Abdelhafid Boussouf University Centre of Mila

Institute of Natural and Life Sciences,

Common Core Department

Abdelhafid Boussouf University Centre of Mila

Thermodynamic and Solutions Chemistry

Course Support

CHAPTER II: Acids and Bases

(Update : 10/02/2024)

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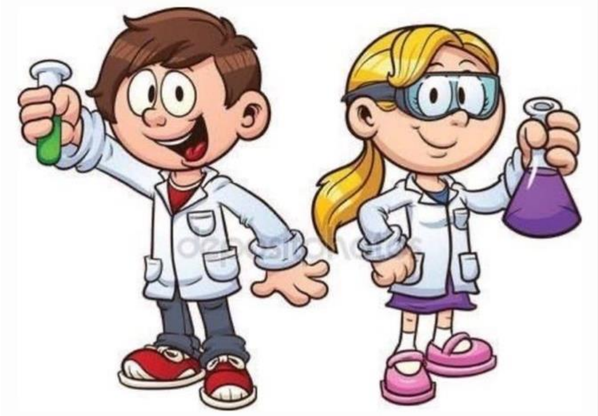


I Acids and bases:

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

Acids and bases are common solutions that exist everywhere. They have opposing chemical properties and are able to neutralize one another to form H_2O, which will be discussed later in a subsection. Acids and bases can be defined by their physical and chemical observations in the table below.

Table I.1. General Properties of Acids and Bases.

Acids	Bases
Produce a piercing pain in a wound	Give a slippery feel
Taste sour	Taste bitter
Are colorless when placed in phenolphthalein (an indicator)	Are pink when placed in phenolphthalein (an indicator)
Are red on blue litmus paper (a pH indicator)	Are blue on red litmus paper (a pH indicator)
Have a pH < 7	Have a pH > 7
Produce hydrogen gas when reacted with metals	
Produce carbon dioxide when reacted with carbonates	
Common examples: lemons, oranges, vinegar, urine, sulfuric acid, hydrochloric acid	Common examples: soap, toothpaste, bleach, cleaning agents, limewater, ammonia water, sodium hydroxide

Acids and bases in aqueous solutions will conduct electricity because they contain dissolved ions. Therefore, acids and bases are electrolytes, with strong acids and bases behaving as strong electrolytes versus weak acids and bases behaving as weak electrolytes.

In chemistry, acids and bases have been defined differently by three sets of theories: First is the Arrhenius definition, which relies on the idea that acids are substances that dissociate (break apart) in an aqueous solution to produce hydrogen (H^+) ions while bases produce hydroxide (OH^-) ions in solution. The other two definitions, discussed in detail in this chapter, include the Brønsted-Lowry definition, which defines acids as proton (H^+) donors and bases as proton acceptors, and the Lewis Theory of acids and bases, which states that acids are electron pair acceptors while bases are electron pair donors. As shown in Figure I.1, as the level of theory expands to include more substances covered under each definition, the closer the theory comes to accurately describing actual acid-base chemistry.

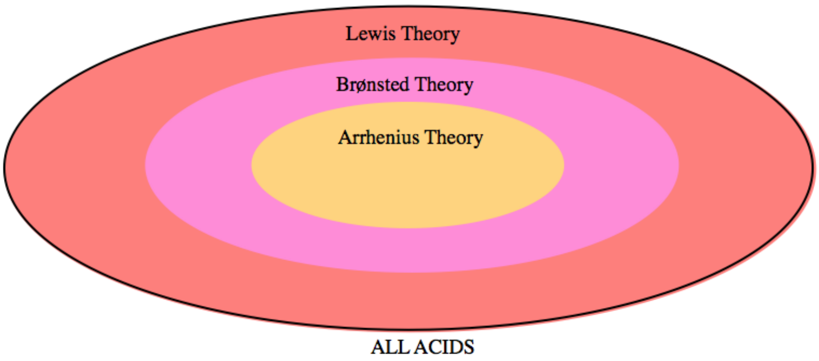


Figure I.1. A Venn diagram representing the three levels of acid classification theory. Arrhenius Theory is the least accurate, and covers only a small subset of substances. Brønsted-Lowry expands upon Arrhenius' definitions and thus is slightly broader. Lewis Theory, the most extensive explanation, most accurately describes all acid-base behavior.

I.1 Arrhenius Definition of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. The Arrhenius definition of acid-base reactions is a development of the "hydrogen theory of acids". It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

According to this theory, an **Arrhenius acid** is a compound that increases the concentration of H+ ions when added to water. This process is represented in what is known as a dissociation reaction in a chemical equation. For example:

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

In this reaction, hydrochloric acid (HCl) dissociates (breaks apart) into hydrogen (H^+) and chloride (Cl^-) ions when dissolved in water, thereby releasing H+ ions into solution.

An **Arrhenius base** is a compound that increases the concentration of hydroxide ions, OH^-, when added to water. For example:

$$\text{NaOH (aq)} \rightarrow \text{Na}^{+}\text{ (aq)} + \text{OH}^{-}\text{ (aq)}$$

In this reaction, an aqueous solution of sodium hydroxide (NaOH) dissociates into sodium ions (Na^+) and hydroxide ions (OH^-) when dissolved in water.

As you can imagine, this Arrhenius level of theory is quite limited. The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure liquid H_2SO_4 or a solution of HCl dissolved in toluene would not be considered to be acidic, despite the fact that both of these acids are known proton donors. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment, and the Arrhenius theory excludes many substances known to display acid-base character.

Another flaw in Arrhenius's theory is its reliance on the concept of dissociation of acids, i.e. an acid "HX" breaking apart in water to form H^+ and X^- ions. We now know that the H^+ cation does not actually exist in this form in aqueous solution; it is more accurately depicted as the hydronium ion, H_3O^+.

Therefore, since the Arrhenius level of theory can only describe acids and bases in an aqueous environment, relies on the flawed concept of acid dissociation, and excludes many substances based on its restrictive definitions, this theory can generally be disregarded moving forward in our discussion.

I.2 Brønsted-Lowry Definition of Acids and Bases

In 1923, the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry expanded upon Arrhenius's ideas by broadening the definitions of acids and bases. The Brønsted-Lowry theory centers on the proton, H^+. A proton is what remains when the most common isotope of hydrogen, ^1H, loses an electron. A compound that donates a proton to another compound is called a **Brønsted-Lowry** acid, and a compound that accepts a proton is called a **Brønsted-Lowry** base. An acid-base reaction is thus defined as the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

Using these very simple definitions, the Brønsted-Lowry level of theory covers the large majority of known acid-base behavior, and thus this theory can be successfully applied for most of this chapter (and this course). However, to be inclusive to all acids and bases, an even more general theory is required.

Acids may be inorganic or organic substances (e.g. HCl vs acetic acid, CH_3COOH), neutral substances or ions (e.g. H_2O vs HSO_4^-). Each of these species contains at least one hydrogen atom; to be defined as a Brønsted-Lowry acid, the substance must be able to donate this atom to another substance in the form of a proton, H^+. Bases may also be inorganic or organic substances (e.g. NaOH vs methyl amine, CH_3NH_2), neutral substances or ions (e.g. NH_3 vs $[Al(H_2O)_5OH]_2^+$). Each of these examples are capable of accepting a proton and may therefore be classified as Brønsted-Lowry bases. The most familiar and recognizable bases tend to be inorganic ionic compounds which contain the hydroxide ion, such as NaOH and $Ca(OH)_2$.

I.3 Lewis Definition of Acids and Bases

A Lewis acid is a chemical species that can accept a pair of electrons. In other words, it is an electron pair acceptor. Lewis acids often have an electron-deficient center, which can be a positively charged ion or a molecule with an incomplete octet of electrons. The most common example of a Lewis acid is a metal cation.

On the other hand, a Lewis base is a chemical species that can donate a pair of electrons. It is an electron pair donor. Lewis bases typically have a lone pair of electrons that they can share with a Lewis acid. A common example of a Lewis base is a molecule with an atom containing a lone pair of electrons, such as ammonia (NH_3) or water (H_2O).

Examples:

Lewis Acid: Aluminum chloride ($AlCl_3$)

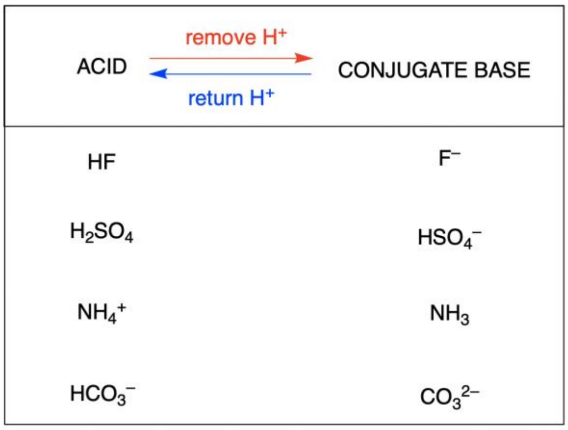
Aluminum chloride is a common Lewis acid because it can accept a pair of electrons. In this case, the aluminum atom is electron-deficient and can form a coordinate covalent bond with a Lewis base.

Lewis Base: Ammonia (NH_3)

Ammonia is a Lewis base because it has a lone pair of electrons on the nitrogen atom that can be donated to a Lewis acid. For example, ammonia can react with boron trifluoride (BF_3) to form a Lewis acid-base adduct. The Lewis acid-base concept is broader than the more traditional Bronsted-Lowry acid-base concept, as it allows for the description of reactions that involve the transfer of electron pairs rather than protons.

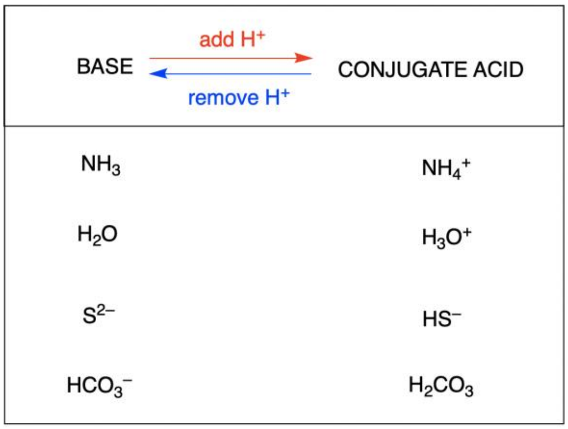
I.4 The conjugate base

The **conjugate base** of an acid is what remains after the acid has donated a proton. This species is a base because it can accept a proton to re-form the original acid:



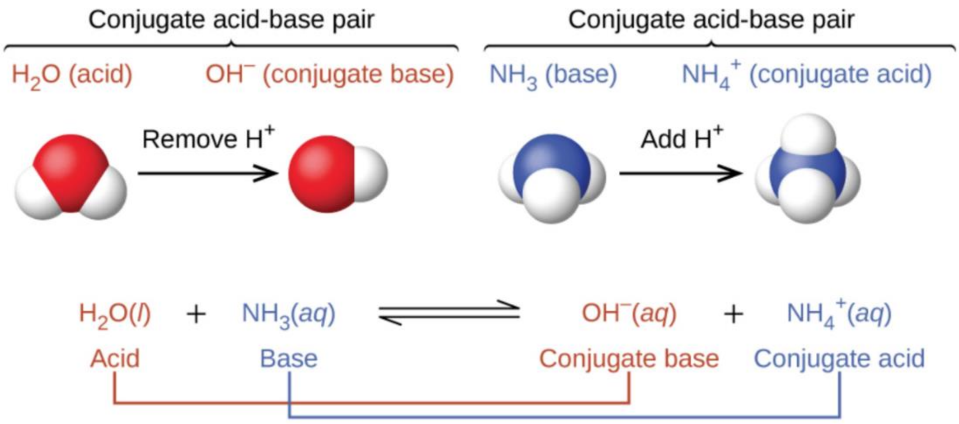
ACID	$\underset{\text{return } H^+}{\overset{\text{remove } H^+}{\rightleftarrows}}$	CONJUGATE BASE
HF		F^-
H_2SO_4		HSO_4^-
NH_4^+		NH_3
HCO_3^-		CO_3^{2-}

The **conjugate acid** of a base is what results after the base has accepted a proton. This species is an acid because it can give up a proton to re-form the original base:

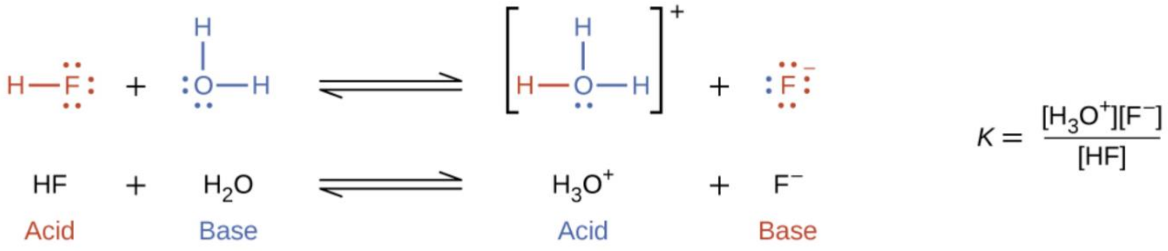


BASE	$\underset{\text{remove } H^+}{\overset{\text{add } H^+}{\rightleftarrows}}$	CONJUGATE ACID
NH_3		NH_4^+
H_2O		H_3O^+
S^{2-}		HS^-
HCO_3^-		H_2CO_3

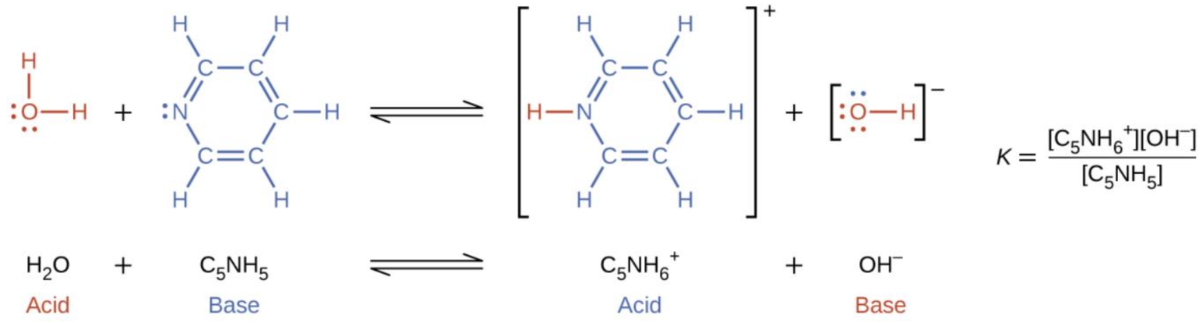
In the two schemes above, the behavior of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. This is quite useful when tasked with exercises asking you to classify reactions, Solution Stoichiometry when we discussed the three types of chemical reactions: acid-base, redox and precipitation reactions. If you can identify all four terms in a proton-transfer reaction (an acid, a base, a conjugate acid, and a conjugate base), you can be certain that it is a Brønsted-Lowry acid-base reaction. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



The reaction between a Brønsted-Lowry acid and base is called **ionization** (note how this differs slightly from the term dissociation defined previously). More specifically, when we add an acid to water, an **acid ionization** occurs, in which protons are transferred from the acid molecules to the water molecules. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



When we add a base to water, a **base ionization** reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter.

All acid-base reactions must have four terms in the chemical equation: an acid, a base, a conjugate acid, and conjugate base. If this is the case, then it can only be an acid-base reaction and not any other reaction type.

Since an acid-base reaction starts with two species and finishes two species, we should not use the term “dissociation” in the context of acids and bases (e.g. the dissociation of an acid in solution). The reason is because the term implies that one species dissociates into two, while in reality the acid-base reaction involves a proton transfer between two species.

II Definitions

"Monoprotic acid and base are terms used in the context of acids and bases, respectively:

a. monoprotic acids:

- A monoacid is a type of acid that can donate only one proton (hydrogen ion) per molecule when dissolved in water. In other words, it has one acidic hydrogen atom that can be ionized in a solution. Examples of monoacids include hydrochloric acid (HCl) and acetic acid (CH_3COOH).

b. Monobasic:

- A monobasic is a type of base that can accept only one proton (hydrogen ion) per molecule when dissolved in water. It has one basic site capable of accepting a proton to form a conjugate acid. Ammonia (NH_3) is an example of a monobasic as it can accept a proton to form ammonium ion (NH_4^+).

In summary, monoacid refers to an acid with one acidic hydrogen atom, while monobasic refers to a base with one basic site capable of accepting a proton.

"Polyacid" and "polybasic" are terms used in the context of acids and bases, respectively, to describe substances that can donate or accept multiple protons (hydrogen ions) in a solution:

c. Polyprotic acids

- A polyacid is an acid that can donate more than one proton (hydrogen ion) per molecule when dissolved in water. Polyacids have multiple acidic hydrogen atoms that can ionize in a solution. Examples of polyacids include sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4). These acids can release more than one proton during ionization reactions.

d. Polybasic:

- A polybasic is a base that can accept more than one proton (hydrogen ion) per molecule when dissolved in water. Polybasic have multiple basic sites capable of accepting protons to form conjugate acids. Examples of polybasic are certain metal oxides and hydroxides, such as calcium hydroxide [$Ca(OH)_2$], which can accept two protons.

In summary, polyacid refers to an acid with multiple acidic hydrogen atoms capable of donating more than one proton, while polybasic refers to a base with multiple basic sites capable of accepting more than one proton.

e. Ampholyte :

An ampholyte, also known as amphiprotic substance, is a molecule or ion that can behave as both an acid and a base. This dual nature allows ampholytes to either donate or accept protons (H^+ ions) depending on the conditions of the surrounding environment, particularly the pH.

In acidic conditions, an ampholyte tends to act as a base, accepting protons. In basic conditions, it acts as an acid, donating protons. The behavior of an ampholyte is determined by the specific environment it is placed in.

Water is a common example of an ampholyte because it can both donate a proton (acting as an acid) and accept a proton (acting as a base). Similarly, **amino acids** and **certain proteins** can also exhibit ampholytic behavior due to the presence of both acidic and basic functional groups in their structures.

Hydrogen sulfide (H_2S) is an example of an ampholyte. It can act as both an acid and a base depending on the conditions. The chemical equation for the ampholytic behavior of hydrogen sulfide is as follows:

1. As an acid (in the presence of a strong base):

$$H_2S+OH^- \rightarrow HS^- +H_2O$$

Here, hydrogen sulfide (H_2S) donates a proton (H^+) to hydroxide ions (OH^-) to form the bisulfide ion (HS^-) and water.

2. As a base (in the presence of a strong acid):

$$H_2S+H_3O^+ \rightarrow H_3S^+ +H_2O$$

In this case, hydrogen sulfide (H_2S) accepts a proton (H^+) from hydronium ions (H_3O^+) to form the hydro sulfonium ion (H_3S^+) and water.

This ability of hydrogen sulfide to both donate and accept protons makes it an ampholyte, demonstrating amphiprotic behavior. The specific behavior depends on the pH and the nature of the other substances present in the system.

A solution is considered **amphoteric** if it contains substances that can act as both acids and bases. In other words, an **amphoteric solution** can react with both acidic and basic substances.

III Acid-base reaction:

Acid–base reaction, a type of chemical process typified by the exchange of one or more hydrogen ions, H+, between species that may be neutral (molecules, such as water, H_2O; or acetic acid, CH_3CO_2H) or electrically charged (ions, such as ammonium, NH_4^+; hydroxide, OH^-; or carbonate, CO_3^{2-}). It also includes analogous behavior of molecules and ions that are acidic but do not donate hydrogen ions (aluminum chloride, $AlCl_3$, and the silver ion Ag^+).

An acid-base reaction involves two conjugated acid-base pairs that exchange protons:

Couple 1: Acid (1) / Base (1): Acid (1) $\rightleftharpoons$ Base (1) + H^+

Couple 2: Acid (2) / Base (2): Base (2) + H^+ $\rightleftharpoons$ Acid (2)

Acid-base reaction: Acid (1) + Base (2) $\rightleftharpoons$ Base (1) + Acid (2)

III.1. Acid-base reaction in aqueous solution.

Water is an ampholyte belonging to the following 2 pairs:

- Couple 1: H_3O^+/H_2O: $\rightleftharpoons$ H_3O^+ $H^+ + H_2O$ (water fixes H^+: it is a base)
- Couple 2: H_2O/OH^-: H_2O $\rightleftharpoons$ $H^+ + OH^-$ (water gives up H^+: it is an acid)

• The ampholytic character of water is then reflected by the superposition of reactions:

H_2O + H_2O $\rightleftharpoons$ OH^- + H_3O^+ ("**autoprotolysis** or **autoionization.**" reaction)

acid (1) + base (2) $\rightleftharpoons$ base (1) + acid (2)

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization.**

IV Equilibrium constant in acid-base reactions.

The equilibrium constant K of any acid-base reaction is given by the law of mass action:

$$a\,A + b\,B \underset{-1}{\overset{1}{\rightleftarrows}} c\,C + d\,D$$

$$\boxed{K = \frac{a_C^c \,.\, a_D^d}{a_A^a \,.\, a_B^b} = \frac{[C]_{éq}^c \cdot [D]_{éq}^d}{[A]_{éq}^a \cdot [B]_{éq}^b}}$$

where: aA, aB, aC and aD are the activities of species A, B, C and D at equilibrium and [A]éq, [B]éq, [C]éq and [D]éq the concentrations of these same species in equilibrium.

IV.1 Water dissociation equilibrium.

Pure water undergoes autoionization to a very slight extent. Only about two out of every billion (10^9) molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the **ion-product constant for water** (**K_w**):

H_2O (l) + H_2O (l) $\rightleftharpoons$ H_3O^+ (aq) + OH^- (aq) $K_w = [H_3O^+][OH^-]$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

IV.2 Acidity constant.

- When a weak acid AH is put in water, dissociation occurs:

AH + H_2O $\rightleftharpoons$ A^- + H_3O^+ (AH/A^- couple)

acid (1) + base (2) $\rightleftharpoons$ base (1) + acid (2)

The equilibrium constant for dissociation of the acid HA, called the “acidity constant” Ka, is written:

$$\boxed{K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{AH} \cdot a_{H_2O}} = \frac{[H_3O^+][A^-]}{[HA]}} \quad (a_{H_2O} = 1)$$

We set: pKa = - log Ka

V Strength of acids and bases.

- An acid is stronger the more easily it gives up an H+ proton.

$$AH + H_2O \underset{-1}{\overset{1}{\rightleftharpoons}} A^- + H_3O^+$$

The stronger an acid, the more the equilibrium is shifted in direction 1 and consequently the greater Ka is: Increasing acidity ⇔ $\boxed{K_a \nearrow ; pK_a \searrow}$

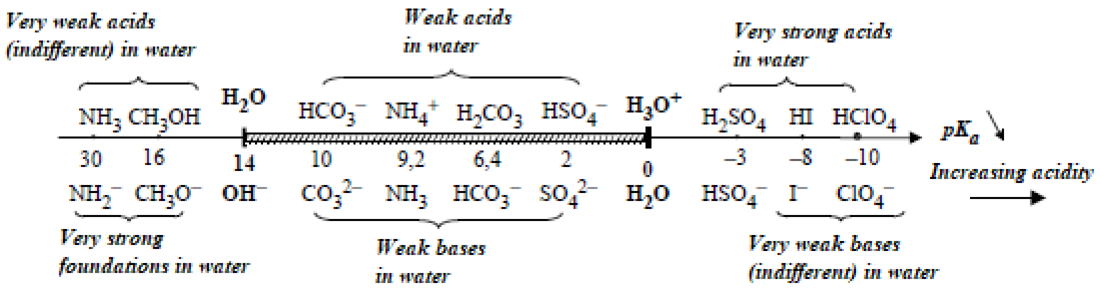
- A base is all the stronger the more easily it captures an H+ proton (the base protonates).

$$A^- + H_3O^+ \underset{-1}{\overset{1}{\rightleftarrows}} AH + H_2O$$

The stronger a base, the more the equilibrium is shifted in direction 1 and consequently the lower the constant Ka of the acid-base couple AH/A^-

increasing basicity ⇔ $\boxed{K_a \searrow \,;\, pK_a \nearrow}$

Examples of acid-base couples:



V.1 Direction of spontaneous evolution of acid-base reactions.

Consider the reaction between two acid-base couples:

$$\text{Acide(1)} + \text{Base(2)} \underset{-1}{\overset{1}{\rightleftharpoons}} \text{Base(1)} + \text{Acide(2)}$$

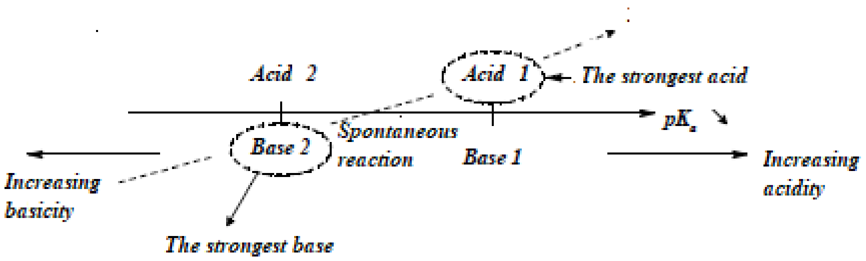
$$K = \frac{[\text{Base(1)}]\,[\text{Acide(2)}]}{[\text{Acide(1)}]\,[\text{Base(2)}]} = \frac{[\text{Base(1)}][\text{H}_3\text{O}^+]}{[\text{Acide(1)}]} \text{x} \frac{[\text{Acide(2)}]}{[\text{H}_3\text{O}^+][\text{Base(2)}]} = \frac{K_{a1}}{K_{a_2}} = \frac{10^{-pK_{a_1}}}{10^{-pK_{a_2}}} = 10^{pK_{a_2} - pK_{a_1}}$$

$$\boxed{K = 10^{\Delta(pK_a)}\ ;\ \textbf{With}\ \Delta(pK_a) = pK_{a_2} - pK_{a_1}}$$

First case: **K_{a1} > K_{a2} or pK_{a2} > pK_{a1}**: the equilibrium constant K is greater than 1.

The previous equilibrium is moved in direction 1.

The reaction therefore takes place between **the strongest base** (largest pK_a) and **the strongest acid** (lowest pKa).



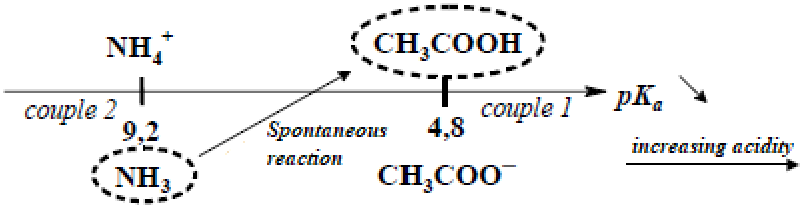
The spontaneous reaction is said to be quantitative or total when it consumes at least 99% of the limiting reagent. This is the case for $K > 10^4$ or $\Delta(pKa) > 4$.

Second case: **K_{a1} < K_{a2} or pK_{a2} < pK_{a1}**: the equilibrium constant K is less than 1.

The balance is shifted in direction -1.

Example of application: We consider the two couples NH_4^+/NH_3 and CH_3COOH/CH_3COO^-

The acid-base reaction is written as: $NH_3 + CH_3COOH \underset{-1}{\overset{1}{\rightleftarrows}} NH_4^+ + CH_3COO^-$



$$K_{éq} = \frac{K_{a_1}}{K_{a_2}} = 10^{(\Delta pK_a)} = 10^{(9,2-4,8)} = 10^{4,4} > 10^4$$

The reaction is quantitative (total) in sense 1.

VI pH (hydrogen potential).

VI.1 Definition of pH.

The pH, or hydrogen potential, is a measure of the acidity or basicity of a solution. It quantifies the concentration of hydrogen ions (H^+) in a solution. The pH scale ranges from 0 to 14, with 7 being neutral.

- A pH value less than 7 indicates an acidic solution, with lower values representing stronger acids.
- A pH value greater than 7 indicates a basic or alkaline solution, with higher values representing stronger bases.
- A pH of 7 is considered neutral, which means the concentration of H_3O^+ ions is equal to the concentration of hydroxide ions (OH^-) in the solution. Water at room temperature is an example of a neutral substance.

The pH is determined by the negative logarithm (base 10) of the hydrogen ion concentration:

$pH = -\log[H_3O^+]$

This relationship means that each unit change in pH represents a tenfold change in the hydrogen ion concentration. For example, a solution with a pH of 3 is ten times more acidic than a solution with a pH of 4. The pH scale is crucial in chemistry, biology, and environmental science, as it provides a standardized way to express the acidity or basicity of solutions.

VI.2 Domain or “predominance diagram”.

Any weak acid/base pair is characterized by its acidity constant:

$$K_a = \frac{[H_3O^+][Base]}{[Acid\ ]} \quad \Rightarrow \quad [H_3O^+] = \frac{K_a.[Acid\ ]}{[Base]} \qquad (1)$$

Knowing that: pH = - log $[H_3O^+]$ and pKa = - log Ka

$pH = pKa + \log \frac{[Base]}{[Acide]}$: Henderson relationship

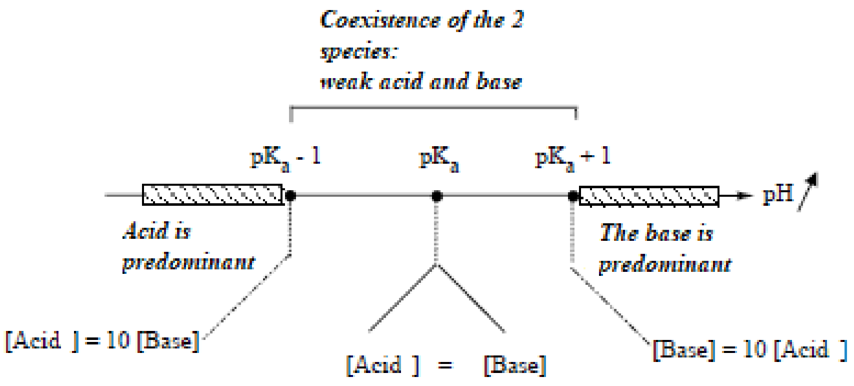
if pH = pKa, [Acid] = [Base]

if pH > pKa, [Acid] < [Base]: the base is the predominant species.

if pH < pKa, [Acid] > [Base]: acid is the predominant species.

A graphical representation delimiting the areas of concentration is called a “predominance diagram”.

The predominance diagram corresponding to the previous example is as follows:



The Henderson-Hasselbalch equation, often referred to as the Henderson equation or Henderson-Hasselbalch relationship, is a mathematical expression that describes the relationship between the pH of a solution and the ratio of its concentrations of weak acid (HA) and its conjugate base (A^-). The equation is commonly used in the context of buffer solutions.

The Henderson-Hasselbalch equation is given by:

$pH = pKa + \log \frac{[A^-]}{[AH]}$:

where:

- pH is the negative logarithm (base 10) of the hydrogen ion concentration in the solution.

- pKa is the negative logarithm (base 10) of the acid dissociation constant (Ka) of the weak acid.
- $[A^-]$ is the concentration of the conjugate base.
- [HA] is the concentration of the weak acid.

The Henderson-Hasselbalch equation is particularly useful for understanding and predicting the behavior of buffer solutions. **A buffer solution** is a solution that resists changes in pH when small amounts of acid or base are added to it. Buffers typically consist of a weak acid and its conjugate base (or a weak base and its conjugate acid), and the Henderson-Hasselbalch equation helps to quantify how the pH of the buffer changes in response to the addition of acidic or basic substances.

• When an acid (AH) or a base (B) is introduced into water, a reaction occurs between the substance introduced and the solvent (water):

VII Determination of pH.

VII.1 pH of water

Pure water at 25 degrees Celsius (77 degrees Fahrenheit) is considered neutral, and its pH is 7. The pH of water is determined by the concentration of hydrogen ions (H_3O^+) and hydroxide ions (OH^-). In neutral water, these concentrations are equal, leading to a pH of 7.

$[H_3O+] = [OH^-] = \sqrt{Ke} = 10^{-7}$ mol. L^{-1} ($Ke = [H_3O+]\,[OH^-] = 10^{-14}$)

The pH of pure water will be $pH = -\log [H_3O^+] = -\log 10^{-7} = 7 = \frac{1}{2} pKe = 7$

- Neutral solutions contain as many H_3O^+ ions as OH^- ions:

$[H_3O^+] = [OH^-] \Rightarrow pH = \frac{1}{2}\ pKe = 7$ at 25°C

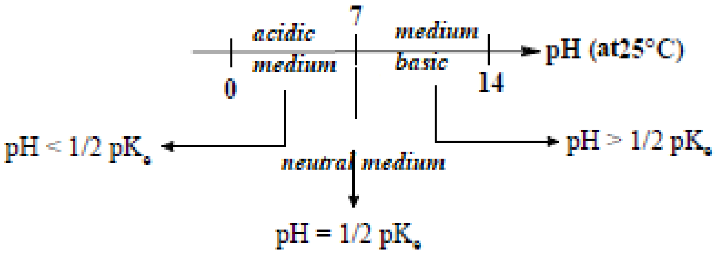
- Acidic solutions contain more H3O+ ions than OH- ions:

$[H_3O^+] > [OH^-] \Rightarrow pH < \frac{1}{2}\ pKw$, or $pH<7$ at 25°C

- Basic solutions contain fewer H_3O^+ ions than OH^- ions:

$[H_3O^+] < [OH^-] \Rightarrow pH > \frac{1}{2}\ pKw$, or $pH>7$ at 25°C

- Hence the pH scale:



VII.2 pH of a strong monoacid.

When a strong acid HA of initial concentration Co is dissolved in water, we have:

Complete dissociation of the acid $HA + H_2O \rightarrow H_3O^+ + A^-$

at t = 0 Co 0 0

at t = equilibrium 0 Co Co

- water autoprotolysis: $2\,H_2O \rightleftharpoons H_3O^+ + OH^-$

In the case of slightly diluted solutions ($Co > 3.10^{-7}$ mol. L^{-1}) the medium is sufficiently acidic so that $[OH^-]$ resulting from the autoprotolysis of water is negligible compared to $[H_3O^+]$.

We have: $[H_3O^+] = Co$ either: $pH = -\log [H_3O^+] = -\log Co$

Approximation validity:

A species such as OH^-, for example, is considered to be in the minority and therefore its concentration is negligible compared to that of $[H_3O^+]$ if: $[OH^-] \leq \frac{1}{10}[H_3O^+]$

By multiplying both sides by $[H_3O^+]$: $[H_3O+]\,[OH^-] = Ke < \frac{1}{10}\,[H_3O^+]^2$

at 25°C: $[H_3O^+]^2 \geq 10\ Ke = 10.10^{-14} = 10^{-13}$; $[H_3O^+] \geq 10^{-6.5}$; i.e. $pH \leq 6.5$

So, the formula: $pH = -\log Co$ is valid up to a pH equal to 6.5

Example: Hydrochloric acid HCl with initial concentration: $Co = 10^{-3}$ mol. L^{-1}

$pH = -\log Co = -\log 10^{-3} = 3 < 6.5$. The formula is therefore validated.

Indeed, we verify that $[H_3O^+] = 10^{-3} >> [OH^-] = \frac{10^{-14}}{10^{-3}} = 10^{-11}$

VII. 3. pH of a strong monobase.

When a strong base B of initial concentration Co is dissolved in water, we have:

Complete dissociation of the base $B + H_2O \rightarrow BH^+ + OH^-$

at t = 0 Co 0 0

at t = equilibrium 0 Co Co

- water autoprotolysis: $2\,H_2O \rightleftharpoons H_3O^+ + OH^-$

In the case of slightly diluted solutions ($Co > 3.10^{-7}$ mol. L^{-1}) the medium is sufficiently basic so that $[H_3O^+]$ resulting from the autoprotolysis of water is negligible compared to $[OH^-]$

We have: $[OH^-] = Co$ => $C_o = \frac{K_w}{[H_3O^+]}$ => $[H_3O^+] = \frac{K_w}{C_o} = \frac{10^{-14}}{C_o}$

pH = pKe + log Co = 14 + log Co at 25°C

This formula is valid for a calculated pH greater than 7.5: pH > 7.5

Example: NaOH soda solution with initial concentration: Co = 10^{-3} mol. L^{-1}

$$pH = 14 + \log Co = 14 + \log 10^{-3} = 11$$

VII. 4. pH of a weak monoacid.

VII. 4. 1. Calculation of pH.

Consider a solution of a weak monoacid HA with initial concentration Co. Two equilibria occur simultaneously:

Acid dissociation: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

Autoprotolysis of water: $2\,H_2O \rightleftharpoons H_3O^+ + OH^-$

Four species are present at equilibrium, in concentration: [HA], [A-], $[H_3O^+]$ and $[OH^-]$

We can write four relationships between these four unknowns:

- ion- product for water: $Kw = [H_3O^+]\,[OH^-]$ (1)
- acidity constant of the HA/A^-couple: $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ (2)

-conservation of the constituent elements of the acid-base couple:

$$C_o = [HA] + [A^-] \qquad (3)$$

- electroneutrality of the solution: $[H_3O^+] = [A^-] + [OH^-]$ (4)

The calculation leads to a 3rd degree equation in $[H_3O^+]$:

$$[H_3O^+]^3 + Ka\,[H_3O^+]^2 - (Kw + KaCo)\,[H_3O^+] - KwKa = 0$$

hence the need to simplify by making the following two approximations simultaneously:

1st approximation: "the medium is acidic": $[H_3O^+] >> [OH^-]$

For a pH below 6.5 ($[H_3O^+] > 3.10^{-7}$), $[OH^-]$ becomes negligible compared to $[H_3O^+]$.

This so-called "acidic medium" approximation is applicable except in the immediate vicinity of pH = 7.

Equation (4) then becomes: $[H_3O^+] = [A^-]$

2nd approximation: “the acid is weak”

Acid dissociation is weak; the concentration of the conjugated monobase A^- is negligible compared to that of the acid HA: $[A^-] << [HA]$.

This approximation will be verified *a posteriori* (after calculating the pH).

Equation (3) then becomes: Co = [HA]

The expression for Ka becomes: $K_a = \frac{[H_3O^+]^2}{C_o}$ ==> $[H_3O^+] = \sqrt{KaCo}$

So, $pH = \frac{1}{2}(pKa - \log Co)$

VII. 4. 2. Domain of validity of the approximation $[A^-] << [HA]$.

An acid is considered to be weakly dissociated if or $\frac{[A^-]}{[HA]} < 10^{-1}$ $\log\frac{[A^-]}{[HA]} < -1$;

By replacing in the equation $pH = pKa + \log\frac{[A^-]}{[AH]}$ from (2) pH < pKa - 1

Example: Calculate the pH of an acetic acid solution CH3COOH (pKa = 4.8) with a concentration Co = 10-1 mol. L^{-1}:

$$pH = 1/2\ (4{,}8 + 1) = 2{,}9$$

The formula which gives the pH is valid, since pH=2.9 < 4.8-1=3.8.

VII.5. pH of a weak monobase.

VII. 5. 1. pH calculation.

Consider a solution of a weak monobase B such as ammonia NH_3(aq) with initial concentration Co.

Two equilibria occur simultaneously:

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad \text{equivalent to: } B + H_3O^+ \rightleftharpoons BH^+ + H_2O$$
$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

Four species present are in equilibrium, in concentration: $[BH^+]$, [B], $[H_3O^+]$ and $[OH^-]$.

We can write the four relationships:

- ion- product for water: $Kw = [H_3O^+]\,[OH^-]$ (1)
- Ka of the BH+/B couple: $Ka = \frac{[H_3O^+]\,[B]}{[BH^+]}$ (2)
- Conservation of matter: Co = [B] + [BH+] (3)
- Electroneutrality: $[H_3O^+] + [BH^+] = [OH^-]$ hence $[BH^+] = [OH^-] - [H_3O^+]$ (4)

The calculation leads to a 3rd degree equation in $[H_3O^+]$:

$$[H_3O^+]^3 + (Co + Ka)\,[H_3O^+]^2 - Kw\,[H_3O^+] - Kw\,Ka = 0$$

Hence the need to simplify by making the following two approximations simultaneously:

1st approximation: “the medium is basic”: $[H_3O^+] << [OH^-]$

For a pH greater than 7.5, $[H_3O^+]$ becomes negligible compared to $[OH^-]$. This so-called approximation "Basic medium" is applicable except in the immediate vicinity of pH = 7.

Equation (4) then becomes: $[BH^+] = [OH^-]$

2nd approximation: "the base is little protonated"

Base protonation is weak; it hardly fixes the protons of water; the concentration of the conjugated acid BH^+ is negligible compared to that of the base B: $[BH^+] << [B]$.

This approximation will be verified *a posteriori* (after calculating the pH).

Equation (3) then becomes: Co = [B]

By replacing [B] and $[BH^+]$ in Ka, we have:

$$K_a = \frac{[H_3O^+].C_o}{[OH^-]} = \frac{[H_3O^+]^2.C_o}{K_w} \text{, d'où : } [H_3O^+] = (K_aK_w)^{1/2}.C_o^{-1/2}$$

Hence: $pH = -\log [H_3O^+] = -\frac{1}{2}\log Ka - \frac{1}{2}\log Kw + \frac{1}{2}\log Co$

Either: pH = (pKw + pKa + log Co)

Or: $pH = 7 + \frac{1}{2} pKa + \frac{1}{2}\log Co$ is valid if $[BH^+] << [B]$ (base is weakly protonated

protonation < 10%) => pH ≥ pKa + 1

Example: Calculate the pH of an ammonia solution NH_3 (pKa = 9.2) with a concentration Co = 10^{-2} mol. L^{-1}:

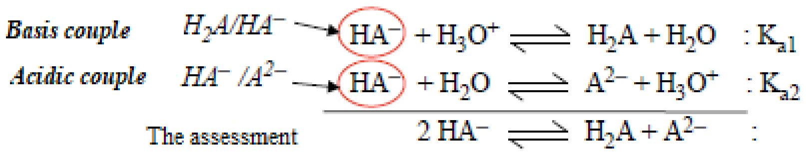
pH = 1/2 (14 + 9,2 - 2) = 10,6 (The formula which gives the pH is valid, since pH=10.6 > 9.2 +1=10.2)

VII.6. pH of an ampholyte solution.

Consider a solution of a NaHA salt (for example $NaHCO_3$) of concentration C. The total dissociation of the salt in water is written as:

$$NaHA_{(solid)} \xrightarrow{Water} Na^+_{(aq)} + HA^-_{(aq)}$$

HA^- is an ampholyte since it is the acid of the HA^-/A^{2-} couple and the base of the H_2A/HA^- couple. Two reactions involving HA- occur:



The assessment of this global reaction indicates that $[H_2A] = [A^{2-}]$

The Ka_1 product. Ka_2 is written:

$$K_{a1} \cdot K_{a2} = \frac{[H_3O^+][HA^-]}{[H_2A]} \frac{[H_3O^+][A^{2-}]}{[HA^-]} = [H_3O^+]^2 \frac{[A^{2-}]}{[H_2A]}$$

Hence: $Ka_1 . Ka_2 = [H_3O^+]^2$

Either: $pH = \frac{1}{2}(pKa1 + pKa2)$ => The pH is independent of C

VII.7. pH of saline solutions.

VII. 7. 1. pH of a solution of a salt of strong acid and strong base.

Example: NaCl (sodium chloride)

$$\bullet\ \underset{\text{Strong Acid}}{HCl} + \underset{\text{Strong Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{NaCl} + H_2O$$

- In aqueous solution, there is total dissolution of the salt:

$$NaCl \xrightarrow{\text{Water}} Na^+_{(aq)} + Cl^-_{(aq)}$$

Cl^-: conjugate base (very weak) of a strong acid (HCl). Cl^- is an indifferent or spectator ion; it does not participate in any acid-base equilibrium.

Na^+: spectator ion, conjugate acid (very weak) of a strong base (NaOH); it does not participate in any acid-base equilibrium.

pH (NaCl) = pH (pure water) = $\frac{1}{2}$ pKe = 7 at 25°C

VII. 7. 2. pH of a solution of a salt of strong acid and weak base.

Example: NH_4Cl (ammonium chloride)

$$\bullet\ \underset{\text{Strong Acid}}{HCl} + \underset{\text{Weak Base}}{NH_3} \longrightarrow \underset{\text{Salt}}{NH_4Cl}$$

- In aqueous solution, there is total dissolution of the salt:

$$NH_4Cl \xrightarrow{\text{Water}} Cl^-_{(aq)} + NH^+_{4(aq)}$$

Cl^-: spectator ion, very weak conjugate base of a strong acid (HCl).

NH_4^+: conjugate acid (weak) of the weak base NH_3 (pKa = 9.2)

$\Rightarrow$ pH (NH_4Cl) = pH (NH_4^+) $\Rightarrow$ pH of a weak acid

If $[OH^-] << [H_3O^{+]}$

$[NH_3] << [NH_4^+]$ (weakly dissociated acid)

$\Rightarrow pH = \frac{1}{2}(pKa - \log [NH_4^+])$

VII. 7. 3. pH of a solution of a salt of a weak acid and a strong base.

Example: CH_3COONa (sodium acetate)

- $\underset{\text{Weak Acid}}{CH_3COOH} + \underset{\text{Strong Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{CH_3COONa} + H_2O$

• In aqueous solution, there is total dissolution of the salt:

$$CH_3COONa \xrightarrow{\text{Water}} CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

Na^+: spectator ion, very weak conjugate acid of a strong base (NaOH)

CH_3COO^-: conjugate base (weak) of the weak acid CH_3COOH (pKa = 4.8)

$\Rightarrow$ pH (CH_3COONa) = pH (CH_3COO^-)$\Rightarrow$ pH of a weak base

If $[H_3O^+] << [OH^-]$

$[CH_3COOH] << [CH_3COO^-]$ (weakly protonated base)

$\Rightarrow pH = \frac{1}{2}\ (pKe + pKa + \log [CH_3COO^-])$

VII. 7. 4. pH of a solution of a salt of a weak acid and a weak base.

Example: CH_3COONH_4 (ammonium acetate) of concentration C (C = $[CH_3COONH_4]$)

- $\underset{\text{Weak Acid}}{CH_3COOH} + \underset{\text{Weak Base}}{NH_3} \longrightarrow \underset{\text{Salt}}{CH_3COONH_4}$

• In aqueous solution, there is <u>total dissolution</u> of the salt:

$$CH_3COONH_4 \longrightarrow CH_3COO^-_{(aq)} + NH_4^+{}_{(aq)}$$

• CH_3COO^- is the weak conjugate base of CH_3COOH, a weak acid.

$$CH_3COOH + H_2O \rightleftharpoons \boxed{CH_3COO^-} + H_3O^+ \quad : K_{a1}$$

• NH_4^+ is the weak conjugate acid of NH_3, weak base.

$$\boxed{NH_4^+} + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad : K_{a2}$$

However, the mixture of a weak acid and a weak base gives a weakly acidic or weakly basic solution $\Rightarrow$ pH is close to 7.
We show that if: $[H_3O^+] << C$ and $[OH^-] << C$, by making the product $Ka_1.Ka_2$:

$pH = \frac{1}{2}(pKa_1 + pKa_2)$: the pH is independent of C. Here: $pH = \frac{1}{2}(4.8 + 9.2) = 7$

VIII Buffer solution

• Buffer solution = mixture of a weak acid AH and its conjugate base A^- in equal or similar proportions (AH/A^- couple).
• Example: HA + NaA salt (solid)

- $NaA_{(s)} \xrightarrow{\text{eau}} Na^+_{(aq)} + A^-_{(aq)}$
- $AH + H_2O \rightleftharpoons A^- + H_3O^+$;

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

Either $[H_3O^+] = K_a \frac{[AH]}{[A^-]}$

or else: $pH = pKa + \log \frac{[A-]}{[AH]}$: Henderson relation, if $[A^-] = [AH] \Rightarrow pH = pKa$: maximum effectiveness of the buffer solution.

- In general, the pH of a buffer solution is between $4 < pH$ (buffer solution) < 10

$[H_3O^+]$ et $[OH^-] < 10^{-4}$ mol. L^{-1}

- For reasons of buffering efficiency: the concentrations C_1 of the weak acid AH and C_2 of the salt NaA are relatively high $\Rightarrow > 10^{-2}$ mol. L^{-1} therefore > at $[H_3O+]$ and $[OH^-]$.

Given that $[H_3O^+]$ and $[OH^-]$ are negligible compared to [AH] and [NaA], we can write:

$C_1 = [AH]$ AH: weak acid, poorly dissociated in water.

$C_2 = [A^-]$ NaA: salt completely dissolved in water.

The pH then becomes: $pH = pKa + \log \frac{\mathbf{C1}}{\mathbf{C2}}$

- Properties of buffer solutions.
- Buffer solutions have the property of minimizing pH variations caused by:
  - ✓ a (moderate) addition of acid or base.
  - ✓ a (moderate) addition of solvent (water): dilution
- Making a buffer solution:
  - ✓ weak acid HA + NaA salt (weak base A-).
  - ✓ weak acid HA + strong base (OH-), because OH^- “consumes” HA $\rightarrow A^-$
  - ✓ weak base A^- (NaA salt) + strong acid (H_3O^+), because H_3O^+ “consumes” $A^- \rightarrow$ HA

Example: Mixture of CH_3COOH (C1) and CH_3COONa (C2), with: $C_1 = C_2 = 10\text{-}1$ mol. L^{-1}

pH of the buffer mixture: $pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a + \log\frac{C_2}{C_1} = pK_a = 4{,}8$

We add n_1 moles of HCl (strong acid) to 1 L of this buffer (with: $n_1 = 10^{-2}$ mol).

What is the new pH? (we assume that the volume remains equal to 1 L after adding HCl).

The addition of HCl causes the reaction: $CH_3COO^- + H^+ \rightarrow CH_3COOH$

n1 moles of CH_3COO^- are “consumed” and n1 moles of CH_3COOH are formed:

$$pH = pK_a + \log\frac{10^{-1} - 10^{-2}}{10^{-1} + 10^{-2}} = pK_a + \log\frac{0{,}09}{0{,}11} = 4{,}7$$

IX Acid-base dosages.

IX.1. Acid-base equivalence.

· In the case where each acid (or base) molecule releases (or captures) one or more protons, the balance equation for the dosage is written:

$$\begin{array}{ll} [\,\text{acid}\ (1) + \lambda_1\, H_2O \rightleftharpoons \text{base}(1) + \lambda_1\, H_3O^+\,] & x\,\lambda_2 \\ [\,\text{base}(2) + \lambda_2\, H_3O^+ \rightleftharpoons \text{acid}\ (2) + \lambda_2\, H_2O\,] & x\,\lambda_1 \\ \hline \lambda_2\,\text{acid}\ (1) + \lambda_1\,\text{base}(2) \rightleftharpoons \lambda_2\,\text{base}(1) + \lambda_1\,\text{acid}\ (2) & \end{array}$$

We thus define "successive equivalences" and "global equivalence": 1st equivalence, 2nd equivalence, *etc*…

· At equivalence, the number of protons released by the acid (1) is equal to the number of protons fixed by the base (2):

λ_1 . n acid (1) = λ_2. n base (2) (n = nb de moles)

Either to the equivalence: $\lambda_1 C_1 V_1 = \lambda_2 C_2 V_2$ Or $\lambda_a C_a V_a = \lambda_b C_b V_b$

with: λa = number of protons released by one mole of acid and λb = number of protons fixed by one mole of base.

At equivalence, the acid and the base have exchanged the same number of protons:

λa n acid (1) (initial) = λb n base (2) (paid for equivalence)

Example 1: Determination of the 1st acidity of H_3PO_4 using the strong OH^- base.

Strong base volume to be added to reach the 1st equivalence (H_3PO_4 involves 1 proton):

$$1\ H_3PO_4 + 1\ OH^- \longrightarrow H_2PO_4^- + H_2O \qquad \lambda b = 1\ ;\ \lambda a = 1$$

At the first equivalence $\lambda_a C_{H3PO4} V_{H3PO4} = \lambda_b C_{OH^-}\ V_{OH^-} \Rightarrow 1\ n_{H3PO4}(\text{initial}) = 1\ n_{OH^-}$ (equivalence)

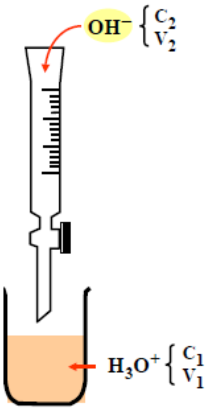
Example 2: Volume of strong base poured to the global equivalence (3rd acidity of H_3PO_4: 3 protons involved per mole of acid):

$$1\ H_3PO_4 + 3\ OH^- \longrightarrow PO_4^{3-} + 3\ H_2O \qquad \lambda b = 1\ ;\ \lambda a = 3$$

At global equivalence: $\lambda_a\ [H_3PO_4]\ V_{H3PO4} = \lambda_b\ [OH^-]\ V_{OH^-} \Rightarrow 3\ n_{H3PO4(\text{initial})} = 1\ n_{OH^-}$ (equivalence)

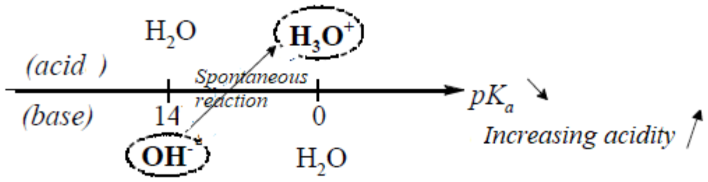
IX .2 . Dosage of a strong monoacid with a strong monobase.

$$HCl \xrightarrow{Water} H_3O^+ + Cl^-$$
$$NaOH \xrightarrow{Water} Na^+ + OH^-$$



The Cl- and Na+ ions being indifferent, the overall reaction which occurs is therefore:

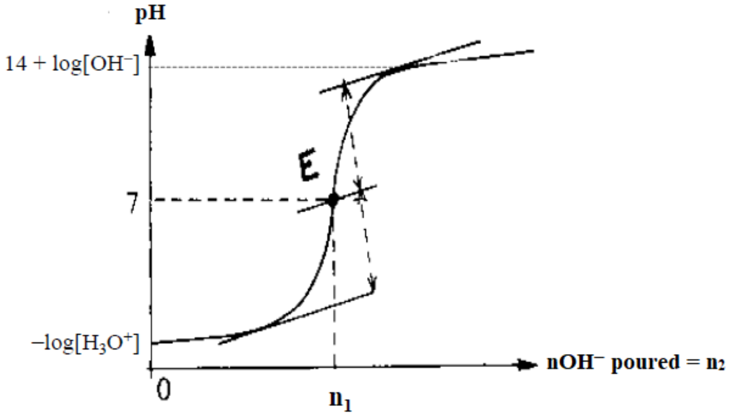
$OH^- + H_3O^+ \rightarrow 2\ H_2O$ $K = 10^{(14-0)} = 10^{14}$



$K > 10^4$, we can therefore consider that the reaction is total (quantitative): $OH^- + H_3O^+ \rightarrow 2H_2O$

The study of an acid-base dosage reaction generally consists of following the evolution of the pH of the solution as a function of the volume V_2 of reagent added (or the number of moles $n_2 = C_2V_2$).

Shape of the pH graph = f (moles of OH- added).

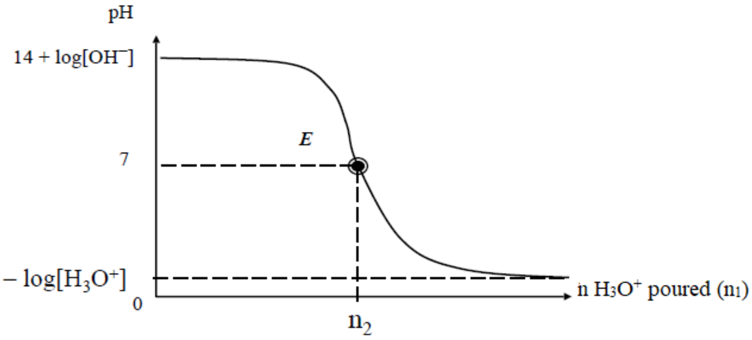


The reaction is total

	Before equivalence: n1 > n2			Equivalence n1 = n2			After equivalence: n1 <n2		
Number of moles	H_3O^+ +	$OH^- \rightarrow 2\ H_2O$		$H_3O^+ + OH^- \rightarrow 2\ H_2O$			$H_3O^+ + OH^- \rightarrow 2\ H_2O$		
Initial state	C_1V_1	C_2V_2	—	C_1V_1	C_2V_2	—	C_1V_1	C_2V_2	
Final state	$C_1V_1 - C_2V_2$	~ 0	—	~ 0	~ 0	Water	~ 0	$C_2V_2 - C_1V_1$	
Final state: H_3O^+ $pH = -\log\left[H_3O^+\right] = -\log\frac{nH_3O^+}{V_{tot}}$ $pH = -\log\frac{C_1V_1 - C_2V_2}{V_{tot}}$				pH = 7			Final state: OH^- $pH = 14 + \log[OH^-]$ $= 14 + \log\frac{C_2V_2 - C_1V_1}{V_{tot}}$		

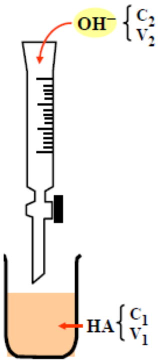
IX .3 . Dosage of a strong monobase with a strong monoacid.

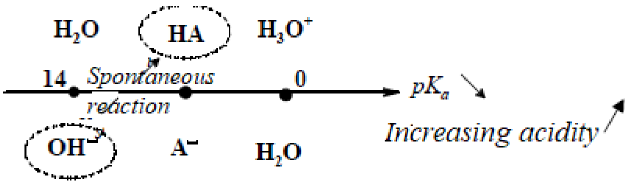
Very similar calculations make it possible to determine the pH during the dosage. We obtain the graph:



IX .4. Determination of a weak monoacid by a strong monobase.

The balance equation for the dosage reaction between the weak acid HA and the strong base OH^- is written: $HA + OH^- \longrightarrow A^- + H_2O$ $K = 10^{(pKe - pKa)}$





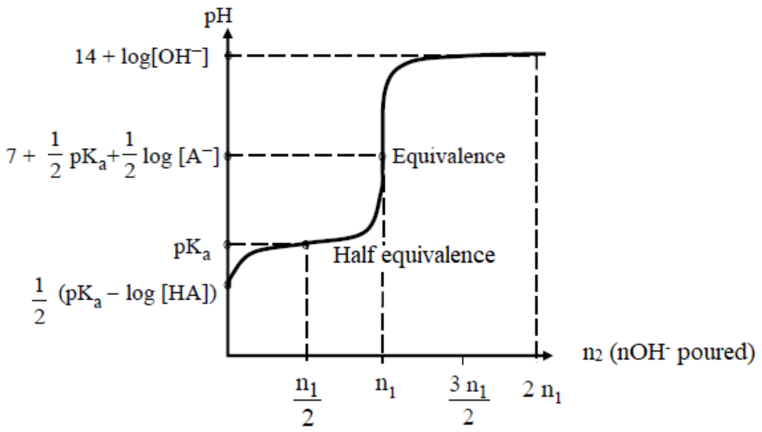
If K is greater than 10^4, the reaction is considered to be quantitative (total).

Example: $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$ pKa = 4.8

$K = 10^{(14 - 4.8)} = 10^{9.2} > 10^4 \Rightarrow$ total reaction

Dosage of a weak monoacid with a strong monobase

Appearance of the graph: pH = f (nOH^- poured)



	n2 < n1				n1 = n2				n2 >n1			
Number of moles	$HA + OH^- \rightarrow A^- + H_2O$				$HA + OH^- \rightarrow A^- + H_2O$				$HA + OH^- \rightarrow A^- + H_2O$			
Initial state	C_1V_1	C_2V_2	~ 0	~ 0	C_1V_1	C_2V_2	~ 0	~ 0	C_1V_1	C_2V_2	~ 0	~ 0
Final state	$C_1V_1 - C_2V_2$	~ 0	C_2V_2	—	~ 0	~ 0	C_1V_1 Or C_2V_2	—	~ 0	$C_2V_2 - C_1V_1$	C_1V_1	—
Final state: [HA]; [A⁻] The pH is calculated using the couple HA/A⁻ ; or : $pH = pKa + \log \frac{[A-]}{[HA]}$					Final state: [HA] and [A⁻] ~ 0 ⇒The A⁻ base imposes the pH If $[HA] << [A^-] et [H_3O^+] << [OH^-]$				Final state: [OH⁻] and [A⁻] The pH is imposed by the base strong: OH⁻			
$pH = pKa + \log \frac{C2V2/Vtotal}{C1V1-C2V2/Vtotal}$					$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log \frac{C2V2}{Vtotal}$				$pH = 14 + \log \frac{C2V2-C1V1}{Vtotal}$			

- **Before equivalence: n2 < n1**

The medium is acidic: $[H_3O^+] >> [OH^-]$. At equilibrium, we have:

$n_{HA} = n_1 - n_2$: $[HA] = \frac{C1V1-C2V2}{V1+V2}$

$n_{A^-} = n_2$: $[A^-] = \frac{C2V2}{V1+V2}$

The pH of the mixture is given by: $pH = pKa + \log \frac{[A-]}{[HA]}$

At half-equivalence: $n_2 = \frac{1}{2} n_1 \Rightarrow pH = pKa$ because: $[HA] = [A^-]$ - it is a buffer mixture

- **At equivalence: $n_1 = n_2$**

From the balance sheet, we see that the pH of the solution is then imposed by the weak monobase A^-. Assuming $[HA] << [A^-]$ and $[OH^-] >> [H_3O^+]$:

pH = $\frac{1}{2}$ (pKe + pKa + log [A⁻]) = 7 + $\frac{1}{2}$ pKa + $\frac{1}{2}$ log [A⁻]

N.B.: At equivalence, the solution is basic.

After the equivalence: n2 > n1: ($n_{OH^-} > n_{H3O^+}$)
The equilibrium solution consists of a mixture of 2 bases OH^- and A^-:

- a strong OH^- base of concentration: $[OH^-] = \frac{n2-n1}{V1+V2} = \frac{C2V2-C1V1}{V1+V2}$

- a weak base A^- of concentration: $[A^-] = \frac{n1}{V1+V2} = \frac{C1V1}{V1+V2}$

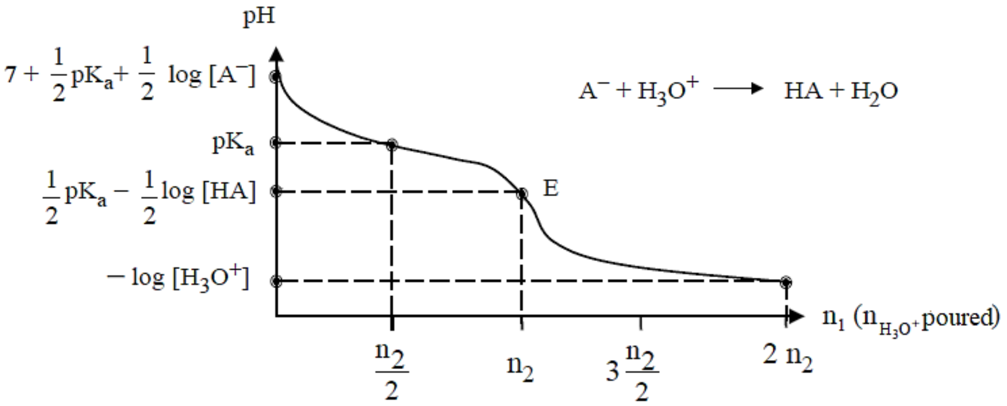
The pH of the mixture of the two bases is imposed by that of the strong base:

Hence: pH = 14 + log [OH^-] or: pH = 14 + log $\frac{C2V2-C1V1}{V1+V2}$

IX .5. Dosage of a weak monobase with a strong monoacid.

Dosage of a weak monobase with a strong monoacid

Appearance of the pH graph = (n_{H3O^+} poured)



At equivalence, the medium is acidic (the pH is imposed by the weak acid HA).