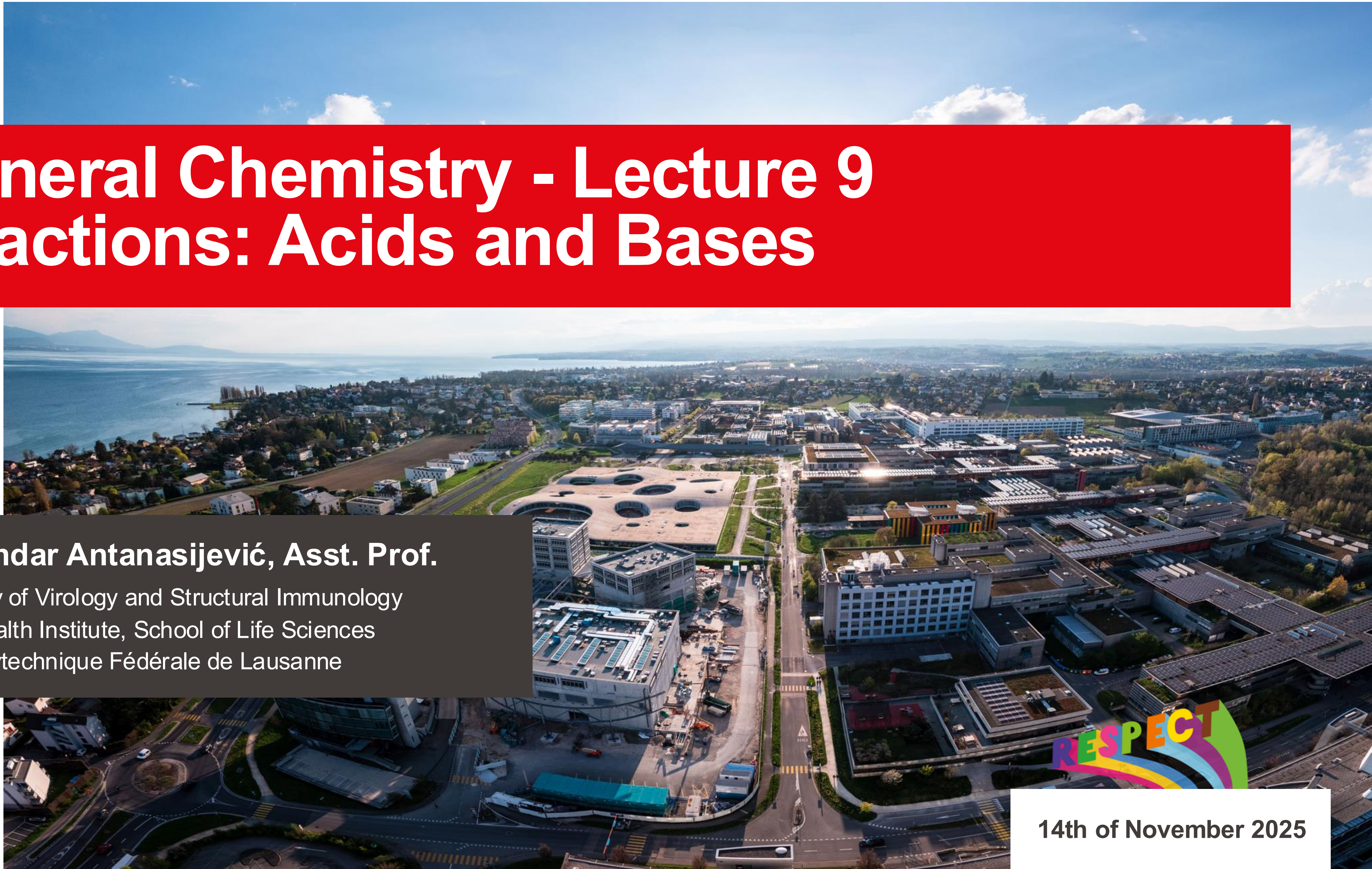

General Chemistry - Lecture 9
Reactions: Acids and Bases

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polytechnique
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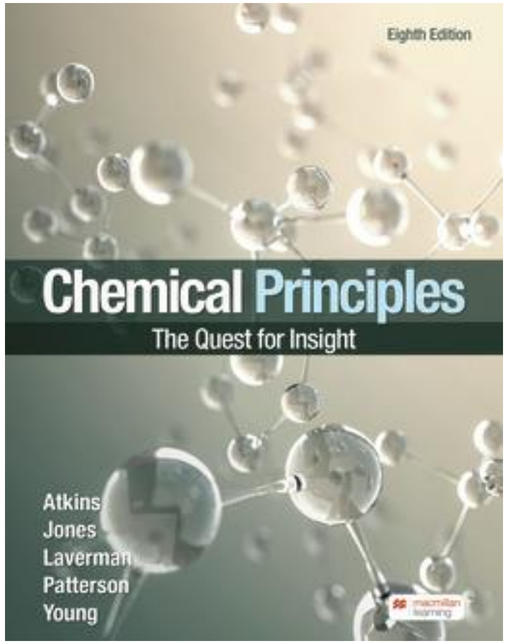
Learning Objectives

- Learning the basic acid and base definitions and their origins
- Acid - base equilibrium and the connection to pH
- Understanding the fundamental constants (pK_a, pK_b)
- Buffer solutions and their applications
- Understanding acid-base titrations

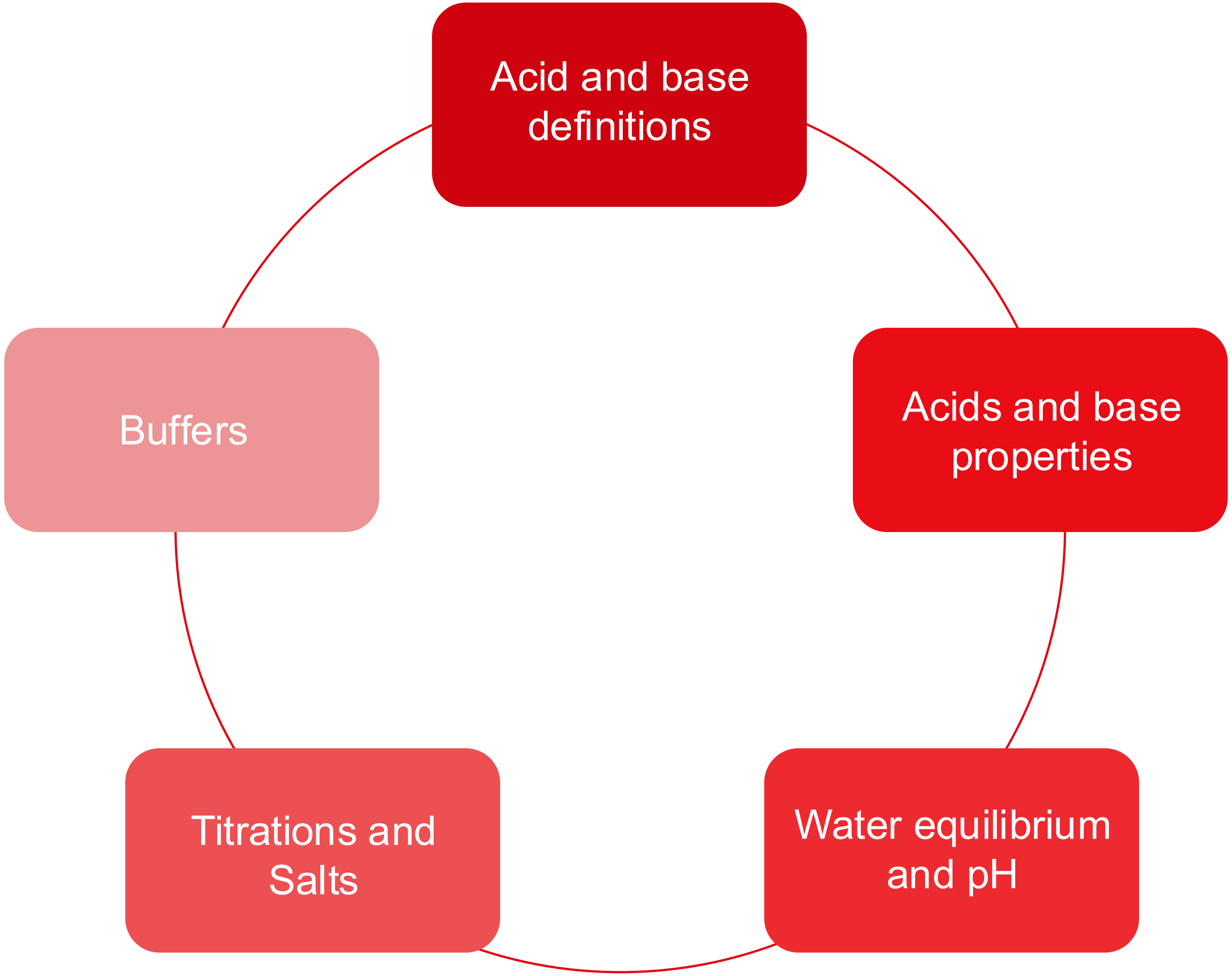
Reading suggestions

- Chemical Principles: The Quest of Insight
  - Chapter 6

Also revise **Lecture 2** of this course



Plan



Acid and base definitions

Acids and base properties

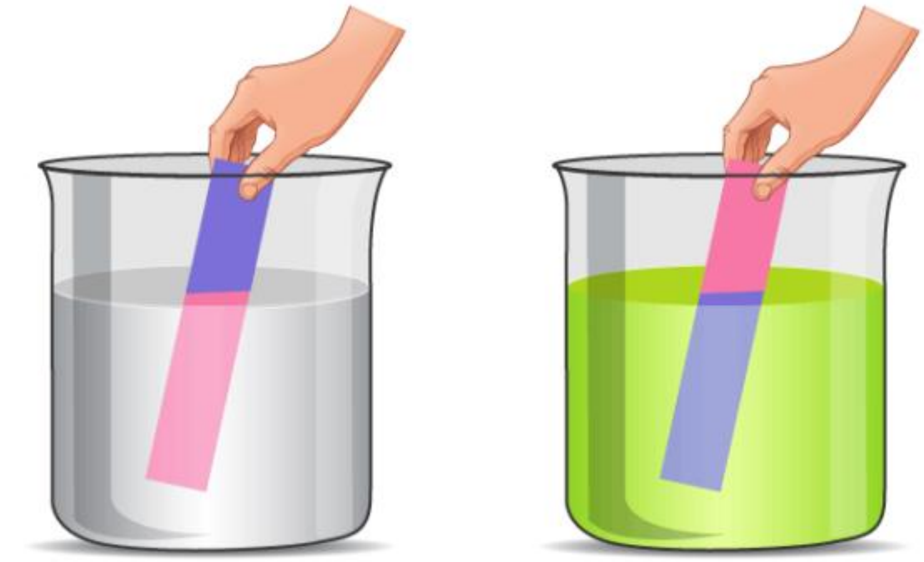
Water equilibrium and pH

Titrations and Salts

Buffers

Acids and Bases

- Early chemists:
  - **Acids** (*lat. acēre*) taste sharp or sour.
  - **Bases** or **alkalis** (*arab. al-qaly*) taste soapy.

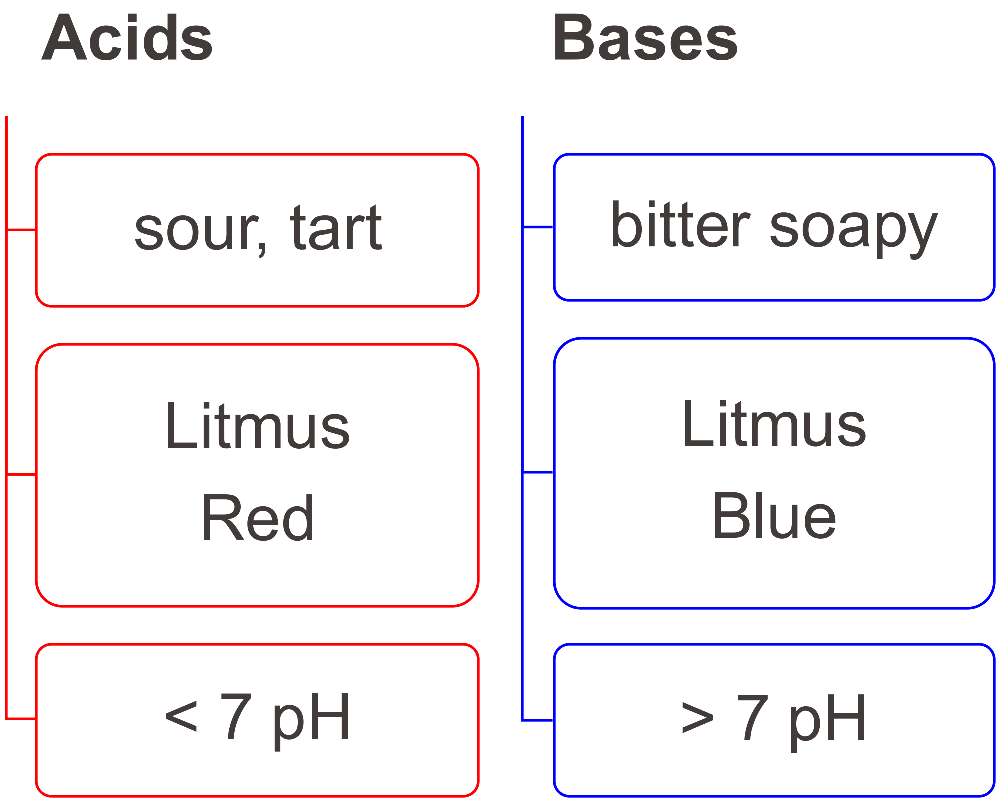


Acid

Blue litmus turns red

Base

Red litmus turns blue



Acids

sour, tart

Litmus Red

< 7 pH

Bases

bitter soapy

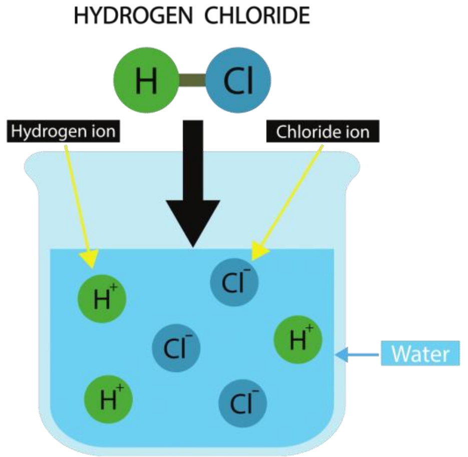
Litmus Blue

> 7 pH

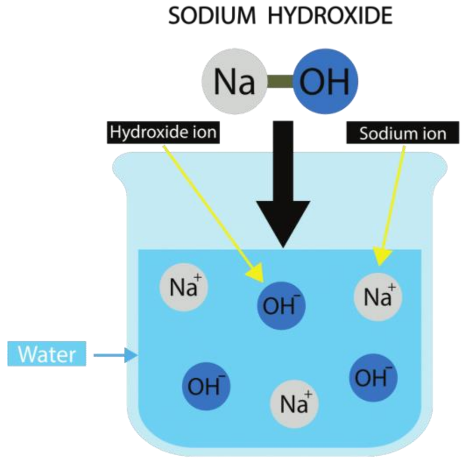
- **Indicators** are molecules that change color when exposed to acid or base.
- This change in color is connected to the **pH** of the solution

General properties of acids and bases

- Generally speaking, **acids** are substances that tend to **donate protons (H^+)** or increase the concentration of hydrogen ions in a system (lowering the pH).
- They often consist of **hydrogen** combined with **nonmetals** or with **polyatomic anions** (e.g., HCl, H_3PO_4).



- In contrast, **bases** are substances that tend to **accept protons (H^+)** or increase the concentration of **hydroxide ions (OH^-)** in a system (increasing the pH).
- They usually contain **metal cations** bonded to **hydroxide** or **oxide** anions (e.g., NaOH), or they are compounds capable of **accepting protons** via free electrons (e.g., NH_3)

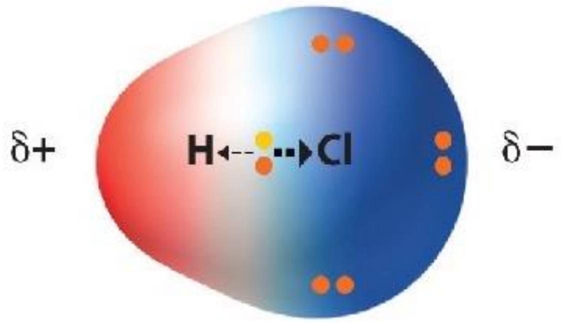


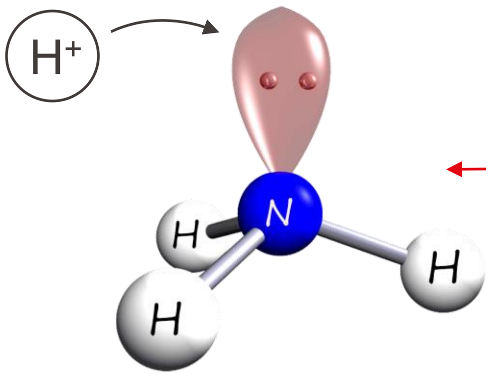
Chemical origins of acids and bases

- The main chemical characteristics of acids:
  - Presence of polar H-X bods → Easier to lose H^+
  - High electronegativity (EN) of the central atom
  - Weak H-X bond → Easier to lose H^+

Acid	**Type**
HF	Binary acid
H_2SO_4	Oxyacid
CH_3COOH	Organic acid

Uneven distribution of shared electrons and/or weak H-X bond favors H^+ release





Free electron pairs or groups with excess electrons can bind free H^+ released by acids

- The main chemical characteristics of bases:
  - Presence of a lone pair of electrons in a valent level
  - Lower electronegativity → Better electron donors
  - Can be formed by both, metals and nonmetals

Base	**Type**
NaOH	Alkali-metal base
$Ca(OH)_2$	Alkaline-earth-metal base
NH_3	Nonmetal base

Arrhenius definition of acids and bases (1884)

- An **acid** is a compound that contains hydrogen and reacts with water to form hydrogen (H^+) ions.
  - Hydrochloric acid, HCl, is an **acid** because it produces hydrogen ion, H^+.

$$\mathbf{HCl\ (aq) \rightarrow Cl^- \ (aq) + H^+ \ (aq)}$$

- A **base** is a compound that produces hydroxide ions (OH^-) in water.
  - Ammonia, NH_3, is a **base** because it produces hydroxide OH^-.

$$\mathbf{NH_3\ (aq) + H_2O\ (l) \rightarrow NH_4^+\ (aq) + OH^-\ (aq)}$$

Svante Arrhenius
(1859-1927)

- **Limitations:** specific to water solvent, not all base reactions produce OH^-

Adapted from Lecture 2

Brønsted-Lowry definition of acids and bases (1923)

- Thomas Lowry in England and Johannes Brønsted in Denmark both developed the proton (H^+) transfer concept.
  - **Acid** – proton donor, **Base** – proton acceptor

$$\mathbf{HCl\ (aq) + H_2O\ (l) \rightarrow Cl^- \ (aq) + H_3O^+ \ (aq)}$$

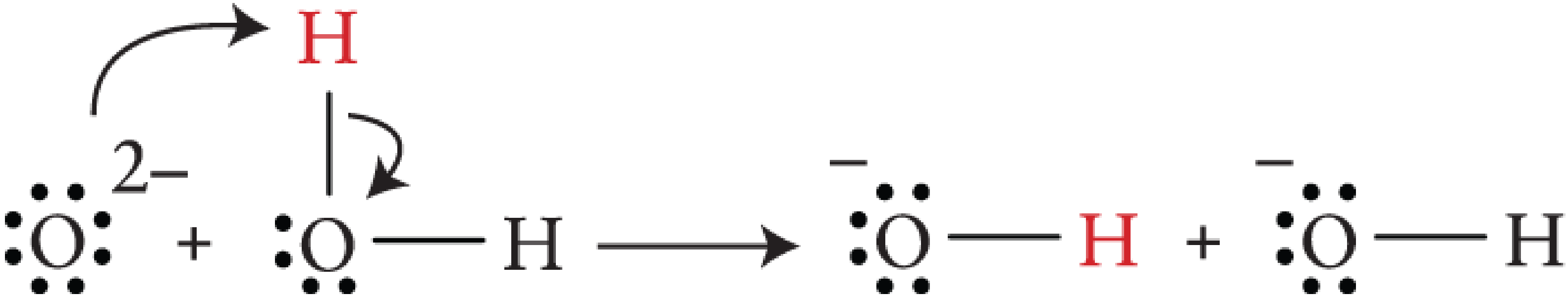
  - HCl is a proton donor (**acid**); H_2O is a proton acceptor (**base**)
  - HCl transfers a hydrogen ion, H^+, to water, producing *hydronium ions* (H_3O^+) and chloride ions.
  - HCl is a Brønsted acid and H_2O is a Brønsted base in this reaction.

- **Limitations:** still limited to protonic solvents and reactions with transferrable H^+

Adapted from Lecture 2

Lewis definition of Acids and Bases (1923)

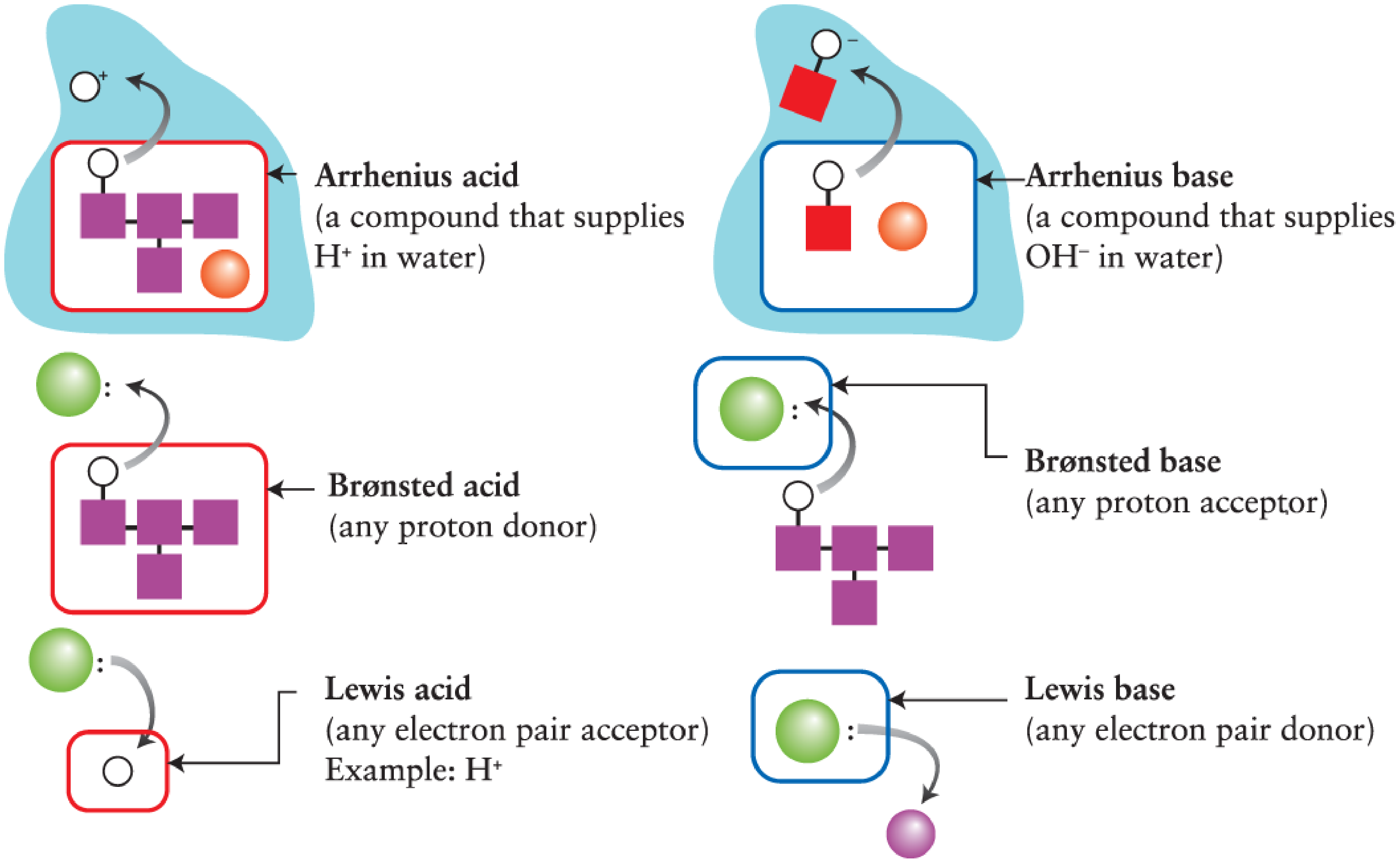
- The focus of Lewis theory is away from protons and instead on lone pairs of electrons; this makes the definition more general than the previous two.
    - A **Lewis acid** is an electron pair acceptor; A **Lewis base** is an electron pair donor.



-
    - A covalent bond forms between the proton (Lewis acid) and oxide (Lewis base) in water.

- These definitions are used frequently in both organic and inorganic chemistry. For instance, it explains how metal atoms can form molecules referred to as complex ions, which neither Brønsted nor Arrhenius theory can explain.

Graphical illustration of acid/base definitions



Arrhenius acid
(a compound that supplies H^+ in water)

Arrhenius base
(a compound that supplies OH^- in water)

Brønsted acid
(any proton donor)

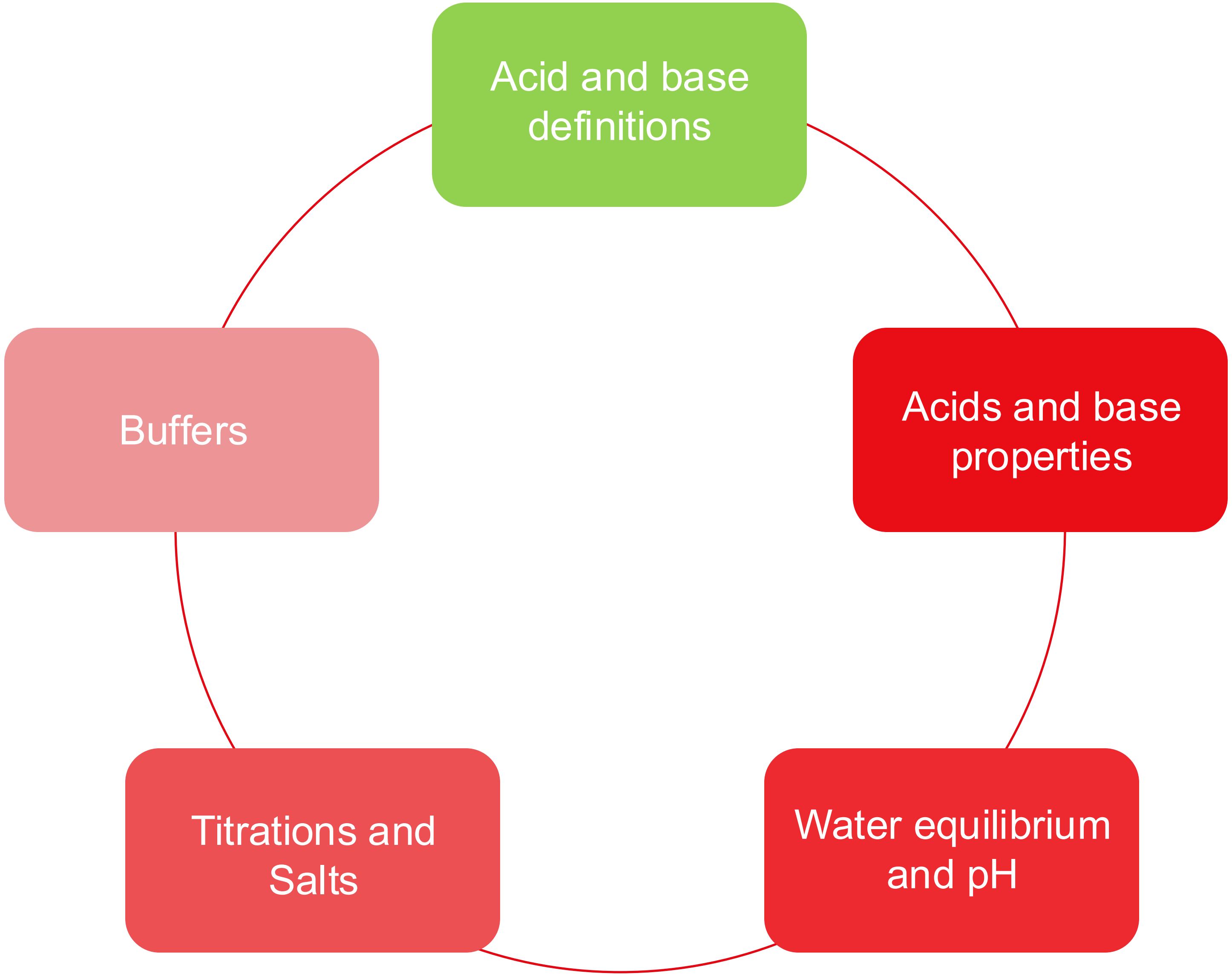
Brønsted base
(any proton acceptor)

Lewis acid
(any electron pair acceptor)
Example: H^+

Lewis base
(any electron pair donor)

- Proton transfer plays a very special role in chemistry, so the Brønsted-Lowry definitions are central for most reactions we will encounter in class.

Plan



Acid and base definitions

Acids and base properties

Water equilibrium and pH

Titrations and Salts

Buffers

The relative strength of acids and bases

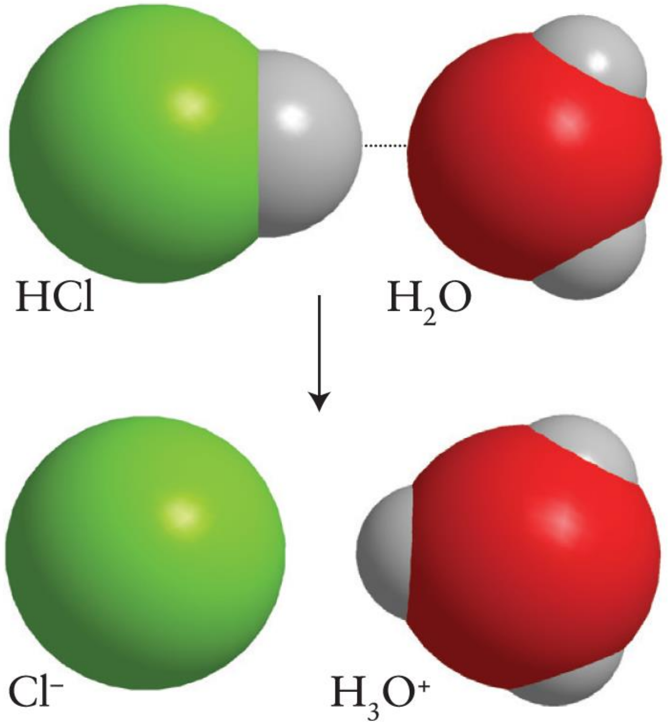
- **Strong** acids and bases undergo complete transition into products (deprotonated acid or protonated base, respectively) in aqueous solution.

$$\mathbf{HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)}$$

$$\mathbf{Ca(OH)_2 + H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq)}$$

Strong acids:
- Hydrobromic acid, HBr (aq)
- Hydrochloric acid, HCl (aq)
- Hydroiodic acid, HI (aq)
- Nitric acid, HNO_3
- Perchloric acid, $HClO_4$
- Chloric acid, $HClO_3$
- Sulfuric acid, H_2SO_4

Strong bases:
- Sodium hydroxide, NaOH
- Potassium hydroxide, KOH
- Lithium hydroxide, LiOH
- Calcium hydroxide, $Ca(OH)_2$
- Barium hydroxide, $Ba(OH)_2$
- Strontium hydroxide, $Sr(OH)_2$
- Cesium hydroxide, CsOH



No residual HCl left

The relative strength of acids and bases

- **Weak** acids and bases undergo partial protonation or deprotonation in aqueous solution, leaving most of the molecules in solution.

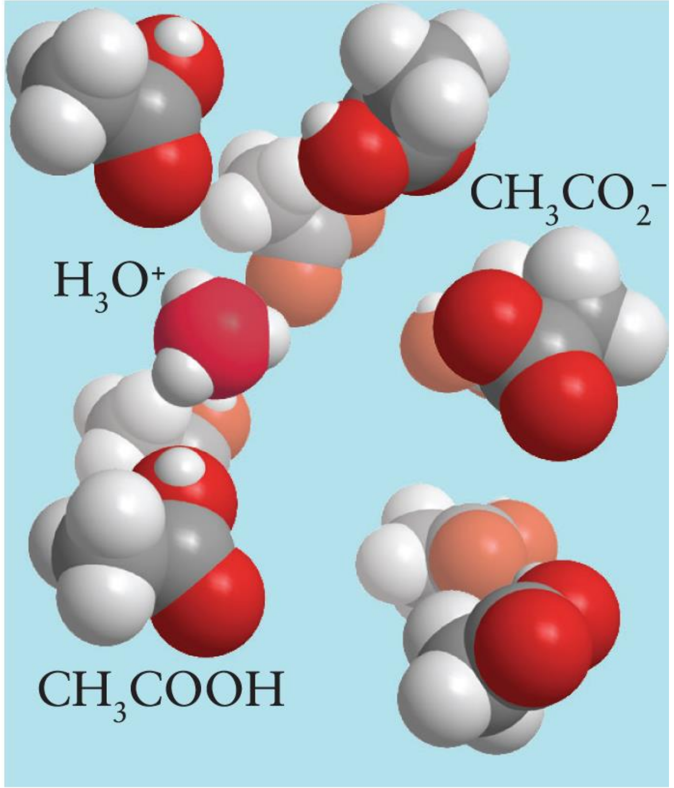
$$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)$$

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

↑ Indicates exchange

Weak acids:
- Acetic acid, CH_3COOH
- Carbonic acid, H_2CO_3
- Phosphoric acid, H_3PO_4
- Hydrofluoric acid, HF
- Formic acid, HCOOH
- Nitrous acid, HNO_2
- Benzoic acid, C_6H_5COOH

Weak bases:
- Ammonia, NH_3
- Methylamine, CH_3NH_2
- Aniline, $C_6H_5NH_2$
- Pyridine, C_5H_5N
- Bicarbonate ion, HCO_3^-
- Carbonate ion, CO_3^{2-}
- Ethylamine, $C_2H_5NH_2$



Residual CH_3COOH remains

Acid - Base Equilibrium

- A reaction is at equilibrium when the rate of formation of products equals the rate of formation of reactants (no net exchange of mass).
- As a result, the concentrations of all reactants and products remain constant over time, even though the forward and reverse reactions continue to occur.

Acid   Conjugate base

$$\mathrm{HA\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{A^{-}\,(aq)} + \mathrm{H_3O^{+}\,(aq)}$$

$$\mathrm{B\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{BH^{+}\,(aq)} + \mathrm{OH^{-}\,(aq)}$$

Base   Conjugate acid

- In the case of acid-base reactions:
  - Deprotonation of acid makes a **conjugate base**
  - Protonation of a base makes **conjugate acid**

Acid dissociation constant (K_a)

- The equilibrium concentrations of all chemical groups participating in the reaction are used to determine the corresponding equilibrium constants (K_{eq})
- In case of acids, it is referred to as **acid dissociation constant (K_a)** and it is a measure of acid's strength.

$$HA\,(aq) \quad + \quad H_2O\,(l) \quad \rightleftharpoons \quad A^-\,(aq) \quad + \quad H_3O^+\,(aq)$$

$$K_{eq} = K_a = \frac{[A^-] \cdot [H_3O^+]}{[HA]} \qquad pK_a = -\log_{10}(K_a)$$

[X] - Concentration of species X in **mol/L**

K_a and pK_a are unitless numbers

- Given that water concentration is usually much, much higher than all other reagents and constant (≈ 55.5mol/L), it is omitted from these equations.
- pK_a value is calculated as a negative logarithm of K_a → Easier to express/analyze

Base dissociation constant (K_b)

- Similarly, **base dissociation constant (K_b)** and its log **(pK_b),** depict the equilibrium upon addition of base to the solution, and are is a relative measure of base strength.

$$B\ (aq) \quad + \quad H_2O\ (l) \quad \rightleftharpoons \quad BH^+\ (aq) \quad + \quad OH^-\ (aq)$$

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

$$pK_b = -\log_{10}(K_b)$$

[X] - Concentration of species X in **mol/L**

K_b and pK_b are unitless numbers

- Gibbs-Helmholtz equation allows to calculate the standard Gibbs free energy difference (ΔG˚) for the reactants and products in equilibrium:

$$\Delta G^\circ = -RT\ln(K_{eq})$$

$K_{eq} = K_a$ or K_b

If **$\Delta G^\circ < 0$** → Reaction favors products

If **$\Delta G^\circ > 0$** → Reaction favors reactants

Example calculation: Acetic acid (CH_3COOH)

- Acetic acid has the K_a of 1.8 x 10^{-5} at 25˚C:

$$\mathbf{CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COO^-\ (aq) + H_3O^+\ (aq)}$$

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{\left[CH_3COOH\right]} = \boxed{1.8 \times 10^{-5}}$$

$$pK_a = 4.74$$

$$\Delta G^\circ = \boxed{27'067\ \text{J/mol}}$$

- Positive ΔG˚ value indicates that the reaction will favor the substrate (CH_3COOH) and only a smaller fraction will be in the form of a product (CH_3COO^-).
- If we assume that we started with 100 molecules of CH_3COOH, in equilibrium there will be less than 1 molecule of CH_3COO^-

Normal ranges of K_a and K_b

- The smaller the dissociation constant (K), the weaker the acid or base.

Acid	K_a	pK_a
Iodic acid, HIO_3	1.7×10^{-1}	0.77
Sulfurous acid, H_2SO_3	1.5×10^{-2}	1.81
Phosphoric acid, H_3PO_4	7.6×10^{-3}	2.12
Hydrofluoric acid, HF	3.5×10^{-4}	3.45
Benzoic acid, C_6H_5COOH	6.5×10^{-5}	4.19
Acetic acid, CH_3COOH	1.8×10^{-5}	4.75
Carbonic acid, H_2CO_3	4.3×10^{-7}	6.37
Boric acid, $B(OH)_3^{\dagger}$	7.2×10^{-10}	9.14
Hydrocyanic acid, HCN	4.9×10^{-10}	9.31
Phenol, C_6H_5OH	1.3×10^{-10}	9.89

Base	K_b	pK_b
Triethylamine, $(C_2H_5)_3N$	1.0×10^{-3}	2.99
Ethylamine, $C_2H_5NH_2$	6.5×10^{-4}	3.19
Trimethylamine, $(CH_3)_3N$	6.5×10^{-5}	4.19
Ammonia, NH_3	1.8×10^{-5}	4.75
Hydrazine, NH_2NH_2	1.7×10^{-6}	5.77
Morphine, $C_{17}H_{19}O_3N$	1.6×10^{-6}	5.79
Nicotine, $C_{10}H_{14}N_2$	1.0×10^{-6}	5.98
Hydroxylamine, NH_2OH	1.1×10^{-8}	7.97
Pyridine, C_5H_5N	1.8×10^{-9}	8.75
Urea, $CO(NH_2)_2$	1.3×10^{-14}	13.90

- Given the (near) complete conversion in equilibrium, strong acids and bases have **very high dissociation constants** ($K_{a/b}$ ~ 100 - ∞), and **negative $pK_{a/b}$** values.

Dissociation constants for conjugate pairs

- Consider the equilibrium between an acid and conjugate base:

Acid　　　　　　　　　　Conjugate base

$$HA\,(aq) \quad + \quad H_2O\,(l) \quad \rightleftharpoons \quad A^-\,(aq) \quad + \quad H_3O^+\,(aq)$$

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

base　　　　　　　　　　Conjugate acid

$$A^-\,(aq) \quad + \quad H_2O\,(l) \quad \rightleftharpoons \quad HA\,(aq) \quad + \quad OH^-\,(aq)$$

$$K_b = \frac{[HA] \cdot [OH^-]}{[A^-]}$$

- Strong acids will have high K_a and negligible conjugate K_b due to: $[HA] \rightarrow 0$
- Strong bases will have high K_b and negligible conjugate K_a due to: $[A^-] \rightarrow 0$
- Weak acids and bases will feature conjugate K_a and K_b values that are within a few orders of magnitude from each other.

Polyprotic acids and bases

- A polyprotic acid is a compound that can donate more than one proton.
  - Examples: H_2SO_4, H_2CO_3, H_3PO_4
- Equivalently, a polyprotic base is a species that can accept more than one proton.
  - Examples: CO_3^{2-}, SO_3^{2-}, PO_4^{3-} anions

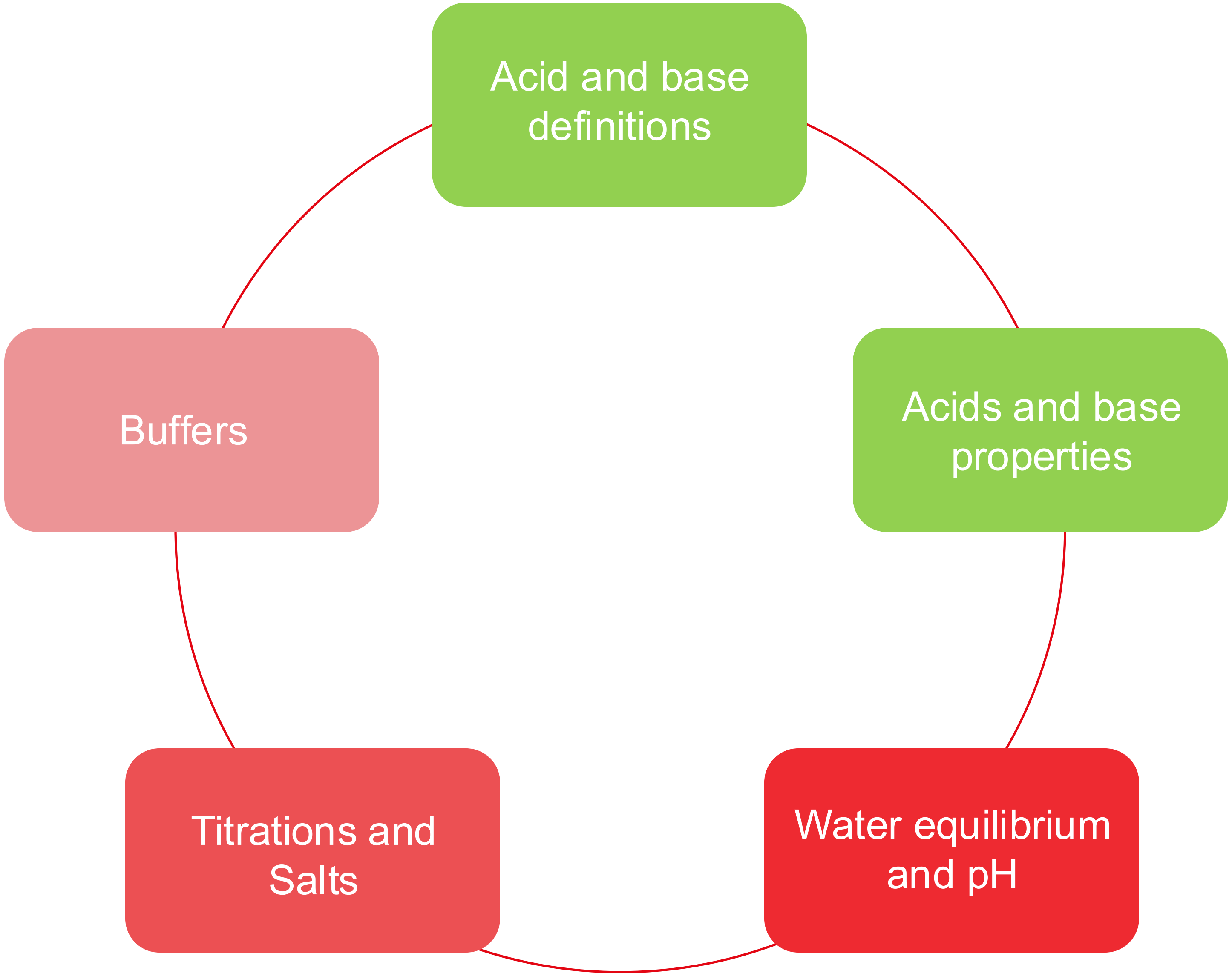
- Carbonic acid takes part in two successive proton transfer equilibria:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.3 \times 10^{-7} \qquad pK_{a1} = 6.37$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 5.6 \times 10^{-11} \qquad pK_{a2} = 10.25$$

- The conjugate base of H_2CO_3 in the first equilibrium, HCO_3^-, acts as an acid in the second equilibrium. That ion produces in turn its own conjugate base, CO_3^{2-}.

Plan



Acid and base definitions

Acids and base properties

Water equilibrium and pH

Titrations and Salts

Buffers

The equilibrium constant of water

- Under equilibrium conditions water will exhibit **amphiprotic** behavior, acting as both acid (releasing protons) and base (accepting protons):

$$\mathbf{2H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)}$$

- The equilibrium constant for this reaction (K_w), sometimes called **autoprotolysis**, will be connected to reagent concentration via:

$$K_w = [H_3O^+] \cdot [OH^-] \qquad \textit{At } 25^\circ C,\ K_w = 1 \cdot 10^{-14}$$

- The K_w is a function of temperature, therefore it remains constant even if the concentrations of H_3O^+ and OH^- change (e.g., by adding acid or base)
- The autoprotolysis process is like a see-saw, if $[H_3O^+]$ ↑, then $[OH^-]$ must ↓, but the multiplication product (K_w) must remain constant

Water and pH

- In pure water at 25°C, the molar concentrations of H_3O^+ and OH^- are equal and are **1.0×10^{-7} mol/L**.
- The equilibrium concentrations of these groups in different settings are used to describe the experimental conditions or results (=very important chemical markers)
- To avoid using exponential concentrations we instead use log values, **pH** and **pOH**

$$pH = -\log_{10} [H_3O^+]$$

$$pOH = -\log_{10} [OH^-]$$

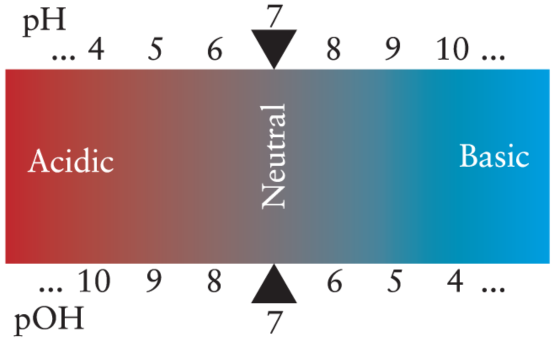
pH (pure water, 25˚C) = 7

pOH (pure water, 25˚C) = 7

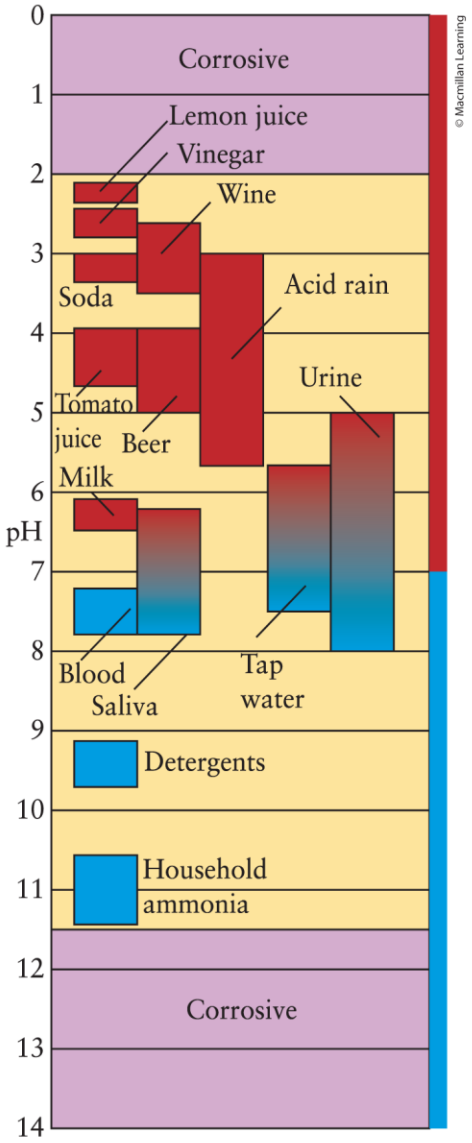
- The pH scale range is 0-14 but values outside of this range are possible (e.g., super-acidic or super-basic solutions)
- Increase by **1 unit** indicates a change in concentration of **1 order of magnitude**
- The **sum of pH and pOH at 25 ˚C is 14**, due to the autoprotolysis constant ($K_w = 10^{-14}$)

pH of different solutions

- pH value can be used to determine whether the solution is overall basic or acidic:
  - The pH of pure water is 7 (neutral pH).
  - The pH of an acidic solution is less than 7 (low pH).
  - The pH of a basic solution is greater than 7 (high pH).



- The normal pH of arterial blood is 7.4, sometimes referred to as **physiological pH**
- Waste is defined as “**corrosive**” if its pH is either lower than or equal to 2 (highly acidic) or higher than 11.5 (highly basic).



Acid rain corrosiveness

- Natural (unpolluted) rain, with an acidity due largely to dissolved carbon dioxide, typically has a pH of about 5.7.

- Air pollution with sulfur dioxide (SO_2) and nitrogen oxides (NO_x) leads to further rain acidification

- The state of the carving on Cleopatra's Needle has deteriorated as a result of the action of acid rain: (a) after 3500 years in the Egyptian desert; (b) after a further 140 years in Central Park, New York City.

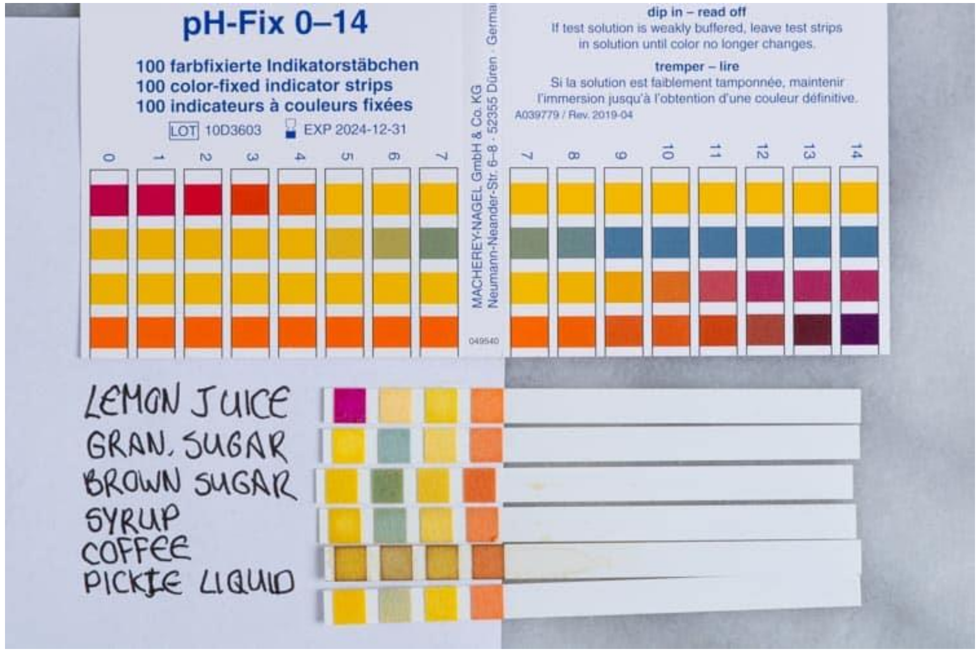
(a)

(b)

Photo (a) Bettmann/Getty Images. Photo (b) chris-mueller/iStock/Getty Images.

Measuring pH

- A digital pH meter, with a pH probe uses a voltmeter to measure conductivity.
- Other less precise methods include pH paper and pH-sensitive dyes.



Color changes is based on the pH

Charles D. Winters/Science Source.

Conductivity is proportional to electrolyte content

The link between conjugate pairs and K_w

- Consider the equilibrium between an acid and conjugate base:

Acid — Conjugate base

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

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

base — Conjugate acid

$$A^-\,(aq) + H_2O\,(l) \rightleftharpoons HA\,(aq) + OH^-\,(aq)$$

$$K_b = \frac{[HA] \cdot [OH^-]}{[A^-]}$$

- If you add these reactions, they lead to an equilibrium for self-ionization of water:

$$2H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

$$K_a \cdot K_b = [H_3O^+] \cdot [OH^-] = K_w$$

The link between conjugate pairs and K_w

- This essentially means that:
  - Water autoprotolysis equilibrium and conjugate pair equilibrium are coupled
  - For any conjugate pair, the product of K_a and K_b equals K_w which is purely a water constant

$$K_a \bullet K_b = [H_3O^+] \bullet [OH^-] = K_w$$

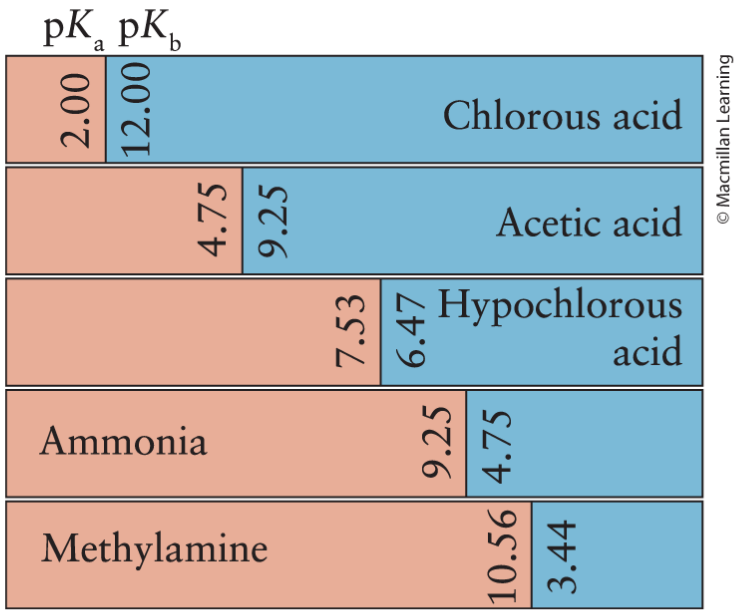
- If we apply negative $\log_{10}$ transformation we get:

$$-\log_{10}(K_a \bullet K_b) = -\log_{10} K_w$$

$$pK_a + pK_b = pK_w$$

pK_w (water, 25˚C) = 14

The pK_a and pK_b values follow the same relative dependence as pH and pOH



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pH after the addition of a strong acid or base

- Imagine that HCl was added to aqueous solution at 0.1 mol/L
- Within minutes 100% of this acid would have underwent this reaction:

$$\mathbf{HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)}$$

- Therefore $[H_3O^+]$ equals the starting concentration of [HCl] which then leads to:

$$\mathbf{pH = -\log_{10}([H_3O^+] / 1\ mol/L) = -\log_{10}(0.1) = 1}$$

$$\mathbf{pOH = 14 - 1 = 13}$$

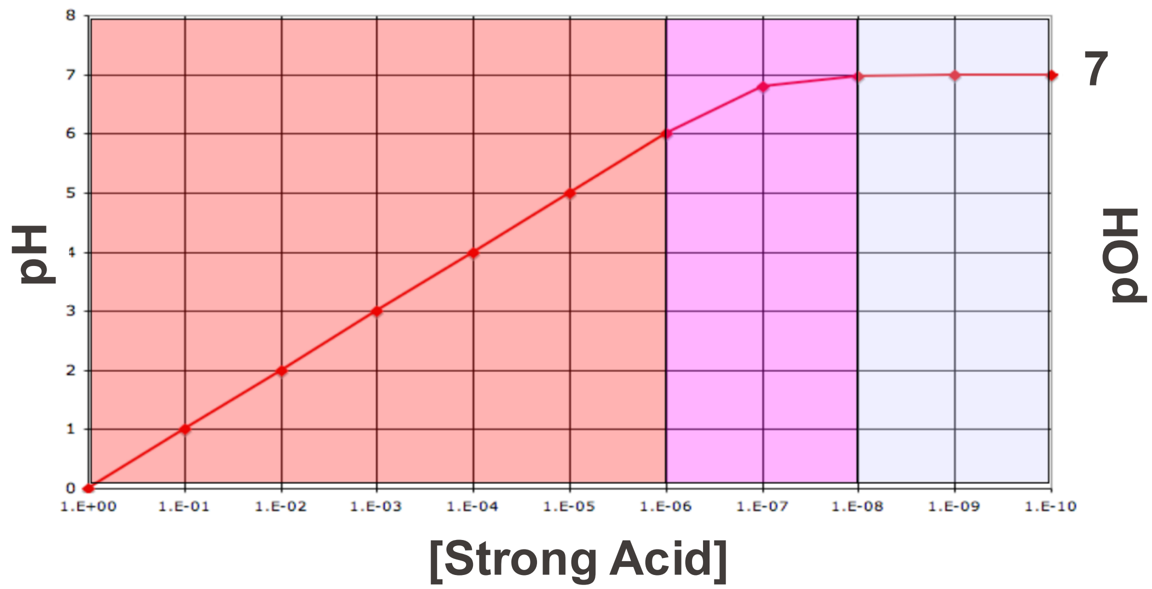
Limitation: It ignores the contribution of water H_3O^+ and OH^- as they are at much lower concentrations

- Similar approach can be applied to solutions of strong bases

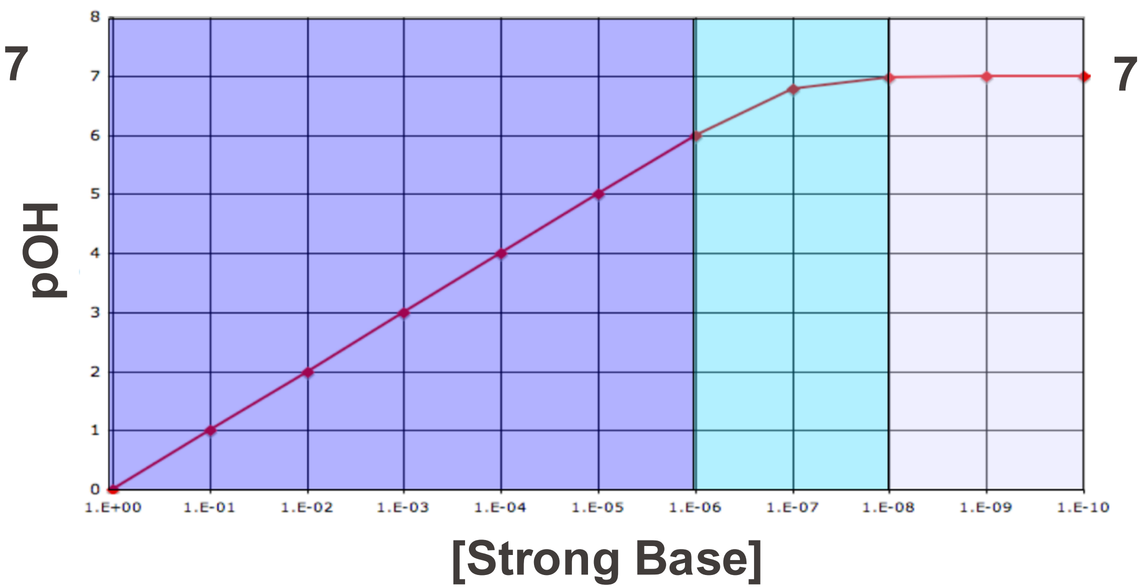
pH after the addition of a strong acid or base

- pH changes linearly with the log of acid concentration (not surprising), until the concentration of strong acid (or strong base) drops below 10^{-6} mol/L
- Given the significant contribution from water H_3O^+ and OH^- groups at such concentrations the change in pH exhibits a slower change

When adding strong acids



When adding strong bases



- Strong acids or bases at concentrations $<10^{-8}$ are insufficient to change the water pH

pH after the addition of a weak acid or base

- Equilibrium calculations for weak acids and bases is complicated by the fact that they undergo only partial protonation or deprotonation.
- Let’s calculate the pH of a water solution after the addition of CH_3COOH at 0.1 mol/L

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

- It is easiest if we perform analyses using tables like the one below:

	CH_3COOH	H_3O^+	CH_3COO^-
Initial	0.1	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.1 - x$	x	x

pK_a (CH_3COOH) = **4.75** K_a (CH_3COOH) = **$1.8 \cdot 10^{-5}$**

$$K_a = \frac{[CH_3COO^-]_{eq} \cdot [H_3O^+]_{eq}}{[CH_3COOH]_{eq}} = \frac{x^2}{0.1 - x}$$

$$x^2 - K_a \cdot (0.1 - x) = 0$$

Quadratic equation

$$x^2 + K_a \cdot x - 0.1 \cdot K_a = 0$$

$$x = 1.33 \cdot 10^{-3} \text{ mol/L}$$

pH after the addition of a weak acid or base

- If the value of **x** is included back in the table we get:

	CH_3COOH	H_3O^+	CH_3COO^-
Initial	0.1	0	0
Change	$-1.33 \cdot 10^{-3}$	$+1.33 \cdot 10^{-3}$	$+1.33 \cdot 10^{-3}$
Equilibrium	0.0987	$1.33 \cdot 10^{-3}$	$1.33 \cdot 10^{-3}$

The resulting pH value is:

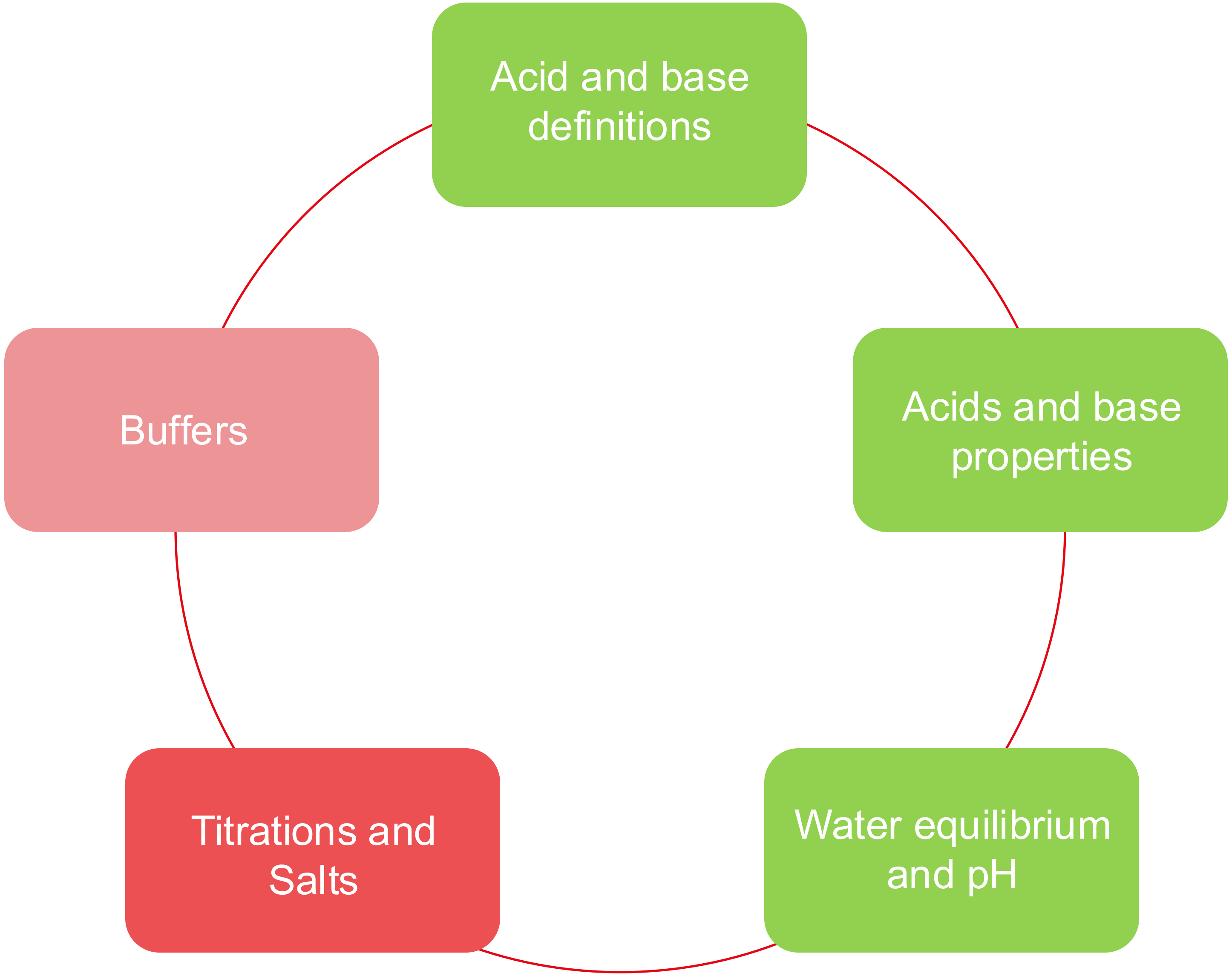
$$pH = -\log_{10}[H_3O^+]$$

$$pH = 2.88$$

- Similar calculations are applied when using a weak base except we replace K_a with K_b

- In practice, to avoid solving quadratic equation we apply these approximations:
  - For weak acids: $[\text{Acid}]_{\text{initial}} >> x \quad \rightarrow \quad x = \sqrt{(Ka \ * [Acid]_{initial}}$
  - For weak bases: $[\text{Base}]_{\text{initial}} >> x \quad \rightarrow \quad x = \sqrt{(Kb \ * [Base]_{initial}}$

Plan



Acid and base definitions

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Buffers

Acid-Base neutralization reactions

- A reaction between an acid and a base is called **neutralization**.
- In case of strong acids and bases the typically have the following form:

Acid + Metal hydroxide → Salt + Water

$$\mathbf{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

$$2\ HNO_3\ (aq) + Ba(OH)_2\ (aq) \rightarrow Ba(NO_3)_2\ (aq) + 2\ H_2O\ (l)$$

Adapted from Lecture 2

Acid-Base neutralization reactions

- Let's take a closer look at this last reaction:

$$2\ HNO_3\ (aq) + Ba(OH)_2\ (aq) \rightarrow Ba(NO_3)_2\ (aq) + 2\ H_2O\ (l)$$

- Complete ionic equations:

$$2\ H^+\ (aq) + 2\ NO_3^-\ (aq) + Ba^{2+}\ (aq) + 2\ OH^-(aq) \rightarrow Ba^{2+}\ (aq) + 2\ NO_3^-\ (aq) + 2\ H_2O\ (l)$$

- Remove the "spectator" ions to obtain the net equation

$$2\ H^+\ (aq) + 2\ OH^-(aq) \rightarrow\ 2\ H_2O\ (l)$$

- Net reaction of any strong acid + strong base neutralization is the formation of **water**

Adapted from Lecture 2

Strong Acid–Strong Base Titrations

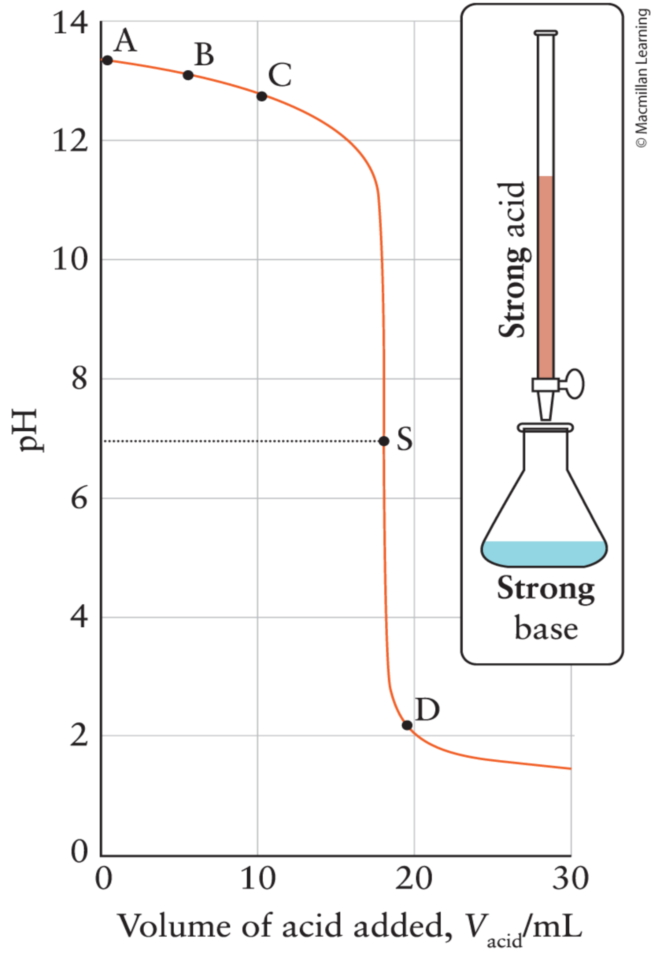
- Acid–base titration is a method used to find the concentration of an acid or base by slowly adding a solution of known concentration until neutralization is reached.

- A plot of the pH against the volume of titrant added during a titration is called a **pH curve**.

- For strong acids and bases the neutralization refers to a state where:

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

Stoichiometric point (S)



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- A strong acid-strong base titration shows at the stoichiometric point a sudden change in pH near 7.

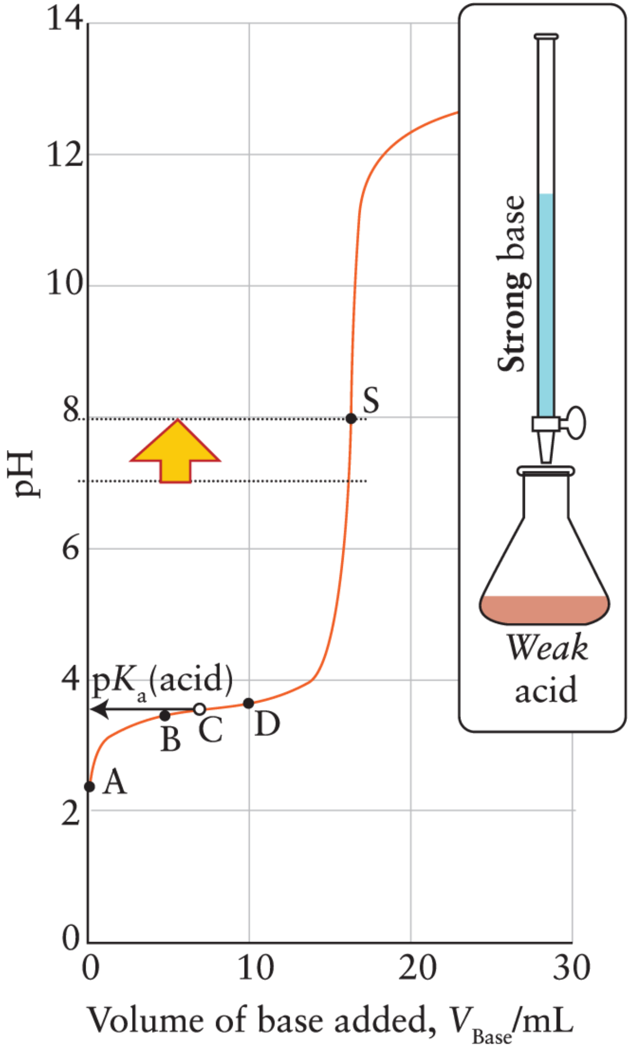
Titrations involving strong and weak acid/base

- A more common titration is between a weak acid and strong base, or the opposite

Conjugate base

$$HCOOH(aq) + NaOH(aq) \rightarrow Na^+ + HCO_2^-(aq) + H_2O(l)$$

- The stoichiometric point (S) in this case will not be reached at **pH 7**
- The pH depends on the conjugate salt produced. If basic, it will contribute to higher pH.
- Note that around the pKa of the weak acid (HCOOH) the pH barely changes with addition of base



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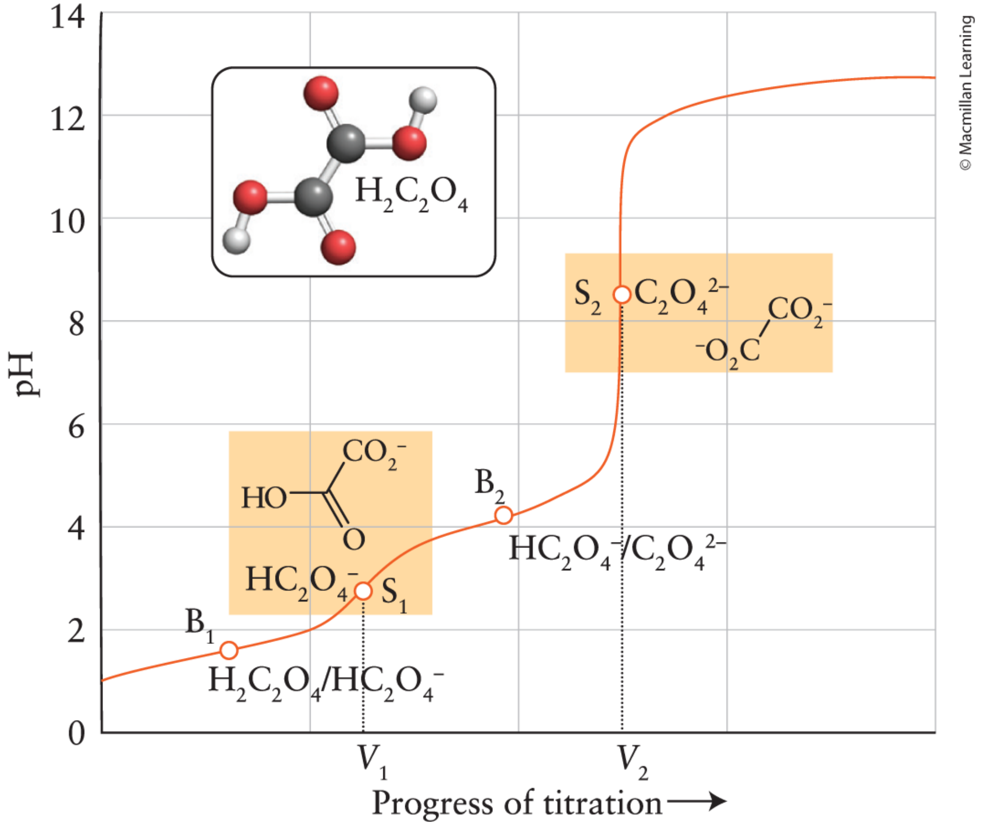
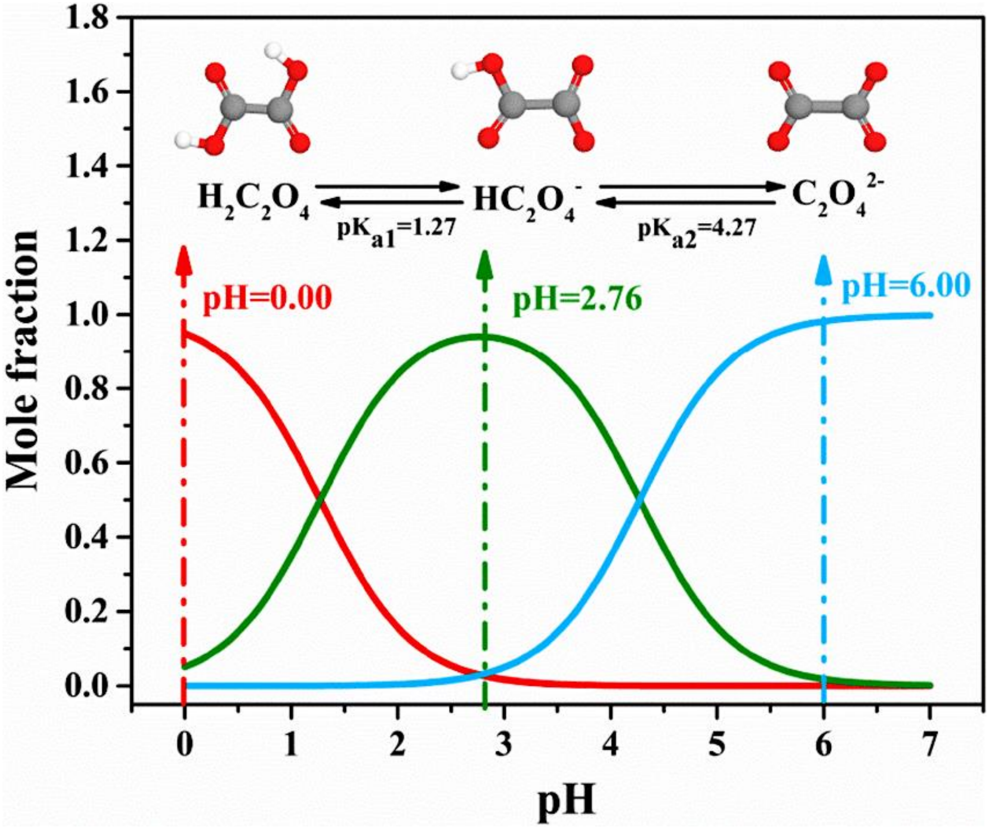
Titrations of polyprotic acids

- The titration of a polyprotic acid proceeds in the same way as a monoprotic acid, except there are many stoichiometric equivalency points since there are many acidic hydrogen atoms.



Chemical species in solution at different pH



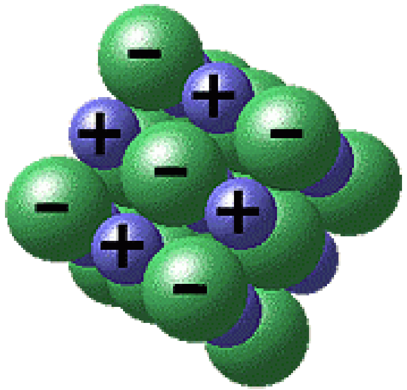
Neutralization reactions and salt

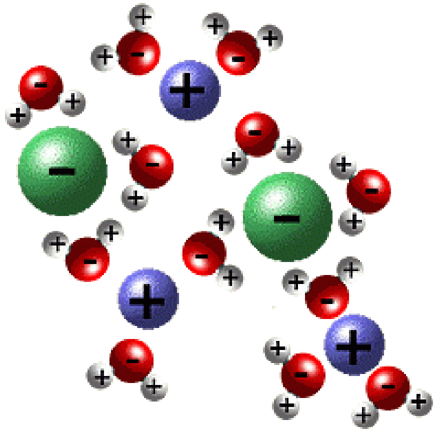
- One of the products of the neutralization reaction is **salt** (e.g., NaCl)

$$\mathbf{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

- Salts are **ionic compounds** consisting of the cation of the base and anion of the acid.

Solid form: crystal





In liquid: Dissolved into ions

- Due to their ionic nature, salts exhibit a tendency to form crystals in solid form, but they often dissolve readily in water dissociating into their constituent cations and anions.

Salts and pH

- The dissolution of certain salts can change the pH of an aqueous solution. The origins of this behavior are closely-related to the composition:

Base

"Acid"

$$CH_3COO^-Na^+(s) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + Na^+(aq) + H_2O(l)$$

- The products from the first reaction can proceed to create their own conjugate pairs:

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

Base ($pK_b = 9.25$)

Conjugate Acid ($pK_a = 4.75$)

Favourable 👍

$$Na^+(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NaOH(aq)$$

"Acid" ($pK_a = 13.8$)

Conjugate Base ($pK_b = 0.2$)

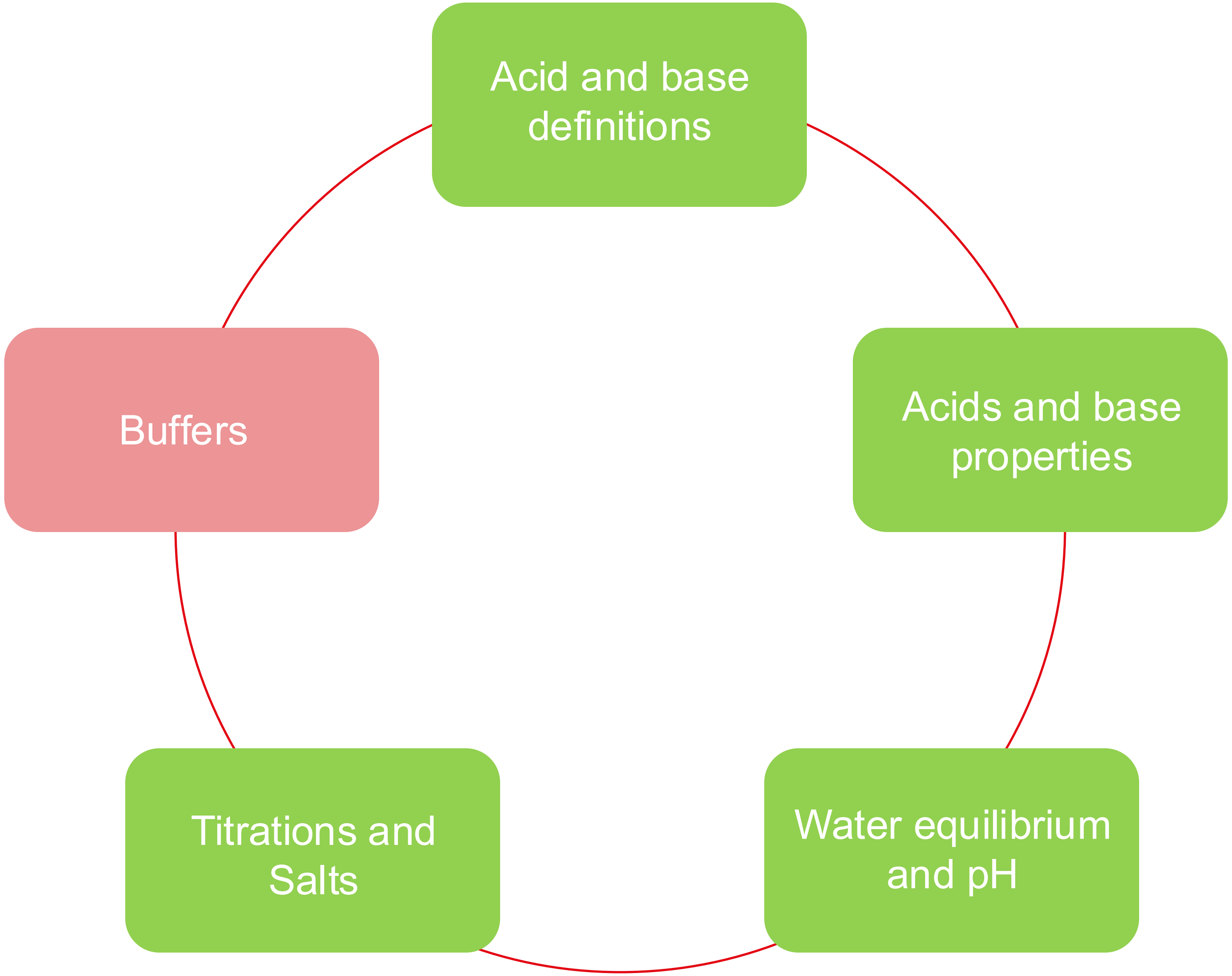
NOT Favourable 👎

Salts and pH

- The resulting pH upon dissolving salt will be influenced by the weak acids or bases released into the aqueous solution.

Parent acid	Parent base	Example salt	pH of solution	Reason
Strong acid	**Strong base**	NaCl, KNO_3	≈ 7 (neutral)	Neither ion hydrolyzes water; both are spectator ions.
Strong acid	**Weak base**	NH_4Cl, $AlCl_3$	< 7 (acidic)	Cation (NH_4^+, Al^{3+}) donates H^+ → acidic solution.
Weak acid	**Strong base**	Na_2CO_3, CH_3COONa	> 7 (basic)	Anion (CO_3^{2-}, CH_3COO^-) accepts H^+ → basic solution.
Weak acid	**Weak base**	NH_4CH_3COO	≈ 7 (depends)	Both ions hydrolyze water; pH depends on relative Ka and Kb values.

Plan



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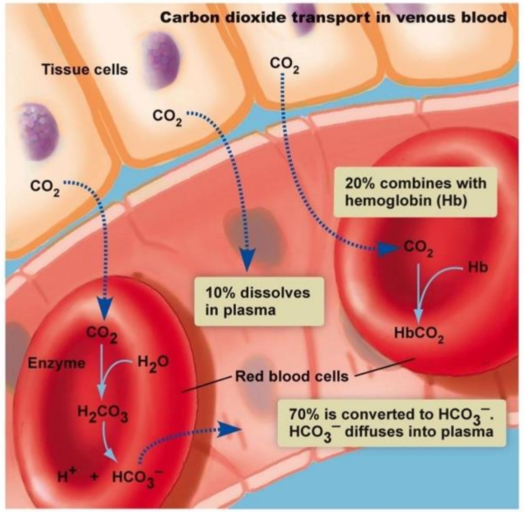
Buffers

Buffers

- A **buffer** is a solution that resists a change in pH when small amounts of strong acids or bases are added.
- Controlling the pH is how our body and environment advert wild acid or base concentration changes.
- In industry, maintaining pH balance of water is essential for manufacturing
- For farming, controlling pH optimizes growing conditions.
- In the laboratory, buffers are essential to produce, purify and maintain the integrity of biomolecules

Peter Dazeley/Getty Images.

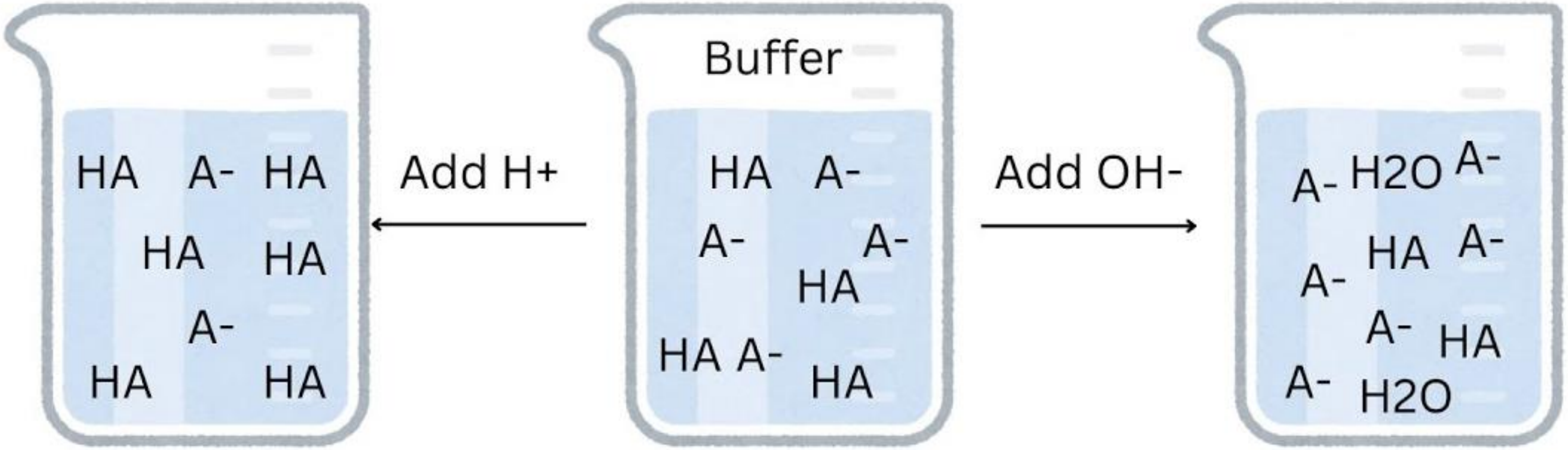


Carbon dioxide in blood produces bicarbonate which helps maintain the blood pH at 7.4

Buffers - Chemical Origins

- A buffer solution contains both a **source** and **sink** for protons (i.e., **HA** and **A$^-$**)

Buffer components (HA and A$^-$) bind H$^+$ and OH$^-$ and maintain the pH



- Through this they maintain the pH when new acids or bases are added to the system
- Typically, a weak acid and a conjugate weak base (e.g., CH_3COOH and CH_3COO^-).

Henderson-Hasselbalch equation

- If we consider a general example for weak acid - conjugate base equilibrium:

Acid

Conjugate base

$$\mathrm{HA\ (aq)} + \mathrm{H_2O\ (l)} \rightleftharpoons \mathrm{A^-\ (aq)} + \mathrm{H_3O^+\ (aq)}$$

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

- And then we apply negative $\log_{10}$ to both sides of the K_a equation we get:

$$-\log_{10} K_a = -\log_{10} [H_3O^+] - \log_{10} \frac{[A^-]}{[HA]} \qquad pK_a = pH - \log_{10} \frac{[A^-]}{[HA]}$$

- If we solve the previous equation for pH we get the **Henderson-Hasselbalch** equation:

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

Henderson-Hasselbalch equation

- HH equation allows to calculate the pH of the solution buffered by a weak acid/base under different experimental conditions

- Let's calculate the pH of a freshly made buffer solution containing:
  - **0.1 mol/L** CH_3COOH
  - **0.1 mol/L** CH_3COONa

pKa (CH_3COOH) = **4.75**

Total volume: **0.5 L**

$$\mathbf{CH_3COO^-Na^+(l) \rightarrow CH_3COO^-(aq) + Na^+(aq)}$$

Salt dissolves completely

$$\mathbf{CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-(aq)}$$

Buffer-making equilibrium

- We can use the assumption that change in concentration (x) is much lower than the starting concentration (HA and A^-) of each reagent. Ultimately, we get:

$$\mathbf{pH = 4.75 + \log_{10}\frac{0.1}{0.1} \approx 4.75}$$

Henderson-Hasselbalch equation

- HH equation allows to calculate the pH of the solution buffered by a weak acid/base under different experimental conditions

- Now let’s see what happens when we add
  - **0.5 L** of NaOH at **0.01 mol/L**

- Here, we first calculate the starting concentrations after dilution with 0.5 L volume:

Initial concentration after dilution: **$[CH_3COOH] = [CH_3COO^-] = 0.05$ mol/L**
Initial concentration of OH^- (from NaOH): **$[OH^-] = 0.005$ mol/L**

- Then we setup the reaction and table as before:

$$CH_3COOH\,(aq) + OH^-\,(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O\,(l)$$

	CH_3COOH	OH^-	CH_3COO^-
Initial	0.05	0.005	0.05
Equilibrium	0.05 - 0.005	0	0.05 + 0.005

Henderson-Hasselbalch equation

- If we use the new concentrations of HA and A^- to calculate the pH we get:

$$pH = 4.75 + \log_{10} \frac{0.055}{0.045} \approx 4.83$$

- This means that the total pH change caused by the addition of NaOH was:

$$\Delta pH = 4.83 - 4.75 = 0.08$$

- For comparison, if there was no buffering component, NaOH at 0.005 mol/L would yield:

$$pH\ (\text{no buffer}) = 11.70$$

Buffering components and their capacity

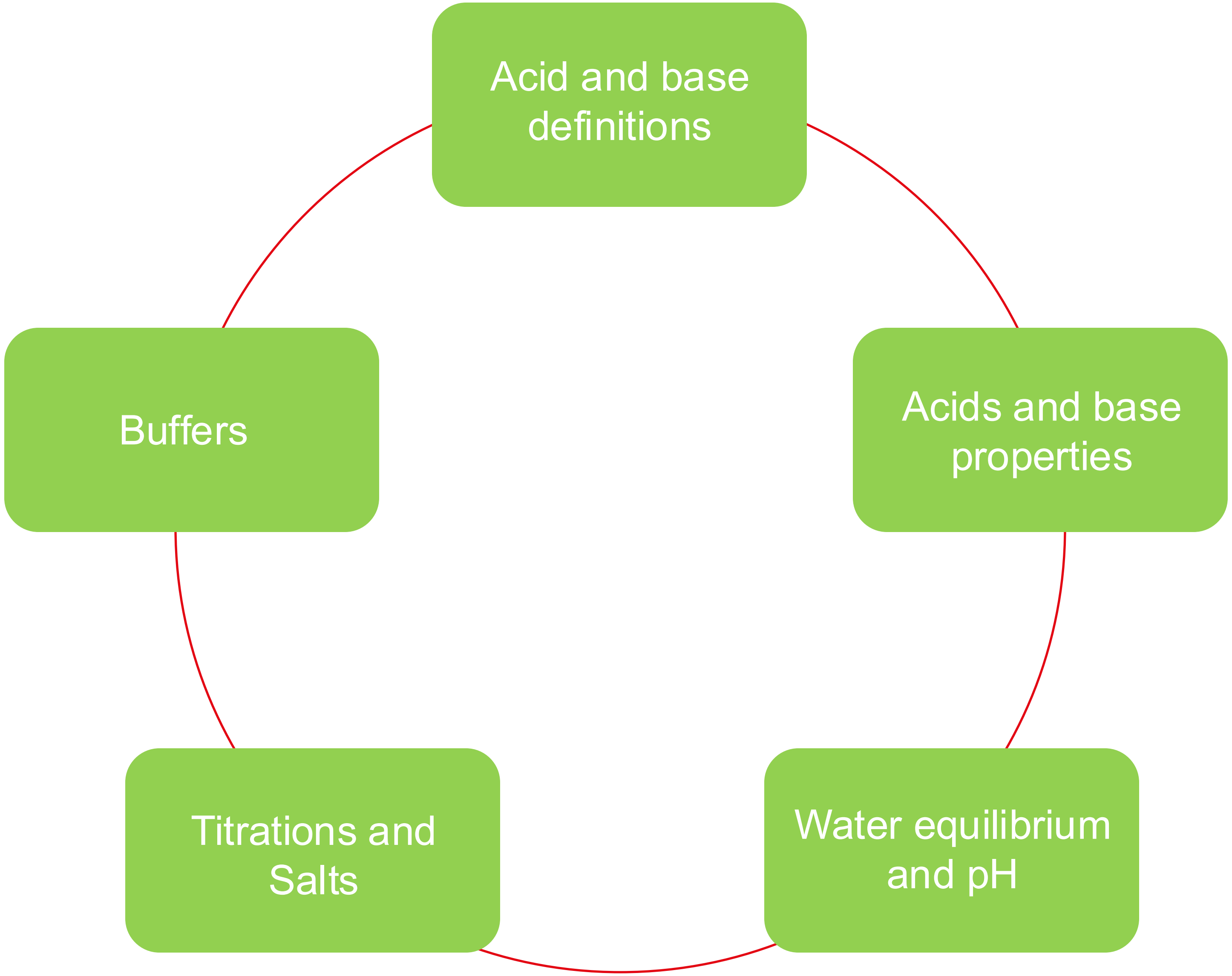
- Experimentally, a buffer works best when it is within ±1 pH range of the pKa of the buffering component.

- This is because the available conjugate acids and bases are at the highest relative level, allowing to absorb the highest amount of H^+ or release them (depending on the scenario)

- Weak acids of different pK_a values can be used to buffer around the desired optimal pH, usually imposed by experimental conditions

Optimal pH range	Acid / Conjugate Base	pK_a
4.7 ± 1	CH_3COOH / CH_3COO^-	4.75
7.2 ± 1	H_2PO_4- / HPO_4^{2-}	7.21
12.3 ± 1	HPO_4^{2-} / PO_4^{3-}	12.32
10.4 ± 1	HCO_3^- / CO_3^{2-}	10.33

Plan



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Have a beautiful day !

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