



# Ch. 1. 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.

## 1.1 The nature of 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 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

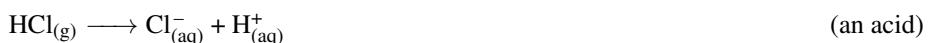
using a single arrow, whereas the dissociation of weak acids and bases is represented using a double harpoon. For example, hydrochloric acid is a strong electrolyte and its dissociation is represented by



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



*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:

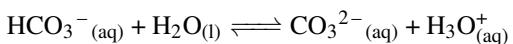


Based on the acid dissociation reaction above, we say chloride is the result of deprotonating hydrochloric acid. In other words, chloride is deprotonated. Based on this dissociation reaction that happens in water, we can say hydrogen chloride also known as hydrochloric acid is an Arrhenius acid, as it produces protons in water. We have that acid 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,  $\text{NaOH}$  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:



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



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▼ Citrus such as lemons or oranges are acidic.



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



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 acids 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

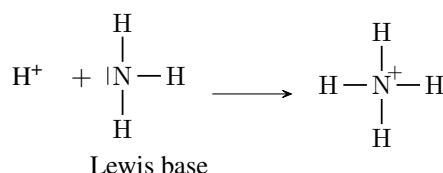
Identify the following chemicals as Arrhenius acids or bases and give their names:  $\text{NaOH}$  and  $\text{H}_2\text{CO}_3$ .

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



© wikipedia

*Lewis acid-base model* This is the most comprehensive acid-base model that we will cover in this chapter. A Lewis acid is a chemical able to receive electron pairs, whereas a Lewis base can give way to electron pairs. In other words, acids are the electron-pair receiver and bases are electron-pair givers. In the example below you can see why ammonia acts as a base:

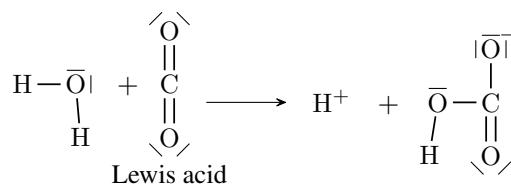


▼ Ashes are basic.



© wikipedia

Ammonia as well as other molecules contain lone pairs. These lone pairs are key in the definition of a Lewis acid-base, as acids and bases receive and give away electron density. Lewis bases contain lone pairs and can give away electron density to an acid. Another example is presented below. The presence of two lone pairs in water makes it a Lewis base that can give electron density to carbon dioxide, a lewis acid.



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



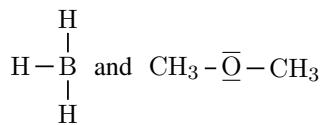
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### Sample Problem 2

Indicate whether the following chemicals are lewis acid or lewis bases: (a)  $\text{BH}_3$  and (b)  $\text{CH}_3-\text{O}-\text{CH}_3$ .

#### SOLUTION

The lewis structure of the molecules are:



$\text{BH}_3$  can receive a lone pair to complete the octet of Boron and hence it will be a Lewis acid. Differently,  $\text{CH}_3-\overline{\text{O}}-\text{CH}_3$  is a Lewis base as oxygen has two lone pairs that can be given away.

## STUDY CHECK

Indicate whether the following chemicals are lewis acid or lewis bases: (a)  $\text{AlH}_3$  and (b)  $\text{OH}^-$ .

In summary, the Arrhenius definition is based on what is on a solution, whereas the Brönsted-Lowry definition is based on giving and receiving protons. Finally, the Lewis definition is based on giving and receiving lone pairs. All these definitions are complementary and all Arrhenius acids are Brönsted-Lowry as well as Lewis acids.

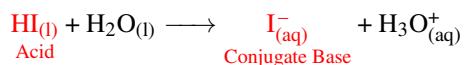
**Table 1.1 Acid-base models**

| Model          | Acid definition         | Base definition          |
|----------------|-------------------------|--------------------------|
| Arrhenius      | H <sup>+</sup> producer | OH <sup>-</sup> producer |
| Brönsted-Lowry | H <sup>+</sup> donor    | H <sup>+</sup> acceptor  |
| Lewis          | electron-pair acceptor  | electron-pair donor      |

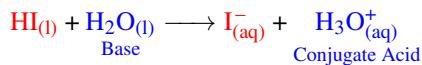
## 1.2 Dissociation of acids and bases

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 H<sup>+</sup>. For example: hydroiodic acid HI and iodate I<sup>-</sup> or water H<sub>2</sub>O and protons H<sub>3</sub>O<sup>-</sup>. The product of the dissociation of acids is a conjugate base. For example:



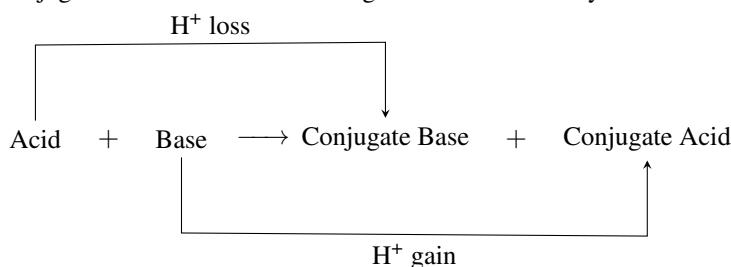
Similarly, bases produce a conjugate acid. In the example below, water acts as a base and a proton is the conjugate acid:



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



Hence, we have that acid reactants 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 3

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



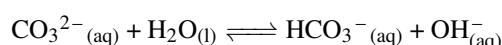
#### SOLUTION

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

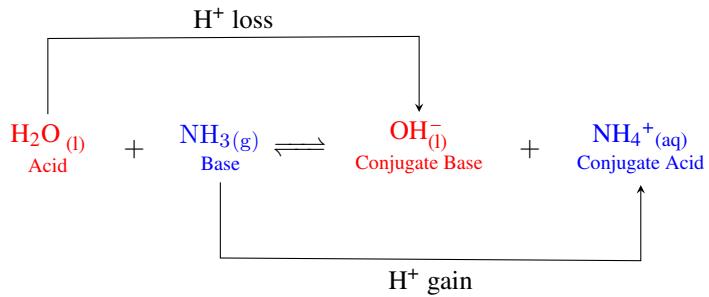
Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:



*Writing down acid-base equilibria* Now let us address how to write down acid-base equilibria from scratch, starting with 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 a hydroxyl and an ammonium ion:



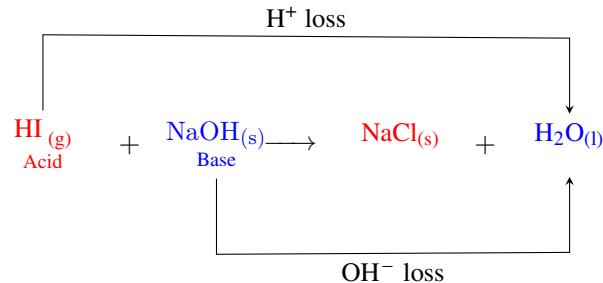
And that will give the dissociation equilibrium of ammonia.



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

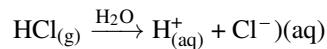


In these types of acid-base reactions, we have that the acid will generate a proton and the base will generate a hydroxyl, which will both combine to produce water and a salt, sodium chloride:

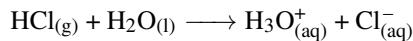


This way, dissociation and acid-base reaction function in a very similar manner.

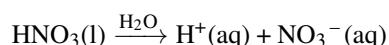
*Including water in the dissociation* Let us consider an acid such as HCl. We know acids produce protons ( $\text{H}^+$  or  $\text{H}_3\text{O}^+$ ) so we can express the acid dissociation as:



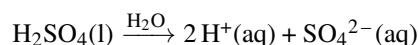
We indicate water on top of the arrow to represent that the dissociation process happens in water. There is an alternative way to represent this process by including explicitly water:



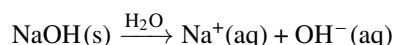
This way we explicitly represent the role of water as a proton receiver. Ultimately, both ways are correct and for some chemicals (e.g.  $\text{NH}_3$ ) it is more convenient to use the role of water whereas for others it makes no difference. In the following, we present more examples. For the case of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



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



#### Sample Problem 4

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:



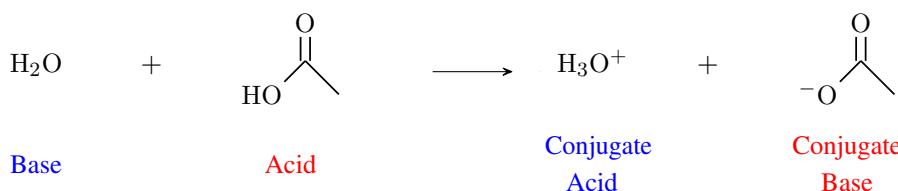
As the molecules contains protons there is no need to explicitly include water in the equilibrium. Ammonia is a base and needs is the only case in which you need to explicitly use water to help dissociate the base. This is because ammonia does not contain hydroxyls.



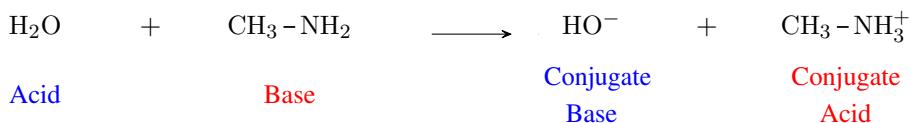
#### ❖ STUDY CHECK

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

*Conjugate organic acids and bases* Organic acids are also called carboxylic acids. Amines tend to be organic bases. A conjugate organic acid-base pair are organic molecule or ions related by the loss of one  $\text{H}^+$ . For example, acetic acid, the acid present in vinegar, is an organic acid that will react with water (the solvent) to produce a conjugate base called acetate. Acetates are used in some printing processes. For example, vinyl acetate is employed in the production of plastics, cellulose acetate is used in making photographic films and textiles. Acids produce protons ( $\text{H}^+$ ) and therefore conjugate bases are negatively charged. The corresponding dissociation equilibrium is shown below:



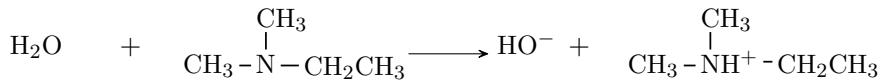
Amines are basic and they will react with water to produce a conjugate acid. Bases receive protons ( $\text{H}^+$ ) from the solvent, hence the conjugate acid of a base is positively charged. An example is presented below.



Again, to review, we have that organic acids produce protons and generate negatively charged conjugate bases. At the same time, organic bases consume protons and generate a conjugate acid that is positively charged. To identify a conjugate acid-base pair we just need to look for a pair of molecules that resemble each other.

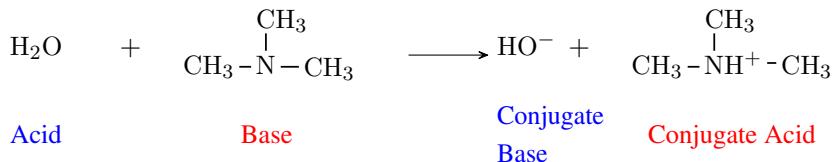
### Sample Problem 5

Identify the acid, the base, the conjugate acid and the conjugate base in the reaction involving organic molecules:



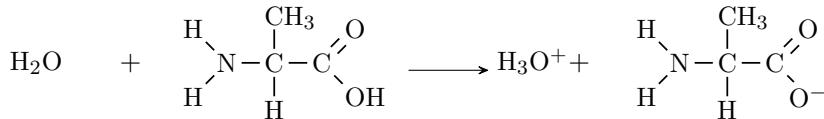
### SOLUTION

We have that acids produce protons and bases receive those protons. In the reaction above, the second reactants received a proton from water and hence, it acts as a base. Hence water will be the acid and the amine, the second reactants, will be the base. The conjugate base would be  $\text{HO}^-$  and the conjugate acid the product on the right. These results make sense as amines are organic bases.

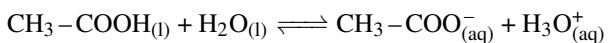


### ❖ STUDY CHECK

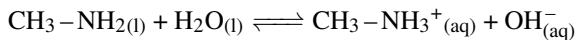
Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:



*Dissociating organic acids and bases* Organic acids and bases often contain numerous hydrogen atoms in their molecular structure. It is critical to dissociate these molecules using the acid and basic centers and not others. For example, acetic acid  $\text{CH}_3 - \text{COOH}$  contains a methyl group and a carboxylic group. When dissociation this molecule, we need to remove the proton only from the acidic group, hence its name:



Methylamine  $\text{CH}_3 - \text{NH}_2$ , on the other hand, is an organic base with a methyl and an amine group. Amine groups are basic per nature—they resemble ammonia—and hence when dissociation this base we need to attach an extra proton to the basic center:



**Sample Problem 6**

Write down the following dissociation or acid-base reaction involving one proton:  $\text{H}_2\text{CO}_{3(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})} \longrightarrow$

**SOLUTION**

As this is a dissociation reaction and carbonic acid is an acid, we will need the help of water. We will have that carbonic acid will lose one proton and water will gain that proton.



As carbonic acid loses a proton to become hydrogencarbonate, its charge becomes negative. Similarly, as water gains a proton to become the hydronium ion, its charge becomes positive so that overall the charge of the reaction is balanced.

**❖ STUDY CHECK**

Write down the following dissociation or acid-base reaction involving one proton:  $\text{HCl}_{(\text{g})} + \text{NH}_{3(\text{g})} \longrightarrow$

### 1.3 Strength of acids and bases

At this point, we are familiar with acids and bases. Acids have a 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 acids and bases. Some acids are weaker while others 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:

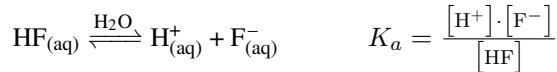


Weak acids or bases that only dissociate partially are represented by a double arrow as the reaction is indeed an equilibrium. Examples of weak acids or bases are  $\text{NH}_3$  or  $\text{HF}$ .

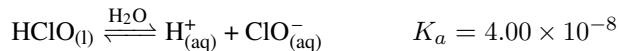
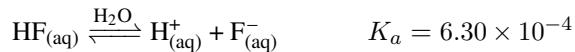


*Strength of acids and bases* How do we quantify the strength of an acid or base? Weak acids dissociate partially in the water. And hence, the dissociation process is in equilibrium. This means we will have at the same time in the same container the molecular form of the acid and its ionic-conjugate 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 the solution. Let's consider the case of HF. We have that the expression of the acidity constant will be:

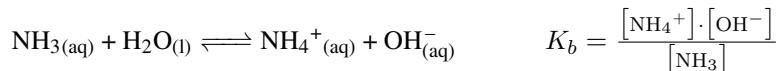


If we compare the acidity constant of two different acids, for example, hydrofluoric acid and hypochlorous acid

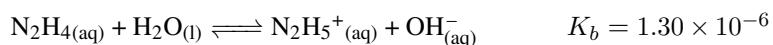
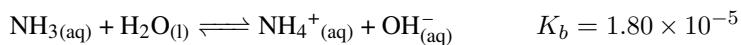


we can conclude that HF is stronger than HClO as its acidity constant is larger.

*Basicity constant* In a very similar way, bases also have what we call base dissociation constants:  $K_b$ . The bigger this value the stronger the base and the more hydroxyls will be produced. In the case of ammonia:



remember liquid water can not be part of an equilibrium constant. If we compare the basicity constant of two different bases, for example, ammonia and hydrazine



we can conclude that NH<sub>3</sub> is stronger than N<sub>2</sub>H<sub>4</sub> as its basicity constant is larger.

$K_a$  and  $K_b$  Acidity and basicity are related concepts. As such, there is a relationship between the constant of acidity and the constant of basicity of an acid or base given by:

$$K_a \cdot K_b = 1.0 \cdot 10^{-14} \quad (1.1)$$

This relationship implies that all acids and bases have a constant of acidity as well as basicity. For example, if the constant of acidity of a given acid is  $1.5 \times 10^{-5}$ , the basicity constant of the same species would be  $6.6 \times 10^{-10}$ . If  $K_a$  is large and the acid is strong  $K_b$  must be small and the basic character of a strong acid is very weak. Further in the chapter, you will find a table listing some acidity and basicity constants. In general, some simple rules predict the acid-base character of an acid-conjugate base pair. Strong acids in general produce weak conjugate bases. For example, HCl is a strong acid and its conjugate base (Cl<sup>-</sup>) is a weak base. Differently, HF is a weak acid and its conjugate base (F<sup>-</sup>) is a moderately strong base. Also, if  $pK_a$  is smaller than 7 we can consider that the chemical is more acidic than basic, and we call the chemical an acid. If  $pK_a$  is larger than 7 (and therefore  $pK_b$  is smaller than 7) we can consider that the chemical is more basic than acidic, and we call the chemical a base.

## Sample Problem 7

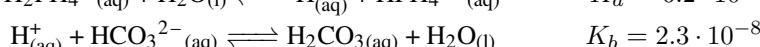
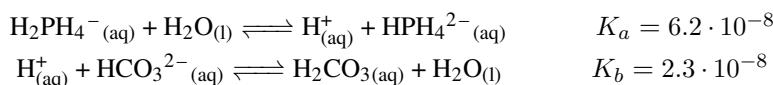
Indicate the strongest acid from:

**SOLUTION**

The acid dissociation constant tells how strong is the acid, hence the larger  $K_a$  the stronger the acid. Comparing both values:  $K_a(\text{HF}) = 7.2 \cdot 10^{-4}$  and  $K_a(\text{HNO}_2) = 4.5 \cdot 10^{-4}$ , HF is the stronger of both.

**◆ STUDY CHECK**

Indicate the strongest of the following acids:



**Table 1.2 Acidity and basicity constants at 25°C**

| Name              | Formula   | $K_a$                  | Name                 | Formula  | $K_a$                 |
|-------------------|---|------------------------|----------------------|--|-----------------------|
| Hypoiodous acid   | HIO   | $3.20 \times 10^{-11}$ | ⋮                    |  |                       |
| Phenol            | C <sub>6</sub> H <sub>5</sub> OH                | $1.00 \times 10^{-10}$ | Fluoroacetic acid    | CH <sub>2</sub> FCO <sub>2</sub> H               | $2.60 \times 10^{-3}$ |
| Hydrocyanic acid  | HCN   | $6.20 \times 10^{-10}$ | Formic acid          | CH <sub>2</sub> O <sub>2</sub>                   | $1.80 \times 10^{-4}$ |
| Hypobromous acid  | HBrO  | $2.80 \times 10^{-9}$  | Bromoacetic acid     | CH <sub>2</sub> BrCO <sub>2</sub> H              | $1.30 \times 10^{-3}$ |
| Hypochlorous acid | HClO  | $4.00 \times 10^{-8}$  | Chloroacetic acid    | CH <sub>2</sub> ClCO <sub>2</sub> H              | $1.30 \times 10^{-3}$ |
| Benzoic acid      | C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H | $6.25 \times 10^{-5}$  | Dichloroacetic acid  | CHCl <sub>2</sub> CO <sub>2</sub> H              | $4.50 \times 10^{-2}$ |
| Hydrazoic acid    | HN <sub>3</sub>                                 | $2.50 \times 10^{-5}$  | Periodic acid        | HIO <sub>4</sub>                                 | $2.30 \times 10^{-2}$ |
| Acetic acid       | CH <sub>3</sub> COOH                            | $1.75 \times 10^{-5}$  | Chlorous acid        | HClO <sub>2</sub>                                | $1.10 \times 10^{-2}$ |
| Iodoacetic acid   | CH <sub>2</sub> ICO <sub>2</sub> H              | $6.60 \times 10^{-4}$  | Trichloroacetic acid | CCl <sub>3</sub> CO <sub>2</sub> H               | $2.20 \times 10^{-1}$ |
| Hydrofluoric acid | HF  | $6.30 \times 10^{-4}$  | Trifluoroacetic acid | CF <sub>3</sub> CO <sub>2</sub> H                | $3.00 \times 10^{-1}$ |
| Nitrous acid      | HNO <sub>2</sub>                                | $5.60 \times 10^{-4}$  | Iodic acid           | HIO <sub>3</sub>                                 | $1.70 \times 10^{-1}$ |
| Cyanic acid       | HCNO  | $3.50 \times 10^{-4}$  | Chromic acid         | HCrO <sub>4</sub>                                | $1.80 \times 10^{-1}$ |
| ⋮                 | ⋮   | ⋮                      | ⋮                    | ⋮  | ⋮                     |
| Name              | Formula   | $K_b$                  | Name                 | Formula  | $K_b$                 |
| Aniline           | C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>   | $7.40 \times 10^{-10}$ | ⋮                    | ⋮  | ⋮                     |
| Pyridine          | C <sub>5</sub> H <sub>5</sub> N                 | $1.70 \times 10^{-9}$  | n-Butylamine         | C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>    | $4.00 \times 10^{-4}$ |
| Hydroxylamine     | NH <sub>2</sub> OH                              | $8.70 \times 10^{-9}$  | Ethylamine           | C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>    | $4.50 \times 10^{-4}$ |
| Hydrazine         | N <sub>2</sub> H <sub>4</sub>                   | $1.30 \times 10^{-6}$  | Methylamine          | CH <sub>3</sub> NH <sub>2</sub>                  | $4.60 \times 10^{-4}$ |
| Ammonia           | NH <sub>3</sub>                                 | $1.80 \times 10^{-5}$  | tert-Butylamine      | (CH <sub>3</sub> ) <sub>3</sub> CNH <sub>2</sub> | $4.80 \times 10^{-4}$ |
| Propylamine       | C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub>   | $3.50 \times 10^{-4}$  | Dimethylamine        | (CH <sub>3</sub> ) <sub>2</sub> NH               | $5.40 \times 10^{-4}$ |
| ⋮                 | ⋮   | ⋮                      | ⋮                    | ⋮  | ⋮                     |

$pK_a$  and  $pK_b$  As acidity and basicity constants tend to be very small numbers there is a convenient form to deal with these values. By using logarithms one can transform a very tiny value into a larger digit. Specifically, if we use the negative value of a logarithm then we can convert a negative power of ten into a larger positive value. For example,

$$-\log(1 \times 10^{-5}) = 5$$

Using this mathematical trick, we define the  $pK_a$  and  $pK_b$ :

$$PK_a = -\log(K_a) \text{ and } PK_b = -\log(K_b) \quad (1.2)$$

For example, as the acidity constant of acetic acid is  $1.75 \times 10^{-5}$  its  $PK_a$  would be 4.74. Similarly, the basicity constant of aniline is  $7.40 \times 10^{-10}$ , and  $PK_b$  would be 9.13. We also use the following expression to convert  $pK_a$  and  $pK_b$  into  $K_a$  and  $K_b$

$$K_a = 10^{-PK_a} \text{ and } K_b = 10^{-PK_b} \quad (1.3)$$

For example, as the  $PK_a$  of nitrous acid is 3.37, the acidity constant of this acid is  $4.26 \times 10^{-4}$ .

*The conjugate seesaw* The strength of an acid and its conjugate base are not independent. Strong acids produce conjugate bases that are moderately weak. Similarly, weak acids produce conjugate bases that are moderately strong. The same reasoning can be applied to bases. This idea is called the conjugate seesaw and helps predict why the conjugate salt of a weak base such as ammonia ( $\text{NH}_4\text{Cl}$ ) gives a moderately strong acidic solution. This idea is summarized in the following relationship and we have that  $pK_a$  and  $pK_b$  are also related:

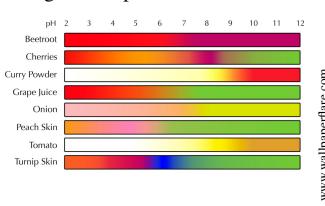
$$PK_a + PK_b = 14 \quad (1.4)$$

▼ A PH meter is used to measure the PH of solutions.



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▼ Color for different natural indicators depending on the pH.



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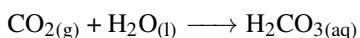
▼ Over breathing causes alkalosis and the PH of blood increases from 7.4. The  $\text{CO}_2$  level in the blood raises after breathing from a plastic bag.  $\text{CO}_2$  is an acid and decreases the PH of blood.



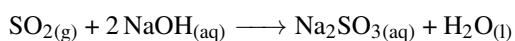
© wikipedia

*Acid-base properties of salts* Remember that strong acids (bases) produce weak conjugate bases (acids). Similarly, weak acids (bases) produce strong conjugate bases (acids). For example, HF is a weak acid, and therefore its conjugate  $\text{F}^-$  acid would be fairly strong. Similarly, NaOH is a strong base and its conjugate acid ( $\text{Na}^+$ ) is therefore fairly weak. Now, let us think about the acid-base properties of NaF, a salt. Remember that salt is just a common name to refer to ionic compounds resulting from the combination of metallic and nonmetallic elements. Without doing any type of calculation we can predict that as  $\text{Na}^+$  is a weak acid and  $\text{F}^-$  a strong base. Therefore, a NaF solution would be basic. Similarly, we can predict that NH<sub>4</sub>Cl would form an acidic solution, as ammonium ( $\text{NH}_4^+$ ) is the conjugate acid of ammonia (a weak base) and  $\text{Cl}^-$  is the conjugate base of a strong acid (HCl).

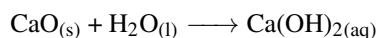
*Acid-base properties of oxides* Metallic oxides can be acidic, basic, or amphoteric. On one hand, acidic oxides react with water (or a base) forming its conjugate base. They tend to be covalent oxides, resulting from the combination of a nonmetal and oxygen. Example of acidic oxides are  $\text{CO}_2$ ,  $\text{NO}_2$  or  $\text{SO}_2$ . For example,  $\text{CO}_2$  can react with water forming carbonic acid:



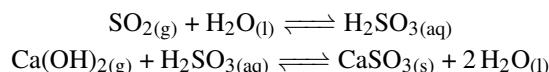
At the same time



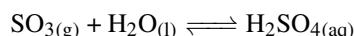
On the other hand, basic oxides react with water of acids to form a conjugate acid. They tend to be ionic compounds with metals from the first and second groups. Examples are MgO, K<sub>2</sub>O or CaO. We have that calcium oxide reacts with water forming calcium hydroxide:



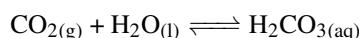
Calcium hydroxide is also known as slaked lime. This hydroxide is used for example in the scrubbing of stack gases from the exhaust of power plants and factories. When this compound reacts with sulfur trioxide the following set of reactions happens:



Group I hydroxides such as NaOH, LiOH or KOH are strong bases. Sodium and potassium hydroxides are common reagents, whereas lithium, rubidium, and cesium hydroxide are expensive and less used. Group II hydroxides such as Ca(OH)<sub>2</sub> or Ba(OH)<sub>2</sub> are also strong bases. However, these hydroxides tend to be insoluble, which can be convenient for some applications. For example, antacids are suspensions of metal hydroxides. The insoluble character helps protect the mouth and esophagus during their ingestion. Calcium hydroxide is called slaked lime and it is extensively used in water treatment plants to soften water—removing calcium and magnesium ions—and in the industry to scrub stack gases from exhaust pipes removing sulfur dioxide (and acidic gas). Calcium oxide—called lime—is also used in combination with soda ash (Na<sub>2</sub>CO<sub>3</sub>) in the softening go water involving the removal of calcium and magnesium ions in solutions. These ions hinder the action of detergents. Finally, amphoteric oxides can act as a basic or acidic oxides. We call this *amphotерism* and these oxides are *amphoteric*. They tend to be oxides containing elements on the line between metals and nonmetals (Be, Al, Ga, Ge, As, In, Sn, Sb, Pb, and Bi). Examples of amphoteric oxides are Al<sub>2</sub>O<sub>3</sub> or BeO. Covalent oxides tend to be acidic. An example is sulfur trioxide that reacts with water to produce sulfuric acid—a reaction involved in acid rain:



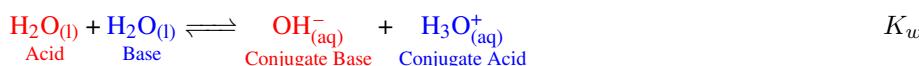
Carbon dioxide produced carbonic acid in the presence of water:



## 1.4 The PH scale

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

*Autoprotoysis of water and K<sub>w</sub>* 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, that can act as a base or an acid, hence giving and receiving protons. We call these types of chemicals *amphiprotic*. Other examples of amphiprotic chemicals are  $\text{HCO}_3^-$  or  $\text{HSO}_4^-$ . The dissociation constant of water is called the ion-product of water  $K_w$ :



$K_w$  is a constant that only depends on the temperature of the 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:

$$[\text{H}^+] \cdot [\text{OH}^-] = 1.0 \cdot 10^{-14} \quad (1.5)$$

*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 the solution is 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 ( $[\text{OH}^-]$ ) and both equal to  $1.0 \cdot 10^{-7}\text{M}$ . When we dissolve an acid or a base into the 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 8

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

#### SOLUTION

We will use Equation 1.5. The value given is  $[\text{H}^+] = 7.0 \cdot 10^{-5}\text{M}$  and the problem ask  $[\text{OH}^-]$ . 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:

$$\text{PH} = -\log [\text{H}^+] \quad (1.6)$$

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

a 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 are defined as:

$$POH = -\log[OH^-] \quad (1.7)$$

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

$$PH + POH = 14 \quad (1.8)$$

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

### Sample Problem 9

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 1.6. 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 1.6. However, before doing that, we need to compute the concentration of protons. In order to do this we will use Equation 1.5 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  $2.0 \cdot 10^{-9} M$ .

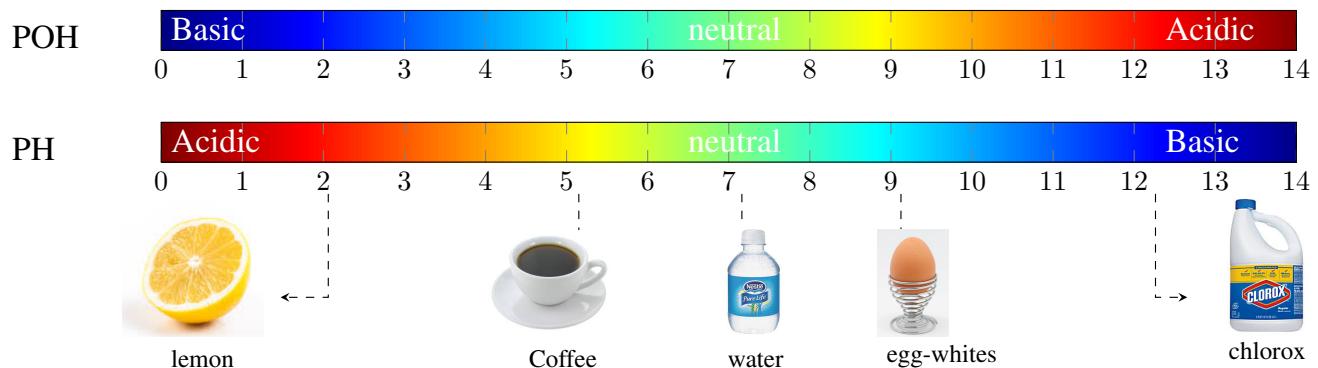


Figure 1.1 The PH scale

*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 using the logarithm with the 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:

$$[H^+] = 10^{-PH} \quad (1.9)$$

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:  $10 \wedge -3.3$ , and the result is  $5.0 \cdot 10^{-4}$ M. Mind that: (a) in some calculators, sometimes the power key looks like  $10^x$ ; (b) you need to use the negative key and not the minus key. The minus sign is used for substations, the negative key is used for numbers. An equivalent relation exists between the concentration of hydroxyls and the POH:

$$[OH^-] = 10^{-POH} \quad (1.10)$$

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

#### Sample Problem 10

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

#### SOLUTION

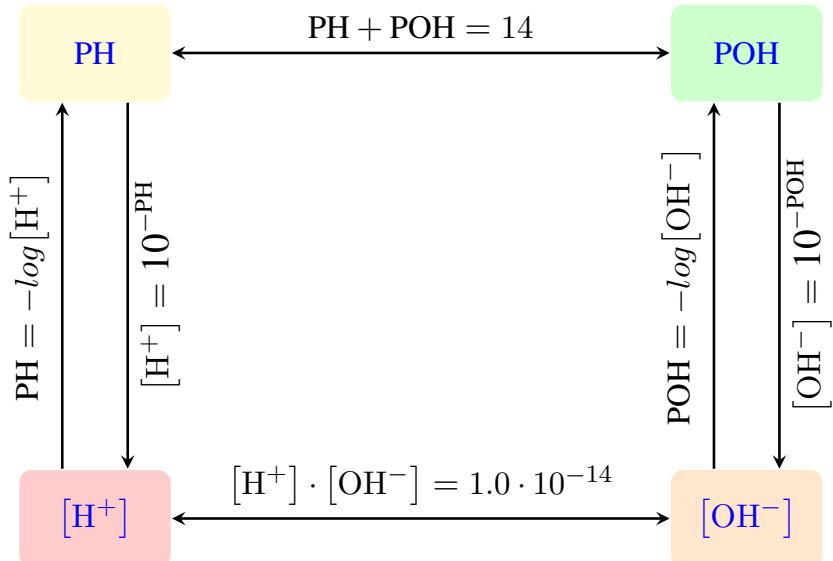
We will use Equation 1.9, given PH and asking  $[H^+]$ .

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

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

#### ❖ STUDY CHECK

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



**Figure 1.2** Diagram with formulas relating the PH, POH and the concentration of protons and hydroxyls in water.

## 1.5 PH of strong acid-base solutions

Imagine we prepare a strong acid solution and we want to estimate the PH of the resulting solution. The solution PH will depend on the molarity of the resulting solution:

$$PH = -\log(n_H \cdot c_a) \quad (1.11)$$

where:

$n_H$  is the number of protons in the acid (e.g. H<sub>3</sub>PO<sub>4</sub> has  $n_H=3$ )

$c_a$  is the molarity of the acid solution

We have an equivalent formula for the POH of a strong base:

$$POH = -\log(n_{OH} \cdot c_b) \quad (1.12)$$

where:

$n_{OH}$  is the number of hydroxyls in the base (e.g. Ca(OH)<sub>2</sub> has  $n_{OH}=2$ )

$c_b$  is the molarity of the base solution

Mind these formulas only work for strong acids and bases, as their molarity is directly related to the concentration of protons and hydroxyls. The following example will demonstrate the use of these formulas.

### Sample Problem 11

Calculate the PH of: (a) a 0.02M HNO<sub>3</sub> solution (b) a 0.02M Ca(OH)<sub>2</sub> solution.

#### SOLUTION

(a) We will use Equation 1.11 given that the molarity of the acid is 0.02M and the acid only has a single proton:

$$PH = -\log(n_H \cdot c_a) = -\log(0.02) = 1.69$$

(b) We will use Equation 1.12 given that the molarity of the base is 0.02M and it has two hydroxyls ( $n_{OH}=2$ ):

$$POH = -\log(n_{OH} \cdot c_b) = -\log(2 \cdot 0.02) = 1.39$$

Now, we will convert POH in PH using Equation 1.8:

$$PH = 14 - POH = 12.61$$

#### ❖ STUDY CHECK

Calculate the PH of: (a) a 0.001M H<sub>2</sub>SO<sub>4</sub> solution (b) a 0.001M NaOH solution.

## 1.6 PH of weak acid-base solutions

*PH of solutions of weak acids and bases* Imagine we prepare a weak acid solution and we want to estimate the PH of the resulting solution. The solution PH will depend on the molarity of the resulting solution. However, as weak acids and

bases do not dissociate completely, the procedure and the formulas involved in the PH calculations differ from those of strong electrolytes, explained previously. In particular, for weak electrolytes, the calculation involves a quadratic equation. These equations can be solved either with the help of a graphic calculator or using a [quadratic equation solver link](#) that can be found in the internet. The resolution of quadratic formulas will lead to two different roots, a positive and a negative root. Only the positive root would make chemical sense. As such, you can directly toss the negative root.

The quadratic formula involved in the PH calculation for a weak acid is shown below:

$$[\text{H}^+]^2 + K_a \cdot [\text{H}^+] - K_a \cdot c_a = 0 \quad \text{with } [\text{H}^+] = x \quad (1.13)$$

where:

$[\text{H}^+] = x$  is concentration of protons in equilibrium

$K_a$  is the acidity constant of the acid

$c_a$  is the molarity of the acid solution

For example, the PH of a 0.1M HF solution, given that HF is a weak acid with  $K_a = 6.3 \times 10^{-4}$ , will be given by:

$$[\text{H}^+]^2 + 6.3 \times 10^{-4} \cdot [\text{H}^+] - 6.3 \times 10^{-5} = 0$$

Solving the quadratic equation, we obtain two roots:  $[\text{H}^+] = 0.0076$  and  $[\text{H}^+] = -0.0082$ . Only the positive root will be valid and hence we have:

$$[\text{H}^+] = 0.0076$$

The PH of the solution will be 2.11. There is an equivalent formula involved in the calculation of the PH of a weak base:

$$[\text{OH}^-]^2 + K_b \cdot [\text{OH}^-] - K_b \cdot c_b = 0 \quad \text{with } [\text{OH}^-] = x \quad (1.14)$$

where:

$[\text{OH}^-] = x$  is concentration of hydroxyls in equilibrium

$K_b$  is the basicity constant of the base

$c_b$  is the molarity of the base solution

Mind that to calculate the PH or POH you will need to employ Equations 1.6 and 1.7. For example, the PH of a 0.1M  $\text{NH}_3$  solution, given that ammonia is a weak base with  $K_b = 1.8 \times 10^{-5}$ , will be given by:

$$[\text{OH}^-]^2 + 1.8 \times 10^{-5} \cdot [\text{OH}^-] - 1.8 \times 10^{-6} = 0$$

Solving the quadratic equation, we obtain two roots:  $[\text{OH}^-] = -0.0013$  and  $[\text{OH}^-] = 0.0013$ . Only the positive root will have chemical meaning and hence we have:

$$[\text{OH}^-] = 0.0013$$

The POH of the solution will be 2.88 and the PH will be 11.11. The following example will further demonstrate the use of these formulas.

**Sample Problem 12**

Calculate the PH of a 0.02M  $\text{CH}_2\text{O}_2$  (formic acid) solution.  $K_a = 1.8 \times 10^{-4}$

**SOLUTION**

As formic acid is a weak acid, we will have to use Equation 1.13 in order to calculate PH:

$$[\text{H}^+]^2 + K_A \cdot [\text{H}^+] - K_a \cdot c_a = 0$$

We have that  $c_a=0.02\text{M}$  and that  $K_a = 1.8 \times 10^{-4}$ . Therefore  $-K_a \cdot c_a$  is  $-3.6 \times 10^{-6}$ . Therefore, the quadratic formula that gives the PH is:

$$[\text{H}^+]^2 + 1.8 \times 10^{-4} \cdot [\text{H}^+] - 3.6 \times 10^{-6} = 0$$

Solving for  $[\text{H}^+]$  and using only the positive root, we have  $[\text{H}^+] = 1.8 \times 10^{-3}\text{M}$  and  $\text{PH}=2.74$ .

**◆ STUDY CHECK**

Calculate the PH of a 0.002M aniline solution.  $K_b = 7.4 \times 10^{-10}$

*PH of salt solutions* As well as hydrcids or hydroxides, salts can exhibit acid or base character. For example, ammonium chloride ( $\text{NH}_4\text{Cl}$ ) is an acidic salt, as ammonium is the conjugate acid of a weak base, and therefore has moderately strong character. Differently, chloride is the conjugate base of a strong acid ( $\text{HCl}$ ) and has a weak character. Let us calculate the PH of a 0.1-M  $\text{NH}_4\text{Cl}$  solution. As the salt is acidic, we will use Equation 1.13 given that  $c_a=0.1\text{M}$  and  $K_a = 5.5 \times 10^{-10}$  (mind for ammonia  $K_b = 1.8 \times 10^{-5}$  and Equation 1.1 relates  $K_a$  and  $K_b$ ):

$$[\text{H}^+]^2 + 5.5 \times 10^{-10} \cdot [\text{H}^+] - 5.5 \times 10^{-11} = 0$$

Solving for  $[\text{H}^+]$  we have that  $[\text{H}^+] = 7.4 \times 10^{-6}\text{M}$  and  $\text{PH}=5.13$ . As predicted, the PH of an ammonium chloride solution is acidic.

**Sample Problem 13**

Calculate the PH of a 0.02M  $\text{HCOONa}$  (sodium formate) solution.  $K_a = 1.8 \times 10^{-4}$

**SOLUTION**

Formate is the conjugate base of an weak acid, therefore it will be moderately basic. We will use 1.14 given that  $K_b = 5.5 \times 10^{-11}$  and  $c_b=0.02\text{M}$ :

$$[\text{OH}^-]^2 + 5.5 \times 10^{-11} \cdot [\text{OH}^-] - 5.5 \times 10^{-12} = 0$$

Solving for  $[\text{OH}^-]$  and using only the positive root, we have  $[\text{OH}^-] = 2.3 \times 10^{-6}\text{M}$  and  $\text{POH}=5.63$ . The final answer would be:  $\text{PH}=8.36$ .

**◆ STUDY CHECK**

Calculate the PH of a 0.01M sodium acetate ( $\text{CH}_3\text{COONa}$ ).  $K_a = 1.75 \times 10^{-5}$

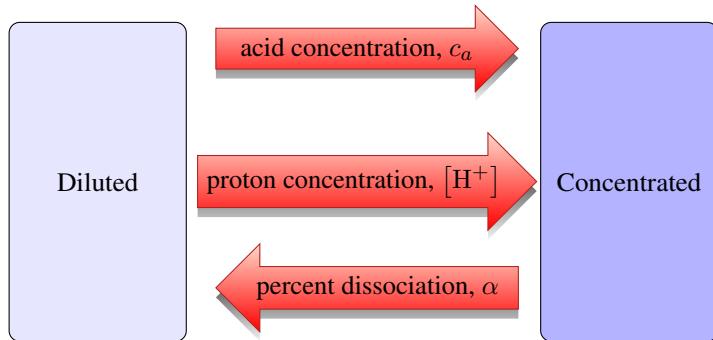
*Percent dissociation of weak acids and bases* Weak acids (and base) are indeed weak electrolytes, which means if we prepare a solution of a given concentration  $c_a$  they will dissociate giving a proton concentration ( $[\text{H}^+]$ ) less than  $c_a$ . We define the percent dissociation  $\alpha$  of an acid (or base) as:

$$\alpha = \frac{\text{amount dissociated}}{\text{initial amount}} \times 100 = \frac{[\text{H}^+]}{c_a} \times 100 \quad (1.15)$$

where:

$[H^+]$  is concentration of protons in equilibrium  
 $c_a$  is the initial acid concentration

For example, a 0.2M HF solution has a proton concentration of 0.0076M. The percent dissociation of this acid at this concentration will be 3.8%. The percent dissociation changes with the acid (or base) concentration and more concentrated acids have in general a larger proton concentration than diluted acids. However, the percent dissociation of more concentrated acids is smaller than the one of less concentrated acids. The diagram below displays this concept.



#### Sample Problem 14

Calculate the percent dissociation of  $\text{CH}_2\text{O}_2$  in 0.01M and 0.09M solutions.

$$K_a = 1.8 \times 10^{-4}$$

#### SOLUTION

We will first calculate  $[H^+]$  for both solutions using Equation 1.13. For the most diluted  $[H^+]$  will be given by:

$$[H^+]^2 + 1.8 \times 10^{-4} \cdot [H^+] - 1.8 \times 10^{-6} = 0$$

Solving and selecting the positive root, we have:  $[H^+] = 1.25 \times 10^{-3}\text{M}$ . For the most concentrated we have:

$$[H^+]^2 + 1.8 \times 10^{-4} \cdot [H^+] - 1.62 \times 10^{-5} = 0$$

Solving and selecting the positive root, we have:  $[H^+] = 3.93 \times 10^{-3}\text{M}$ . We can now calculate the degree of dissociation using Equation 1.15. For the most diluted we have:

$$\alpha = \frac{[H^+]}{c_a} \times 100 = \frac{1.25 \times 10^{-3}}{0.01} \times 100 = 12.5\%$$

For the most concentrated we have:

$$\alpha = \frac{3.93 \times 10^{-3}}{0.09} \times 100 = 4.36\%$$

We have that for more concentrated solutions of the same acid, the concentration of protons is larger than for more diluted solutions. In contrast, the degree of dissociation is larger for more diluted solutions.

#### ◆ STUDY CHECK

Calculate the percent dissociation of a 0.05M methylamine  $\text{CH}_3\text{NH}_2$  solution.

$$K_b = 4.4 \times 10^{-4}$$

## 1.7 Buffer solutions

We have previously addressed the properties of acids and bases. Buffers are specific solutions able to accommodate acids or bases without changing their PH. Buffers play a key role for example in our blood where a buffer system absorbs 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 or base. Buffers are solutions of a weak acid with its conjugate base, or weak bases and its conjugate acid. For example, a mixture of 0.1M NH<sub>3</sub> and 0.1M NH<sub>4</sub>Cl is a buffer. You can find acidic or basic buffers. 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 lose their capacity to modulate the PH.

**PH of a Buffer solution** A buffer solution consists 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:

$$PH = PK_a + \log\left(\frac{c_b}{c_a}\right) \quad (1.16)$$

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 15

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:

$$PH = PK_a + \log\left(\frac{V_b \cdot c_b + (V_b \cdot c_b)^{\text{added}} - (V_a \cdot c_a)^{\text{added}}}{V_a \cdot c_a + (V_a \cdot c_a)^{\text{added}} - (V_b \cdot c_b)^{\text{added}}}\right) \quad (1.17)$$

where most of the symbols of Equation 1.17 are the same as in Equation 1.16:

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

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

The following example illustrates how to use Equation 1.16.

**Sample Problem 16**

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  $PK_a = 9.25$ ,  $V_a = V_b = 20\text{mL}$ ,  $c_a = 0.1\text{M}$  and  $c_b = 0.2\text{M}$ . As we are adding an acid we have  $(V_b \cdot c_b)^{\text{added}} = 0$  and  $(V_a \cdot c_a)^{\text{added}} = 1 \cdot 0.3 = 0.3\text{mM}$ . Using Equation 1.16:

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

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**

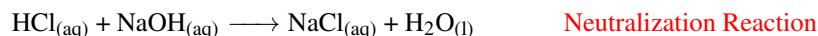
Calculate the PH of 5mL of a 0.2M HF/0.3M KF ( $K_a = 6.30 \times 10^{-4}$ ) after adding 1mL of HCl 0.2M.

## 1.8 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, Erlenmeyer, 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 involve a neutralization reaction in which an acid neutralizes a base. Acids produce protons  $H^+$  and bases hydroxyls  $OH^-$  that neutralize forming water,  $H_2O$ . 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 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 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.

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

$$n_H \cdot c_a \cdot V_a = n_{OH} \cdot c_b \cdot V_b \quad (1.18)$$

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 at the volume of base needed to the endpoint to calculate 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 1.18 can also be used to identify if we already passed the endpoint in a titration. For example, we titrate 2mL of 3M  $H_2SO_4$  (titrant) with 2mL of 1M NaOH (titrate). The question would be: are we before, after, or at the endpoint? We have to neutralize completely the titrant ( $H_2SO_4$ ), and using Equation 1.18 we would need:

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

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

Sample Problem 17

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 1.18, 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**

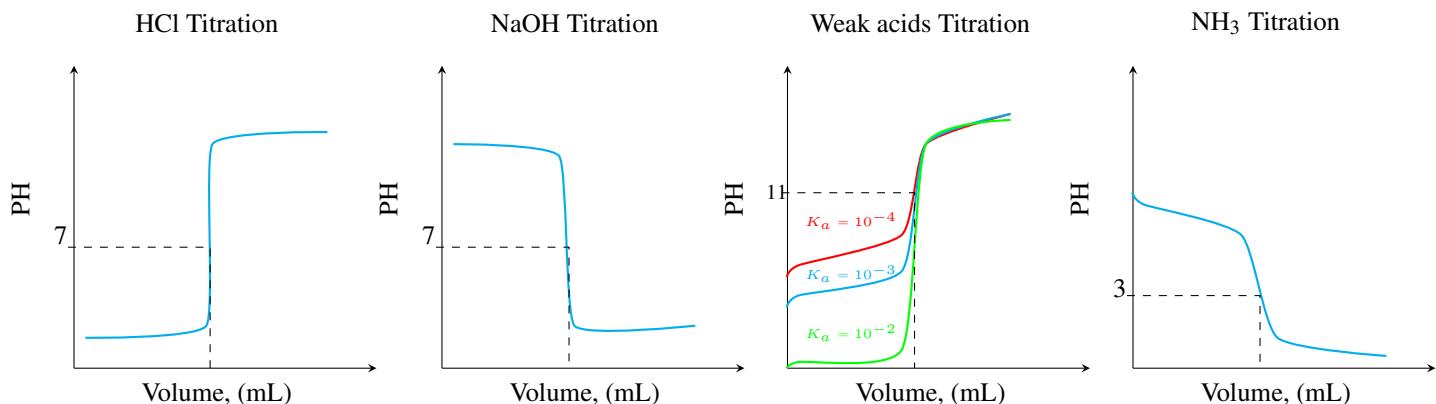
A 15mL sample of an unknown acid is neutralized with 45 mL of a NaOH 1M solution. Calculate the molarity of the unknown acid.

*The mid-point* In titrations, there is another important point called the mid-point. The mid-point is reached at half the equivalency point. For example, the end-point of the titration of 10 mL of 0.1M HCl by 10 mL of 0.1M NaOH happens when we add 10 mL of the base. The mid-point hence will happen when we add 5mL of the base. We have that the volumes of the end ( $V_{EP}$ ) and the midpoint ( $V_{MP}$ ) are related by the formula below:

$$V_{MP} = \frac{V_{EP}}{2} \quad (1.19)$$

## 1.9 Titrations curves

A titration plot or PH curve represents the change in the PH during titration as the volume of the titrant increases. In the vertical axis, it represents PH, in the horizontal axis, it resents volume. The species present in the titrate change as the titration proceed. For example, in the case of the titration of a weak acid with a strong base, before it starts, the major species is solution is the weak acid HA. When the titration proceeds and before reaching the endpoint, the major species in solution are the weak acid and the conjugate base ( $A^-$  and HA), as the titrant neutralizes some of the acids. At the endpoint, the major specie present is the conjugate base  $A^-$ . After the endpoint, the PH is given by the excess of the titrant.



**Figure 1.3** 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.

*Titration curve differences* Titration curves look slightly different depending on the 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 an acidic PH. The PH at the endpoint is also neutral. The titration ends with a strong basic PH. When titrating a weak acid, the curve starts at a high acidic PH, and near the endpoint, PH rises smoothly and not sharply until reaching a plateau at a low 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. For weak acids and bases, the location of the starting plateau depends on the equilibrium constant. For the titration of a weak acid, the plateau lowers as the acidity constant increases. In other words, stronger acids have a lower starting plateau, and stronger bases have a higher starting plateau. Still, the equivalence point does not depend on the nature of the acid but on the stoichiometry. Overall, we have that 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 bases, 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.

Table 1.3 PH Titration formulas

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

## 1.10 Quantitative analysis of a titration

We spoke at this point about the idea behind titrations, its most important points, and how to graphically represent the PH changes that happen. Now we will focus on calculating the PH value at different points along a titration. The formula involved behind titration can be complex and often involves quadratic formulas. In particular, the formulas to be used depends on the nature of the titrate and the titrant.

*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 that 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 Table 1.3 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 concentrations  $c_R$  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 the solution. The formula for  $c_R$  is:

$$c_R = \frac{|n_H \cdot c_a \cdot V_a - n_{OH} \cdot c_b \cdot V_b|}{V_a + V_b} \quad (1.20)$$

where all variable refer to Equation 1.18. 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 the solution. The formula for  $c_F$  is:

$$c_F = \frac{\min(n_H \cdot c_a \cdot V_a, n_{OH} \cdot c_b \cdot V_b)}{V_a + V_b} \quad (1.21)$$

where all variable refer to 1.18. 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 18

A 25mL sample of 3M HCl is titrated by 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 1.2 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 1.18 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 1.18:

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

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  $c_R$ :

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

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

#### STUDY CHECK

A 5mL sample of 2M  $\text{H}_2\text{SO}_4$  is titrated by 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

*PH at the midpoint* The PH at the midpoint depends on the type of acid or base that is being titrated. For strong electrolytes, the PH at the midpoint will be given by the molarity of the initial solution. For example, when titrating a 0.1M HCl solution with 0.1M NaOH, the PH at the midpoint will be close to 1. Differently, the PH at the midpoint for weak electrolytes is given by the acidity or basicity constant of the acid. Specifically, it corresponds to the  $PK$  of the acid or base. For example, when titrating a 0.1M HAc (acetic acid,  $K_a = 1.8 \times 10^{-5}$ ) solution with 0.1M NaOH, the PH at the midpoint will be close to 4.7.

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 1.6-1.8)

#### Sample Problem 19

A 1mL sample of 2M acetic acid ( $\text{CH}_3\text{COOH}$ ,  $K_b = 1.75 \times 10^{-5}$ ) is titrated by 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 1.2 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 1.18 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 1.18:

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

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 by 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



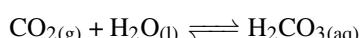
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**Figure 1.4** An acid base titration using phenolphthalein as indicator. From left to right, before, at and after the end point.

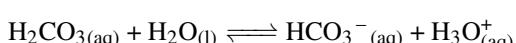
## 1.11 Blood as a buffer

Carbon dioxide acts as a buffer in the blood, hence regulating its PH. Here, we will discuss some chemical aspects that impact its role as buffer.

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

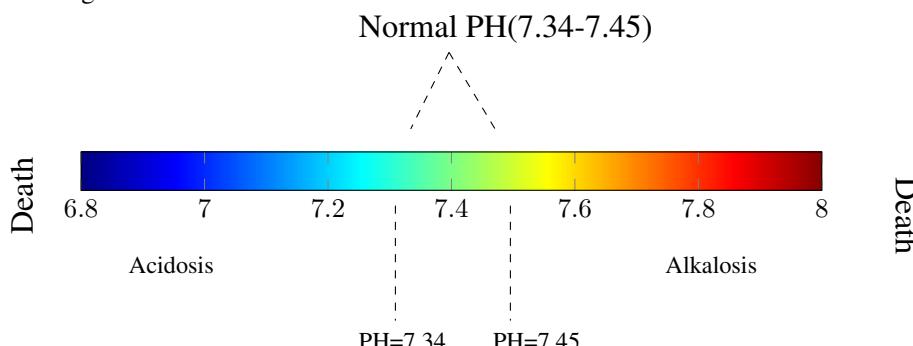


At the same time  $\text{H}_2\text{CO}_3$  partially dissociates in water as a weak acid producing bicarbonate—also known as hydrogen carbonate:



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 which is slightly above the neutral value of 7.

The dangerous change in blood PH Most biological molecules are very sensitive to 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 in PH below 6.8 or above 8.0 can cause death.



**Figure 1.5** 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 becoming 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 is unable to 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 20

Explain why CO<sub>2</sub> decreases the PH of blood.

#### SOLUTION

CO<sub>2</sub> is an acid and when dissolved in water it generates protons, H<sup>+</sup>. Increasing the amount of protons decreases PH as PH is a measure the concentration of protons in solution.

#### ❖ STUDY CHECK

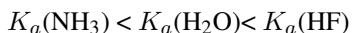
The PH of a patient's blood sample is 7.3. Indicate whether the patient suffers alkalosis, acidosis, or perhaps none of the afflictions. Can the PH level cause death?

## 1.12 Molecular mechanisms behind acid-base strength

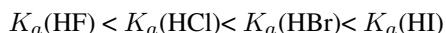
Why are some acids stronger than others? There is not simple answer to this question. The strength of a given acid depends not only on its molecular structure but also on energetic

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. HClO), and carboxylic acids (e.g. CH<sub>3</sub>COOH).

*Binary acids* Binary acids result from the combination of an element (e.g. N, O, F) with hydrogen: NH<sub>3</sub>, H<sub>2</sub>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. NH<sub>3</sub>). 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



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 atom to withdraw electron density from hydrogen and hence the bond becomes weaker (*acidity factor 1*). The less 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

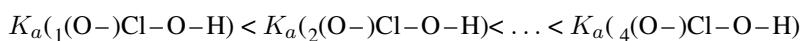


This trend corresponds with an increase in the atomic weight of the central atom and an increase in the capacity of the corresponding anion to stabilize the negative charger. Acid dissociation necessarily implies the formation of an anion (e.g. Cl<sup>-</sup> or even NH<sub>2</sub><sup>-</sup>). The more stable this anion the stronger its 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: <sub>n</sub>(O<sup>-</sup>)Cl—O—H. For example, Cl—O—H is called hypochlorous acid (HClO), and <sub>3</sub>(O<sup>-</sup>)Cl—O—H is called perchloric acid (HClO<sub>4</sub>). 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

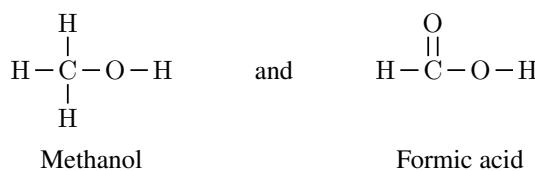


In other words, acidity increases from bottom to top across a group. That is the greater the electronegativity of the halogen the stronger the acid character. This trend is indeed opposite to the one found in binary acids. As the electronegativity of the halogen increases more electron density is withdrawn 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

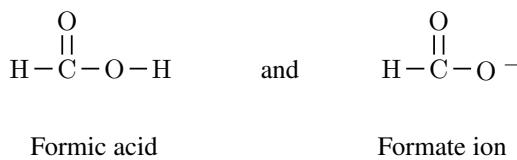


In other words, acidity increases as the number of oxygen atoms connected to the central halogen increases. As the number of electronegative oxygen atoms connected to the central halogen atoms increases, more electron density will be withdrawn from the central Cl. This will also impact the oxygen connected to the acidic hydrogen weakening the O–H bond and 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.

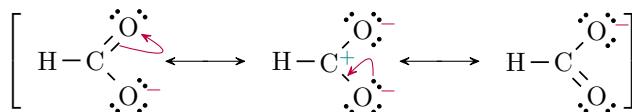
*Carboxylic acids* We can start by comparing the acidity of two different organic compounds, methanol, the simplest of all alcohols, and formic acid, the simplest carboxylic acid. The structure of both molecules is presented below:



Indeed, methanol, as well as other alcohols, are not acidic whereas carboxylic acids and in particular formic acid are in general weak acids. We can understand this trend through two factors. On one hand, following *acidity factor 4* carboxylic acids have two oxygen atoms connected to the central carbon. Both withdraw electron density from carbon hence weakening the O–H bond and increasing acidity. There is a new acidity factor that contributes 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 contributes to the acidity of the carboxylic acids *acidity factor 5*.



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

Five different factors 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 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 acid increases acidity strength.

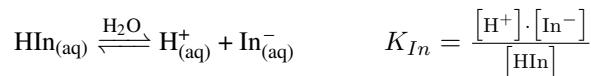
There are several techniques to locate the endpoint during titration. On one hand, we can use a PH meter and measure PH during the titration. The endpoint locates between the initial and final plateau. We can also use an automatic titrator, a machine that automatically mixes the acid and the base while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

**Table 1.4 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       |

*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 in an 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. Turmeric is a specie that turns 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 different colors due to differences in their electronic structure that transform into differences in 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 endpoint (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 color change 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:  $PH = PK_{In} \pm 0.7$

*Selecting an indicator* A good indicator will turn into a different color within the transition between acid and basic PH during 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 which 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 endpoint.

*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, for example, ammonia vapor would turn blue on a piece of wet red litmus paper.

### Sample Problem 21

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

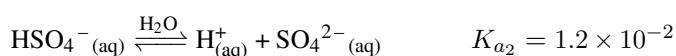
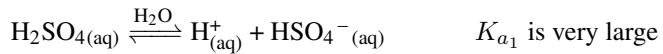
 **STUDY CHECK**

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.

## 1.14 Titrations of polyprotic acids

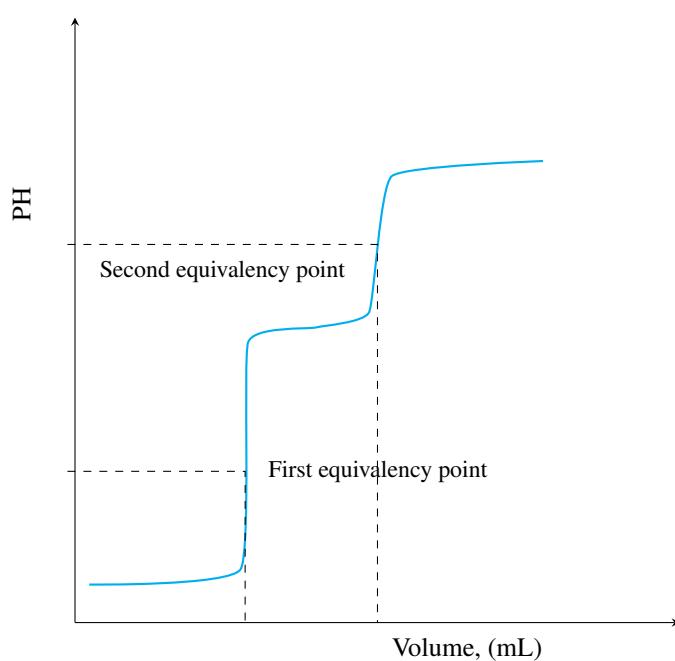
Monoprotic acids contain a single proton. Examples are hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>). Polyprotic acids contain more than one proton. Examples are sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), a diprotic acid, and phosphoric acid, (H<sub>3</sub>PO<sub>4</sub>). When titrating an acid, the number of protons determines the number of endpoints observed. Monoprotic acids go through a single endpoint, 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 transitions and inclined plateaus. For polyprotic acids, these principles are applied to each endpoint 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 bases 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 1.6** PH curve for a diprotic acid showing two equivalency points

