Chapter 17: Acids and Bases II

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Review

- Neutral solution: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M} \text{ (at } 25 \, {}^{\text{O}}\text{C}\text{)}$
- Acidic solution: $[H_3O^+] > [OH^-]$
- Basic solution: $[OH^-] > [H_3O^+]$
- In all aqueous solutions both H_3O^+ and OH^- are present:

 $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} (at 25 {}^{\circ}C)$

 $pH = -log([H_3O^+])$



Finding [H₃O⁺] and pH

<u>General assumption</u>: The major source of the H_3O^+ or OH^- is the *acid* or *base* in the solution:

- H₃O⁺ or OH⁻ from water auto ionization is small enough to ignore
- Only exception would be very dilute acids/bases with concentrations $< \sim \! 10^{-5}$ M



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pH of a strong acid

- Strong acid: completely ionizes in solution
- $[H_3O^+]$ = concentration of the acid
 - **Example:** 0.10 M HNO₃(*aq*) gives pH = -log(0.10) = 1
 - **Exercise:** Write the above reaction in water.







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pH of a mixture of strong acids

Add up the $[H_3O^+]$ from each acid separately (both acids dissociate fully to form $[H_3O^+]$).

Example:

Consider a mixture of 0.10 M HNO₃ and 0.20 M HCl. We get pH = $-\log(0.10 + 0.20) \approx 0.5$.



pH of a weak acid



- Now the acid ionizes only partially!
- Need to consider equilibrium (ICE chart)
- \bullet Assume that the water does not contribute much H_3O^+
- Solve using the 5% rule (if needed)
- Generic weak acid equilibrium:

 $HA(aq) + H_2O(\ell) \Longrightarrow H_3O^+(aq) + A^-(aq)$

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





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Example: pH of weak acid solution

Calculate [H₃O⁺] and pH of 0.20 M acetic acid solution with $K_a = 1.8 \times 10^{-5}$. Set up the ICE chart:

	CH₃COOH(aq)	H ₂ O(I)	⇒	H₃O+(aq)	CH₃COO⁻(aq)
Ī	0.2 M	_		~0 M	0 M
<u>C</u>	-X	_		+x	+x
<u>E</u>	0.2 - <i>x</i>	-		X	X

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



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	CH₃COOH(aq)	H ₂ O(I)	4	H₃O+(aq)	CH₃COO⁻(aq)
l	0.2 M	-		~0 M	0 M
<u>C</u>	-X	-		+x	+x
<u>E</u>	0.2 - <i>x</i>	-		X	X

$$1.8 \times 10^{-5} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$
$$x \approx 1.9 \times 10^{-3} M$$
$$Test: \quad \frac{1.9 \times 10^{-3} M}{0.20M} \times 100 = 0.95\% < 5\%$$

 $pH = -log(1.9 \times 10^{-3} M) = 2.72$



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Using quadratic (rel. large K_a or low conc.)

Exercise: Calculate pH of 0.100 M HClO₂ solution ($K_a = 0.011$).

Try it yourself:

- 1. Write the chemical equation.
- 2. Set up ICE the table.
- 3. Solve for `x' in the expression for K_a .

(must use quadratic equation)

4. Calculate pH from $-\log([H_3O^+])$.



Percent ionization of a weak acid



Note: This is the same calculation as the "5% rule" check for chemical equilibrium.



Mixture of a strong acid with a weak acid



<u>General assumption</u>: The strong acid contributes most of the H_3O^+ to the solution. Weak acid has very little effect.

Example: Solution of 0.10 M HCl with 0.10 M Acetic Acid (HA). The three sources of H_3O^+ are:

 $\begin{aligned} \mathrm{HCl}(\mathrm{aq}) + \mathrm{H}_2\mathrm{O}(\ell) &\longrightarrow \mathrm{H}_3\mathrm{O}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq}) & \mathrm{Strong} \\ \mathrm{HA}(\mathrm{aq}) + \mathrm{H}_2\mathrm{O}(\ell) & \Longrightarrow \mathrm{H}_3\mathrm{O}^+(\mathrm{aq}) + \mathrm{A}^-(\mathrm{aq}) & K_a = 1.8 \times 10^{-5} \\ \mathrm{H}_2\mathrm{O}(\ell) + \mathrm{H}_2\mathrm{O}(\ell) & \Longrightarrow \mathrm{H}_3\mathrm{O}^+(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq}) & K_a = 1.0 \times 10^{-14} \end{aligned}$



Mixture of a strong acid with a weak acid



HCl completely dissociates, so $[H_3O^+] = 0.10$ M.

	CH₃COOH(aq)	H ₂ O(I)	⇒	H₃O+(aq)	CH₃COO⁻(aq)
<u> </u>	0.10 M	-		0.10 M	0 M
<u>C</u>	-X	-		+x	+x
<u>E</u>	0.10 - <i>x</i>	-		0.10 + <i>x</i>	X

$$K_a = 1.8 \times 10^{-5} = \frac{(0.10 + x)x}{(0.10 - x)} \Rightarrow x = 1.8 \times 10^{-5}$$

Acetic acid did not affect the pH!

 $[H_3O^+] = 0.100018 \ M \approx 0.10 \ M \Rightarrow pH = 1.00$



Mixture of a strong acid with a weak acid



- <u>In general</u>: For a strong acid mixed with a weak acid, the strong acid mostly controls the pH.
- Shifts weak acid equilibrium so far to the left that it contributes very little to [H₃O⁺].
- Calculate pH using the strong acid only.
- <u>Careful:</u> May depend on the concentration of the strong acid vs. the weak acid. For example, a dilute strong acid with a concentrated weak acid.

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Mixture of two weak acids

If the concentrations are roughly similar, the acid with the larger K_a value will control the pH.

Example: 0.10 M acetic acid with 0.10 M HClO.

 $HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = 1.8 \times 10^{-5}$ $HClO(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + ClO^-(aq) \qquad K_a = 2.9 \times 10^{-8}$ $H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_a = 1.0 \times 10^{-14}$

In this case, K_a for acetic acid is ~ 10³ times larger than for HClO, so acetic acid will dominate acidity.



Mixture of two weak acids

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- <u>In general</u>: The larger *K*_a dominates.
- Shifts weaker acid equilibrium so far to the left that it contributes very little to [H₃O⁺].
- Could calculate pH using the stronger acid only.
- <u>Careful</u>: May depend on relative concentrations of the weak acids!



- Generally, the strong bases are Group I and II hydroxides.
- The M(OH)₂ hydroxides lose both OH groups at the same time, not sequentially like for acids.

TABLE 16.7 Strong Bases	
Lithium hydroxide (LiOH)	Strontium hydroxide [Sr(OH) ₂]
Sodium hydroxide (NaOH)	Calcium hydroxide [Ca(OH) ₂]
Potassium hydroxide (KOH)	Barium hydroxide [Ba(OH) ₂]

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Strong bases



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Strong bases



- 1. Calculate $[OH^-] \rightarrow [H_3O^+] \rightarrow pH$
- 2. Calculate [OH⁻] \rightarrow pOH \rightarrow pH

Example: Consider 0.10 M Sr(OH)₂ solution.

$$Sr(OH)_2(aq) \longrightarrow Sr^{2+}(aq) + 2OH^-(aq)$$

Note the stoichiometry! Two moles of OH^{-} formed. [OH^{-}] = 0.20 M, pOH = 0.70, and pH = 14.0 – 0.70 = 13.3. Since pH >> 7, the solution is very alkaline.



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Weak bases

• Generic weak base reaction:

$$B(aq) + H_2O(\ell) \Longrightarrow BH^+(aq) + OH^-(aq)$$

• Base ionization constant: $K_b = \frac{|BH|}{|BH|}$

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

- Common weak bases are amines or conjugates of acids
- Base strength: higher K_b = stronger base



TABLE 16.8 Some Common Weak Bases				
Weak Base	Ionization Reaction	K _b (at 25 °C)		
Carbonate ion $(CO_3^{2-})^*$	$CO_3^{2^-}(aq) + H_2O(I) \Longrightarrow HCO_3^-(aq) + OH^-(aq)$	$1.8 imes10^{-4}$		
Methylamine (CH_3NH_2)	$CH_3NH_2(aq) + H_2O(I) \Longrightarrow CH_3NH_3^+(aq) + OH^-(aq)$	$4.4 imes 10^{-4}$		
Ethylamine ($C_2H_5NH_2$)	$C_2H_5NH_2(aq) + H_2O(I) \Longrightarrow C_2H_5NH_3^+(aq) + OH^-(aq)$	$5.6 imes10^{-4}$		
Ammonia (NH ₃)	$NH_3(aq) + H_2O(I) \Longrightarrow NH_4^+(aq) + OH^-(aq)$	$1.76 imes10^{-5}$		
Bicarbonate ion (HCO ₃ ⁻)* (or hydrogen carbonate)	$HCO_3^{-}(aq) + H_2O(I) \Longrightarrow H_2CO_3(aq) + OH^{-}(aq)$	$2.3 imes10^{-8}$		
Pyridine (C ₅ H ₅ N)	$C_5H_5N(aq) + H_2O(I) \Longrightarrow C_5H_5NH^+(aq) + OH^-(aq)$	$1.7 imes10^{-9}$		
Aniline (C ₆ H ₅ NH ₂)	$C_6H_5NH_2(aq) + H_2O(I) \Longrightarrow C_6H_5NH_3^+(aq) + OH^-(aq)$	$3.9 imes10^{-10}$		

*The carbonate and bicarbonate ions must occur with a positively charged ion such as Na^+ that serves to balance the charge but does not have any part in the ionization reaction. For example, it is the bicarbonate ion that makes sodium bicarbonate (NaHCO₃) basic. We look more closely at ionic bases in Section 16.8. © 2017 Pearson Education, Inc.





Relationship between K_b and K_a

$$B(aq) + H_2O(\ell) \Longrightarrow BH^+(aq) + OH^-(aq)$$
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

For the conjugate acid, BH⁺:

 $BH^{+}(aq) + H_{2}O(\ell) \rightleftharpoons B(aq) + H_{3}O^{+}(aq)$ $K_{a} = \frac{[B][H_{3}O^{+}]}{[BH^{+}]} = \frac{K_{w}}{K_{b}}$ $K_{a} \times K_{b} = K_{w} \qquad pK_{a} + pK_{b} = 14$



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Weak base pH

Exercise: Calculate $[OH^{-}]$, $[H_{3}O^{+}]$, pOH, and pH for 0.10 M NH₃(aq) with $K_{b} = 1.76 \times 10^{-5}$.

Try it yourself:

- 1. Write the chemical equation.
- 2. Set up ICE table.
- 3. Solve for `x' in the expression for K_b .
- 4. Calculate pOH from -log([OH-]).
- 5. Calculate $[H_3O^+] = K_w / [OH^-]$ and then pH.



Acid-base properties of salts

- Think of any anion as the conjugate base of an acid (if it were to react with water):
 - Cl⁻ is the conjugate base of HCl
 - F⁻ is the conjugate base of HF
 - $NO_{3^{-}}$ is the conjugate base of HNO_{3}
 - etc.
- Think of any cation as the conjugate acid of a base (if it were to react with water):
 - Na⁺ is the conjugate acid of NaOH
 - Ca²⁺ is the conjugate acid of Ca(OH)₂



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Acid-base properties of anions

Every <u>anion</u> can potentially act as a base:

- The conjugate base of <u>weak</u> acid is a weak base
 It will react with water to produce that weak acid (will change pH; e.g., HF/F⁻)
- The conjugate base of <u>strong</u> acid is (extremely) weak base (pH neutral)

It will not react with water because it is extremely weak base (no change in pH; e.g., HCI/CI⁻)



Example: Will dissolving NaF in water change pH?



 F^{-} is the conjugate base of HF. HF is a <u>weak acid</u>, so when F^{-} encounters water, it will react to form HF:

$F^{-}(aq) + H_2O(\ell) \Longrightarrow HF(aq) + OH^{-}(aq)$ Weak acid "prefers" to be HF

This produces OH⁻ so the pH must increase!

Note: Would need to consider Na⁺ separately but it turns out not to change the pH (conjugate acid of a strong base NaOH).



Example: Will dissolving NaCl in H₂O change pH?

Cl⁻ is the conjugate base of HCl. HCl is a <u>strong acid</u>, so when Cl⁻ encounters water, it will not react because HCl is a strong acid:

$$Cl^{-}(aq) + H_2O(\ell) \xrightarrow{no!} HCl(aq) + OH^{-}(aq)$$

Strong acid
"prefers" to be Cl⁻

Does not produce H⁺ or OH⁻, so *no change in pH*!

Note: Would need to consider Na⁺ separately but it turns out not to change the pH (conjugate acid of a strong base NaOH).











Acid-base properties of cations



Every <u>cation</u> can potentially act as an acid:

- The conjugate acid of <u>weak</u> base is a weak acid It will react with water to produce that weak base (changes pH; e.g., NH₄⁺)
- The conjugate acid of <u>strong</u> base is pH neutral

It will not react with water because it is extremely weak acid (no change in pH; e.g., Na⁺)

Note: Small, highly charged cations can form hydrated ions that act as proton donors (e.g., Al³⁺ or Fe³⁺).



Example: Does NH₄Cl in H₂O change pH?



 NH_4^+ is the conjugate acid of NH_3 . NH_3 is a <u>weak base</u>, so when NH_4^+ encounters water, it will react to form NH_3 :

$$NH_4^+(aq) + H_2O(\ell) \Longrightarrow NH_3(aq) + H_3O^+(aq)$$

Weak base
"prefers" to be NH_3

This produces H_3O^+ and hence lowers the pH.

Note: Would also need to consider Cl⁻ separately. But as shown before, Cl⁻ does not change pH.



Example: Does dissolving NaCl in water change pH?

Na⁺ is the conjugate acid of NaOH. NaOH is a <u>strong</u> <u>base</u>, so when Na⁺ encounters water, it will not react because NaOH is a strong base:

$$Na^+(aq) + H_2O(\ell) \xrightarrow{no!} NaOH(aq) + H^+(aq)$$

Strong base
"prefers" to be Na⁺

The pH remains unchanged (Cl⁻ is also neutral).





Predict whether aqueous solutions of the following would be acidic, basic, or neutral



- Br^{-} ($Br^{-} + H_{2}O$ does not produce OH^{-} ; HBr is a strong acid)
- CN^{-} ($CN^{-} + H_{2}O \rightleftharpoons HCN + OH^{-}$; HCN is a weak acid)
- K⁺ (K⁺ + H₂O does not produce KOH!)
- NaCl (Na⁺ + H_2O does not produce NaOH;

and Cl⁻ + H₂O does no produce HCl)

 $NO_3^{-} + H_2O$ does not produce HNO_3)

• NH₄Cl (NH₄⁺ + H₂O \rightleftharpoons NH₃ + H₂O⁺)

• Al(NO₃)₃ (Al³⁺(aq) + $nH_2O \rightleftharpoons$ Al(OH)_n⁽³⁻ⁿ⁾⁺ + nH^+ ;

- NaF(Na⁺ neutral; $F^- + H_2O \rightleftharpoons HF + OH^-$)



More difficult example



What if the cation is an acid but the cation is a base? Compare K_a and K_b . Larger value dominates: $NH_4F(aq) \longrightarrow NH_4^+(aq) + F^-(aq)$ • NH₃ $K_b = 1.76 \times 10^{-5}$ • HF $K_a = 3.5 \times 10^{-4}$ acidic basic $K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} = 5.68 \times 10^{-10}$ • K_a (NH₄⁺) > K_b (F⁻) $K_b(F^-) = \frac{K_w}{K_a(HF)} = 2.9 \times 10^{-11}$ Therefore the solution will be acidic



Practice: pH of a salt solution



[Consider: $F^- + H_2O \rightleftharpoons HF + OH^-$ with $K_b = K_w/K_a$. Set up ICE table and solve for OH⁻, then pOH and finally pH.]



pH of polyprotic acid solutions



 $H_2CO_3(aq) + H_2O(\ell) \Longrightarrow H_3O^+(aq) + HCO_3^-(aq)$ $HCO_3^-(aq) + H_2O(\ell) \Longrightarrow H_3O^+(aq) + CO_3^{2-}(aq)$

- First dissociation: $K_{a1} = 4.3 \times 10^{-7}$
- Second dissociation: $K_{a2} = 5.6 \times 10^{-11}$

This relationship is always true for a polyprotic acid: $K_{a1} > K_{a2}$ (> K_{a3})

- To calculate pH: treat as by using K_{a1} (need $K_{a1} >> K_{a2}$)
- 2nd or 3rd proton will (usually) contribute relatively little to $[H_3O^+]$ and pH.





Example

What is the pH of a 0.100 M H₃PO₄(*aq*) solution? The equilibrium constants are given as $K_{a1} = 7.5 \times 10^{-5}$, $K_{a2} = 6.2 \times 10^{-8}$, $K_{a3} = 4.2 \times 10^{-13}$.

<u>Solution</u>: H⁺(*aq*) from the 2nd and 3rd steps will be small and can be ignored. **Treat like a monoprotic acid** with $K_{a1} = 7.5 \times 10^{-5}$:

$$H_{3}PO_{4}(aq) \rightleftharpoons H_{2}PO_{4}(aq) + H^{+}(aq)$$
$$K_{a} = 7.5 \times 10^{-5} = \frac{[H_{2}PO_{4}] \cdot [H^{+}]}{[H_{3}PO_{4}]}$$



Example (continued)

Set up an ICE table:

	$H_{3}PO_{4}(aq)$	$H_2PO_4(aq)$	H+(aq)
Initial	0.100	0	0
Change	- <i>X</i>	+X	+X
Equilibrium	0.100 - <i>x</i>	X	X

Substitute values into K_a expression and solve.



Example (continued)



$$H_3PO_4(aq) \rightleftharpoons H_2PO_4(aq) + H^+(aq)$$

$$K_a = 7.5 \times 10^{-5} = \frac{[H_2PO_4^{-}] \cdot [H^{+}]}{[H_3PO_4]} = \frac{x^2}{0.100 - x}$$



 $pH = -log(2.7 \times 10^{-3}) = 2.57$





Exercise

Calculate the pH of a 0.050 M H_2CO_3 solution.

$[K_{a1} = 4.3 \times 10^{-7}, K_{a2} = 5.6 \times 10^{-11};$ weak acid with only K_{a1}]





Contribution of second deprotonation

- If first dissociation is large, **be careful** because second dissociation may contribute to pH.
- Treat first as a strong acid, then calculate the second as equilibrium.
- **Exercise:** Calculate pH and $[SO_4^{2-}]$ for 0.02 M H₂SO₄

(1st full dissociation provides starting [H⁺] and [HSO₄⁻] for the 2nd step ($K_a = 0.012$); construct ICE table)

Note that the 2nd dissociation step here will have a very small effect.



2nd deprotonation: Did you notice?



For a solution of H₂A, we have $[A^{2-}] \approx K_{a2}$ because:







2nd deprotonation: Did you notice?

2.

$HA^{-}_{(aq)} \rightleftharpoons H^{+}_{(aq)} + A^{2-}_{(aq)}$				
I	X	X	0	
С	- <i>Y</i>	+ <i>y</i>	+ <i>y</i>	
E	х-у	x+y	У	

$$K_2 = \frac{\left[\mathrm{H}^+\right] \left[\mathrm{A}^{2-}\right]}{\left[\mathrm{H}\mathrm{A}\right]} = \frac{(x+y)y}{x-y} \approx y = \left[\mathrm{A}^{2-}\right]$$

Note that this assumes that y is small compared to x (5% rule).

In general, two ICE tables & two eqs. needed but we assume that the two equilibria are not "connected" and can be treated separately.





Predicting acid strength from molecular structure

Binary acids

- Polarity affects how "positive" the H is
- Must be slightly positive to be an acid





Bond strength matters too

Acid	Bond Energy (kJ/mol)	Type of Acid
H—F	565	Weak
H—CI	431	Strong
H—Br	364	Strong
H-Br	364	Strong





Predicting acid strength from molecular structure

Binary acids:

Combined polarity and bond strength results in the relative acidity of group 6 and 7 acids.



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Predicting acid strength from molecular structure

<u>Oxyacids</u>

• General structure: H—O—Y



- The more electronegative Y is, the more the electrons are pulled away from the H
- Bond becomes more polar and hence more acidic

Acid	Electronegativity of Y	K _a
H-O-I	2.5	$2.3 imes10^{-11}$
H-O-Br	2.8	$2.0 imes10^{-9}$
	3.0	$2.9 imes10^{-8}$

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Predicting acid strength from molecular structure

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H - O - Y



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Acid	Structure	Ka
HCIO ₄	$\begin{array}{c} \mathbf{H} - \mathbf{O} - \begin{array}{c} \mathbf{O} \\ \ \\ \mathbf{C} \ = \mathbf{O} \\ \ \\ \mathbf{O} \end{array}$	Strong
HCIO ₃	$\begin{array}{c} 0 \\ \parallel \\ H - 0 - CI = 0 \end{array}$	1
HCIO ₂	H-0-CI=0	$1.1 imes 10^{-2}$
HCIO	H	$2.9 imes10^{-8}$
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Example

Which would be more acidic?

Red H^+ is the proton to be considered.





Lewis acids

- Lewis acid: accepts electron pair
- Lewis base: donates electron pair





Lewis acids



Lewis acid: Needs an empty orbital or be able to rearrange to make one.

