

# 10

## Acids & Bases

**A**CIDS and bases are very important chemicals in our everyday life. Think about vinegar or Sour Patch Kids. On one hand, vinegar tastes sour as it contains acetic acid. Sour Patch Kids, on the other hand, are coated in a combination of sugar and acids. Acids help us digest food and help bacteria produce yogurt or cottage cheese. Bases on the other hand are used in drain openers, oven cleaners, or the production of soap. This chapter covers the properties of acids and bases qualitatively and quantitatively. You will learn how to identify each of these chemicals and categorize them according to their strength. Yes! acids and bases are strong, and some of them can seriously hurt you. More importantly, this chapter introduces the idea of PH, which quantifies the acidity of a solution. The PH of an acid or base depends on its strength and here we will cover how to compute the PH of solutions of strong and weak acids and bases. Balancing PH is crucial for health. Finally, we will briefly cover the idea of a buffer that helps regulate the PH of solutions and titrations used to elucidate the molarity of an unknown acid or base.



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### 10.1 The nature of acids and Bases

*Acids and bases* Acids have very different properties than bases. Acids are acidic, have a sour taste, and can sting to the touch. Bases are basic, have a bitter–chalky–taste, and they feel soapy–slippery–to the touch. On one hand, acids are extensively used in the food and perfume industry. For example, vinegar—a liquid solution of acetic acid—is used in pickles and food preparations. On the other hand, lemon and orange juice, containing citric acid, is used in the preparation of effervescent salts and as food preservatives. Acids are also used in the production of batteries. For example, car batteries contain corrosive sulphuric acid. On the other hand, bases are extensively used in manufacturing. As a first example, sodium hydroxide is used in the manufacture of soap, medicines, and even paper. As a second example, calcium hydroxide—also known as slaked lime—is used to neutralize the acid in water supplies or as an antidote for food poisoning. This hydroxide is also used in the construction industry, mixed with sand and water to make mortar. As a third example, potassium hydroxide (KOH), is used in alkali batteries. Finally, ammonia is an extensively used cleaning product, also used to remove ink spots from clothes or grease from window-panes.

*Strong and weak acids and bases* Strong acids are strong electrolytes that completely dissociate to produce protons. Similarly, strong bases completely dissociate in solution generating hydroxyls. On the contrary, weak acids and bases are just weak electrolytes that dissociate partially in solution generating only a small amount of

protons and hydroxyls. The dissociation of strong acids and bases is represented by means of a single arrow, whereas the dissociation of weak acids and bases is represented by means of a double harpoon. For example, hydrochloric acid is a strong electrolyte and its dissociation is represented by

▼ Hydrofluoric acid is a weak acid used to dissolve glass.



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whereas hydrofluoric acid is a weak electrolyte and its dissociation is represented by



▼ Citrus such as lemons or oranges are acidic.



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▼ Pickles contain vinegar that is a solution of acetic acid in water.



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*Arrhenius acid-base model* In general terms, we can identify some acids and bases by inspecting its formula. Svante Arrhenius claimed around 1884 that acids are acidic because contain hydrogen in their structure and when dissolved in water they produce *protons*:  $\text{H}^+$ , also called hydronium ion written as  $\text{H}_3\text{O}^+$ . Let us consider these chemicals: HF,  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . All these chemicals, named hydrofluoric acid, sulfuric acid, and nitric acid, are Arrhenius acidic. The reaction below described the process of dissociation of hydrogen chloride to produce chloride and a proton:

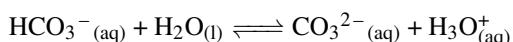


Based on the acid dissociation reaction above, we say chloride is the result of deprotonating hydrochloric acid. In other words, chloride is deprotonated. Based on this dissociation reaction that happens in water, we can say hydrogen chloride also known as hydrochloric acid is an Arrhenius acid, as it produces protons in water. We have that acids are classified as monoprotic, diprotic, and polyprotic. Monoprotic acids have only one acidic H on their molecule (e.g.  $\text{HNO}_3$ ), whereas diprotic acids have two (e.g.  $\text{H}_2\text{NO}_4$ ) and polyprotic acids have more than two (e.g.  $\text{H}_3\text{PO}_4$ ). Differently, bases are basic because when dissolved in water they produce *hydroxyls*:  $\text{OH}^-$ . Hydroxides are Arrhenius bases and for example, NaOH and  $\text{Ca}(\text{OH})_2$ , named sodium hydroxide and calcium hydroxide, are well-known bases. Let us address now the dissociation of sodium hydroxide in water:



This chemical is an Arrhenius base as it produces hydroxyls. Therefore, Arrhenius acids and bases produce protons and hydroxyls in water, respectively. However, the Arrhenius model does not explain why chemicals unsolved in water can also be acidic or even why chemicals such as  $\text{NH}_3$ —a molecule without OH on its structure—can be basic.

*Brönsted-Lowry acid-base model* In 1923 two different chemists Thomas Lowry and Johannes Brönsted proposed what is now known as the Brönsted-Lowry model of acids and bases. The Brönsted-Lowry model is a more advanced acid-base model. This model claims acids are chemicals that give away protons ( $\text{H}^+$ ) whereas bases receive protons. This way, Brönsted-Lowry extends the Arrhenius model to other solvents different than water, as the solvent is not part of the definition. Based on this model, we can understand how  $\text{HCO}_3^-_{(\text{aq})}$  can act as an acid giving away protons to water and as a base receiving protons from water. When acting as an acid:



When acting as a base:



As you can see, an acid-base reaction is essentially a proton transfer reaction, in which a proton  $\text{H}^+$  transfers from an acid into a base. Compounds that can act as acid or bases are referred to as *amphiprotic* as they can act as a proton donor or acceptor. Other examples are:  $\text{H}_2\text{O}$ ,  $\text{HS}^-$  or  $\text{HSO}_4^-$ . Still, the Brönsted-Lowry model does not explain why chemicals such as ammonia are a base and carbon dioxide an acid. In particular, the model does not justify what structural particularity makes ammonia behave as a base and carbon dioxide (with no hydrogen on its structure) as an acid.

### Sample Problem 1

Identify the following chemicals as Arrhenius acids or bases and give their names:  $\text{HCl}$ ,  $\text{KOH}$ ,  $\text{H}_3\text{PO}_4$  and  $\text{CH}_3\text{COOH}$ .

#### SOLUTION

The acids are:  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$  and  $\text{CH}_3\text{COOH}$ . Their names are: hydrochloric acid, phosphoric acid and acetic acid, the later is a common name.  $\text{KOH}$  is a base called potassium hydroxide.

#### ❖ STUDY CHECK

Identify the following chemicals as Arrhenius acids or bases and give their names:  $\text{NaOH}$  and  $\text{H}_2\text{CO}_3$ .

▼ Bath bombs are made of acidic and basic ingredients that combine in water to make a fizzy bath time experience.

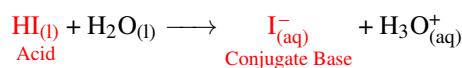


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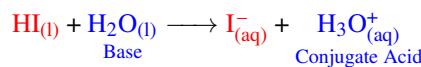
## 10.2 Dissociation of acids and bases

This second section will cover the acid and base dissolution in water. Water plays a key role in the acid-base character of a chemical as these chemicals ultimately react with water. When acids and bases solve in water, they dissociate producing a byproduct called the conjugate base and conjugate acid. We will describe how to set up the dissociation equilibrium and how to identify conjugate acid-base pairs.

*Conjugate acids and bases* A conjugate acid-base pair are molecules or ions related by the loss of one  $\text{H}^+$ . For example: hydroiodic acid  $\text{HI}$  and iodate  $\text{I}^-$  or water  $\text{H}_2\text{O}$  and protons  $\text{H}_3\text{O}^-$ . The product of the dissociation of an acids is a conjugate base. For example:



Similarly, bases produce a conjugate acid. In the example below, water acts as a base and a proton is the conjugate acid:



At the same time acids react with bases as they have opposite character. Following the previous example:



▼ Ashes are basic.



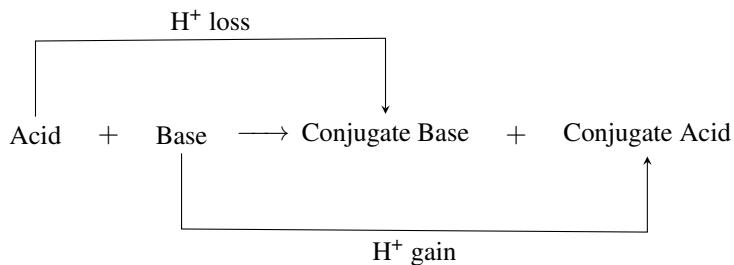
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▼ Limestone reactant with hydrochloric acid to give carbon dioxide bubbles.



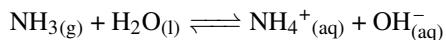
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Hence, we have that an acid reacts with a base to produce a conjugate base and a conjugate acid. We can use the diagram below to identify the acid-conjugate base pairs:



### Sample Problem 2

Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:



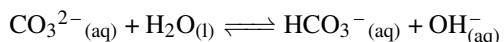
### SOLUTION

The trick is first identifying the acid and the base starting for the left side of the formula. In this case  $\text{NH}_3\text{(g)}$  is the base and hence water is the acid. Now connect the acid and the base with the other side of the arrow, and use conjugate with the opposite term. For example:  $\text{NH}_3$  is a base and should be related with  $\text{NH}_4^+$  that is the conjugate acid. Similarly,  $\text{H}_2\text{O}$  is an acid, being related with  $\text{OH}^-$  that is the conjugate base. In summary:



### ❖ STUDY CHECK

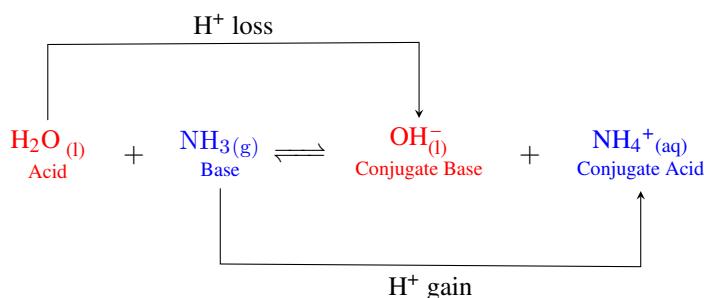
Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:



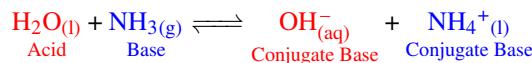
*Writing down acid-base equilibria* Now let us address how to write down acid-base equilibria from scratch, starting by the dissociation of ammonia ( $\text{NH}_3$ ). Dissociation reactions are the reaction of an acid or base and water:



We have that ammonia is a base and hence water will act as an acid. Bases receive protons whereas acids give protons away. In the equilibrium, we will remove one proton from water and add it to ammonia, producing respectively an hydroxyl and an ammonium ion:



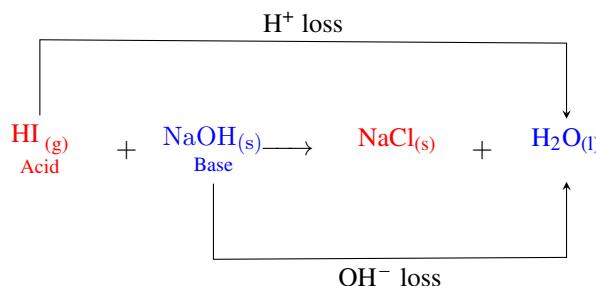
And that will give the dissociation equilibrium of ammonia.



We can now address the reaction between an acid and a base for example, between sodium hydroxide and hydroiodic acid:



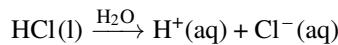
In these types of acid-base reaction, we have that the acid will generate a proton and the base will generate an hydroxyl, which will both combine to produce water and a salt, sodium chloride:



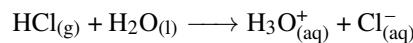
This way, dissociation and acid-base reaction function in a very similar manner.

*Including water in the dissociation* Let us consider an acid such as HCl.

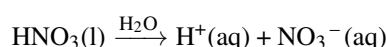
We know acids produce protons ( $\text{H}^+$  or  $\text{H}_3\text{O}^+$ ) so we can express the acid dissociation as:



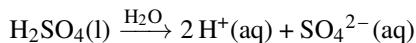
We indicate water on top of the arrow in order to represent that the dissociation process happens in water. There is an alternative way to represent this process by including explicitly water:



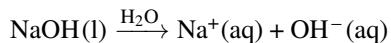
This way we explicitly represent the role of water as a proton receiver. Ultimately, both ways are correct and for some chemicals (e.g.  $\text{NH}_3$ ) it is more convenient to use the role of water whereas for others it makes no difference. In the following, we present more examples. For the case of  $\text{HNO}_3$ , nitric acid, we have:



that means once dissolved in water, nitric acid gives a proton and forms a nitrate  $\text{NO}_3^-$  cation. Some other acids, such as  $\text{H}_2\text{SO}_4$  are diprotic, as they have two protons and hence they can lose both while reaction with water:



Bases produce hydroxyls ( $\text{OH}^-$ ) and an example of a base dissociation would be:

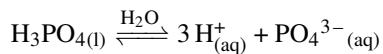


### Sample Problem 3

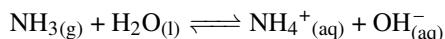
Write down the dissociation reaction using double arrows for the following chemicals:  $\text{H}_3\text{PO}_4(\text{l})$  and  $\text{NH}_3(\text{g})$ .

#### SOLUTION

Phosphoric acid is a triprotic acid with three possible protons that can be given away:



As the molecules contain protons there is no need to explicitly include water in the equilibrium. Ammonia is a base and needs is the only case in which you need to explicitly use water to help dissociate the base. This is because ammonia does not contain hydroxyls.



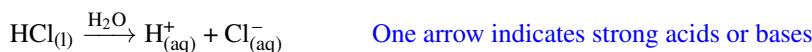
#### ❖ STUDY CHECK

Write down the dissociation reaction using double arrows for the following chemicals:  $\text{HI}(\text{g})$  and  $\text{HClO}_2(\text{l})$ .

## 10.3 Strength of acids and bases

At this point we are familiar with acids and bases. We have that acids have sour taste and produce protons in water. Differently bases feel soupy to the touch and produce hydroxyls. Both acids and bases react together giving conjugate species. This section gains further insight into the strength of acid and bases. Some acids are weaker whether other are stronger. The same idea can be applied to bases. Here we will also learn how to quantify the strength of an acid or base and how to compare the acidic or basic character of a chemical.

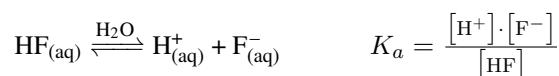
*Review of acid-base strength* Acids and bases are indeed electrolytes. Remember electrolytes can be weak or strong depending on the degree to which they dissociate. Strong acids are strong electrolytes that dissociate completely in water producing large quantities of protons  $\text{H}^+$ . Strong bases are strong electrolytes that dissociate completely to produce this time large quantities of hydroxyls  $\text{OH}^-$ . Weak acids or weak bases dissociate only partially and hence they produce fewer protons or hydroxyls. Examples of strong electrolytes are:  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ . As they dissociate completely we use a single arrow to indicate they are strong electrolytes:



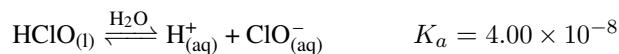
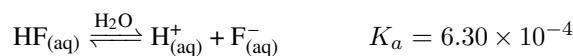
Weak acids or bases that only dissociate partially are represented by a double arrow as the reaction is indeed an equilibrium. Examples of weak acids or bases are NH<sub>3</sub> or HF.



*Strength of acids and bases* How do we quantify the strength of an acid or base? Weak acids dissociate partially in water. And hence, the dissociation process is in equilibrium. This means we will have at the same time in the same container the molecular form of the acid and its ionic-conjugate form. For this reason, we can employ equilibrium constant  $K_a$ —in this chapter they are called acidity constant equivalent to  $K_c$ —to characterize the degree of dissociation. The larger  $K_a$  the stronger the acid and hence the more protons will the acid produce in solution. Let's consider the case of HF. We have that the expression of the acidity constant will be:



If we compare the acidity constant of two different acids, for example, hydrofluoric acid and hypochlorous acid

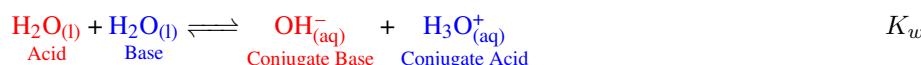


we can conclude that HF is stronger than HClO as its acidity constant is larger.

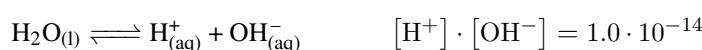
## 10.4 The PH scale

This section describes the PH scale that simply transforms a concentration value—often times a very small number—into a simple round value. In short, the PH value tells you how much protons are there in a solution so that the larger PH the fewer protons are there in solution. It also informs about the hydroxyl concentration, as protons and hydroxyls are connected by means of the dissociation equilibrium of water.

*Autoprotolysis of water and  $K_w$*  Water is a weak electrolyte. The dissociation equilibrium of water is listed below:



This chemical equilibrium representing the dissociation of water is called the autoprotolysis of water. We have that water, as well as many other chemicals, can act as a base or an acid giving and receiving protons. We call these type of chemicals *amphiprotic*. Other examples of amphiprotic chemicals are: HCO<sub>3</sub><sup>-</sup> or HSO<sub>4</sub><sup>-</sup>. The dissociation constant of water is called the ion-product of water  $K_w$ :



$K_w$  is constant that only depends on the temperature of water being  $1.0 \cdot 10^{-14}$  at  $25^\circ\text{C}$ . The ion-product of water established a relationship between protons and hydroxyls in solution:

$$[\text{H}^+] \cdot [\text{OH}^-] = 1.0 \cdot 10^{-14} \quad (10.1)$$

*Protons and Hydroxyls* Acids and bases exist in solution with water. That means that as they produce protons or hydroxyls water receives these ions as it ionizes as well. Hence, the concentration of protons and hydroxyls in solution are not independent. Indeed, the ion-product of water relates the concentration of protons ( $[\text{H}^+]$ ) and the concentration of hydroxyls ( $[\text{OH}^-]$ ):

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

Water is neutral, which means that the concentration of protons ( $[\text{H}^+]$ ) and the concentration of hydroxyls ( $[\text{OH}^-]$ ) are both equal to  $1.0 \cdot 10^{-7}\text{M}$ . When we dissolve an acid or a base into water,  $[\text{OH}^-]$  and  $[\text{H}^+]$  change drastically. When dissolving an acid,  $[\text{H}^+]$  increases as acids produce protons, while  $[\text{OH}^-]$  decreases. Differently, when dissolving a base,  $[\text{OH}^-]$  increases, as bases produce hydroxyls, while  $[\text{H}^+]$  decreases.

#### Sample Problem 4

The proton concentration in an acid solution is  $7.0 \cdot 10^{-5}\text{M}$ . Calculate  $[\text{OH}^-]$ .

#### SOLUTION

We will use Equation 10.1. The value given is  $[\text{H}^+] = 7.0 \cdot 10^{-5}\text{M}$  and the problem asks  $[\text{OH}^-]$ . Solving for  $[\text{OH}^-]$  we have:

$$7.0 \cdot 10^{-5} \cdot [\text{OH}^-] = 1.0 \cdot 10^{-14}$$

Hence  $[\text{OH}^-] = 1.4 \cdot 10^{-10}\text{M}$ .

#### ◆ STUDY CHECK

The hydroxyl concentration in a basic solution is  $2.3 \cdot 10^{-6}\text{M}$ . Calculate the concentration of protons.

*The PH scale* The proton concentrations in aqueous solutions tend to be rather small. For example, the proton concentration in normal vinegar is  $2 \cdot 10^{-3}\text{M}$ . As it is hard to work with these small concentrations, scientists developed the PH scale that transforms  $[\text{H}^+]$  into a larger number. The formula for the PH is:

$$\text{PH} = -\log[\text{H}^+] \quad (10.2)$$

The PH scale normally ranges from 0 to 14. PH values lower than 7 correspond to acidic solutions, whereas PH values larger than 7 correspond to basic solutions. Solutions with PH of 7 are neutral. For example, the PH for vinegar is  $-\log(2 \cdot 10^{-3})$  that is 2.69. However, it exists PH values out of the scale for very concentrated solutions. Examples of PH values and common chemicals are given in the figure below. An equivalent scale is also defined for the concentration of hydroxyls. The POH values is defined as:

$$\text{POH} = -\log[\text{OH}^-] \quad (10.3)$$

The POH scale also ranges from 0 to 14. POH values lower than 7 correspond to this time to basic solutions, whereas POH values larger than 7 correspond to acidic solutions.

Solutions with POH of 7 are neutral. The values of PH and POH are hence related by the following equation:

$$PH + POH = 14 \quad (10.4)$$

For example, if the PH of a solution is 4 therefore the POH will be 10. Both indicators suggest that the solution would be acidic.

### Sample Problem 5

Calculate the PH for: (a) an acid solution with proton concentration of  $7.0 \cdot 10^{-5} M$  (b) a basic solution with a hydroxyl concentration of  $7.0 \cdot 10^{-5} M$ .

#### SOLUTION

(a) We will use Equation 10.2. Given is  $[H^+] = 7.0 \cdot 10^{-5} M$  and the problem ask for the PH. Solving for PH we have:

$$PH = -\log(7.0 \cdot 10^{-5})$$

and the results is 4.15. This is an acidic PH. (b) We will also use Equation 10.2. However, before doing that, we need to compute the concentration of protons. In order to do this we will use Equation 10.1 given  $[OH^-] = 8.0 \cdot 10^{-2} M$

$$[H^+] \cdot 8.0 \cdot 10^{-2} = 1.0 \cdot 10^{-14}$$

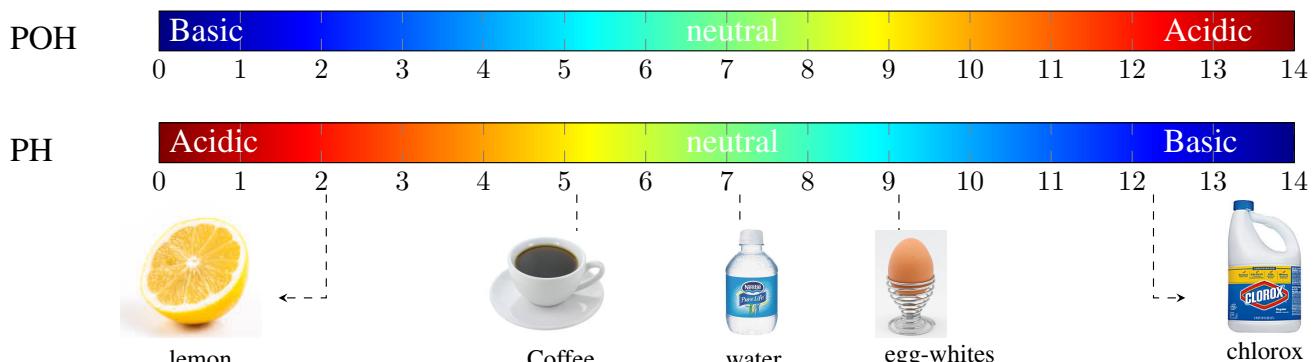
We have  $[H^+] = 1.25 \cdot 10^{-13} M$ . Now we can compute the PH. Solving for PH we have:

$$PH = -\log(1.25 \cdot 10^{-13})$$

and the results is 12.90. This is a basic PH.

#### ❖ STUDY CHECK

Calculate the PH for: (a) a basic solution with proton concentration of  $3.0 \cdot 10^{-8} M$  (b) a basic solution with a hydroxyl concentration of  $2.0 \cdot 10^{-9} M$ .



**Figure 10.1** The PH scale

*From PH to proton concentration* At this point we know that the PH quantifies the proton concentration of a solution. So given  $[H^+]$  we can calculate PH by means of the logarithm with opposite sign. But what if we know the PH and we want to calculate the corresponding proton concentration? We can do this by using the formula:

$$[H^+] = 10^{-PH} \quad (10.5)$$

In order to use the previous formula you need to use the power key in your calculator. For example if the PH is 3.3 and we need to calculate the proton concentration you

will need to type:  $10 \left[ \begin{array}{l} \wedge \\ - \end{array} \right] 3.3$ , and the result is  $5.0 \cdot 10^{-4}\text{M}$ . Mind that: (a) in some calculators, sometime the power key looks like:  $10^x$ ; (b) you need to use the negative key and not the minus key. Minus is used for substations, the negative key is used for number. An equivalent relation exist between the concentration of hydroxyls and the POH:

$$[\text{OH}^-] = 10^{-\text{POH}} \quad (10.6)$$

The diagram below displays some of the most important equations involved in this section:

### Sample Problem 6

The PH of a solution is 4.5. Calculate the proton concentration of that solution.

#### SOLUTION

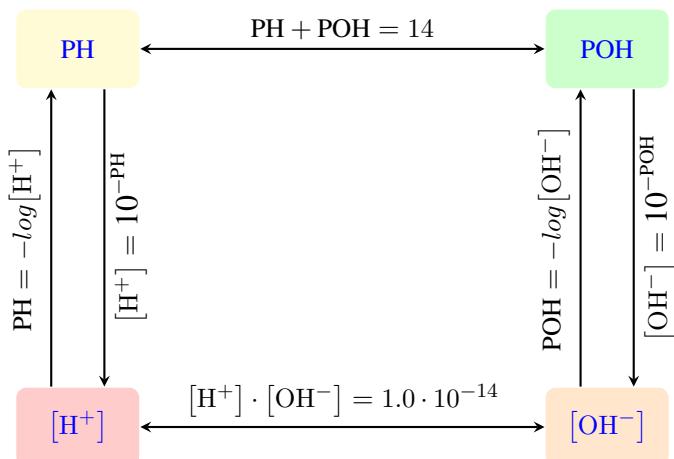
We will use Equation 10.5, given PH and asking  $[\text{H}^+]$ .

$$[\text{H}^+] = 10^{-\text{PH}} = 10^{-4.5}$$

and the results is  $3.16 \cdot 10^{-5}\text{M}$ .

#### ❖ STUDY CHECK

The PH of a solution is 9.5. Calculate the proton concentration of that solution.



## 10.5 Buffer solutions

We have previously addressed the properties of acids and bases. Buffers are specific solutions able to accommodate acids or bases without changing its PH. Buffers play a key role for example in the our blood where a buffer system absorb small quantities of acids and bases produced during biological reactions while keeping its PH constant. This section covers the properties of buffers. You will learn what are buffer, what are they made of. You will also learn how to compute the PH of a buffer system and the PH of a buffer after an acid or a base it is been added.

*Buffers* Buffers are solutions of an acid and a base. But not any kind of acid and base. Buffers are solutions of an weak acid with its conjugate base, or weak bases and its conjugate acid. For example a mixture of 0.1M  $\text{NH}_3$  and 0.1M  $\text{NH}_4\text{Cl}$  is a

buffer. You can find acidic or basic buffer. For example, the previous example was a basic buffer, whereas a mixture of 0.1M CH<sub>3</sub>COOH and 0.1M NaCH<sub>3</sub>COO is an acidic buffer. Acidic buffers contain a mixture of a weak acid and its conjugate base. Basic buffers contain a mixture of a weak base and its conjugate acid. Buffer function thanks to the equilibrium that links the acid and base so that when small quantities of acid or base are added the conjugate species contra rest this external action keeping the PH constant. Still, buffers have a limit of action and if large quantities of external acid or bases are added the buffer equilibrium can be broken and they loose their capacity to modulate the PH.

*PH of a Buffer solution* A buffer solution consist of a solution containing both a weak electrolyte and its conjugate counterpart in the same or different concentration. For example, the PH of a 0.01M CH<sub>3</sub>COOH/0.1M NaCH<sub>3</sub>COO ( $K_a = 1.75 \times 10^{-5}$ ) acidic buffer can be computed using the following formula:

$$PH = PK_a + \log\left(\frac{c_b}{c_a}\right) \quad (10.7)$$

where:

$PK_a$  is the PK of the acid in the buffer

$c_a$  is the acid concentration in the buffer

$c_b$  is the base concentration in the buffer

This formula is called the Henderson-Hasselbalch equation. Using the date above, we have that:  $PH = 4.76 + \log\left(\frac{0.1}{0.01}\right) = 5.75$ . The following example will further demonstrate how to calculate the PH of buffer solutions.

#### Sample Problem 7

Calculate the PH of 20mL of a 0.1M NH<sub>4</sub>Cl/0.2M NH<sub>3</sub> ( $K_b = 1.80 \times 10^{-5}$ ).

#### SOLUTION

This is a basic buffer and the main equilibrium involves ammonia, a weak base. In order to calculate the PH we need the concentration of the acid and base counter parts. The buffer volume is not important as it will be cancel out in the the Henderson-Hasselbalch equation. We would also need  $K_a$ , as we have  $K_b$  we can easily compute  $K_a$ , giving  $5.5 \times 10^{-10}$ . The final PH will be:

$$PH = 9.25 + \log\left(\frac{20 \cdot 0.2}{20 \cdot 0.1}\right) = 9.56$$

#### ◆ STUDY CHECK

Calculate the PH of a 0.2M HF/0.3M KF ( $K_a = 6.30 \times 10^{-4}$ ).

*PH of Buffer solution mixed with acids or bases* This section covers the PH calculation of buffers when external acids or bases different than the ones involved in the buffer equilibrium, are added to the solution. For example, the PH of 5mL of a 0.01M CH<sub>3</sub>COOH/0.1M NaCH<sub>3</sub>COO ( $K_a = 1.75 \times 10^{-5}$ ) after adding 1mL of NaOH 3M would be calculated with the following formula:

$$PH = PK_a + \log\left(\frac{V_b \cdot c_b + (V_b \cdot c_b)^{added} - (V_a \cdot c_a)^{added}}{V_a \cdot c_a + (V_a \cdot c_a)^{added} - (V_b \cdot c_b)^{added}}\right) \quad (10.8)$$

where most of the symbols of Equation 10.8 are the same as in Equation 10.7:

$(V_b \cdot c_b)^{added}$  is volume and molarity of added base

$(V_a \cdot c_a)^{added}$  is volume and molarity of added acid

The following example illustrates how to use Equation 10.7.

### Sample Problem 8

Calculate the PH of 20mL of a 0.1M NH<sub>4</sub>Cl/0.2M NH<sub>3</sub> ( $K_b = 1.80 \times 10^{-5}$ ) after adding 1mL of HCl 0.3M.

#### SOLUTION

In this example, we are adding an acid to a basic buffer. We have that  $PK_a = 9.25$ ,  $V_a = V_b = 20mL$ ,  $c_a = 0.1M$  and  $c_b = 0.2M$ . As we are adding an acid we have  $(V_b \cdot c_b)^{added} = 0$  and  $(V_a \cdot c_a)^{added} = 1 \cdot 0.3 = 0.3\text{mM}$ . Using Equation 10.7:

$$PH = 9.25 + \log\left(\frac{20 \cdot 0.2 - (1 \cdot 0.3)^{added}}{20 \cdot 0.1 + (1 \cdot 0.3)^{added}}\right) = 9.46$$

We have that the original PH of the buffer is 9.56. After adding an acid, the PH remains close to the original buffer PH.

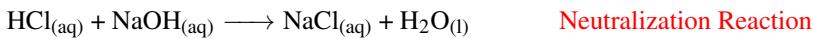
#### ❖ STUDY CHECK

Calculate the PH of 5mL of a 0.2M HF/0.3M KF ( $K_a = 6.30 \times 10^{-4}$ ) after adding 1mL of HCl 0.2M.

## 10.6 Titrations

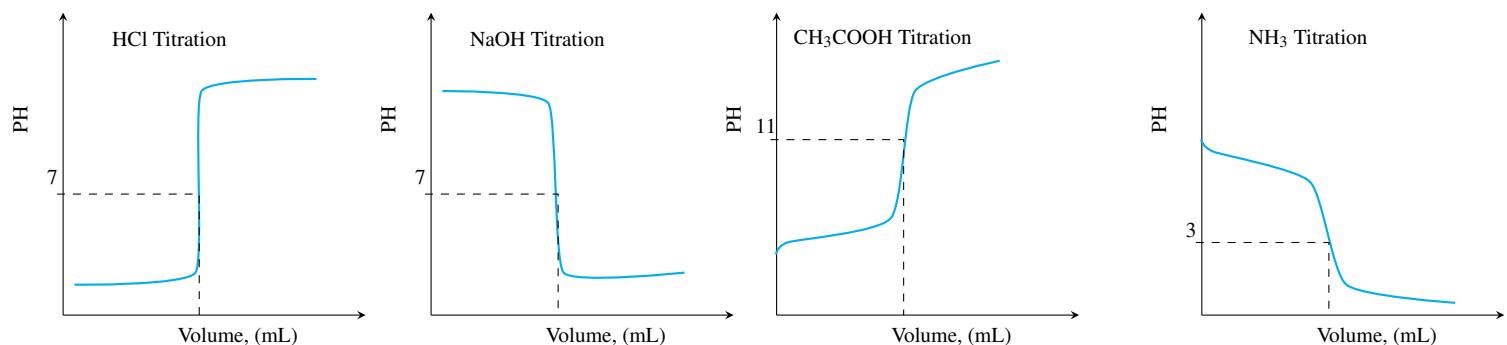
Titration is a chemical technique used to calculate the unknown molarity of an acid or base. It is based on the principle that acids neutralize bases and we can figure out the molarity of the unknown chemical (the titrate) by knowing the reacting amounts. A titration uses chemical equipment: a burette, erlenmeyers and an indicator. The unknown chemical is called the titrate and the known chemical is called the titrant. The goal of a titration is to calculate the volume of titrant needed to neutralize the titrate. We reach the endpoint of a titration when the titrant and titrate completely neutralize. At the end point the mixture of titrant and titrate has a specific PH. Even though the chemical procedure in the lab is similar when titrating strong or weak acids or bases, the calculations needed to calculate the PH at the endpoint differ. This section will cover the principles and calculations involved in titrations.

*Neutralization Reactions* Titrations involves a neutralization reaction in which an acid neutralizes a base. Acids produce protons H<sup>+</sup> and bases hydroxyls OH<sup>-</sup> that neutralize forming water, H<sub>2</sub>O. More importantly they react in very specific ratios. Let us take a look at the reaction of hydrochloric acid with sodium hydroxide to produce water and sodium chloride:



In this reaction, one mole of HCl reacts with one mole of NaOH. The fact that one more reacts with one more can be used as a principle for an acid-base titration. We will have to use the stoichiometry of the reaction to calculate the volume of titrant needed to neutralize the titrate. Imagine you have an unknown sample of HCl and

you need to know the amount of acid in the solution. If you know that this sample reacts with a specific amount of NaOH as you know that they react in a one-2-one ratio then you would know the acidic content. This is the idea behind a titration: a laboratory procedure in which an unknown sample is neutralized with a known solution. A chemical *indicator*, which changes color depending on the acidity of the medium, is used to visually reveal the moment in which the acid and the base are completely neutralized. The point at which the indicator changes color is called the *equivalency point* or the *endpoint*. At the endpoint, the acid and the base are neutralized.



**Figure 10.2** Different shapes of titration curves. Plateaus are flat for the PH curves of strong acids and bases, while being inclined for weak electrolytes. For weak electrolytes, plateaus are referred to as buffer areas.

*Endpoint formula* At the equivalency point the moles of acid and the moles of base are the same. A simple formula is extensively used to calculate the unknown acid concentration in a titration:

$$n_H \cdot c_a \cdot V_a = n_{OH} \cdot c_b \cdot V_b \quad (10.9)$$

where:

$n_H \cdot c_a \cdot V_a$  and  $n_{OH} \cdot c_b \cdot V_b$  is moles of protons and hydroxyls, respectively

$c_a$  and  $V_a$  is acid concentration and volume respectively

$c_b$  and  $V_b$  is base concentration and volume respectively

$n_H$  and  $n_{OH}$  is the number of protons of the acid and hydroxyls of the base

Regarding the units in this formula, the units in  $V_a$  and  $V_b$  can either be *L* or *mL*. They just need to be the same units. This formula can be used for example when we titrate a given acid amount with a known base and we arrive to the volume of based needed to the end point with the aim of calculating the molarity of the acid. This formula can also be used when we titrate a known acid with a known base and we need to calculate the volume of titrant needed to reach the endpoint.

Equation 10.9 can also be used to identify if we already passed the endpoint in a titration. For example, we titrate 2mL of 3M H<sub>2</sub>SO<sub>4</sub> (titrant) with 2mL of 1M NaOH (titrate). The question would be: are we before, after or at the endpoint? We have that in order to neutralize completely the titrant (H<sub>2</sub>SO<sub>4</sub>), and using Equation 10.9 we would need:

$$2 \cdot 3M \cdot 2mL = 1 \cdot 1M \cdot V_b$$

that is we would need 12 mL of base. Therefore, as we only used 2mL we would be before the end point and we would have not reached the endpoint.

### Sample Problem 9

A 50mL sample of an unknown acid is neutralized with 25 mL of a NaOH 3M solution. Calculate the molarity of the unknown acid.

#### SOLUTION

We will use Equation 10.9, given:  $c_b = 3\text{M}$ ,  $V_b = 25\text{mL}$  and  $V_a = 50\text{mL}$ .

$$c_a \cdot 50\text{mL} = 3\text{M} \cdot 25\text{mL}$$

and the results is 1.5M.

#### ◆ STUDY CHECK

A 15mL sample of an unknown acid is neutralized with 45 mL of a NaOH 1M solution. Calculate the molarity of the unknown acid.

Table 10.1 PH Titration formulas

Titrate	Before the EndPoint	At the EndPoint	After the EndPoint
Strong Acid	$[\text{H}^+] = c_R$	$\text{PH}=7$	$[\text{OH}^-] = c_R$
Strong Base	$[\text{OH}^-] = c_R$	$\text{PH}=7$	$[\text{H}^+] = c_R$
Weak Acid	$[\text{H}^+] = \frac{c_R}{c_F} \cdot K_a$	$[\text{OH}^-]^2 + K_b \cdot [\text{OH}^-] - K_b \cdot c_F = 0$	$[\text{OH}^-] = c_R$
Weak Base	$[\text{OH}^-] = \frac{c_R}{c_F} \cdot K_b$	$[\text{H}^+]^2 + K_a \cdot [\text{H}^+] - K_a \cdot c_F = 0$	$[\text{H}^+] = c_R$

## 10.7 Titrations curves

*Titration curves* A titration plot or PH curve represents the change on the PH during a titration as the volume of titrant increases. In the vertical axis it represents PH whereas in the horizontal axis it represents volume. Titration curves looks slightly different depending on nature of the chemical to be titrated. When titrating a strong acid, the curve starts at an acidic PH and near the endpoint PH rises sharply until reaching a plateau at a basic PH. The PH at the endpoint is neutral. When titrating a strong base, the curve starts at a basic PH and near the endpoint PH decreases sharply until reaching a plateau at a acidic PH. The PH at the endpoint is also neutral. When titrating a weak acid, the curve starts at an acidic PH and near the endpoint PH rises smoothly and not sharply until reaching a plateau at a basic PH. The PH at the endpoint is basic and the difference between the initial and final plateaus is small. Finally, when titrating a weak base, the curve starts at a basic PH and near the endpoint PH decreases smoothly and not sharply until reaching a plateau at an acidic PH. The PH at the endpoint is basic and the difference between the initial and final plateaus is small. The main difference between acid and base titration curves is the starting PH, whereas the difference between strong and weak titration curves is the PH at the equivalency point, being basic for weak acids

and acidic for weak bases. For weak acids and base, the plateaus are called buffer areas, and in this PH range both the acid and conjugate base coexist. At the same time, and also for weak electrolytes, the PH in the half-point corresponds to the  $pK$  value of the acid or base.

*Titration PH formulas* The goal of this section is to quantify—calculate the value—the PH at the equivalency point, when titrating an acid or a base with a strong chemical. For example, we will have a weak acid which will be titrated with a strong base and we will have to determine the PH at the equivalency point. There is a series of formulas to calculate the PH at the equivalency point. The formulas are given in the Table 10.1 and the formula to use will depend on the nature of the substance to be titrated. If we titrate a strong acid or base, the formulas are relatively simple. Differently, if we titrate a weak acid or base, the formulas are quadratic equations. Also, independently of the nature of the titrate, there are certain concentration  $c_R$  and  $c_F$  that appear in most of the formulas. In the following, we will address the meaning of these concentrations.

$c_R$  and  $c_F$  First,  $c_R$  is the concentration of protons or hydroxyls remaining in solution.

The formula for  $c_R$  is:

$$c_R = \frac{|n_H \cdot c_a \cdot V_a - n_{OH} \cdot c_b \cdot V_b|}{V_a + V_b} \quad (10.10)$$

where all variables refer to 10.9. For example, if we titrate 1mL of NaOH 3M with 4mL of HCl 2M,  $C_R$  would be:

$$c_R = \frac{|1 \cdot 2 \cdot 4 - 1 \cdot 3 \cdot 1|}{4 + 1} = 1M$$

Second,  $c_F$  is the concentration of the conjugate species formed in solution. The formula for  $c_F$  is:

$$c_F = \frac{\min(n_H \cdot c_a \cdot V_a, n_{OH} \cdot c_b \cdot V_b)}{V_a + V_b} \quad (10.11)$$

where all variables refer to 10.9. Let us calculate  $c_F$  when mixing 1mL of NaOH 3M with 4mL of HCl 2M. We will have to compute  $n_H \cdot c_a \cdot V_a$  and  $n_{OH} \cdot c_b \cdot V_b$ , and choose the smallest value. We have that  $n_H \cdot c_a \cdot V_a = 8\text{mmol}$  and  $n_{OH} \cdot c_b \cdot V_b = 3\text{mmol}$ . The smallest value is 3mmol, therefore  $c_F = 0.6\text{M}$ . The following example demonstrate how to select the appropriate PH formula for a titration. They key is to identify the location in terms of the endpoint (before, at or after) and the nature of the titrate (strong, weak, acid or base).

#### Sample Problem 10

A 25mL sample of 3M HCl is titrated with 25 mL of a NaOH 2M solution.

- (a) identify the titrate and titrant, and indicate whether you are before, after or at the endpoint
- (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte
- (c) indicate the formula that would need to be used from Table 10.2 to calculate the PH
- (d) calculate the PH

#### SOLUTION

As they say HCl is titrated with NaOH, therefore hydrochloric acid is the titrate (the one that is being titrated) and sodium hydroxide is the titrant—the one used to titrate. The titrant is a strong acid. In order to find out whether we are before,

at or after the endpoint, we will have to use Equation 10.9 and calculate the volume of titrant needed to neutralize the titrate. If the volume of titrant we have used is less than the endpoint volume then we will be before the end point. If it is larger then we will be beyond the end point. We will be at the endpoint if the volume of titrant used is the same as the endpoint volume. We have that  $c_a = 3\text{M}$ ,  $V_a = 25\text{mL}$ , and  $n_H = 1$ . We also have that  $c_b = 2\text{M}$ , and  $n_{OH} = 1$ . We will calculate  $V_b$  that fulfills Equation 10.9:

$$1 \cdot 3 \cdot 25 = 1 \cdot 2 \cdot V_b$$

Therefore,  $V_b = 37.5\text{mL}$ . As we have used only 25mL of base, we would be before the endpoint and the formula to use for the endpoint PH would be:  $[\text{H}^+] = c_R$ . We can calculate  $c_R$ :

$$c_R = \frac{|n_H \cdot c_a \cdot V_a - n_{OH} \cdot c_b \cdot V_b|}{V_a + V_b} = \frac{|1 \cdot 3\text{M} \cdot 25\text{mL} - 1 \cdot 2\text{M} \cdot 25\text{mL}|}{(25 + 25)\text{mL}} = 0.5\text{M}$$

We have that  $\text{PH}=0.30$ .

#### STUDY CHECK

A 5mL sample of 2M  $\text{H}_2\text{SO}_4$  is titrated with 25 mL of a NaOH 1M solution. (a) indicate whether you are before, after or at the endpoint (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte (c) indicate the formula that would need to be used to calculate the PH (d) calculate the PH

The following examples will cover titration in which the titrate is a weak electrolyte, acid or base. For these case, the corresponding PH formula involves a quadratic equation that will lead to the calculation to the concentration of protons or hydroxyles. Afterwards, the PH would need to be calculated using the regular logarithmic formulas (Equations 10.2-10.4)

#### Sample Problem 11

A 1mL sample of 2M acetic acid ( $\text{CH}_3\text{COOH}$ ,  $K_b = 1.75 \times 10^{-5}$ ) is titrated with 0.66 mL of a NaOH 3M solution. (a) indicate whether you are before, after or at the endpoint (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte (c) indicate the formula that would need to be used from Table 10.2 to calculate the PH (d) calculate the PH

#### SOLUTION

We have that  $\text{CH}_3\text{COOH}$  is the titrant and NaOH is the titrate. This is because the question indicates that you titrate  $\text{CH}_3\text{COOH}$  and therefore the chemical to be titrated is the titrant. The titrant is a weak acid. In order to find out whether we are before, at or after the endpoint, we will have to use 10.9 and calculate the volume of titrant needed to neutralize the titrate. If the volume of titrant we have used is less than the endpoint volume then we will be before the end point. If it is larger then we will be beyond the end point. We will be at the endpoint if the volume of titrant used is the same as the endpoint volume. We have that  $c_a = 2\text{M}$ ,  $V_a = 1\text{mL}$ , and  $n_H = 1$ . We also have that  $c_b = 3\text{M}$ , and  $n_{OH} = 1$ . We will calculate  $V_b$  that fulfills 10.9:

$$1 \cdot 2 \cdot 1 = 1 \cdot 3 \cdot V_b$$

Therefore,  $V_b = 0.66\text{mL}$ . Therefore, we are at the endpoint and the PH is given by:

$$[\text{OH}^-]^2 + K_b \cdot [\text{OH}^-] - K_b \cdot c_f = 0$$

as we have that  $K_a = 1.75 \times 10^{-5}$  and therefore  $K_a = 1.33 \times 10^{-9}$ , and  $c_f = 2/0.66 = 1.2\text{M}$ :

$$[\text{OH}^-]^2 + 1.33 \times 10^{-9} \cdot [\text{OH}^-] - 1.59 \times 10^{-9} = 0$$

Solving for  $[\text{OH}^-]$  we have  $[\text{H}^+] = 3.98 \times 10^{-5}\text{M}$  and therefore  $\text{POH}=4.4$  and  $\text{PH}=9.59$ .

#### ❖ STUDY CHECK

A 1mL sample of 2M  $\text{NH}_3$  ( $1.80 \times 10^{-5}$ ) is titrated with 2 mL of a HCl 1M solution. (a) indicate whether you are before, after or at the endpoint (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte (c) indicate the formula that would need to be used to calculate the PH (d) calculate the PH



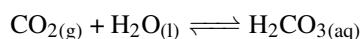
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**Figure 10.3** An acid base titration using phenolphthalein as indicator. From left to right, before, at and after the end point.

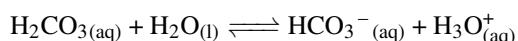
## 10.8 Blood as a buffer

We will finally discuss the role of CO<sub>2</sub> as a buffer in the blood.

*Carbon dioxide is an acid* Carbon dioxide is an acid gas. When it dissolved reversibly in water it produces carbonic acid:

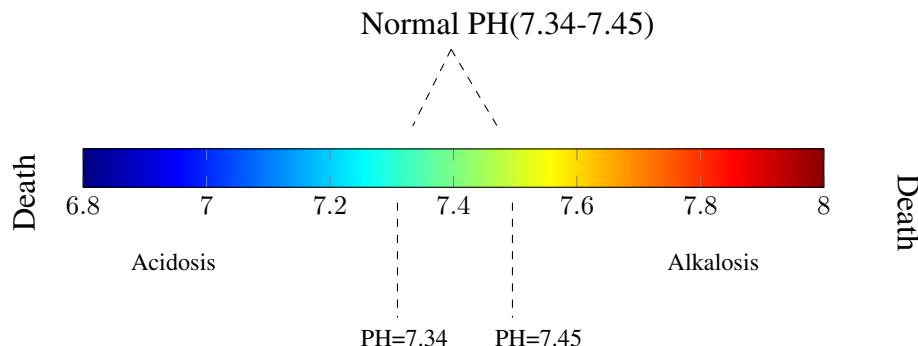


At the same time H<sub>2</sub>CO<sub>3</sub> partially dissociates in water as a weak acid producing bicarbonate—also known as hydrogen carbonate:



As a result, the dissolution of carbon dioxide in the blood produced a buffer containing carbonic acid and bicarbonate—the conjugate base of carbonic acid. This buffer system keeps the PH of blood constant to a value of 7.4 that is slightly above the neutral value of 7.

*The dangerous change in blood PH* Most biological molecules are very sensitive PH changes. Small deviations in PH can be dangerous or even fatal. If the blood PH falls below 7.34 it becomes more acidic causing a clinical condition called *acidosis*. On the other hand, if the PH rises above 7.45, the blood becomes more basic causing a condition called *alkalosis*. Changes of PH below 6.8 or above 8.0 can cause death.



**Figure 10.4** PH range that leads to acidosis and alkalosis

*Alkalosis and carbon dioxide* Our body needs oxygen to function properly. When you inhale, you introduce oxygen into the lungs. When you exhale, you release carbon dioxide, which is a waste product. Normally, the respiratory system keeps these two gases in balance. Respiratory alkalosis occurs when you breathe too fast or too deep. This hyperventilation—also known as over-breathing—causes carbon dioxide levels to drop too low. This means there is not enough CO<sub>2</sub> in the blood and that causes the PH to increase and become too alkaline. Treating the condition is a matter of raising carbon dioxide levels in the blood. You can do this by breathing from a plastic bag. Respiratory acidosis occurs when too much CO<sub>2</sub> builds up in the body. Normally, the lungs remove CO<sub>2</sub> while you breathe. However, sometimes your body can't get rid of enough CO<sub>2</sub>. Treatments for this condition are usually designed to help your lungs. For example, you may be given drugs to dilate your airway. You might also be given oxygen or a continuous positive airway pressure (CPAP) device. The CPAP device can help you breathe if you have an obstructed airway or muscle weakness.

**Sample Problem 12**

Explain why  $\text{CO}_2$  decreases the PH of blood.

**SOLUTION**

$\text{CO}_2$  is an acid and when dissolved in water it generates protons,  $\text{H}^+$ . Increasing the amount of protons decreases PH as PH is a measure the concentration of protons in solution.

**❖ STUDY CHECK**

The PH of a patients blood is 7.3. Indicate whether the patient suffers alkalosis, acidosis or perhaps none of the afflictions. Can the PH level cause death?

## 10.9 Molecular mechanisms behind acid-base strength

Why are some acids stronger than others? There is not a simple answer to this question. The strength of a given acid depends not only on its molecular structure but also on energetic and electronic arguments. In this section, we will explore the mechanisms responsible for acidity in three different families of chemicals: binary acids (e.g. HCl), oxoacids (e.g.  $\text{HClO}$ ), and carboxylic acids (e.g.  $\text{CH}_3\text{COOH}$ ).

*Binary acids* Binary acids result from the combination of an element (e.g. N, O, F) with hydrogen:  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , HF, HCl, HBr, and HI. Mind that ammonia and even methane are indeed very weak acids. Here we will compare the acidity of well-known acids (e.g. HCl) as well as other hydrogen-based chemicals (e.g.  $\text{NH}_3$ ). We find two different acidity trends across periods and groups of the periodic table. On one hand, we have that across a period from left to right acidity increases

$$K_a(\text{NH}_3) < K_a(\text{H}_2\text{O}) < K_a(\text{HF})$$

For this set of acids, the dominant contribution to acidity is the electronegativity character of the central atom: the larger the electronegativity of the central atom the larger the tendency of this atoms to withdrawn electron density from hydrogen and hence the bond becomes weaker (*acidity factor 1*). The fewer electron density localized in the bond the larger acidity—the easier would be to break this bond. On the other hand, across a group, acidity increases when going from HF to HI, that is from top to bottom. We have that across a group

$$K_a(\text{HF}) < K_a(\text{HCl}) < K_a(\text{HBr}) < K_a(\text{HI})$$

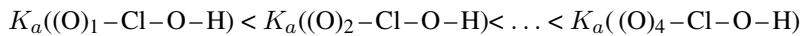
This trend corresponds with an increase in the atomic weight of the central atom and an increase of the capacity of the corresponding anion to stabilize negative charger. Acid dissociation necessarily implies the formation of an anion (e.g.  $\text{Cl}^-$  or even  $\text{NH}_2^-$ ). The more stable this anion the stronger acidity. Heavier atoms are more capable to stabilize negative charges and hence they are more stable. Therefore, the larger the atomic weight of the central atom the stronger acidity (*acidity factor 2*). At this point we saw two different factors that contribute to acidity. These factors play a key role as well in other types of acids as we will see in the following.

*Oxoacids* Oxoacids contain a central halogen atom bonded to one or more oxygen atoms as well as hydrogen. These acids normally have the following general structure:

$(O)_n - X - O - H$ . For example,  $Cl - O - H$  is called hypochlorous acid ( $HClO$ ), and  $(O)_3 - Cl - O - H$  is called perchloric acid ( $HClO_4$ ). We will first address the changes in acidity with the nature of the central halogen and then address the changes in acidity with the number of oxygen atoms in the molecule. When comparing the acidity of hypochlorous acid, hypobromous acid and hypoiodous acid, we find that

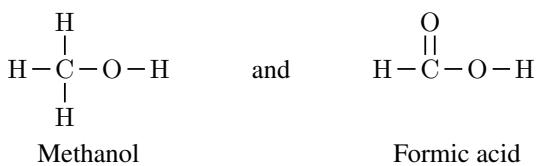


In other words, acidity increases from bottom to top across a group. That is the greater the electronegativity of the halogen the stronger the acid character. This trend is indeed opposite to the one found in binary acids. As the electronegativity of the halogen increases more electron density is withdrawn towards the  $X - O$  bond and less electronic density is available for the  $O - H$ . As a consequence, the  $O - H$  bond becomes weaker due to the indirect changes of the  $O - X$  bond as acidity increases. Hence, we have a new factor that controls acidity: the larger the electronegative of the central halogen in an oxoacid the stronger acidity (*Acidity factor 3*). When comparing the acidity of hypochlorous acid, chlorous acid, chloric acid and perchloric acid, we find that

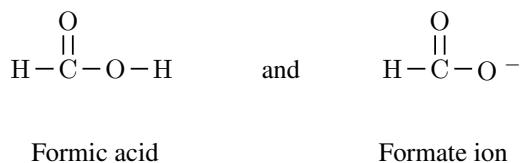


In other words, acidity increases as the number of oxygen atoms connected to the central halogen increases. As the number of electronegative oxygen atoms connected to the central halogen atoms increases, more electron density will be withdrawn from the central  $Cl$ . This will also impact the oxygen connected to the acidic hydrogen weakening the  $O - H$  bond increasing acidity. The more oxygens are connected to the central halogen the stronger acidity (*Acidity factor 4*). To summarize, two different factors impact the acid character of oxoacids: the electronegativity of the central halogen and the number of oxygens connected to the central halogen.

*Carboxylic acids* We can start by comparing the acidity of two different organic compounds, methanol, the simplest of all alcohols and formic acid, the simplest carboxylic acid. The structure of both molecules is presented below:

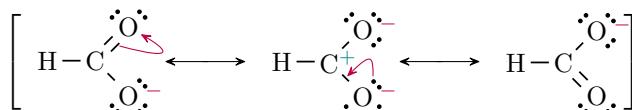


Indeed, methanol as well as other alcohols are not really acidic whereas carboxylic acids and in particular formic acid are in general weak acids. We can understand this trend by two factors. On one hand, following *acidity factor 4* carboxylic acids have two oxygen atoms connected to the central carbon. Both withdrawn electron density from carbon hence weakening the  $O - H$  bond and increasing acidity. There is a new acidity factor that contribute to the acidity of carboxylic acids. The result of dissociating a carboxylic acid is a negatively charged carboxylate ion



The negative charge in the oxygen is stabilized by resonance, that is, it is not localized on a single oxygen but distributed between the two oxygen atoms as shown below.

Hence carboxylates are stabilized by resonance and this contribute to the acidity of the carboxylic acids *acidity factor 5*.



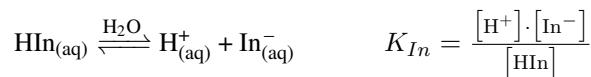
#### *Molecular mechanisms behind acid-base strength: a review*

There are five different factors that contribute to the acidity of a chemical. First, the larger the electronegativity of the atom directly connected to hydrogen the stronger acidity. Second, the heavier the atom connected to hydrogen the stronger acidity. Third, the larger the electronegativity of an atom secondarily connected to a hydrogen the stronger acidity. Fourth, the larger the number of electronegative atoms indirectly connected to hydrogen the stronger acidity. Fifth, a possible stabilization of the corresponding anion generated by the dissociation of an acid increases acidity strength.

## 10.10 Indicators

There are several techniques to locate the endpoint during a titration. On one hand, we can use a PH meter and measure PH during the titration. The endpoint locates between the initial and final plateau. We can also use an automatic titrator, a machine that automatically mixes the acid and the base while displaying the PH. Another technique uses an indicator that changes color when the PH changes from acidic to basic or the opposite.

*How do indicators function?* Acid-base indicators are water-soluble organic dyes that have a different color depending on PH. Halochromism is the effect of changing color due to changes on a external force such as PH. Many flowers or plants exhibit this quality. For example, the french hydrangea is a plant that changes color depending on the acidity of the soil. Turmenic is a specie that turn from yellow to brown when the PH increases. Indicator can be extracted from many plants and fruits such as red cabbage, geranium, poppy, rose petals or blueberries. Indeed, indicators are weak acids that exist in a conjugate base form as well. Both the acid (the indicator form with the hydrogen attached) and the conjugate base have a different color due to differences in their electronic structure that transform into differences absorbing light. For example, phenolphthalein is a common acid-base indicator that is transparent when the PH is acidic and pink when the PH is basic. The equivalency point of a titration (when acid and base are neutralized) is not necessarily the end point (when the indicator changes color). However, if both points are close enough chemical indicators are an accurate way to visually locate the equivalency point during a titration. As indicators are weak acids, each particular indicator is characterized by a constant of acidity referred to as  $K_{In}$  so that



The change in color is considered to happen when the difference between the acidic and basic form of the indicator is an order or magnitude—ten times—different. This is the ten times rule. For this difference, we have that

$$PH = PK_{In} \pm 1$$

We can always use a different value for the difference ( $\Delta$ ) between the acid and basic form of an indicator so that the PH range will be given by

$$PH = PK_{In} \pm \log(\Delta)$$

This expression helps with the selection of the indicator for a given titration. For example, if we want to select an indicator that changes color when the difference between acid and base form is 5 times ( $\Delta = 5$ ), then the OH range would be:  $PH = PK_{In} \pm 0.7$

**Table 10.2 Acid-base indicators showing ample representations of their colors**

Name	PH Range	Color acid form	Color basic form
Thymol Blue	1.2-2.8	red	yellow
Pentamethoxy red	1.2-2.3	red-violet	colorless
Methyl yellow	2.9-4.0	red	yellow
Methyl orange	3.1-4.4	red	orange
Bromophenol blue	3.0-4.6	yellow	blue-violet
Tetrabromophenol blue	3.0-4.6	yellow	blue
Alizarin sodium sulfonate	3.7-5.2	yellow	violet
$\alpha$ -Naphthyl red	3.7-5.0	red	yellow
p-Ethoxychrysoidine	3.5-5.5	red	yellow
Bromocresol green	4.0-5.6	yellow	blue
Methyl red	4.4-6.2	red	yellow
Bromocresol purple	5.2-6.8	yellow	purple
Bromophenol blue	6.2-7.6	yellow	blue
Azolitmin	5.0-8.0	red	blue
Phenol red	6.4-8.0	yellow	red
Neutral red	6.8-8.0	red	yellow
Rosolic acid	6.8-8.0	yellow	red
Cresol red	7.2-8.8	yellow	red
$\alpha$ -Naphtholphthalein	7.3-8.7	rose	green
Tropeolin	7.6-8.9	yellow	rose-red
Thymol blue	8.0-9.6	yellow	blue
Phenolphthalein	8.0-10.0	colorless	red
$\alpha$ -Naphtholbenzein	9.0-11.0	yellow	blue
Thymolphthalein	9.4-10.6	colorless	blue
Nile blue	10.1-11.1	blue	red
Diazo violet	10.1-12.0	yellow	violet
Tropeolin	11.0-13.0	yellow	orange-brown
Nitramine	11.0-13.0	colorless	orange-brown
Trinitrobenzoic acid	12.0-13.4	colorless	orange-red

*Selecting an indicator* A good indicator will turn into a different color within the transition between acid and basic PH during a titration. For example, for the titration of hydrochloric acid with sodium hydroxide, the PH changes from 5 before the equivalency point to 8 after. Any indicator with  $PK_{In}$  between 5 and 8 would be able to accurately indicate the stoichiometric point. Examples are bromothymol blue, m-nitrophenol, and even phenolphthalein that transition color at 8. For the titration of a weak acid and a strong base, the selection of an indicator is more difficult as the difference between the acidic and basic plateaus during the titration is less pronounced. We must choose an indicator that changes color more closely to the end point.

*Litmus paper* Litmus paper is an indicator heavily used for quick PH testing in labs. It contains a mixture of dyes that were extracted originally from lichens. There are two main types of litmus paper, red and blue litmus. Light blue litmus paper turns red when the medium is acidic, whereas red litmus paper turns blue in basic mediums. By wetting a piece of litmus paper one can also test for the acidity of gases, and for example, ammonia vapor would turn blue a piece of wet red litmus paper.

### Sample Problem 13

When titrating hydrochloric acid with sodium chloride using p-Nitrophenol ( $K_a = 6.3 \times 10^{-8}$ ), indicate the PH at which the ratio between the acid and base form if the indicator is 10%.

#### SOLUTION

We have that the PH at which an indicator changes color depends on the  $pK_a$  of the indicator.  $pK_a$  for p-Nitrophenol is 7.2, hence the PH for color transition will be  $7.2 \pm \log(\Delta)$ , given that  $\Delta$  is the difference in concentration between acid and basic form. For a 10% difference, we have that  $7.2 \pm \log(10)$  and the color change will start at 6.2 and finish at 8.2

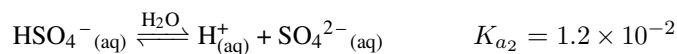
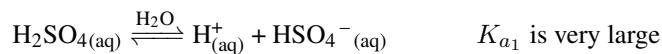
#### ❖ STUDY CHECK

When titrating an acid with a strong base using Methyl orange ( $K_a = 3.9 \times 10^{-4}$ ), indicate the PH at which the concentration of the acid form of the indicator is four times the one of the base base.

## 10.11 Titrations of polyprotic acids

Monoprotic acids contain a single proton. Examples are hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>). Polyprotic acids contain more than one proton. Examples are sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), a diprotic acid, and phosphoric acid, (H<sub>3</sub>PO<sub>4</sub>). When titrating an acid, the number of protons determines the number of endpoints observed. Monoprotic acids go through a single end point, whereas diprotic acids go through two different end points.

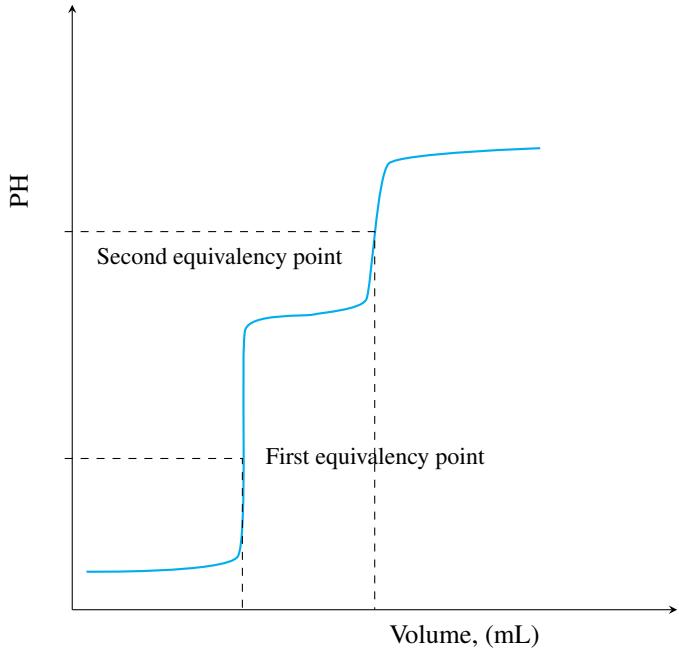
*PH curves of polyprotic acids* The principles that control the shape of PH curves of monoprotic acids also apply to polyprotic acids. PH curves of strong acids have well-defined plateaus, whereas PH curves of weak acids or bases have shorter PH transition and inclined plateaus. For polyprotic acids, these principles are applied to each end point in the PH curve. For example, sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) can give away two protons. The first proton dissociation equilibrium is characterized by a very large  $K_a$ , whereas the second dissociation corresponds to a weak acid dissociation:



The PH curve of this acid should reflect these facts and the first transition is well-defined, whereas the second one is shorter. For weak electrolytes, the plateaus represent buffer areas where the acid and conjugate base exist. At the half-point the PH is the same as the  $pK$  of each dissociation.

*End points of polyprotic acids* We can also employ the endpoint formula to locate the volume of titrant needed to reach each of the end points during the titration.

For example, when titrating a 10mL sample of 0.1M phosphoric acid with 0.1M-NaOH, we would need 10mL to reach the first end point, 20mL to reach the second end point, and a total of 30mL to reach the third and last end point, completely neutralizing the acid.



**Figure 10.5** PH curve for a diprotic acid showing two equivalency points