Acid-Base Equilibria

Chapter 16

Chemistry, The Central Science 11th edition



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• Acids and bases are found in many common substances and are important in life processes.

• A range of chemical processes from industrial to biological ones, from reactions in the lab to those occurring in the environment, involve either an acid or a base.

• As such, a massive amount of chemistry can be understood in terms of acid-base reactions.

• There are several models for what constitutes an acid or a base - <u>three models</u> to be discussed in this chapter.

Acid	Base	
Tastes sour	Tastes bitter	
Stings skin	Feels slippery	
Turns litmus red	Turns litmus blue	
Turns phenolphthalein colourless	Turns phenolphthalein pink	
Corrosive to metals	Fouling on metal surfaces	
<u>Examples</u> : - Ascorbic acid (vitamin C) - Citric acid (lemon and orange)	Examples: -CaCO ₃ is used in antacid tables - NaOH to unblock drains	

• React together to form a salt with loss of the characteristic acid/base properties.

Arrhenius Theory

- Acid: substance that produces H⁺ in aqueous solution
- Base: substance that produces OH⁻ in aqueous solution

Examples of Arrhenius acids and bases:

- Acid $HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$
- **Base** NaOH(g) $\xrightarrow{H_2O}$ Na⁺ (ag) + OH⁻(aq)
- HCl + NaOH \rightarrow Na⁺ + Cl⁻ + H₂O
- acid + base \rightarrow salt + water.

The Arrhenius concept is limited to substances that <u>dissolve</u> in water.

In 1923 two chemists, Brønsted and Lowry suggested a more general definition of acids and bases.

- Their concept was based on the fact that acid-base reactions to involve the <u>transfer of a proton</u>, (a proton is an H⁺ ion), from an acid to a base.
- •This transfer may or may not involve water.
- An acid is a species that _____ a proton.
- A base is a species that _____a proton.

Examples

• Acids: $HCl(aq) + H_2O(I) \implies H_3O^+(aq) + Cl^-(aq)$ $NH_4^+(aq) + H_2O(I) \implies H_3O^+(aq) + NH_3(aq)$

• Bases:

 $\begin{aligned} \mathsf{NH}_3(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) & \Longrightarrow & \mathsf{OH}^-(\mathsf{aq}) + \mathsf{NH}_4^+(\mathsf{aq}) \\ \mathsf{CO}_3^{2-}(\mathsf{aq}) + \mathsf{H}_2\mathsf{O}(\mathsf{I}) & \longmapsto & \mathsf{OH}^-(\mathsf{aq}) + \mathsf{HCO}_3^{--}(\mathsf{aq}) \end{aligned}$

The H⁺ Ion in Water

- If acid-base reactions are proton (H⁺ ion) transfer reactions, we need to know what the H⁺ ion is.
- The hydrogen ion, H⁺ ion , is a very small "bare" proton with no surrounding valence electron.
- This small, positively charged particle interacts with the nonbonding electron pairs (lone pair) of H₂O molecules to form a <u>hydronium ion, H₃O⁺</u>.

The H⁺ Ion in Water

$$H^{+} + : \stackrel{..}{O} - H \longrightarrow \begin{pmatrix} ..\\ H : \stackrel{..}{O} - H \\ I \\ H \end{pmatrix}^{+}$$
$$\longrightarrow H^{+} + H_{2}O \longrightarrow H_{3}O^{+}$$
The hydronium ion

- H⁺ and H₃O⁺ represent the same thing hydrated proton.
- The can be used interchangeably.

Proton-Transfer Reactions

Let us see what happens when an acid dissolves in water...

Consider: $HCl(g) + H_2O(I) \rightarrow H_3O^+(aq) + Cl^-(aq)$



The polar H_2O molecule promotes the ionization of acids in an aqueous (water) solution by accepting a proton to form H_3O^+ .

Proton-Transfer Reactions

Brønsted and Lowry proposed that acids and bases should be defined as follows:

ACID : An acid is a substance (molecule or ion) that can transfer a proton to another substance.

BASE : A base is a substance that can accept a proton from another substance.

These are termed Brønsted-Lowry acids and bases.

Proton-Transfer Reactions

• Simply put, according to the Brønsted-Lowry definitions:

An acid is a proton donor A base is a proton acceptor

 The Brønsted–Lowry concept is on proton transfer and also applies to reactions that do not occur in aqueous solution.



• This reaction occurs in the gas phase

Proton-Transfer Reactions

Amphiprotic substances

• Consider the reaction of H_2O with HCl in [1] and NH_3 in [2].



In [1] H₂O is a Bronsted-Lowry base it ______ a proton.
In [2] H₂O is a Bronsted-Lowry acid it ______ a proton.

Proton-Transfer Reactions

A substance that is capable of acting as either an acid or a base is called amphiprotic.

Conjugate Acid-Base Pairs

- From the Latin word *conjugare*, meaning "to join together."
- Reactions between acids and bases always yield their conjugate bases and acids.



Conjugate Acid-Base Pairs

• Consider the reaction of an acid (HA) with water:

 $HA(aq) + H_2O(l) \implies H_3O^+(aq) + A^-(aq)$

- After HA (acid) loses its proton it is converted into A⁻ (base). Therefore HA and A⁻ are conjugate acid-base pairs.
- After H_2O (base) gains a proton it is converted into H_3O^+ (acid). Therefore, H_2O and H_3O^+ are conjugate acid-base pairs.
- Conjugate acid-base pairs differ by only one proton.



Conjugate Acid-Base Pairs

Examples

<u>conjugate acid</u>		<u>conjugate base</u>
H ₃ O ⁺	H ₂ O	OH⁻
NH ₄ ⁺	NH ₃	NH_2^-
H_2CO_3	HCO ₃ -	CO ₃ ²⁻
$H_2^{PO_4^{2-}}$	HPO ₄ -	PO ₄ ²⁻

Conjugate Acid-Base Pairs

More examples

- $H_3PO_4(aq) + H_2O(\ell) = H_3O^+(aq) + H_2PO_4^-(aq)$ acid base conjugate conjugate acid base
- CH₃COOH (aq) + H₂O(ℓ) ⇒ H₃O⁺(aq) + CH₃COO⁻ (aq) acid base conjugate conjugate acid base
- H₂CO₃(aq) + H₂O(ℓ) ⇒ H₃O⁺(aq) + HCO₃⁻ (aq) acid base conjugate conjugate acid base

Relative Strengths of Acids and Bases

- <u>Strong acids</u> are completely dissociated in water.
 - Their conjugate bases are quite weak.
 - They are good proton donors.
 - examples: HCl, HI, HBr, HNO₃, H₂SO₄, HClO₄
- <u>Example</u>: HCl(aq) + H₂O(l) \rightarrow H₃O⁺(aq) + Cl⁻ (aq) 1.2 M 1.2 M 1.2 M 1.2 M
- Acid fully dissociates. No equilibrium occurs between the acid and its ions.
- A large acid dissociation constant, K_a, is expected.
- K_a is the equilibrium constant for the dissociation of an acid.

Relative Strengths of Acids and Bases

- <u>Weak acids</u> only dissociate partially in water.
 - Their conjugate bases are weak bases.
 - When weak acids are in solution, there is an equilibrium between the acid molecules and the constitute ions.
 - Examples: CH₃COOH, HNO₂, H₂CO₃, H₃BO₃, HF.
- <u>Example</u>:

 $CH_3COOH(aq) + H_2O(I) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

- The K_a is very small (1.8 x 10⁻⁵).
- Some of the CH_3COOH remains undissociated.

Relative Strengths of Acids and Bases

- **<u>Strong bases</u>** are completely dissociated in water.
 - They have a great attraction to protons.
 - They have a pair of electrons to form a bond with the proton.
 - examples: NaOH, KOH, Ca(OH)₂, O^{2-} , H⁻
 - Example:

 $O^{2-}(aq) + H_2O(I) \rightarrow OH^{-}(aq) + OH^{-}(aq)$

- Expect a large base dissociation constant, K_b.
- K_b is the equilibrium constant for the dissociation of a base.

Relative Strengths of Acids and Bases

- <u>Weak bases</u> are molecules or ions that are partially ionized in water to give OH-
 - They are poor proton acceptors
 - examples: NH_3 , $CH_3CO_2^-$
 - <u>Example</u>

 $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

- The equilibrium constant, K_b , is small, 1.8 x 10⁻⁵. Therefore the base is weak.
- Some NH₃ molecules remain undissociated.

Relative Strengths of Acids and Bases

- Substances with negligible acidity such as CH₄ do not dissociate in water.
 - Their conjugate bases are exceedingly strong and react completely with water.

Relative Strengths of Acids and Bases

Strong and weak vs concentrated and dilute

Do not confuse the meaning of the terms 'strong' and 'weak' with the terms 'concentrated' and 'dilute'.

Examples:

1.0 M HCl = a <u>concentrated</u> solution of a <u>strong</u> acid.
0.0001 M HCl = a <u>dilute</u> solution of a <u>strong</u> acid.
1.0 M HOAc = a <u>concentrated</u> solution of a <u>weak</u> acid.
0.001 M HOAc = a <u>dilute</u> solution of a <u>weak</u> acid.

Relative Strengths of Acids and Bases

- A strong acid has a weak conjugate base.
- The stronger the acid the weaker is its conjugate base.
- Very strong acids have conjugate bases with negligible base strength.
- The more easily an acid gives up a proton, the less easily its conjugate base accepts a proton.
- A <u>strong base</u> has a <u>weak conjugate acid</u>.
- The stronger the base the weaker is its conjugate acid.
- Very strong bases have conjugate acids with negligible acid strength.
- The more readily a base accepts a proton, the less easily its conjugate acid gives up a proton.

Relative Strengths of Acids and Bases

- A weak acid has a weak conjugate base.
- A weak acid only partially dissociates in aqueous solution.
- The conjugate base of a weak acid shows a slight ability to remove protons from water.

Relative strengths of some conjugate-acid base pairs.



Relative Strengths of Acids and Bases

Which base is the weakest?

- F-
- NH₃
- OH^{-}
- SO₄²⁻
 C₂H₃O₂⁻



Relative Strengths of Acids and Bases

Which acid is the strongest?

- H₂O
- H₃O⁺
- HF
- $HC_2H_3O_2$
- NH₄⁺



The Autoionization of Water

- We have seen that water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.
- This is referred to as <u>autoionization</u>.
- H₂O can therefore act as a <u>Brønsted acid or base</u>.
- At room temp. no molecules stay ionized for long.
- Thus pure water consists entirely of H₂O molecules.

The Autoionization of Water

The Ion Product Constant

- The autoionization of water is an equilibrium process: H₂O(I) = H₃O⁺(aq) + OH⁻(aq)
- The equilibrium-constant expression for this process is:

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

- This special equilibrium constant is referred to as the ion-product constant for water, K_w.
- At 25 C,

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

The Autoionization of Water

The Ion Product Constant

In <u>NEUTRAL</u> solutions [H+] = [OH-] In <u>ACIDIC</u> solutions [H+] > [OH-] In <u>BASIC</u> solutions [OH-] > [H+]

Summary so far

- Acids proton donors
- Bases proton acceptors
- Weak acids and weak bases partly dissociate
- Strong acids and strong bases fully dissociate
- Conjugate acid-base pair one H+ difference
- Autoionisation of water

 $H_2O(I) + H_2O(I) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

• $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

The pH Scale

- The concentration of H₃O⁺ or OH⁻ in solution can vary over a wide range, but these concentrations are usually small.
- We define

The pH Scale



- In neutral water at 25 °C, pH = pOH = 7.00.
- In acidic solutions, $[H^+] > 1.0 \times 10^{-7}$, so pH < 7.00.
- In basic solutions, $[H^+] < 1.0 \times 10^{-7}$, so pH > 7.00.
- •The higher the pH, the lower the pOH, the more basic the solution.
| Solution Type | [H ⁺] (<i>M</i>) | [OH ⁻] (<i>M</i>) | pH Value |
|---------------|--------------------------------|---------------------------------|----------|
| Acidic | $>1.0 \times 10^{-7}$ | $<1.0 \times 10^{-7}$ | <7.00 |
| Neutral | =1.0 × 10 ⁻⁷ | =1.0 × 10 ⁻⁷ | =7.00 |
| Basic | <1.0 × 10 ⁻⁷ | >1.0 × 10 ⁻⁷ | >7.00 |

• In pure water,

 $K_w = [H_3O^+] [OH^-] = 1.0 \times 10^{-14}$

• Because in pure water $[H_3O^+] = [OH^-]$, $[H_3O^+] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}$ pH values of some common solutions

More acidic

More basic

Note that a change in [H⁺] by a factor of 10 causes the pH to increase by 1

 $[H^+](M)$ pH pOH $[OH^{-}](M)$ 1×10^{-14} $-1(1 \times 10^{-0})$ 0.0 14.0 1×10^{-13} -1×10^{-1} 1.0 13.0 Gastric juice - - - 1×10^{-12} -1×10^{-2} 2.0 12.0 Lemon juice - - - - -Cola, vinegar $---- - 1 \times 10^{-3}$ 1×10^{-11} 3.0 11.0 Wine -1×10^{-4} 1×10^{-10} 4.0 10.0 Tomatoes -----Banana 1×10^{-5} 1×10^{-9} Black coffee 5.0 9.0 Rain $\cdot 1 \times 10^{-6}$ 1×10^{-8} 6.0 8.0 Saliva 1×10^{-7} 1×10^{-7} 7.0 7.0 Human blood, tears Egg white, seawater -- 1×10^{-8} 1×10^{-6} 8.0 6.0 Baking soda -- 1×10^{-9} 1×10^{-5} 9.0 5.0 Borax -----Milk of magnesia – – – – 1×10^{-10} 1×10^{-4} 10.0 4.0 Lime water 1×10^{-11} 1×10^{-3} 11.0 3.0 Household ammonia - - -1×10^{-12} 1×10^{-2} 12.0 2.0 Household bleach--- -1×10^{-13} 1×10^{-1} NaOH, 0.1 M-----13.0 1.0 1×10^{-14} $1(1 \times 10^{-0})$ 14.0 0.0

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pOH and other "p" scales

• The "p" in pH tells us to take the negative log of the quantity (in this case, hydrogen ions).

• We can express concetration of OH⁻ as pOH pOH = $-\log [OH^{-}]$ $pK_w = -\log K_w$

pOH and other "p" scales

Because at 25°C, $[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$, we know that

 $-\log [H_3O^+] + -\log [OH^-] = -\log K_w = 14.00$

or, in other words,

pH + pOH = pK_w **= 14.00** (at 25°C)

pOH and other "p" scales

Exercise

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:

(a) $[H^+] = 4 \times 10^{-9} M$; (b) $[OH^-] = 1 \times 10^{-7} M$; (c) $[OH^-] = 7 \times 10^{-13} M$.

<u>Exercise</u>: What is the pH of an aqueous solution of $[OH^-]$ = $1.0 \times 10^{-3} M$?

- 1. 2.22
- 2. 3.00
- 3. 7.00
- 4. 10.78
- 5. 11.00

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

pH = 14.00 - pOH

= 14.00 - 3.00 = 11.00

Exercise:

If the pOH of a solution is 3.00, what is the pH of the solution? Is the solution acidic or basic?

 $pH + pOH = pK_w = 14.00$

pH = 14.00 - 3.00 = 11.00

pH = 11.00 basic

Measuring pH

- For less accurate measurements, one can use
 - Litmus paper
 - "Red" paper turns blue above ~pH = 8
 - "Blue" paper turns red below ~pH = 5
 - An indicator
 - Certain dyes change color as pH changes. These are indicators.
 - Many indicators do not have a sharp color change as a function of pH.
 - Most indicators tend to be red in more acidic solutions.

Measuring pH



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Measuring pH

For <u>more accurate</u> measurements, one uses a pH meter, which measures the voltage in the solution.



Strong acids

- Recall that strong acids e.g. HCl, HBr, HI, HNO₃, H₂SO₄, HClO₃, and HClO₄ dissociate completely to form H₃O⁺.
- By definition, these are strong electrolytes and exist totally as ions in aqueous solution.
- Thus for the monoprotic strong acids,

 $[acid] = [H_3O^+]$ pH = -log[H₃O⁺]; pH + pOH = 14

Strong acids

Exercise:

Calculate the pH of a solution made of 0.723g perchloric acid in 500mL of solution.

Strong bases

- Strong bases also dissociate completely in aqueous solution.
- The pOH (and hence pH) of a strong base is given by the initial molarity of the base.
- In order for a hydroxide to be a base, it must be soluble.
- Bases do not have to contain the OH⁻ ion e.g. O²⁻
- As with strong acids, the calculation of pH for strong bases is simple.

[base] = [OH⁻]

 $pOH = -log[OH^-]; pH + pOH = 14$

Strong bases

Exercise

If 3.56g of pure NaOH is dissolved in 10 dm³ of water, what is the pH of the solution?

- Weak acids are only partially ionized in solution.
- There is a mixture of ions and unionized acid in solution.
- Therefore, weak acids are in equilibrium:

 $HA(aq) + H_2O(l) \implies H_3O^+(aq) + A^-(aq)$

$$K_a = \frac{[\mathrm{H}_3\mathrm{O}^+][\mathrm{A}^-]}{[\mathrm{H}\mathrm{A}]}$$

$$HA(aq) \implies H^+(aq) + A^-(aq)$$

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

Dissociation Constants

• For a generalized acid dissociation,

 $HA(aq) + H_2O(l) \implies H_3O^+(aq) + A^-(aq)$

the equilibrium expression would be

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

 This equilibrium constant is called the aciddissociation constant, K_a.

Dissociation Constants

The greater the value of K_a , the stronger the acid.

Acid	Structural Formula	Conjugate Base	Equilibrium Reaction	K _a
Hydrofluoric (HF)	HF	F^{-}	$HF(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + F^-(aq)$	$6.8 imes10^{-4}$
Nitrous	H0N===-0	NO_2^-	$HNO_2(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + NO_2^-(aq)$	$4.5 imes 10^{-4}$
(HNO ₂) Benzoic (HC ₇ H ₅ O ₂)	н-оЁ()	$C_7 H_5 O_2^{-}$	$\mathrm{HC}_{7}\mathrm{H}_{5}\mathrm{O}_{2}(aq) + \mathrm{H}_{2}\mathrm{O}(l) \Longrightarrow \mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{C}_{7}\mathrm{H}_{5}\mathrm{O}_{2}^{-}(aq)$	$6.3 imes 10^{-5}$
Acetic (HC ₂ H ₃ O ₂)	H-0-C-C-H H	$C_2H_3O_2^-$	$\mathrm{HC}_{2}\mathrm{H}_{3}\mathrm{O}_{2}(aq) + \mathrm{H}_{2}\mathrm{O}(l) \Longrightarrow \mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{C}_{2}\mathrm{H}_{3}\mathrm{O}_{2}^{-}(aq)$	1.8×10^{-5}
Hypochlorous (HClO)	н —о—а	ClO ⁻	$HClO(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + ClO^-(aq)$	$3.0 imes 10^{-8}$
Hydrocyanic (HCN)	HC≡≡N	CN^{-}	$HCN(aq) + H_2O(l) \Longrightarrow H_3O^+(aq) + CN^-(aq)$	$4.9 imes 10^{-10}$
Phenol (HC ₆ H ₅ O)	H-0-{O	$C_6H_5O^-$	$\mathrm{HC}_{6}\mathrm{H}_{5}\mathrm{O}(aq) + \mathrm{H}_{2}\mathrm{O}(l) \Longrightarrow \mathrm{H}_{3}\mathrm{O}^{+}(aq) + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{O}^{-}(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.

• If $K_a >> 1$, then the acid is completely ionized and the acid is a strong acid.

Calculating K_a from the pH

- Calculate H_3O^+ and hence pH from K_a
 - K_a is usually small therefore use a approximation to simplify the problem.
 - Test the assumption made.
 - Use quadratic equation if "x" is out by more the 5% of the original acid concentration.
- Calculate K_a from pH

Calculating K_a from the pH

Exercise:

- The pH of a 0.10 *M* solution of formic acid, HCOOH, at 25 C is 2.38. Calculate K_a for formic acid at this temperature.
- HCOOH(aq) + $H_2O(aq) \implies H_3O^+(aq) + COO^-(aq)$
- To calculate K_a , we need the equilibrium concentrations of all three species.
- We can find [H₃O⁺], which is the same as [HCOO⁻], from the pH.

$$K_a = \frac{[H_3O^+] [HCOO^-]}{[HCOOH]}$$

Calculating K_a from the pH

Weak acids are simply equilibrium calculations.

- The pH gives the equilibrium concentration of H⁺.
- Using K_a, the concentration of H⁺ (and hence the pH) can be calculated.
 - Write the balanced chemical equation clearly showing the equilibrium.
 - Write the equilibrium expression. Find the value for K_a .
 - Write down the initial and equilibrium concentrations for everything except pure water.

Calculating K_a from the pH

$$\mathcal{K}_{a} = \frac{[H_{3}O^{+}] [HCOO^{-}]}{[HCOOH]}$$

$$pH = -\log [H_{3}O^{+}] = 2.38$$

$$-2.38 = \log [H_{3}O^{+}]$$

$$[H_{3}O^{+}] = 10^{-2.38}$$

$$[H_{3}O^{+}] = [HCOO^{-}] = 4.2 \times 10^{-3} \text{ M}$$

Now we can set up a table...

Calculating K_a from the pH

 $HCOOH(aq) + H_2O(I) \implies H_3O^+(aq) + HCOO^-(aq)$

	[HCOOH], M	[H ₃ O+], M	[HCOO ⁻], M
Initially	0.10	0	0
Change	-4.2 × 10 ⁻³	+4.2 × 10 ⁻³	$+4.2 \times 10^{-3}$
At Equilibrium	$0.10 - 4.2 \times 10^{-3}$ = 0.0958 ~ 0.10	4.2 × 10 ⁻³	4.2 × 10 ⁻³

$$K_a = \frac{[4.2 \times 10^{-3}] [4.2 \times 10^{-3}]}{[0.10]} = 1.8 \times 10^{-4}$$

Calculating [H₃O⁺] and pH from Ka

Example

What is the $[H_3O^+]$ in a 0.20 *M* solution of benzoic acid? ($K_a = 6.3 \times 10^{-5}$)

Solution

- Benzoic acid, C₇H₅O₂H
- We have a weak acid does not fully dissociate
- We construct a table

Calculating [H₃O⁺] and pH from Ka

$C_7H_5O_2H + H_2O$	⇒ H₃O⁺	+ C ₇ H ₅ O ₂ -
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Initially	0.20 M	0 M	0 M
Change	- x	+ X	+ x
Equilibrium	0.20 – x M	хM	хM

 $K_{a} = [C_{7}H_{5}O_{2}^{-1}][H_{3}O^{+}] = 6.3 \times 10^{-5}$ $[C_{7}H_{5}O_{2}H]$ $(x)(x) = 6.3 \times 10^{-5}$ (0.20 - x)

Calculating [H₃O⁺] and pH from Ka

This could be solved using a quadratic equation. But since this is a weak acid, we know that "x" is very small, in fact much smaller than 0.20 M.

Therefore it is assumed that $(0.20 - x) \approx 0.20$

Calculating [H₃O⁺] and pH from Ka

If
$$(x)(x) = 6.3 \times 10^{-5}$$

 $(0.20 - x)$
and we assume $(0.20 - x) \approx 0.20$
then, $x^2 = 6.3 \times 10^{-5}$
 $x = \sqrt{(0.20) \times (6.3 \times 10^{-5})}$
 $= 3.5 \times 10^{-3} \text{ M}$
Therefore, $[\text{H}_3\text{O}^+] = 3.5 \times 10^{-3} \text{ M}$
 $p\text{H} = 2.46$

Calculating [H₃O⁺] and pH from Ka

Test the assumption

(0.20 – X) = 0.20 - (3.5 x 10⁻³) = 0.196 ~ 0.20 therefore assumption is valid

or

<u>3.5 x 10⁻³ M</u> x 100 = 1.8% 0.20 M

Calculating [H₃O⁺] and pH from Ka

If the *assumption is not valid*, one must use the quadratic equation:

$$x = -b \pm \sqrt{b^2 - 4ac}$$
2a

Calculating [H₃O⁺] and pH from Ka

Guidelines on how to tackle the previous exercise

1) Write the ionization equilibrium of benzoic acid. If you don't know the actual formula of the acid use the general formula:

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

- 2) Write the equilibrium constant expression using the given value of Ka.
- 3) Substitute the equilibrium concentrations into the equilibrium constant expression.
- 4) Simplify the equation by making an assumption.
- 5) Check the assumption.
- 6) If the quantity "x" is more than about 5% of the concentration of the acid, use the quadratic equation.

Calculating [H₃O⁺] and pH from Ka

Exercise:

Calculate the pH of 0.10 mol L⁻¹ HF solution $(K_a = 6.8 \times 10^{-4})$.

Percent Ionization

- Magnitude of K_a indicates the strength of a weak acid.
- Likewise percent ionization is a measure of acid strength.

Percent Ionization = $[H^+]_{equilibrium} \times 100\%$ [HA]_{initial}

• In the previous example $[H^+]_{eq} = 4.2 \times 10^{-3} \text{ M}$ $[HCOOH]_{initial} = 0.10 \text{ M}$ Percent Ionization = $\frac{4.2 \times 10^{-3}}{0.10} \times 100$ = 4.2%

Percent Ionization



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(a) The flask on the left contains $1 M HC_2H_3O_2$; the one on the right contains 1 M HCl. Each balloon contains the same amount of magnesium metal. (b) When the Mg metal is dropped into the acid, H_2 gas is formed. The rate of H_2 formation is higher for the 1 M HCl solution on the right as evidenced by more gas in the balloon.

Percent Ionization

- Percent ionization relates the equilibrium H⁺ concentration, [H⁺]_{eqm}, to the initial HA concentration, [HA]₀.
- The higher percent ionization, the stronger the acid.
- Percent ionization of a weak acid decreases as the molarity of the solution increases.

Percent Ionization



For acetic acid 0.05 *M* solution is 2.0 % ionized whereas a 0.15 *M* solution is 1.0 % ionized.

Polyprotic Acids

- Polyprotic acids have more than one ionizable H atom.
- The protons (H atoms) are removed in steps. For example: $H_2SO_3(aq) \implies H^+(aq) + HSO_3^-(aq) \quad K_{a1} = 1.7 \times 10^{-2}$ $HSO_3^-(aq) \implies H^+(aq) + SO_3^{-2}(aq) \quad K_{a2} = 6.4 \times 10^{-8}$
- It is always easier to remove the first proton in a polyprotic acid than the second.
- Therefore, $K_{a1} > K_{a2} > K_{a3}$ etc.

Polyprotic Acids

 If the difference between the K_a for the first dissociation and subsequent K_a values is 10³ or more, the pH generally depends only on the first dissociation.

Name	Formula	K _{a1}	K _{a2}	K _{a3}
Ascorbic Carbonic	$H_2C_6H_6O_6$ H_2CO_3	$8.0 imes 10^{-5}$ $4.3 imes 10^{-7}$	$1.6 imes 10^{-12}$ $5.6 imes 10^{-11}$	
Citric	$H_3C_6H_5O_7$	7.4×10^{-4}	1.7×10^{-5}	$4.0 imes 10^{-7}$
Oxalic	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	10
Phosphoric	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Sulfurous	H_2SO_3	$1.7 imes 10^{-2}$	$6.4 imes10^{-8}$	
Sulfuric	H_2SO_4	Large	$1.2 imes 10^{-2}$	
Tartaric	$H_2C_4H_4O_6$	1.0×10^{-3}	$4.6 imes10^{-5}$	
Weak Acids

Summary so far



Calculate pH – weak acid \rightarrow Equilibrium equation $\rightarrow K_a \rightarrow pH$ $\rightarrow Assumption$ $\rightarrow If not valid, use$ weak bases (next) $\rightarrow Calculate K_a from pH.$

- Weak bases react with water to remove protons from water.
- There is an equilibrium between the base and the resulting ions:

Weak base + $H_2O \implies$ conjugate acid + $OH^ NH_3(aq) + H_2O(l) \implies NH_4^+(aq) + OH^-(aq)$ add H^+ $NH_3(aq) + H_2O(l) \Longrightarrow NH_4^+(aq) + OH^-(aq)$ Acid Base Conjugate Conjugate base acid remove H

• The equilibrium constant expression for a weak base is

$$K_b = \frac{[\mathsf{HB}] [\mathsf{OH}^-]}{[\mathsf{B}^-]}$$

where K_b is the base-dissociation constant.

 K_b can be used to find [OH⁻] and, consequently, pH.

Base	Lewis Structure	Conjugate Acid	Equilibrium Reaction	K_b
Ammonia (NH ₃)	H-N-H H	$\mathrm{NH_4}^+$	$NH_3 + H_2O \Longrightarrow NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C ₅ H ₅ N)		$C_5H_5NH^+$	$C_5H_5N + H_2O \Longrightarrow C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H ₂ NOH)	H-N-ÖH	H ₃ NOH ⁺	$H_2NOH + H_2O \Longrightarrow H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH ₂ CH ₃)	HNCH3 H	NH ₃ CH ₃ ⁺	$NH_2CH_3 + H_2O \Longrightarrow NH_3CH_3^+ + OH^-$	4.4×10^{-4}
Hydrosulfide ion (HS ⁻)	[H	H_2S	$HS^- + H_2O \Longrightarrow H_2S + OH^-$	1.8×10^{-7}
Carbonate ion (CO ₃ ^{2–})		HCO ₃ ⁻	$CO_3^{2-} + H_2O \Longrightarrow HCO_3^- + OH^-$	1.8×10^{-4}
Hypochlorite ion (ClO ⁻)	[:¤—¤]-	HClO	$CIO^- + H_2O \Longrightarrow HClO + OH^-$	3.3×10^{-7}

Types of Weak Bases

1. Neutral (uncharged) substances that have an atom with a nonbonding pair of electrons that can accept a proton.

Examples:

- Ammonia :NH₃
- Amines

CH₃ ^{̈́} NH₂	primary amine
сн₃йнсн₃	secondary amine
CH ₃ -N-CH ₃ I CH ₃	tertiary amine

Types of Weak Bases

2. The conjugate bases (anions) of weak acids.

- Acetate ion, CH₃COO⁻ conjugate base of acetic acid.
 Example: in sodium acetate, CH₃COONa.
- Hypochlorite ion, ClO⁻ conjugate base of hypochlorous acid.

Example: in calcium hypochlorite, Ca(ClO)₂

- Carbonates, bicarbonates, phosphates.
- 3. Alkaloids.

Naturally occurring basic substances e.g. cocaine, ephedrine, quinine, mescaline, morphine

pH of Basic Solutions

Example: What is the pH of a 0.15 M solution of NH_3 ?

Solution:

 $NH_{3}(aq) + H_{2}O(l) = NH_{4}^{+}(aq) + OH^{-}(aq)$ $K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{3}]} = 1.8 \times 10^{-5}$

Tabulate the data...

pH of Basic Solutions

	[NH ₃], <i>M</i>	[NH ₄ +], <i>M</i>	[OH ⁻], <i>M</i>
Initially	0.15	0	0
Change	- X	+ X	+ X
At Equilibrium	0.15 - <i>x</i> ≈ 0.15	X	X

pH of Basic Solutions $1.8 \times 10^{-5} = \frac{(x)^2}{(0.15)}$ $(1.8 \times 10^{-5}) (0.15) = x^2$ $2.7 \times 10^{-6} = x^2, x = 1.6 \times 10^{-3}$

Test the assumption: Percent ionization = (0.0016/0.15) x 100 % = 1.07%

$$Or 0.15 - x = 0.15 - 0.0016 = 0.1484$$

pH of Basic Solutions

Therefore,

 $[OH^{-}] = 1.6 \times 10^{-3} M$ pOH = -log (1.6 × 10⁻³) pOH = 2.80 pH = 14.00 - 2.80 pH = 11.20

Relationship between K_a and K_b

• When two reactions are added to give a third, the equilibrium constant for the third reaction is the product of the equilibrium constants for the first two:

Reaction 1 + Reaction 2 = Reaction 3

has

$$K_3 = K_1 \times K_2$$

Relationship between K_a and K_b

• K_a and K_b are related in this way:

$$K_a \times K_b = K_w$$

- Therefore, if you know one of them, you can calculate the other.
- For a conjugate acid-base pair $K_w = K_a \times K_b$
- The larger the K_a , the smaller the K_b . That is, the stronger the acid, the weaker the conjugate base.
- In terms of pK_a and pK_b

$$pK_w = pK_a + pK_b = 14$$
 (at 25°C)

Relationship between K_a and K_b

Acid	K _a	Base	K _b
HNO ₃ HF HC ₂ H ₃ O ₂ H ₂ CO ₃ NH ₄ ⁺	(Strong acid) 6.8×10^{-4} 1.8×10^{-5} 4.3×10^{-7} 5.6×10^{-10}	NO_{3}^{-} F^{-} $C_{2}H_{3}O_{2}^{-}$ HCO_{3}^{-} NH_{3}	(Negligible basicity) 1.5×10^{-11} 5.6×10^{-10} 2.3×10^{-8} 1.8×10^{-5}
HCO_3^-	$5.6 imes 10^{-11}$	CO_3^{2-}	$1.8 imes10^{-4}$
HCO_3^-	5.6×10^{-11} (Negligible acidity)	$CO_3^{2^-}$	1.8×10^{-4} (Strong base)
011	(ivegigible actuity)	0	(Strong base)

Acid-Base Properties of Solutions

- Nearly all salts are strong electrolytes.
- Therefore, salts exist entirely of ions in solution.
- Acid-base properties of salts are a consequence of the reaction of their *ions* in solution.
- The reaction in which ions produce H⁺ or OH⁻ in water is called <u>hydrolysis</u>.
- Anions from weak acids are basic.
- Anions from strong acids are neutral.

Acid-Base Properties of Solutions Reactions of Anions with Water

- In general, anions, X⁻, are bases in solution i.e. can be considered as the conjugate base of an acid.
- E.g. Cl⁻ is the conjugate base of HCl, CH₃COO⁻ is the conjugate base of CH₃COOH.
- As such, anions can react with water in a hydrolysis reaction to form OH⁻ and the conjugate acid:

 $X^{-}(aq) + H_2O(I) \implies HX(aq) + OH^{-}(aq)$

Acid-Base properties of Solutions Reactions of Cations with Water

- Cations with acidic protons (like NH₄⁺) will lower the pH of a solution.
- They can be considered as the conjugate acids of weak bases.
- $NH_4^+(aq) + H_2O(I) \implies NH_3(aq) + H_3O^+(aq)$
- Most metal cations that are hydrated in solution also lower the pH of the solution.

Acid-Base Properties of Solutions

Combined Effect of Cation and Anion in Solution



- An anion that is the conjugate base of a strong acid will not affect the pH. Example, Br⁻
- An anion that is the conjugate base of a weak acid will increase the pH. Example, CN⁻
- A cation that is the conjugate acid of a weak base will decrease the pH. Example, CH₃NH₃⁺

Acid-Base Properties of Solutions

Combined Effect of Cation and Anion in Solution

- Cations of the strong Arrhenius bases will not affect the pH.
- 5. Other metal ions will cause a decrease in pH.
- 6. When a solution contains both the conjugate base of a weak acid and the conjugate acid of a weak base, the affect on pH depends on the K_a and K_b values.



- In this section we discuss briefly the effects of chemical structure on acid base behavior.
- An acid must contain at least one H bonded to an X atom, i.e. H-X
- <u>Three</u> factors affect the strengths of acids

Factors that Affect Acid Strength

(i) Polarity of the H-X

• H-X bond must be polar with H $\delta +$ and X $\delta -$



- •The more polar the bond, the stronger the acid.
- If X is a metal then the bond polarity is $H\delta$ -, $X\delta$ + and the substance is a base, the H-X bond must be weak enough to be broken, the conjugate base, X-, must be stable.

Factors that Affect Acid Strength

(ii) The Strength of the bond

- Release of a proton implies the breaking of the X-H bond.
- The weaker the bond stronger the acid.
- The H-F bond is the most polar. However it has the highest bond strength amongst the hydrogen halides, hence it is a *weak acid*.

Factors that Affect Acid Strength

(iii) Stability of the conjugate base, X⁻

- The conjugate base, X⁻, must be stable.
- Any feature that lowers the energy of the conjugate base in comparison with the acid increases its stability.
- The greater the stability of the conjugate base, the stronger the acid.

The strength of an acid is often a combination of the <u>polarity</u> of the H-X bond, the <u>strength</u> of the H-X bond, and the <u>stability</u> of the conjugate base, X⁻.

Binary Acids

- Binary acids contain H and just one other element. E.g. HF, H₂S, HI, HCl, etc.
- The more polar the H-X bond and/or the weaker the H-X bond, the more acidic the compound.

	GROUP				th	
	4A	5A	6A	7A	eng	1gt
Period 2	CH ₄ No acid or base properties	NH ₃ Weak base	H ₂ O 	HF Weak acid	ng acid stre	t base strer
Period 3	SiH ₄ No acid or base properties	PH ₃ Weak base	H ₂ S Weak acid	HCl Strong acid	Increasi	Increasing

Increasing acid strength

Increasing base strength

Binary Acids

Which acid is the strongest?

- H₂S
- HF
- HCl
- HBr
- HI

					8A 18
3A	4A	5A	6A	7A	2
13	14	15	16	17	He
5	6	7	8	9	10
B	C	N	0	F	Ne
13	14	15	16	17	18
Al	Si	P	S	Cl	Ar
31	32	33	34	35	36
Ga	Ge	As	Se	Br	Kr
49	50	51	52	53	54
In	Sn	Sb	Te	I	Xe
81	82	83	84	85	86
Tl	Pb	Bi	Po	At	Rn
113	114	115	116		

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Binary Acids

Which base is the strongest?

- CIO_4^{-}
- BrO_3^-
- BrO_4^-
- 10₃⁻
- 10₄-

						18
	3A	4A	5A	6A	7A	2
	13	14	15	16	17	He
	5	6	7	8	9	10
	B	C	N	0	F	Ne
	13	14	15	16	17	18
	Al	Si	P	S	Cl	Ar
	31	32	33	34	35	36
	Ga	Ge	As	Se	Br	Kr
102	49	50	51	52	53	54
	In	Sn	Sb	Te	I	Xe
	81	82	83	84	85	86
	Tl	Pb	Bi	Po	At	Rn
8	113	114	115	116		

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8A

Binary Acids

- Acid strength increases across a period and down a group.
- Conversely, base strength decreases across a period and down a group.
- HF is a weak acid because the bond energy is high.
- The electronegativity difference between C and H is so small that the C-H bond is non-polar and CH₄ is neither an acid nor a base.

Oxyacids

- Oxyacids contain O-H bonds (and often also =O groups).
- Exmaple: sulphuric acid. о н—о—s—о—н
- All oxyacids have the general structure Y-O-H.
- The strength of the acid depends on Y and the atoms attached to Y. The OH group/s in these molecules can ionise as follows:

$$\ge Y - O - H \longrightarrow \ge Y - O^- + H^+$$

Oxyacids

- This only happens in practice if the atom Y is a strongly electronegative atom, e.g., P, S, N, etc. Atom Y can then attract electron density towards itself, thereby polarising the O-H bond and facilitating ionisation:
- If Y is a metal (low electronegativity), then the substances are bases.
- If Y has intermediate electronegativity (e.g. I, EN = 2.5), the electrons are between Y and O and the substance is a weak oxyacid.

Oxyacids

 If Y has a large electronegativity (e.g. Cl, EN = 3.0), the electrons are located closer to Y than O and the O-H bond is polarized to lose H⁺.



Oxyacids

Summary

1. For oxyacids that have the same number of OH groups and the same number of O atoms, acid strength increases with increasing electronegativity of the central atom.

H-O-Y

Acid	EN of Y	K _a
HClO HBrO HIO	3.0 2.8 2.5	$3.0 imes 10^{-8} \ 2.5 imes 10^{-9} \ 2.3 imes 10^{-11}$

Oxyacids

Summary

2. For a series of oxyacids that have the same central atom Y, acidity increases with the number of oxygen atoms attached to Y increases.



Carboxylic Acids

 Carboxylic acids are organic acids that contain the carboxyl group:

- Often written as –COOH or as –CO₂H.
- All carboxylic acids are weak acids.
- When the carboxylic acid loses a proton, it generate the carboxylate anion, COO⁻.



Acetic acid







Benzoic acid

Carboxylic Acids

- It is of interest to note that methanol, CH₃OH, does not have acidic properties in water, while acetic acid [CH₃COOH] does. Why?
- Compare the molecular structures:



Carboxylic Acids

- Two factors contribute to acidic behaviour of carboxylic acids:
- Additional O atom attached to the carbon attracts electron density from the O-H bond increasing its polarity and stabilising the conjugate base
- Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.



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Carboxylic Acids

- The acid strength of carboxylic acids also increases as the number of electronegative atoms in the molecule increases.
- Example:



Lewis Acids and Bases

- In previous sections we discussed Brønsted-Lowry acids and bases.
- In the Brønsted-Lowry view, an acid is a proton donor. When a proton is donated to another molecule, where does it actually go on the acceptor molecule ?
- It invariably goes onto a lone pair of electrons situated on some atom (e.g., a N or O-) belonging to the base.
Lewis Acids and Bases

- G.N. Lewis proposed that what was characteristic of acids and bases wasn't so much that a proton is always exchanged between an acid and a base, but that a lone pair of electrons is always involved.
- This led to the definition of Lewis acids and bases.
- According to the Lewis view:

A Lewis acid is an electron pair acceptor. A Lewis base is electron pair donor.

• Note: Lewis acids and bases do not need to contain protons. Therefore, the Lewis definition is the most general definition of acids and bases.

Lewis Acids



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
- Lewis acids generally have an incomplete octet e.g. BF₃
- Compounds with π-bonds can act as Lewis acids.

Lewis Bases



base acid

- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted–Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.

Metal Complexes

- A central metal atom bonded to a group of molecules or ions is a metal complex e.g. $[Ag(NH_3)_2]^+$.
- If the complex bears a charge, it is a complex ion.
- Compounds containing complexes are coordination compounds.



Metal Complexes

The metal-ligand bond

- The molecules or ions that bond to the metal ion in a complex are known as **ligands**.
- They are usually anions or polar molecules. They have at least one unshared pair of valence electrons.
- Examples of ligands:

$$\begin{array}{ccc} & H \\ & | \\ \vdots \\ H & H \end{array} \\ H & H \end{array} : C \equiv N : \overline{}$$

Metal Complexes

The metal-ligand bond

- The bond between a ligand and a metal ion is an example of an interaction between a Lewis base and acid.
- The ligands have nonbonding electrons and are Lewis bases.
- The metal has empty orbitals and is a Lewis acid.
- A metal-ligand bond is formed between the Lewis acid (metal) and the Lewis base (ligand).



End of Chapter 16

Acid-Base Equilibria