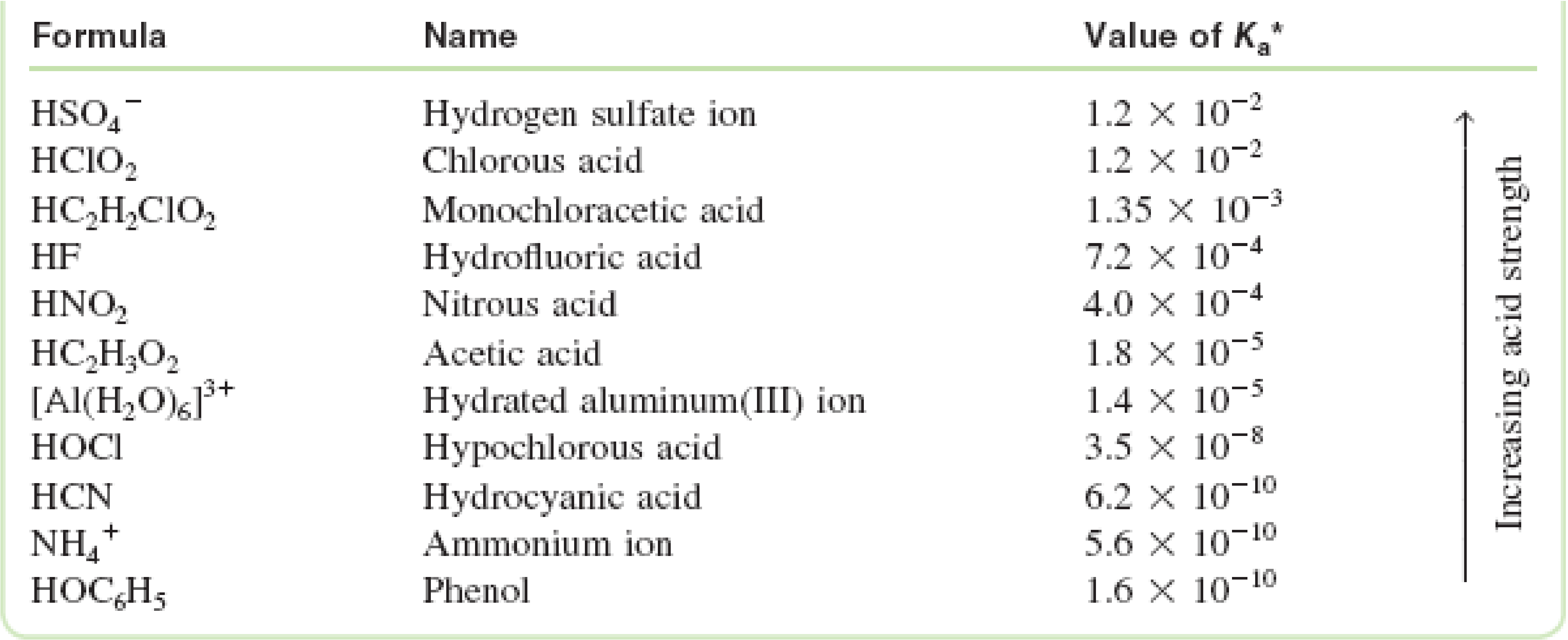
Strong Acids

- sulfuric acid [$H_2SO_4(aq)$],
- hydrochloric acid [$HCl(aq)$],
- nitric acid [$HNO_3(aq)$],
- perchloric acid [$HClO_4(aq)$].

Weak Acids

- phosphoric acid (H_3PO_4),
- nitrous acid (HNO_2),
- hypochlorous acid ($HOCl$),
- acetic acid (CH_3COOH),
- benzoic acid (C_6H_5COOH).

K_a for common monoprotic Acids



Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

Exercise

- Arrange the following species according to their strengths as bases:
  - **H_2O, F^-, Cl^-, NO_2^-, and CN^-.**

Solution

- Remember that water is a stronger base than the conjugate base of a strong acid but a weaker base than the conjugate base of a weak acid. This leads to the following order:

$$Cl^- < H_2O < \text{conjugate bases of weak acids}$$

Weakest bases →→→ Strongest bases

- Recognize that the strength of an acid is inversely related to the strength of its conjugate base.

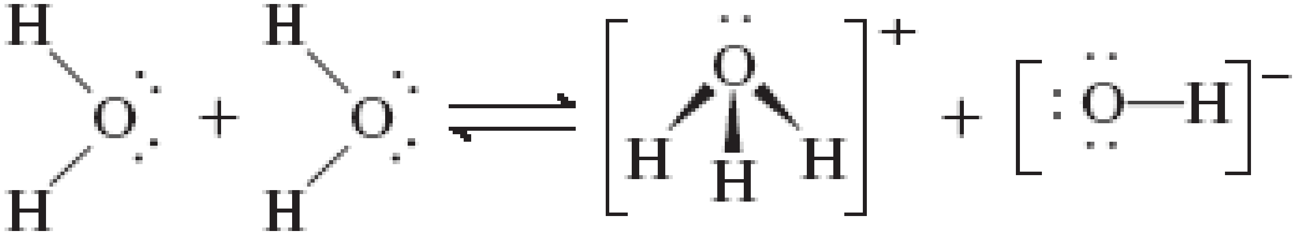
$$K_a \text{ for } HF > K_a \text{ for } HNO_2 > K_a \text{ for } HCN$$

- The combined order of increasing base strength is

$$Cl^- < H_2O < F^- < NO_2^- < CN^-$$

Water as an Acid and a Base

- **Amphoteric substances** behave as an acid or as a base.



Autoionization

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

K_w : the ion-product constant (**dissociation constant** of water). Experiment shows that at 25°C in pure water,

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} M$$

$$\boxed{\begin{aligned} &K_W = [H^+][OH^-] = \\ &(1.0 \times 10^{-7}) \times (1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14} \end{aligned}}$$

Exercise

- Calculate [H⁺] or [OH⁻] as required for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

  a) 1.0×10^{-5} M OH^-, b) 1.0×10^{-7} M OH^-,

  c) 10.0 M H^+

Solution

$$[H^+] = \frac{K_W}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9} M$$

Basic

$$[\mathrm{H^+}] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}\mathrm{M}$$

Neutral

$$[\mathrm{OH^-}] = \frac{1.0 \times 10^{-14}}{[\mathrm{H^+}]} = \frac{1.0 \times 10^{-14}}{10.0}$$
$$= 1.0 \times 10^{-15}\mathrm{M}$$

Acidic

pH Scale

$$pK = -\log K$$

$$pH = -\log[\mathrm{H}^+]$$

$$pOH = -\log[\mathrm{OH}^-]$$

$$pH + pOH = 14$$

At 25 °C

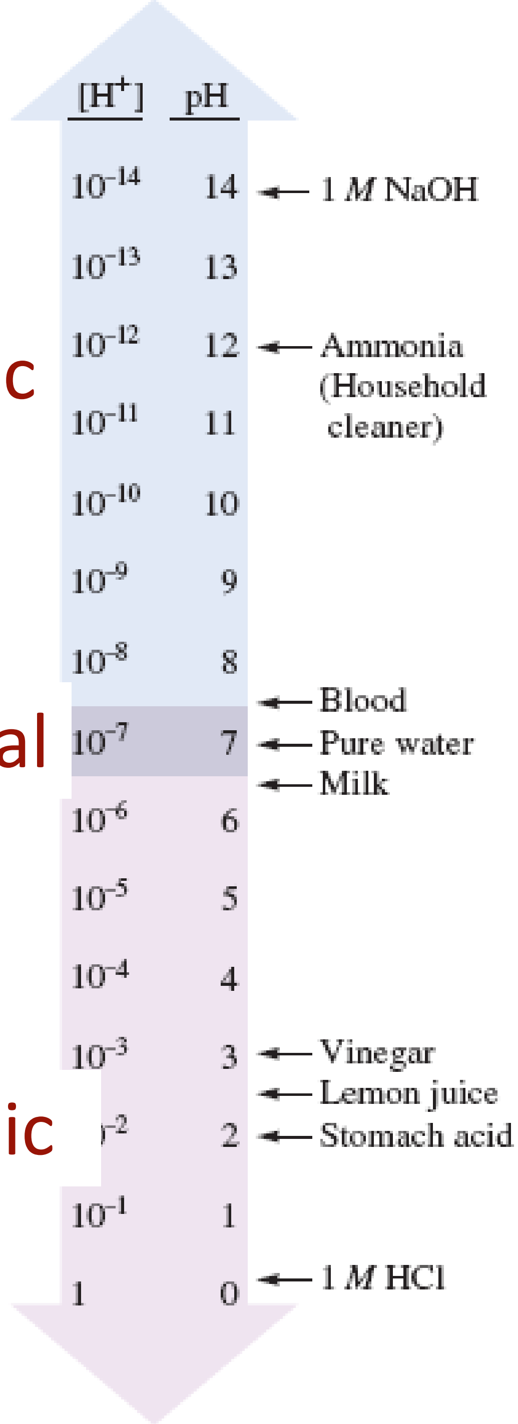
$$[\mathrm{H}^+] = 1.0 \times 10^{-7}\,\mathrm{M}$$

$$\boxed{pH = -(-7) = 7}$$

Basic

Neutral

Acidic



$[H^+]$	pH	
10^{-14}	14	1 *M* NaOH
10^{-13}	13	
10^{-12}	12	Ammonia (Household cleaner)
10^{-11}	11	
10^{-10}	10	
10^{-9}	9	
10^{-8}	8	
		Blood
10^{-7}	7	Pure water
		Milk
10^{-6}	6	
10^{-5}	5	
10^{-4}	4	
10^{-3}	3	Vinegar
		Lemon juice
$^{-2}$	2	Stomach acid
10^{-1}	1	
1	0	1 *M* HCl

Exercise

- Calculate pH and pOH for 1.0×10^{-3} M OH^- solution at 25°C?

Solution

$$[\mathrm{H}^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\mathrm{M}$$

$$\mathrm{pH} = -\log(1.0 \times 10^{-11}) = 11.00$$

$$\mathrm{pOH} = -\log(1.0 \times 10^{-3}) = 14.00 - 11.00$$
$$= 3.00$$

pH of Strong Acid Solutions

Exercise

- Calculate the pH of 1.0 M HCl?

Solution

Find major species in solution:

H^+, Cl^-, and H_2O

Major species that can produce H^+ are:

✓ the dissociation of HCl

$$HCl \rightarrow H^+ + Cl^-$$

✓ Autoionization of H_2O

$$H_2O \leftrightarrow H^+ + OH^-$$

- In pure H_2O at 25 °C, $[H^+] = 10^{-7}$ M.

- In 1.0 M HCl solution, water will produce even less than 10^{-7} M H^+ (Le Châtelier's principle) (can be ignored compared to 1.0 M H^+ from 1.0 M HCl).

$$\boxed{\mathrm{pH} = -\log[\mathrm{H}^+] = -\log(1.0) = 0}$$

Exercise

- Calculate the pH of 1.0×10^{-10} M HNO_3?

Solution

Find major species in solution:

H^+, NO_3^-, and H_2O

- Major species that can produce H^+ are:
  - ✓ the dissociation of HNO_3
  - ✓ Autoionization of H_2O
- In pure H_2O at 25 °C, $[H^+] = 10^{-7}$ M.
- In 1.0×10^{-10} M HNO_3 solution, the amount of HNO_3 in solution is so small that it has **no effect**; the only major species is H_2O.
- Thus the pH will be that of pure water, or pH = 7.00.

pH of Weak Acid Solutions

Exercise

- Calculate the pH of a 1.00 M HF soln. ($K_a = 7.2 \times 10^{-4}$)?

Solution

Major species in solution: **HF and H_2O**

Major species that can produce H^+ are:

✓Dissociation of HF

$$\mathrm{HF} \leftrightarrow \mathrm{H}^+ + \mathrm{F}^- \qquad \mathrm{K_a} = 7.2 \times 10^{-4}$$

$$\mathrm{K_a} = \frac{[\mathrm{H}^+][\mathrm{F}^-]}{[\mathrm{HF}]} = 7.2 \times 10^{-4}$$

✓Autoionization of H_2O

$$\mathrm{H_2O} \leftrightarrow \mathrm{H}^+ + \mathrm{OH}^- \qquad \mathrm{K_w} = 1.0 \times 10^{-14}$$

Compare K_a for HF and K_w for H_2O,

- HF, although weak, is still a much stronger acid than water. Thus we will assume that HF will be the dominant source of H^+. We will ignore the tiny contribution by water.

Before dissociation of HF,

$$[\mathrm{HF}]_0 = 1.0\mathrm{M}, \qquad [\mathrm{F}^-]_0 = 0, \qquad [\mathrm{H}^+]_0 = 10^{-7} \approx 0$$

Assume to reach equilibrium, x mol/L HF will dissociate to produce x mol/L H^+ and x mol/L F^-.

Equilibrium concentrations can be defined in terms of x:

$$[\mathrm{HF}] = [\mathrm{HF}]_0 - \mathrm{x} \;= 1.0 - \mathrm{x},$$
$$[\mathrm{F}^-] = [\mathrm{F}^-]_0 + \mathrm{x} = 0 + \mathrm{x} = \mathrm{x},$$
$$[\mathrm{H}^+] = [\mathrm{H}^+]_0 + \mathrm{x} \approx 0 + \mathrm{x} = \mathrm{x}$$

As x is very small compared to 1.0, 1.0–x ≈ 1.0

$$\mathrm{K_a} = 7.2 \times 10^{-4} = \frac{[\mathrm{H}^+][\mathrm{F}^-]}{[\mathrm{HF}]} = \frac{(\mathrm{x})(\mathrm{x})}{1.0 - \mathrm{x}}$$

$$\mathrm{x}^2 \approx (7.2 \times 10^{-4})(1.0)$$
$$\mathrm{x} \approx \sqrt{7.2 \times 10^{-4}} = 2.7 \times 10^{-2}$$

$$x = [H^+] = 2.7 \times 10^{-2} \text{mol/L}$$
$$pH = -\log[H^+] = -\log(2.7 \times 10^{-2}) = 1.57$$

Solving a quadratic equation of the general form

$$ax^2 + bx + c = 0$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

pH of Weak Acid Mixtures

Exercise

Calculate the pH of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO_2 ($Ka = 4.0 \times 10^{-4}$). Also calculate the concentration of cyanide ion (CN^-) in this solution at equilibrium?

Solution

Major species in solution:

HCN, HNO_2 and H_2O

Major species that can produce H^+ are:

$$\begin{aligned}
&HCN \leftrightarrow H^+ + CN^- && K_a = 6.2 \times 10^{-10}\\
&HNO_2 \leftrightarrow H^+ + NO_2^- && K_a = 4.0 \times 10^{-4}\\
&H_2O \leftrightarrow H^+ + OH^- && K_w = 1.0 \times 10^{-14}
\end{aligned}$$

Compare K_a for HCN, HNO_2 and K_w for H_2O,

HNO_2, although weak, is still a much stronger acid than HCN and water. Thus we will assume that HNO_2 will be the dominant source of H^+.

$$\boxed{K_a = 4.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]}}$$

Initial Concentration (mol/L)	→	Equilibrium Concentration (mol/L)
$[HNO_2]_0$= 5.00	X mol/L HNO_2 dissociates	$[HNO_2]$ = 5.00–x
$[NO_2^-]_0$= 0		$[NO_2^-]_0$= x
$[H^+]_0$= ≈0		$[H^+]_0$= ≈x

	$HNO_2 \leftrightarrow$	$H^+ +$	NO_2^-
Initial	5.00	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$5.00 - x$	x	x

$$K_a = 4.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{(x)(x)}{5.0 - x} \approx \frac{x^2}{5.0}$$

$$x = 4.5 \times 10^{-2} = [H^+] \qquad pH = 1.35$$

Calculation of equilibrium $[CN^-]$:

$$HCN \leftrightarrow H^+ + CN^- \qquad K_a = 6.2 \times 10^{-10}$$

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]}$$

- There is only one kind of H^+ in this solution. It does not matter from which acid the H^+ ions originate. $[H^+] = 4.5 \times 10^{-2}$ M

- Since K_a for HCN is so small, a negligible amount of HCN will dissociate.

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} = \frac{4.5 \times 10^{-2}[CN^-]}{1.00}$$

$$[CN^-] = 1.4 \times 10^{-8} \text{mol/L}$$

pH of Weak Acid Solutions

Generally

$$HA \leftrightarrow H^+ + A^-$$

Initial	C	0	0
Change	$-x$	$+x$	$+x$
Eqm.	$C-x$	x	x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x\,.x}{C-x} \approx \frac{x^2}{C} = \frac{[H^+]^2}{C}$$

$$[H^+]^2 = K_a C$$

$$[H^+] = \sqrt{K_a C}$$

Percent Dissociation

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100 \quad \%$$

In a 1.00 M solution of HF, $[H^+] = 2.7 \times 10^{-2}$ M.

To reach equilibrium, 2.7×10^{-2} mol/L of the original 1.00 M HF dissociates, so

$$\text{Percent dissociation} = \frac{2.7 \times 10^{-2}\,\text{mol/L}}{1.00\ \text{mol/L}} \times 100 = 2.7\ \%$$

For a given weak acid, the percent dissociation increases as the acid becomes more dilute.

Exercise

The pH of a 0.050 M weak acid is 3.00. What is the percentage ionization?

Solution

$$\mathrm{pH} = 3.00 = -\log[\mathrm{H}^+]$$
$$[\mathrm{H}^+] \;= 0.001\ \mathrm{mol/L}$$

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100 \quad \%$$
$$= \frac{0.001\ (\mathrm{mol/L})}{0.050\ (\mathrm{mol/L})} \times 100 = 2.0\ \%$$

HOMEWORKS

- Calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in 1.00 and 0.100 M $HC_2H_3O_2$?

- Lactic acid ($HC_3H_5O_3$) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a 0.100 M aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid?

Bases

Strong Bases

dissociating completely when dissolved in aqueous solution, e.g., sodium hydroxide (NaOH) and potassium hydroxide (KOH).

$$\boxed{\mathrm{NaOH\ (s)} \rightarrow \mathrm{Na^{+}(aq)} + \mathrm{OH^{-}(aq)}}$$

Virtually no undissociated NaOH left. Thus a 1.0 M NaOH solution really contains 1.0 M Na^+ and 1.0 M OH^-.

Exercise

- Calculate the pH of a 5.0×10^{-2} M NaOH solution?

Solution

Major species in solution: Na^+, OH^-, $\mathbf{H_2O}$

Although autoionization of water also produces OH^- ions, the pH will be dominated by the OH^- ions from the dissolved NaOH.

$$[\mathrm{OH^-}] = 5.0 \times 10^{-2} \mathrm{mol/L}$$

$$[\mathrm{H^+}] = \frac{\mathrm{K_w}}{[\mathrm{OH^-}]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13} \mathrm{mol/L}$$

$$\mathrm{pH} = 12.70$$

Note that this is a basic solution for which

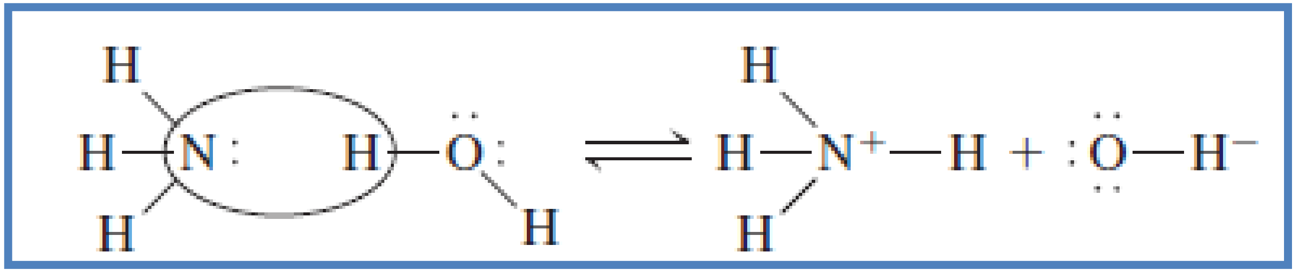
$$\boxed{[\mathrm{OH}^-] > [\mathrm{H}^+] \text{ and } \mathrm{pH} > 7.0}$$

The added OH⁻ from NaOH has shifted the water autoionization equilibrium to left, significantly lowering [H⁺] compared with that in pure water.

$$\boxed{\mathrm{H_2O} \leftrightarrow \mathrm{H}^+ + \mathrm{OH}^- \quad \mathrm{K_w} = 1.0 \times 10^{-14}}$$

Bases having no OH^-

- Many bases do not contain the hydroxide ion.



- However, when dissolved in water $[OH^-]$ increases because of their reaction with water.

$$\begin{array}{lllll} B\,(aq) + H_2O\,(l) & \leftrightarrow & BH^+(aq) & + & OH^-(aq) \\ \text{Base} \quad \text{Acid} & & \text{Conjugate Acid} & & \text{Conjugate Base} \end{array}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$B\ (aq)$	$+$	$H_2O\ (l)$	$\leftrightarrow$	$BH^+(aq)$	$+$	$OH^-(aq)$
Base		Acid		Conjugate Acid		Conjugate Base

Note the competition between the weak base, B, and OH^-, which is a very strong base, for H^+ ion. Thus their K_b values tend to be small.

Exercise

- Calculate the pH for a 15.0 M solution of NH_3 ($K_b = 1.8 \times 10^{-5}$)?

Solution

Major species in solution: NH_3 and H_2O (as K_b is very small)

Major species that can produce OH^- are:

$$NH_3 + H_2O \leftrightarrow NH_4{}^+ + OH^- \qquad K_b = 1.8 \times 10^{-5}$$

$$H_2O \leftrightarrow H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$

The contribution from water can be neglected, since

$K_b >>> K_w$

$$\boxed{K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}}$$

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[NH_3]_0 = 15.0$		$[NH_3] = 15.0 - x$
$[NH_4^+]_0 = 0$	$\xrightarrow[\text{H}_2\text{O to reach equilibrium}]{x\text{ mol/L NH}_3\text{ reacts with}}$	$[NH_4^+] = x$
$[OH^-]_0 \approx 0$		$[OH^-] = x$

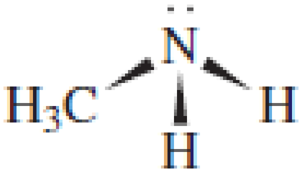
$$\boxed{K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{15.0 - x} \approx \frac{x^2}{15.0}}$$

$$\boxed{x \approx 1.6 \times 10^{-2}}$$

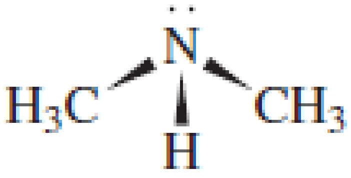
$$\boxed{[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13}\, M}$$

$$\boxed{pH = -\log(6.3 \times 10^{-13}) = 12.20}$$

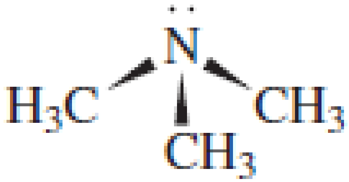
Weak Bases_ examples



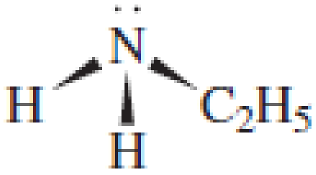
Methylamine



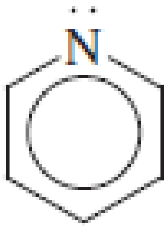
Dimethylamine



Trimethylamine



Ethylamine



Pyridine

TABLE 14.3 › Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Exercise

Calculate $[H_3O^+]$, $[OH^–]$, and $[Ba^{2+}]$ in a 50.0 mL sample of 0.010 M $Ba(OH)_2$?

Solution

$Ba(OH)_2$ is considered the sole source of $OH^–$

$$Ba(OH)_2 \rightarrow Ba^{2+} + 2\ OH^–$$

$[Ba^+] = 0.010$ M

$[OH^–] = 2\ [Ba^+] = 0.020$ M

$$K_w = [H_3O^+]\ [OH^–] =[H_3O^+](0.020) = 1.0 \times 10^{–14}$$

$$[H_3O^+] = 5.0 \times 10^{–13}\ M$$

pH of Weak Bases Solutions

Generally

$$\mathrm{BOH} \leftrightarrow \mathrm{B}^{+} + \mathrm{OH}^{-}$$

Initial	C	0	0
Change	$-x$	$+x$	$+x$
Eqm.	$C-x$	x	x

$$K_b = \frac{[\mathrm{B}^{+}][\mathrm{OH}^{-}]}{[\mathrm{BOH}]} = \frac{x\,.x}{C-x} \approx \frac{x^2}{C} = \frac{[\mathrm{OH}^{-}]^2}{C}$$

$$[\mathrm{OH}^{-}]^2 = K_b C \qquad [\mathrm{OH}^{-}] = \sqrt{K_b C}$$

$$\mathrm{pOH} = -\log[\mathrm{OH}^{-}] \qquad \mathrm{pH} + \mathrm{pOH} = 14$$

The pH of a Polyprotic Acid

- Sulfuric acid is unique among the common acids in that it is a strong acid in its first dissociation step and a weak acid in its second step:

$$\mathrm{H_2SO_4} \rightarrow \mathrm{H^+} + \mathrm{HSO_4{}^-} \qquad \mathrm{K_{a_1}} = \text{very large}$$

$$\mathrm{HSO_4{}^-} \leftrightarrow \mathrm{H^+} + \mathrm{SO_4{}^{2-}} \qquad \mathrm{K_{a_2}} = 1.2 \times 10^{-2}$$

Exercise

Calculate the pH of a 1.0 M H_2SO_4 solution.

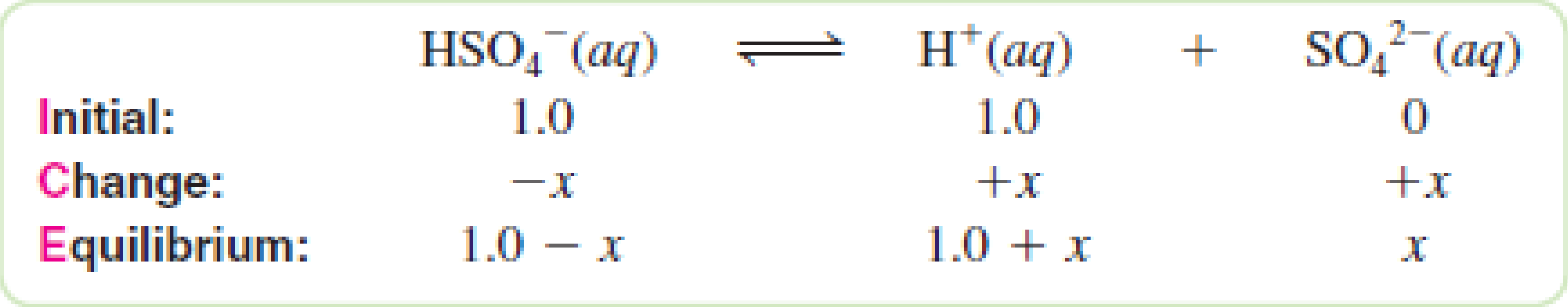
Solution

Major species in solution: H^+, HSO_4^-, and H_2O

$[H^+] = 1.0 + x$ (obtained from the dissociation of HSO_4^-)

To calculate x

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$



	$HSO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$SO_4^{2-}(aq)$
Initial:	1.0		1.0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$1.0 - x$		$1.0 + x$		x

Note that $[H^+]_0 \neq 0$, as it usually is for a weak acid, because the first dissociation step has already occurred.

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(1.0 + x)(x)}{1.0 - x} \approx \frac{(1.0)(x)}{1.0} \approx x$$

$$[H^+] = 1.0 \text{ M} \qquad pH = 0.00$$

$$[H^+] = 1.0 \text{ M} + x = 1.0\text{M} + 1.2 \times 10^{-2}\text{M} \approx 1.0 \text{ M}$$

Dissociation of HSO_4^- does not contribute to $[H^+]$

(H) Calculate the pH of a 1.0×10^{-2} M H_2SO_4 solution ?

Acid-Base Properties

of

Salts

Salts Producing Neutral Solutions

- When a salt (ionic compound) dissolves in water, it breaks up into its ions, which move independently, at least in dilute solutions.

- Under certain conditions, these ions can behave as acids or bases.

- Salts that consist of the cations of strong bases (K^+, Na^+) and the anions of strong acids (Cl^-, NO_3^-) have no effect on $[H^+]$ when dissolved in water

- Aqueous solutions of salts such as KCl, $NaCl$, $NaNO_3$, and KNO_3 are neutral (have a pH of 7).

Salts Producing Basic Solutions

- Salts whose cations have neutral properties (such as K^+, Na^+) and whose anions are the conjugate bases of weak acids always produce basic aqueous solutions.

- The pH of aqueous solution of sodium acetate ($NaC_2H_3O_2$) is determined by the $C_2H_3O_2^-$ ion (strong conjugate base of acetic acid)

$$C_2H_3O_2^-(aq) + H_2O\,(l) \leftrightarrow H\,C_2H_3O_2(aq) + OH^-(aq)$$

$$K_b = \frac{[H\,C_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

- What is the relationship between K_b and K_a of acetic acid?

$$K_a \times K_b = \frac{[H^+][C_2H_3O_2{}^-]}{[H\,C_2H_3O_2]} \times \frac{[H\,C_2H_3O_2][OH^-]}{[C_2H_3O_2{}^-]}$$

$$= [H^+] \times [OH^-] = 1.0 \times 10^{-14} = K_w$$

Exercise

- Calculate the pH of a 0.30 M NaF solution? The K_a value for HF is 7.2×10^{-4}.

Solution

Major species in solution Na^+, F^-, and H_2O

Since HF is a weak acid, the F^- ion must have a significant affinity for protons, and the dominant reaction will be

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

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{K_w}{K_a(HF)} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

	$F^-(aq)$	$+ H_2O(l) \leftrightarrow$	$HF(aq) +$	$OH^-(aq)$
Initial	0.30	$-$	0	≈ 0
Change	$-x$	$-$	$+x$	$+x$
Eq.	$0.30 - x$	$-$	x	x

$$K_b = 1.4 \times 10^{-11} = \frac{[HF][OH^-]}{[F^-]} = \frac{(x)(x)}{0.3 - x} \approx \frac{x^2}{0.3}$$

$$x \approx 2.0 \times 10^{-6} = [OH^-]$$

$$pOH = 5.69$$

$$pH = 14.00 - 5.69 = 8.31$$

As expected, the solution is basic

Salts Producing Acidic Solutions

Salts whose anion is a weak base (Cl^-, NO_3^-) and whose cation is a conjugate acid of a weak base (such as NH_4^+) produce acidic solutions

Exercise

- Calculate the pH of a 0.10 M NH_4Cl solution. The K_b value for NH_3 is 1.8×10^{-5}.

Solution

Major species in solution NH_4^+, Cl^-, and H_2O

both NH_4^+ and H_2O can produce H^+. The dissociation reaction for the NH_4^+ ion is

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$K_a(\text{for } NH_4^{+}) = \frac{K_w}{K_b(\text{for } NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

NH_4^+ is a very WA (see K_a) but still stronger than H_2O. Hence, it will dominate in the production of H^+.

$$NH_4^{+}(aq) \leftrightarrow H^{+}(aq) + NH_3(aq)$$

Initial	0.10	≈ 0	0
Change	$-x$	$+x$	$+x$
Eq.	$0.10 - x$	x	x

$$\boxed{K_a = 5.6 \times 10^{-10} = \frac{[H^{+}][NH_3]}{[NH_4^{+}]} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}}$$

$x \approx 7.5 \times 10^{-6} = [H^{+}]$ $\qquad$ $pH = 5.13$

As expected, acidic solution

Salts whose cations and anions influence pH

- We can predict whether the solution will be basic, acidic, or neutral by comparing the K_a value for the acidic ion with the K_b value for the basic ion.

$K_a > K_b$ $\quad$ $pH < 7$ $\quad$ (acidic)

$K_a < K_b$ $\quad$ $pH > 7$ $\quad$ (basic)

$K_a = K_b$ $\quad$ $pH = 7$ $\quad$ (neutral)

Exercise

Predict whether an aqueous solution of $NH_4C_2H_3O_2$ salt will be acidic, basic, or neutral.

Solution

Major species in soln: NH_4^+ and $C_2H_3O_2^-$

$$K_a \text{ for } NH_4^+ = 5.6 \times 10^{-10}$$

$$K_b \text{ for } C_2H_3O_2^- = 5.6 \times 10^{-10}$$

$$K_a \text{ for } NH_4^+ = K_b \text{ for } C_2H_3O_2^-$$

Neutral solution pH =7

Solutions of Acids Containing a Common Ion

Consider a solution containing a weak acid 1.0 M HF ($K_a = 7.2 \times 10^{-4}$) and 1.0 M NaF. How does F^- influence the dissociation of HF?

Major species in soln: Na^+, F^-, HF, and H_2O

The common ion in this solution is F^-.

$$\mathrm{HF(aq)} \leftrightarrow \mathrm{H^+(aq)} + \mathrm{F^-(aq)}$$

$$\mathrm{NaF(s)} \xrightarrow{\mathrm{H_2O}} \mathrm{Na^+(aq)} + \mathrm{F^-(aq)}$$

Le Châtelier's

Common ion effect makes a solution of NaF and HF less acidic than a solution of HF alone.

Solutions of Bases Containing a Common Ion

Consider the addition of solid NH_4Cl to a 1.0 M NH_3 solution.

$$\begin{aligned} &NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq) \\ &NH_3(aq) + H_2O \leftrightarrow NH_4^+(aq) + OH^-(aq) \end{aligned}$$

Le Châtelier's ➡

The position of the ammonia–water equilibrium shifts to the left reducing the equilibrium concentration of OH^- ions.

Polyprotic acids

- Common ion effect is important in solutions of polyprotic acids (e.g., H_2SO_4, H_3PO_4).

- The production of H^+ by the first dissociation step greatly inhibits the succeeding dissociation steps, which also produce protons “common ion”

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \qquad K_{a_1} = \text{very large}$$

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-} \qquad K_{a_2} = 1.2 \times 10^{-2}$$

Exercise

The equilibrium concentration of H^+ in a 1.0 M HF solution is 2.7 × 10^{-2} M, and the percent dissociation of HF is 2.7%. Calculate $[H^+]$ and the percent dissociation of HF in a solution containing 1.0 M HF (K_a = 7.2 x 10^{-4}) and 1.0 M NaF.

Solution

Major species in soln. Na^+, F^-, HF, H_2O

- Na^+ ions have neither acidic nor basic properties
- H_2O is a very weak acid (or base).
- Important species are HF and F^-.

$$\mathrm{HF(aq)} \leftrightarrow \mathrm{H^+(aq)} + \mathrm{F^-(aq)}$$

$$\boxed{K_a = \frac{[\mathrm{H^+}][\mathrm{F^-}]}{[\mathrm{HF}]} = 7.2 \times 10^{-4}}$$

Initial Conc. (mol/L)	Change (mol/L)	Eq. Conc. (mol/L)
$[HF]_0 = 1.0$ From dissolved HF	x mol/L HF dissociates	$[HF] = 1.0 – x$
$[F^–]_0 = 1.0$ From dissolved NaF		$[F^–] = 1.0 + x$
$[H^+]_0 = 0$ Neglect contribution from H_2O		$[H^+]_0 = x$

$$\boxed{K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(1.0 + x)}{(1.0 - x)} \approx x = [H^+]}$$

$$[H^+] = 7.2 \times 10^{-4} \Rightarrow pH = 3.14$$

The percent dissociation of HF in this solution is

$$\frac{[H^+]}{[HF]_0} \times 100 = \frac{7.2 \times 10^{-4} M}{1.0 M} \times 100 = 0.072\%$$

As expected, F^- ions inhibited the dissociation of HF and position of acid dissociation equilibrium is shifted to the left

Buffered Solution BS

- A BS is that resisting a change in its pH when either hydroxide ions or protons are added
- Buffered systems are especially important in living systems, which can survive only in a relatively narrow pH range.
- For example, although human blood contains many buffering systems, the most important of these consists of a mixture of carbonic acid (0.0012 M) and bicarbonate ion (0.024 M). These concentrations produce a pH of 7.4 for normal blood.

Buffered Solutions

- Because our cells are so sensitive to pH, it is important that this pH value be maintained.

- When reactions occur in our bodies, such as the formation of lactic acid ($HC_3H_5O_3$) when our muscles are exerted, the buffering systems must be capable of neutralizing the effects of this acid to maintain the pH at 7.4.

- A buffered solution may contain a WA and its salt (HF and NaF) or a WB and its salt (NH_3 and NH_4Cl).

- By choosing the appropriate components, a solution can be buffered at virtually any pH.

Exercise

- A buffered solution contains 0.50 M acetic acid ($HC_2H_3O_2$, K_a= 1.8 × 10^{-5}) and 0.50 M sodium acetate ($NaC_2H_3O_2$). Calculate the pH of this solution?

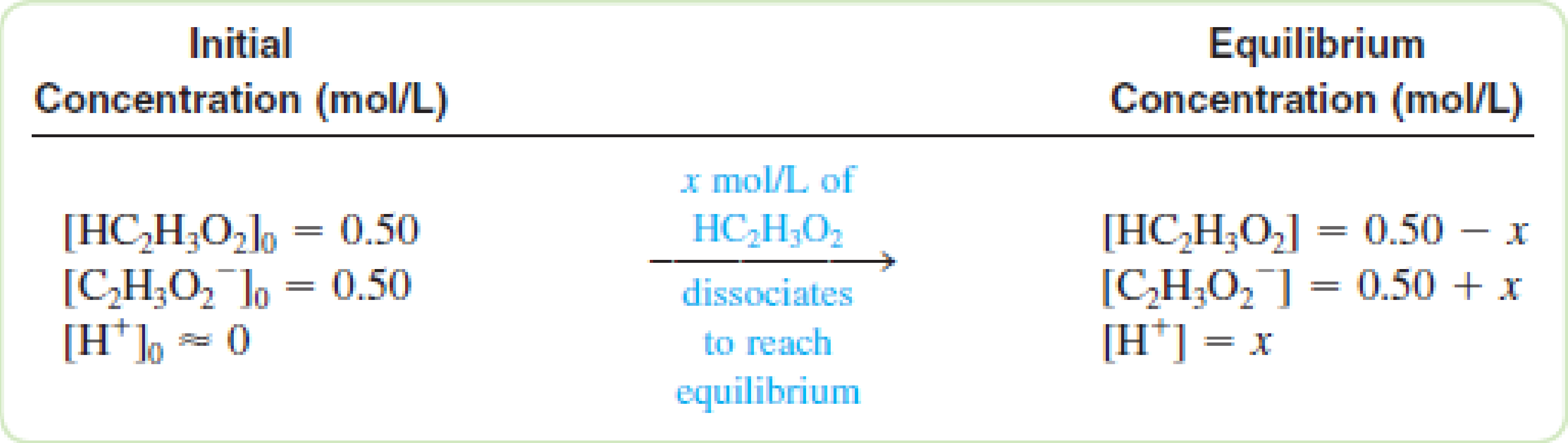
Solution

Major species in soln.

$HC_2H_3O_2$,	Na^+,	$C_2H_3O_2^-$,	H_2O
Weak acid	neutral	base	weak acid/base

$$\mathrm{H\,C_2H_3O_2(aq) \leftrightarrow H^+(aq) + C_2H_3O_2{}^-(aq)}$$

$$\mathrm{K_a} = 1.8 \times 10^{-5} = \frac{[\mathrm{H^+}][\mathrm{C_2H_3O_2{}^-}]}{[\mathrm{H\,C_2H_3O_2}]}$$



Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[HC_2H_3O_2]_0 = 0.50$		$[HC_2H_3O_2] = 0.50 - x$
$[C_2H_3O_2^-]_0 = 0.50$	$\xrightarrow[\text{dissociates to reach equilibrium}]{x \text{ mol/L of } HC_2H_3O_2}$	$[C_2H_3O_2^-] = 0.50 + x$
$[H^+]_0 \approx 0$		$[H^+] = x$

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2{}^-]}{[H\,C_2H_3O_2]} = \frac{(x)(0.5 + x)}{(0.5 - x)} \approx x$$

$$[H^+] = 1.8 \times 10^{-5} \Rightarrow pH = 4.74$$

Calculate the change in pH that occurs when 0.010 mole of solid NaOH is added to 1.0 L of the abovementioned buffered solution? Compare this pH change with that which occurs when 0.010 mole of solid NaOH is added to 1.0 L water?

- Na^+ ions have neither **acidic** nor **basic** properties
- NaOH will completely dissociate, so the major species in solution before any reaction occurs are

  $HC_2H_3O_2$, Na^+, $C_2H_3O_2^-$, OH^-, and H_2O.

- The solution contains a relatively large amount of the very strong base OH^-, which has a great affinity for H^+.

- The best source of H^+ is $HC_2H_3O_2$, and the reaction that will occur is

$$OH^- + H\,C_2H_3O_2 \rightarrow H_2O + C_2H_3O_2^-$$

- Although acetic acid is a weak acid, the hydroxide ion is such a strong base that their reaction will proceed essentially to completion (until the OH^- ions are consumed).

- The best approach to this problem involves two distinct steps:
  - assume that the reaction goes to completion, and carry out the stoichiometric calculations, and then
  - carry out the equilibrium calculations.

Stoichiometry

	$HC_2H_3O_2$ +	OH^- →	$C_2H_3O_2^-$	+ H_2O
BR	$1L \times 0.5\ M = 0.5\ mol$	$0.01\ mol$	$1L \times 0.5\ M = 0.5\ mol$	
AR	$0.5 - 0.01 = 0.49\ mol$	$0.01 - 0.01 = 0\ mol$	$0.5 + 0.01 = 0.51\ mol$	

Eqm.

After the reaction between OH^- and $HC_2H_3O_2$ is complete, the major species in solution are

$HC_2H_3O_2$, Na^+, $C_2H_3O_2^-$, and H_2O.

	$H\,C_2H_3O_2$ $\leftrightarrow$	H^+ $+$	$C_2\,H_3O_2^-$
Initial	0.49	0	0.51
Change	–x	+x	+x
Eq.	0.49–x	x	0.51+x

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[H\,C_2H_3O_2]} = \frac{(x)(0.51 + x)}{(0.49 - x)}$$

$$\approx \frac{(x)(0.51)}{(0.49)}$$

$$x = 1.7 \times 10^{-5} = [H^+]$$

$$\Rightarrow pH = 4.76$$

The change in pH produced by the addition of 0.01 mole of OH^- to this buffered solution is then

$$\text{Change in pH} = 4.76 - 4.74 = \quad +0.02$$

The pH increased by 0.02 pH units.

What does it happen if 0.01 mole of solid NaOH is added to 1.0 L water?

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

$$\Rightarrow pH = 12$$

$$\text{Change in pH} = 12 - 7 = \quad +5$$

Buffering mechanism

Consider the addition of OH^- to a buffered solution containing relatively large quantities of a weak acid HA and its conjugate base A^-. OH^- will be consumed immediately

$$\mathrm{HA} + \mathrm{OH}^- \rightarrow \mathrm{A}^- + \mathrm{H_2O}$$

pH will be justified by the equilibrium of HA dissociation:

$$\mathrm{K_a} = \frac{[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{H\,A}]} \quad \Rightarrow \quad [\mathrm{H}^+] = \mathrm{K_a}\frac{[\mathrm{H\,A}]}{[\mathrm{A}^-]}$$

- The equilibrium concentration of H^+, and thus pH, is determined by the ratio $[HA]/[A^-]$.
- When OH^- ions are added, HA is converted to A^-, and the ratio $[HA]/[A^-]$ decreases.

- If [HA] and [A⁻] originally very large compared to [OH⁻] added, the change in the [HA]/[A⁻] ratio will be small.

Prev. Ex.

$$\frac{[\mathrm{H\,A}]}{[\mathrm{A}^-]} = \frac{0.50}{0.50} = 1.0 \quad \text{Initially}$$

$$\frac{[\mathrm{H\,A}]}{[\mathrm{A}^-]} = \frac{0.49}{0.51} = 0.96 \quad \text{after adding } 0.01\ \mathrm{M\ OH}^-$$

- The change in [HA]/[A] ratio is very small. Thus [H⁺] and pH remain essentially constant.

The essence of buffering is that [HA] and [A⁻] are large compared with the amount of OH⁻ added

If H⁺ are added to a buffered solution of a weak acid and a salt of its conjugate base: $\mathrm{H}^+ + \mathrm{A}^- \rightarrow \mathrm{HA}$

Henderson–Hasselbalch equation

It is used to calculate the pH of buffered solutions when the ratio $[HA]/[A^-]$ is known.

Exercise

- Calculate $[H^+]$ in a buffered solution containing 0.10 M HF ($K_a = 7.2 \times 10^{-4}$) and 0.30 M NaF?

Solution

$$[\mathrm{H}^+] = \mathrm{K_a}\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} = (7.2 \times 10^{-4}) \times \frac{0.10}{0.30} = 2.4 \times 10^{-4}\mathrm{mol/L}$$

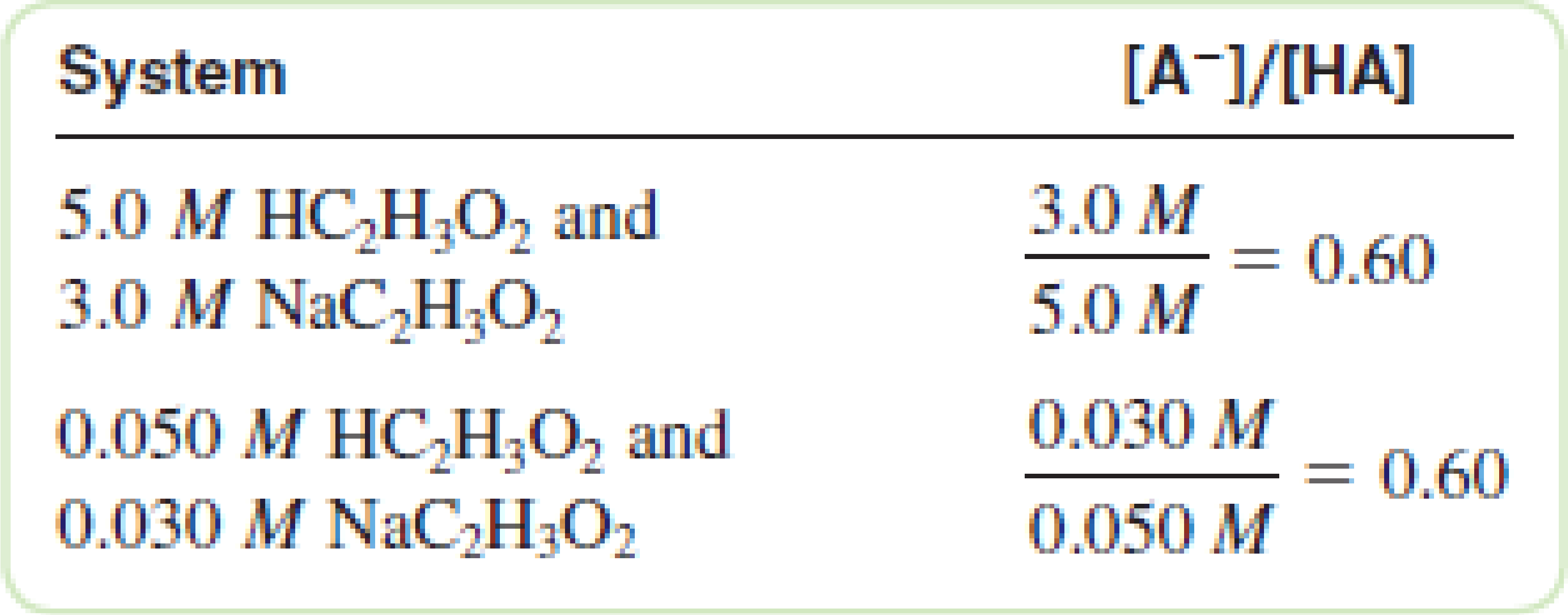
$$\boxed{[\mathrm{H}^+] = \mathrm{K_a}\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}}$$

$$-\log[\,\mathrm{H}^+] = -\log(\,\mathrm{K_a}) - \log\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

$$\boxed{\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}}$$

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

For a particular buffering system (conjugate acid–base pair), all solutions that have the same ratio $[\mathrm{A}^-]/[\mathrm{HA}]$ will have the same pH.



System	$[A^-]/[HA]$
5.0 M $HC_2H_3O_2$ and 3.0 M $NaC_2H_3O_2$	$\frac{3.0\ M}{5.0\ M} = 0.60$
0.050 M $HC_2H_3O_2$ and 0.030 M $NaC_2H_3O_2$	$\frac{0.030\ M}{0.050\ M} = 0.60$

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[C_2H_3O_2{}^-]}{[H\,C_2H_3O_2]}$$

$$= 4.74 + \log(0.60) = 4.74 - 0.22 = 4.52$$

Exercise

- Calculate the pH of a solution containing 0.75 M lactic acid ($K_a = 1.4 \times 10^{-4}$) and 0.25 M sodium lactate?

Solution

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{C_3H_5O_3}^-]}{[\mathrm{H\,C_3H_5O_3}]}$$

$$= 3.85 + \log\left(\frac{0.25}{0.75}\right) = 3.38$$

Buffering_Bases

- Buffered solutions also can be formed from a weak base and the corresponding conjugate acid.

- Weak base B reacts with any H^+ added:

$$\boxed{B + H^+ \rightarrow BH^+}$$

- Conjugate acid BH^+ reacts with any added OH^-:

$$\boxed{BH^+ + OH^- \rightarrow B + H_2O}$$

Exercise

- Calculate the pH of a buffered solution containing 0.25 M NH_3 ($K_b = 1.8 \times 10^{-5}$) and 0.40 M NH_4Cl?

Solution

Major species in soln.

$$NH_3 \qquad \underbrace{NH_4^+ \qquad\qquad Cl^-}_{\text{from } NH_4Cl} \qquad H_2O$$

Weak base

from NH_4Cl

weak acid/base

As Cl^- is a WB and water is a WA or WB, the important equilibrium is

$$\underbrace{NH_3(aq)}_{\text{Base}} + \underbrace{H_2O\ (l)}_{\text{Acid}} \leftrightarrow \underbrace{NH_4^+\ (aq)}_{\text{Conjugate Acid}} + \underbrace{OH^-(aq)}_{\text{Conjugate Base}}$$

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

	NH_3 +	H_2O ↔	NH_4^+ +	OH^-
Initial	0.25	–	0.40	≈0
Change	–x	–	+x	+x
Eq.	0.25–x	–	0.40+x	x

$$K_b = 1.8 \times 10^{-5} == \frac{[NH_4{}^{+}][OH^{-}]}{[NH_3]} = \frac{(0.40 + x)(x)}{(0.25 - x)}$$

$$\approx \frac{(0.40)(x)}{(0.25)}$$

$$x = 1.1 \times 10^{-5} = [OH^{-}]$$

$$\Rightarrow pOH = 4.95$$

$$\Rightarrow pH = 14 - 4.95 = 9.05$$

Alternatively

Using the dissociation equilibrium for NH_4^+

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Henderson–Hasselbalch

$$pH = pK_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

$$pH = 9.25 + \log\frac{0.25}{0.4} = \quad 9.25 - 0.20 = 9.05$$

Adding a SA to a BS

Exercise

- Calculate the pH of the solution that results when 0.10 mole of gaseous HCl is added to 1.0 L of a buffered solution containing 0.25 M NH_3 ($K_b = 1.8 \times 10^{-5}$) and 0.40 M NH_4Cl?

Solution

Major species in soln.

NH_3 Weak base

NH_4^+

$\underbrace{Cl^- \qquad H^+}_{\text{from HCl}}$

H_2O WA/WB

✓ H^+ will not react with Cl^- to form HCl.

✓ NH_3 will react with H^+ to form NH_4^+

$$\boxed{NH_3 + H^+ \leftrightarrow NH_4^+}$$

This Rx is assumed to go essentially to completion. Hence, we will do the stoichiometry calculations before the equilibrium calculations.

Stoichiometry

	NH_3 $+$	H^+ $\rightarrow$	NH_4^+
BR	$1\text{L} \times 0.25\ \text{M}$ $= 0.25\ \text{mol}$	$0.1\ \text{mol}$ **Limiting**	$1\text{L} \times 0.4\ \text{M}$ $= 0.4\ \text{mol}$
AR	$0.25 - 0.1$ $= 0.15\ \text{mol}$	0	$0.4 + 0.1$ $= 0.5\ \text{mol}$

Major species in soln. after reaction

NH_3 NH_4^+ Cl^- H_2O

$$[\mathrm{NH_3}]_0 = \frac{0.15\ \mathrm{mol}}{1.0\ \mathrm{L}} = 0.15\ \mathrm{M}$$

$$[\mathrm{NH_4}^+]_0 = \frac{0.5\ \mathrm{mol}}{1.0\ \mathrm{L}} = 0.5\ \mathrm{M}$$

Eqm.

$$[\mathrm{NH_3}] \approx [\mathrm{NH_3}]_0 = 0.15\ M$$

$$[\mathrm{NH_4}^+] \approx [\mathrm{NH_4}^+]_0 = 0.5\ M$$

$$\boxed{\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{NH_3}]}{[\mathrm{NH_4}^+]}}$$

$$\boxed{= 9.25 + \log\frac{0.15}{0.5} = 8.73}$$

Adding HCl decreases slightly pH as expected in a BS

Buffering Capacity_ BC

- **BC** of a **BS** represents the amount of H^+ or OH^- that **BS** absorb without a significant change in pH.

- A **BS** containing large concentrations of buffering components will have a large **BC**.

- The pH of a **BS** is related to the **$[A^-]/[HA]$** ratio.

- **BC** is determined by the magnitudes of $[HA]$ and $[A^-]$.

Exercise

Calculate the change in pH that occurs when 0.010 mole of gaseous HCl is added to 1.0 L of each of the following solutions (K_a for acetic acid = 1.8×10^{-5}):

- **Solution A**: 5.00 M $HC_2H_3O_2$ and 5.00 M $NaC_2H_3O_2$
- **Solution B**: 0.050 M $HC_2H_3O_2$ and 0.050 M $NaC_2H_3O_2$

Solution

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[C_2H_3O_2{}^-]}{[H\,C_2H_3O_2]}}$$

$$[C_2H_3O_2{}^-] = [H\,C_2H_3O_2]$$

$$\mathrm{pH} = \mathrm{p}K_a = -\log\left(1.8 \times 10^{-5}\right) = 4.74$$

After adding HCl

Major species in soln. before reaction

$HC_2H_3O_2$ Na^+ $C_2H_3O_2^-$ $\underbrace{H^+ \qquad Cl^-}_{\text{from HCl}}$ H_2O

- H^+ will not react with Cl^- to form HCl.
- $C_2H_3O_2^-$ will react with H^+ to form $HC_2H_3O_2$

$$H^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2$$

- Because $HC_2H_3O_2$ is a weak acid, the Rx is assumed to go to **completion**.
- Hence, we will do the **stoichiometry** calculations before the equilibrium calculations.

Stoichiometry_Soln A

	H^+ +	$C_2H_3O_2^-$ →	$HC_2H_3O_2$
BR	0.01 M **Limiting**	5 M	5 M
AR	0	4.99	5.01 M

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[C_2H_3O_2^-]}{[H\,C_2H_3O_2]}}$$

$$\mathrm{pH} = 4.74 + \log\frac{4.99}{5.01} = \quad 4.74 - 0.0017 = 4.74$$

No Change in pH

Stoichiometry_Soln B

	H^+	$+ \quad C_2H_3O_2^- \rightarrow$	$HC_2H_3O_2$
BR	0.01 M **Limiting**	0.05 M	0.05 M
AR	0	0.04	$0.06\ M$

$$\boxed{\mathrm{pH} = \mathrm{pK_a} + \log \frac{[C_2H_3O_2^-]}{[H\,C_2H_3O_2]}}$$

$$\mathrm{pH} = 4.74 + \log \frac{0.04}{0.06} = \quad 4.74 - 0.18 = 4.56$$

BC decreased

Change in [$C_2H_3O_2^-$]/[$HC_2H_3O_2$]

If 0.01 mol H^+ is added to 1.0 L of each solution

Soln.	$\left(\frac{[C_2H_3O_2^-]}{[H\,C_2H_3O_2]}\right)_{orig}$	$\left(\frac{[C_2H_3O_2^-]}{[H\,C_2H_3O_2]}\right)_{new}$	**Change**	**Change %**
A	$\frac{1.0}{1.0} = 1.0$	$\frac{0.99}{1.01} = 0.98$	1.00→ 0.98	2.0 %
B	$\frac{1.0}{0.01} = 100$	$\frac{0.99}{0.02} = 49.5$	100→ 49.5	50.5 %

The **optimal** **buffering**, most resistant to change when H^+ or OH^- are added to the buffered solution, occurs when **[HA] is equal to [A^-]**.

If [A]/[HA] = 1

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = \mathrm{pK_a} + \log(1) = \mathrm{pK_a}$$

$\mathrm{pK_a}$ of WA in the buffer should be as close as possible to the desired pH.

Exercise

- A chemist needs a solution buffered at pH 4.30 and can choose from the following acids (and their sodium salts):

  a. chloroacetic acid (K_a = 1.35 × 10^{-3})

  b. propanoic acid (K_a = 1.3 × 10^{-5})

  c. benzoic acid (K_a = 6.4 × 10^{-5})

  d. hypochlorous acid (K_a = 3.5 × 10^{-8})

  Calculate the ratio [HA]/[A] required for each system to yield a pH of 4.30. Which system will work best?

Solution

A pH of 4.30 corresponds to

$$\boxed{[\mathrm{H^+}] = \mathrm{K_a}\frac{[\mathrm{HA}]}{[\mathrm{A^-}]}}$$

$$[\mathrm{H^+}] = 10^{-4.30} = antilog\,(-4.30) = 5.0 \times 10^{-5}\ \mathrm{M}$$

	Acid	$[H^+] = K_a \frac{[HA]}{[A^-]}$	$\frac{[HA]}{[A^-]}$
a.	chloroacetic acid	$5.0 \times 10^{-5} = 1.35 \times 10^{-3} \frac{[HA]}{[A^-]}$	3.7×10^{-2}
b.	propanoic acid	$5.0 \times 10^{-5} = 1.3 \times 10^{-5} \frac{[HA]}{[A^-]}$	3.8
c.	benzoic ac	$5.0 \times 10^{-5} = 6.4 \times 10^{-5} \frac{[HA]}{[A^-]}$	0.78
d.	hypochlorous acid	$5.0 \times 10^{-5} = 3.5 \times 10^{-8} \frac{[HA]}{[A^-]}$	1.4×10^{3}

- As $[HA]/[A^-]$ for benzoic acid is closest to 1, the system of benzoic acid and its sodium salt will be the best choice.

- The optimal buffering system has a **pK_a** value close to the desired pH. (The pK_a for benzoic acid is 4.19)

End of Course

Good Luck