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Ch. 10. Acids & Bases

ACIDS 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.

10.1 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

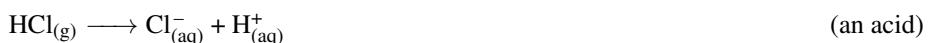
using a single arrow, whereas the dissociation of weak acids and bases is represented using a double harpoon. For example, hydrochloric acid is a strong electrolyte and its dissociation is represented by



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*: H^+ , also called hydronium ion written as H_3O^+ . Let us consider these chemicals: HF, H_2SO_4 and 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:

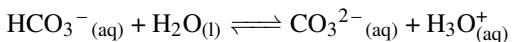


Based on the acid dissociation reaction above, we say chloride is the result of deprotonating hydrochloric acid. In other words, chloride is deprotonated. Based on this dissociation reaction that happens in water, we can say hydrogen chloride also known as hydrochloric acid is an Arrhenius acid, as it 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. HNO_3), whereas diprotic acids have two (e.g. H_2NO_4) and polyprotic acids have more than two (e.g. H_3PO_4). Differently, bases are basic because when dissolved in water they produce *hydroxyls*: OH^- . Hydroxides are Arrhenius bases and for example, NaOH and $\text{Ca}(\text{OH})_2$, named sodium hydroxide and calcium hydroxide, are well-known bases. Let us address now the dissociation of sodium hydroxide in water:



This chemical is an Arrhenius base as it produces hydroxyls. Therefore, Arrhenius acids and bases produce protons and hydroxyls in water, respectively. However, the Arrhenius model does not explain why chemicals unsolved in water can also be acidic or even why chemicals such as 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 (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.



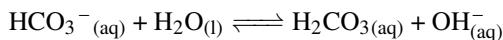
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▼ Citrus such as lemons or oranges are acidic.



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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 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: H_2O , HS^- or 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: HCl , KOH , H_3PO_4 and CH_3COOH .

SOLUTION

The acids are: HCl , H_3PO_4 and CH_3COOH . Their names are: hydrochloric acid, phosphoric acid and acetic acid, the later is a common name. KOH is a base called potassium hydroxide.

❖ STUDY CHECK

Identify the following chemicals as Arrhenius acids or bases and give their names: NaOH and H_2CO_3 .

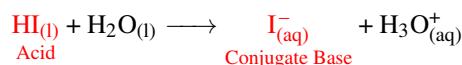
▼ Bath bombs are made of acidic and basic ingredients that combine in water to make a fizzy bath time experience.


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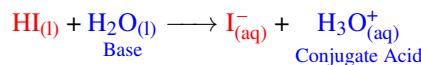
10.2 Dissociation of acids and bases

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

Conjugate acids and bases A conjugate acid-base pair are molecules or ions related by the loss of one H^+ . For example: hydroiodic acid HI and iodate I^- or water H_2O and protons H_3O^+ . 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:



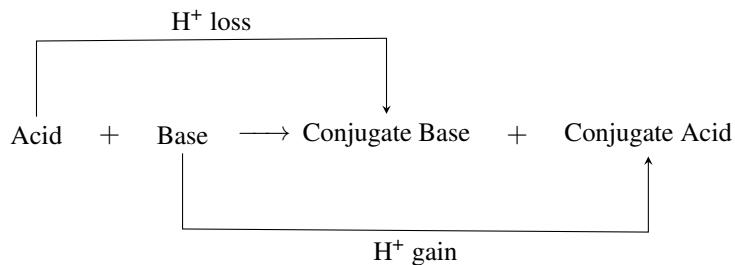
▼ Ashes are basic.


© wikipedia

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

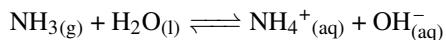

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Hence, we have that acid reactants with a base to produce a conjugate base and a conjugate acid. We can use the diagram below to identify the acid-conjugate base pairs:



Sample Problem 2

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



SOLUTION

The trick is first identifying the acid and the base starting for the left side of the formula. In this case $\text{NH}_3\text{(g)}$ is the base and hence water is the acid. Now connect the acid and the base with the other side of the arrow, and use conjugate with the opposite term. For example: NH_3 is a base and should be related with NH_4^+ that is the conjugate acid. Similarly, H_2O is a acid, being related with OH^- that is the conjugate base. In summary:



❖ STUDY CHECK

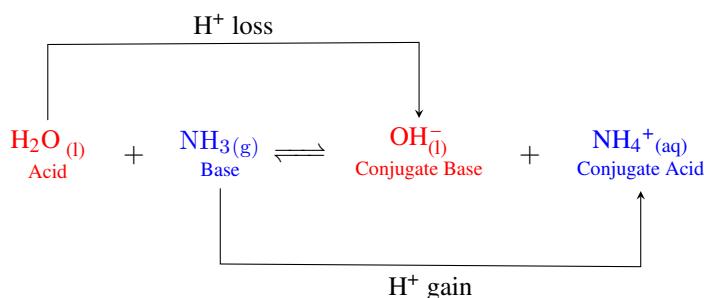
Identify the acid, the base, the conjugate acid and the conjugate base in the reaction:



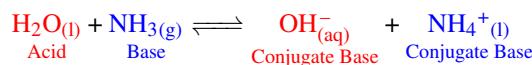
Writing down acid-base equilibria Now let us address how to write down acid-base equilibria from scratch, starting with the dissociation of ammonia (NH_3). Dissociation reactions are the reaction of an acid or base and water:



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:



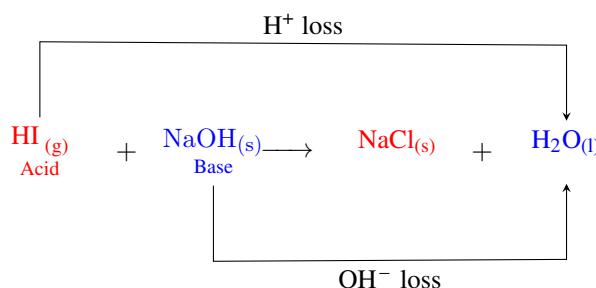
And that will give the dissociation equilibrium of ammonia.



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

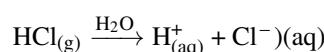


In these types of acid-base reactions, we have that the acid will generate a proton and the base will generate a hydroxyl, which will both combine to produce water and a salt, sodium chloride:

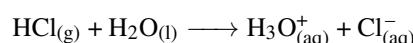


This way, dissociation and acid-base reaction function in a very similar manner.

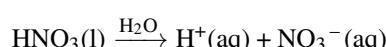
Including water in the dissociation Let us consider an acid such as HCl. We know acids produce protons (H^+ or H_3O^+) so we can express the acid dissociation as:



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:



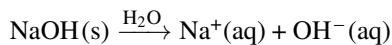
This way we explicitly represent the role of water as a proton receiver. Ultimately, both ways are correct and for some chemicals (e.g. NH₃) it is more convenient to use the role of water whereas for others it makes no difference. In the following, we present more examples. For the case of HNO₃, nitric acid, we have:



that means once dissolved in water, nitric acid gives a proton and forms a nitrate NO_3^- cation. Some other acids, such as H_2SO_4 are diprotic, as they have two protons and hence they can lose both while reacting with water:



Bases produce hydroxyls (OH^-) and an example of a base dissociation would be:

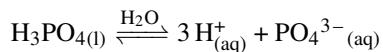


Sample Problem 3

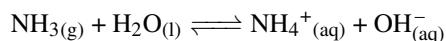
Write down the dissociation reaction using double arrows for the following chemicals: $\text{H}_3\text{PO}_4(\text{l})$ and $\text{NH}_3(\text{g})$.

SOLUTION

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



As the molecules 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.



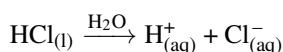
◆ STUDY CHECK

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

10.3 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 if 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 H^+ . Strong bases are strong electrolytes that dissociate completely to produce this time large quantities of hydroxyls OH^- . Weak acids or weak bases dissociate only partially and hence they produce fewer protons or hydroxyls. Examples of strong electrolytes are: HCl , H_2SO_4 or HNO_3 . As they dissociate completely we use a single arrow to indicate they are strong electrolytes:

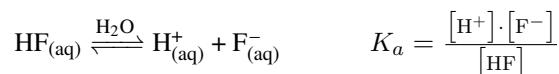


One arrow indicates strong acids or bases

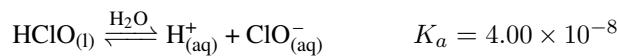
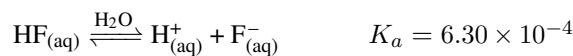
Weak acids or bases that only dissociate partially are represented by a double arrow as the reaction is indeed an equilibrium. Examples of weak acids or bases are NH₃ or HF.



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:

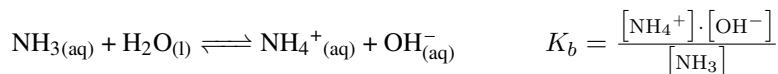


If we compare the acidity constant of two different acids, for example, hydrofluoric acid and hypochlorous acid

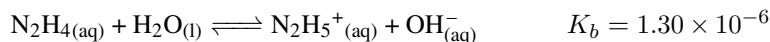
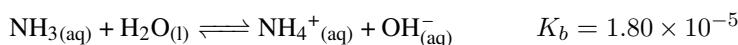


we can conclude that HF is stronger than HClO as its acidity constant is larger.

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 NH₃ is stronger than N₂H₄ 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:

$$K_a \cdot K_b = 1.0 \cdot 10^{-14} \quad (10.1)$$

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 1.5×10^{-5} , the basicity constant of the same species would be 6.6×10^{-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^-) is a weak base. Differently, HF is a weak acid and its conjugate base (F^-) 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 4

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:

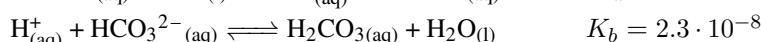
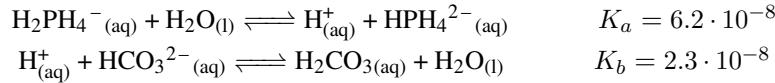


Table 1.1 Acidity and basicity constants at 25°C

Name	Formula	K_a	Name	Formula	K_b
Hypoiodous acid	HIO	3.20×10^{-11}	Fluoroacetic acid	$\text{CH}_2\text{FCO}_2\text{H}$	2.5
Phenol	$\text{C}_6\text{H}_5\text{OH}$	1.00×10^{-10}	Formic acid	CH_2O_2	1.8
Hydrocyanic acid	HCN	6.20×10^{-10}	Bromoacetic acid	$\text{CH}_2\text{BrCO}_2\text{H}$	1.7
Hypobromous acid	HBrO	2.80×10^{-9}	Chloroacetic acid	$\text{CH}_2\text{ClCO}_2\text{H}$	1.6
Hypochlorous acid	HClO	4.00×10^{-8}	Dichloroacetic acid	$\text{CHCl}_2\text{CO}_2\text{H}$	4.4
Benzoic acid	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	6.25×10^{-5}	Periodic acid	HIO_4	2.2
Hydrazoic acid	HN_3	2.50×10^{-5}	Chlorous acid	HClO_2	1.1
Acetic acid	CH_3COOH	1.75×10^{-5}	Trichloroacetic acid	$\text{CCl}_3\text{CO}_2\text{H}$	2.2
Iodoacetic acid	$\text{CH}_2\text{ICO}_2\text{H}$	6.60×10^{-4}	Trifluoroacetic acid	$\text{CF}_3\text{CO}_2\text{H}$	3.3
Hydrofluoric acid	HF	6.30×10^{-4}	Iodic acid	HIO_3	1.1
Nitrous acid	HNO_2	5.60×10^{-4}	Chromic acid	HCrO_4	1.1
Cyanic acid	HCNO	3.50×10^{-4}	⋮	⋮	⋮
<hr/>					
Name	Formula	K_a	Name	Formula	K_b
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	7.40×10^{-10}	n-Butylamine	$\text{C}_4\text{H}_9\text{NH}_2$	4.0
Pyridine	$\text{C}_5\text{H}_5\text{N}$	1.70×10^{-9}	Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	4.0
Hydroxylamine	NH_2OH	8.70×10^{-9}	Methylamine	CH_3NH_2	4.0
Hydrazine	N_2H_4	1.30×10^{-6}	tert-Butylamine	$(\text{CH}_3)_3\text{CNH}_2$	4.0
Ammonia	NH_3	1.80×10^{-5}	Dimethylamine	$(\text{CH}_3)_2\text{NH}$	5.0
Propylamine	$\text{C}_3\text{H}_7\text{NH}_2$	3.50×10^{-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 :

$$PK_a = -\log(K_a) \text{ and } PK_b = -\log(K_b) \quad (10.2)$$

For example, as the acidity constant of acetic acid is 1.75×10^{-5} its PK_a would be 4.74. Similarly, the basicity constant of aniline is 7.40×10^{-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

$$K_a = 10^{-PK_a} \text{ and } K_b = 10^{-PK_b} \quad (10.3)$$

For example, as the PK_a of nitrous acid is 3.37, the acidity constant of this acid is 4.26×10^{-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 (NH_4Cl) 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:

$$PK_a + PK_b = 14 \quad (10.4)$$

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

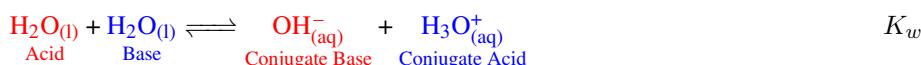


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10.4 The PH scale

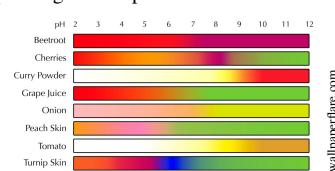
This section describes the PH scale that simply transforms a concentration value—oftentimes a very small number—into a simple round value. In short, the PH value tells you how many protons are there in a solution so that the larger PH the fewer protons are there in the solution. It also informs about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

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



This chemical equilibrium representing the dissociation of water is called the autoprotolysis of water. We have that water, as well as many other chemicals, 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 HCO_3^- or HSO_4^- . The dissociation constant of water is called the ion-product of water K_w :

▼ 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 CO_2 level in the blood raises after breathing from a plastic bag. CO_2 is an acid and decreases the PH of blood.



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

$$[\text{H}^+] \cdot [\text{OH}^-] = 1.0 \cdot 10^{-14} \quad (10.5)$$

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 ($[\text{OH}^-]$) are 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 5

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 asks $[\text{OH}^-]$. Solving for $[\text{OH}^-]$ we have:

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

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

❖ STUDY CHECK

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

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

$$\text{PH} = -\log [\text{H}^+] \quad (10.6)$$

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:

$$\text{POH} = -\log [\text{OH}^-] \quad (10.7)$$

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:

$$PH + POH = 14 \quad (10.8)$$

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 6

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 $2.0 \cdot 10^{-9} M$.

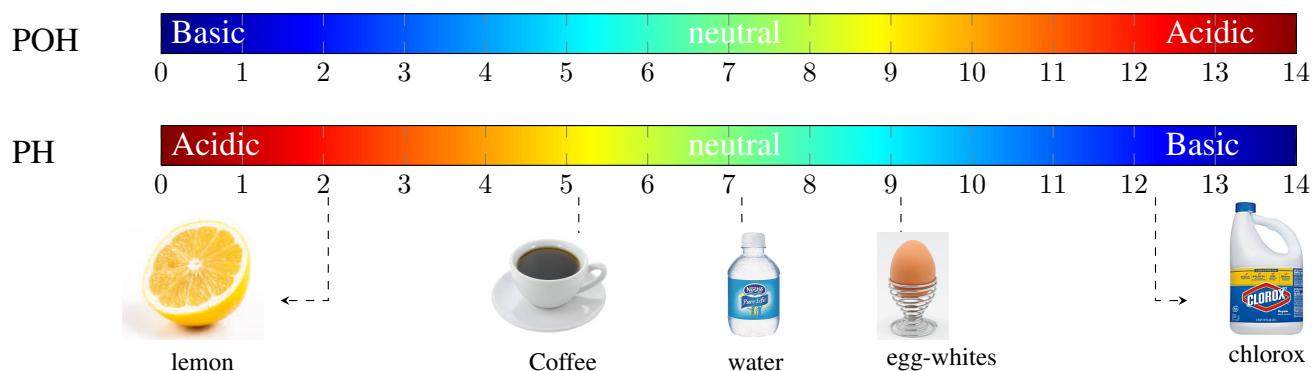


Figure 1.1 The PH scale

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:

$$[H^+] = 10^{-PH} \quad (10.9)$$

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 substitutions, the negative key is used for numbers. An equivalent relation exists between the concentration of hydroxyls and the POH:

$$[\text{OH}^-] = 10^{-\text{POH}} \quad (10.10)$$

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

Sample Problem 7

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 $[\text{H}^+]$.

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

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.

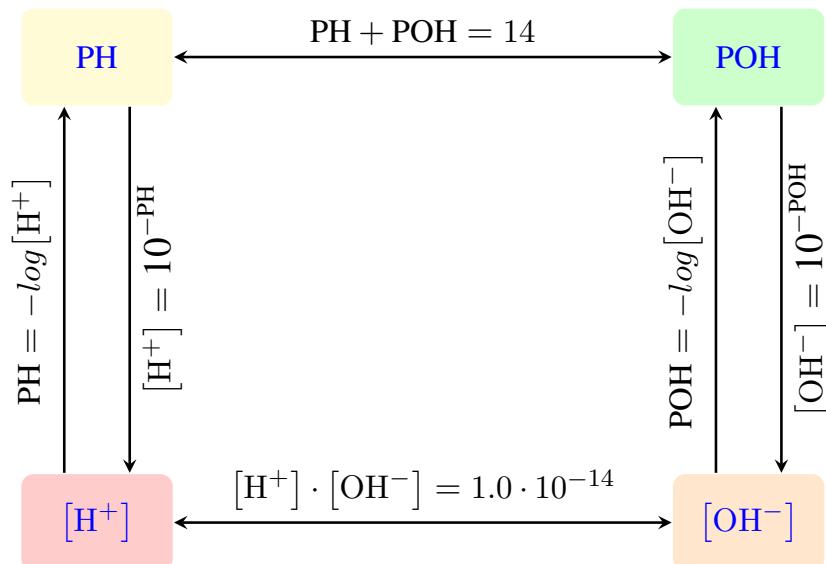


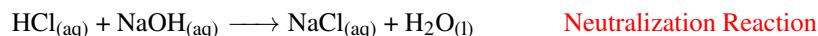
Figure 1.2 Diagram with formulas relating the PH, POH and the concentration of protons and hydroxyls in water.

10.5 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:

$$n_H \cdot c_a \cdot V_a = n_{OH} \cdot c_b \cdot V_b \quad (10.11)$$

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 that 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 8

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.

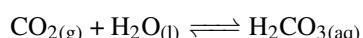
The mid-point In titrations, there is another important point called the mid-point. The mid-point is reached at half the equivalency point. For example, the end-point of the titration of 10 mL of 0.1M HCl by 10 mL of 0.1M NaOH happens when we add 10 mL of the base. The mid-point hence will happen when 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:

$$V_{MP} = \frac{V_{EP}}{2} \quad (10.12)$$

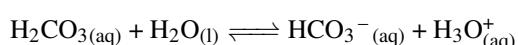
10.6 Blood as a buffer

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 H_2CO_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.

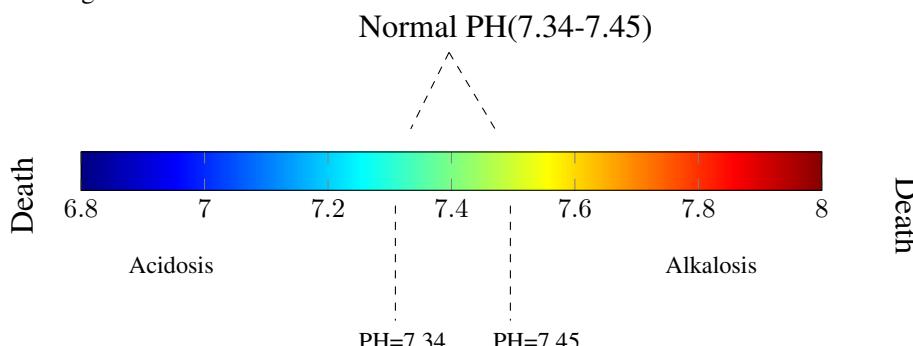


Figure 1.3 PH range that leads to acidosis and alkalosis

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 CO₂ 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 CO₂ builds up in the body. Normally, the lungs remove CO₂ while you breathe. However, sometimes your body is unable to get rid of enough CO₂. 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 9

Explain why CO₂ decreases the PH of blood.

SOLUTION

CO₂ is an acid and when dissolved in water it generates protons, H⁺. Increasing the amount of protons decreases PH as PH is a measure of 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?

CHAPTER 10

THE NATURE OF ACIDS AND BASES

10.1 Classify the following species as Arrhenius acids, or bases: (a) H_2SO_4 (b) NaOH (c) HNO_3 (d) HCl (e) $\text{Ca}(\text{OH})_2$

10.2 Classify the following species as Arrhenius acids, or bases: (a) KOH (b) H_3PO_4 (c) HI (d) $\text{Mg}(\text{OH})_2$

10.3 Classify the following species as Brönsted-Lowry acids, bases or both: (a) H_2O (b) OH^- (c) NH_3 (d) NO_2^-

10.4 Classify the following species as Brönsted-Lowry acids, bases or both: (a) HCO_3^- (b) HI (c) HCN (d) HSO_4^- (e) HCOONa

DISSOCIATIONS OF ACIDS & BASES

10.5 From the following pairs, select the strongest acid:

- (a) HIO_3 ($K_a = 1.6 \cdot 10^{-1}$) or H_2SO_3 ($K_a = 1.5 \cdot 10^{-2}$)
 (b) HN_3 ($K_a = 1.9 \cdot 10^{-5}$) or H_2CO_3 ($K_a = 4.3 \cdot 10^{-7}$)

10.6 From the following pairs, select the strongest base:

- (a) CN^- ($K_a = 6.2 \cdot 10^{-10}$) or H_2O ($K_a = 1.0 \cdot 10^{-14}$)
 (b) $\text{H}_2\text{C}_6\text{H}_5\text{O}^-$ ($K_a = 1.8 \cdot 10^{-5}$) or HCOOH ($K_a = 1.7 \cdot 10^{-4}$)

10.7 Write down the formula of the conjugate bases:

- (a) H_2O (b) HCl (c) HNO_3 (d) H_2SO_4

10.8 Write down the formula of the conjugate bases:

- (a) HSO_4^- (b) H_2S (c) HCOOH (d) H_2PO_4^-

10.9 Write down the formula of the conjugate acids:

- (a) NH_4^+ (b) CH_3COO^- (c) HS^- (d) CN^-

10.10 Identify the conjugate acid-base pairs:

- (a) $\text{HCl}_{(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{Cl}_{(\text{aq})}^- + \text{H}_3\text{O}_{(\text{aq})}^+$
 (b) $\text{CH}_3\text{COO}_{(\text{l})}^- + \text{HCl}_{(\text{g})} \rightleftharpoons \text{Cl}_{(\text{aq})}^- + \text{CH}_3\text{COOH}_{(\text{aq})}$
 (c) $\text{CO}_3^{2-}_{(\text{aq})} + \text{HCN}_{(\text{g})} \rightleftharpoons \text{CN}_{(\text{aq})}^- + \text{HCO}_3^-_{(\text{aq})}$
 (d) $\text{HNO}_3_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightleftharpoons \text{NO}_3^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{aq})}$

10.11 Write down the following dissociation or acid-base reaction involving the exchange of one proton:

- (a) $\text{HNO}_3_{(\text{l})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$
 (b) $\text{H}_2\text{SO}_4_{(\text{l})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$
 (c) $\text{HCl}_{(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$
 (d) $\text{NH}_3_{(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons$

10.12 Write down the following dissociation or acid-base reaction involving the exchange of one proton:

- (a) $\text{CO}_3^{2-}_{(\text{aq})} + \text{HCN}_{(\text{g})} \rightleftharpoons$
 (b) $\text{HCO}_3^-_{(\text{aq})} + \text{HCN}_{(\text{g})} \rightleftharpoons$
 (c) $\text{HCO}_3^-_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightleftharpoons$

THE PH SCALE

10.13 Answer the following questions: (a) The proton concentration of a solution is $3 \times 10^{-3}\text{M}$. Calculate the hydroxyl concentration in the same solution (b) The hydroxyl concentration of a solution is $8 \times 10^{-6}\text{M}$. Calculate the proton concentration in the same solution.

10.14 Answer the following questions: (a) The PH of a solution is 1.34. Calculate the POH of the same solution (b) The POH of a solution is 12. Calculate the PH of the same solution.

10.15 Answer the following questions: (a) The PH of a solution is 1.56. Calculate the concentration of protons. (b) The POH of a solution is 10.34. Calculate the hydroxyl concentration in the same solution. (c) The PH of a solution is 12.4. Calculate the hydroxyl concentration in the same solution.

10.16 Fill the table below:

$[\text{H}^+]$	$[\text{OH}^-]$	Acidic/Basic/Neutral?
1.5×10^{-4}	6.6×10^{-11}	
4.9×10^{-12}	2.0×10^{-3}	
1.9×10^{-6}	5.3×10^{-9}	
1.0×10^{-7}	1.0×10^{-7}	

10.17 Fill the table below:

[H ⁺]	[OH ⁻]	PH	POH
4.5×10^{-3}		—	—
	3.2×10^{-7}	—	—
—	—	5.1	
—	—		6.9

10.18 Fill the table below:

[H ⁺]	[OH ⁻]	PH	POH
3.5×10^{-1}	—	—	
—	—	—	2

BUFFER SOLUTIONS

10.19 Which of the following mixtures of solutions can act as a buffer: (a) 0.1M-H₂SO₄/0.1M-Na(SO₄)₂ (b) 0.01M-NH₃/0.01M-NH₄Cl (c) 0.2M-HNO₂/0.2M-NaNO₂

10.20 Which of the following mixtures of solutions can act as a buffer: (a) 0.4M-H₂SO₄/0.1M-NaHSO₄ (b) 0.23M-HCl/0.20M-KCl (c) 0.56M-HCN/0.22M-NaCN

10.21 Which of the following mixtures of solutions can act as a buffer: (a) KCl/HCl (b) H₂SO₄/NaHSO₄ (c) Na₂SO₄/NaHSO₄

10.22 Which of the following mixtures of solutions can act as a buffer: (a) H₃PO₄/NaH₂PO₃ (b) Na₃PO₄/NaH₂PO₃ (c) HNO₂/NaNO₂

10.23 Which of the following substances can be mixed together to prepare a buffer: (a) CH₃COOH (b) CH₃COONa (c) NaOH (d) HCl (e) NaCl

10.24 Which of the following substances can be mixed together to prepare a buffer: (a) NH₃ (b) NH₄Cl (c) Na₂SO₄ (d) H₂SO₄ (e) NaCl (f) HCl

10.25 Calculate the PH of the following buffers:

- (a) 0.15 M-HCN/0.35M-NaCN, $K_a = 6.20 \times 10^{-10}$
- (b) 0.15 M-HCN/0.15M-NaCN, $K_a = 6.20 \times 10^{-10}$
- (c) 0.25 M-HCN/0.15M-NaCN, $K_a = 6.20 \times 10^{-10}$

10.26 Calculate the PH of the following buffers:

- (a) 0.25 M-NH₃/0.45M-NH₄Cl, $K_b = 1.80 \times 10^{-5}$
- (b) 0.15 M-HNO₂/0.05M-NaNO₂, $K_a = 5.60 \times 10^{-4}$

10.27 Calculate the PH of the following buffers:

- (a) 0.02 M-C₆H₅NH₂/0.05M-C₆H₅NHCl, $K_b = 7.40 \times 10^{-10}$
- (b) 0.4 M-HCNO/0.5M-NaCNO, $K_a = 3.50 \times 10^{-4}$

10.28 The PH of a C₆H₅NH₂/C₆H₅NHCl ($K_b = 7.40 \times 10^{-10}$) buffer is 4.0. Calculate the ratio of [C₆H₅NH₂]/[C₆H₅NHCl].

TITRATIONS

10.29 Solve the following titration scenarios: (a) In a titration experiment, 13.5 mL of 0.34 M HCl neutralize 34.3 mL of KOH. What is the concentration of the KOH solution? (b) In a titration experiment, 20.4 mL of 0.10 M HCl neutralize 12.4 mL of Ca(OH)₂. What is the concentration of the base solution? (c) In a titration experiment, 10.4 mL of 0.20 M H₂SO₄ neutralize 8.4 mL of Ca(OH)₂. What is the concentration of the base solution?

10.30 A 5mL sample of a monoprotic acid neutralizes 10mL of a 0.01M-KOH solution. Calculate the molarity of the acid.

10.31 A 10mL sample of a monoprotic acid neutralizes 5mL of a 0.2M-Ca(OH)₂ solution. Calculate the molarity of the acid.

10.32 A 5 grams sample of an acid neutralizes 30mL of a 0.5M-NaOH solution. Calculate the molar mass of the acid.

10.33 You prepare a base solution by dissolving 3-g of the base into 250mL of solution. Five milliliters of this solution neutralizes 5mL of a 0.3MH₂SO₄ solution. Calculate the molar mass of the base.

Answers

10.1 (a) H₂SO₄ (acid) (b) NaOH (base) (c) HNO₃ (acid) (d) HCl (acid) (e) KOH (base) (f) H₃PO₄ (acid) (g) HI (acid) (h) Mg(OH)₂ (base)

10.2 (a) NH₃ (base) (b) NO₂⁻ (base)

10.3 (a) H₂O (both) (b) HIO₃ (b) H₂CO₃

10.4 (a) HCO₃⁻ (both) (b) HI (acid) (c) HCN (acid) (d) HSO₄⁻ (base)

10.5 (a) H₂SO₄ (HSO₄⁻) (b) H₂S (HS⁻) (c) HCOOH (HCOO⁻)

10.6 (a) CN⁻ (b) HCOOH

10.7 (a) H₂O (OH⁻) (b) HCl (NO₃⁻) (d) H₂SO₄ (HSO₄⁻)

10.8 (a) HSO₄⁻ (SO₄²⁻) (b) H₂S (HS⁻) (c) HCOOH (HCOO⁻)

10.9 (a) NH₄⁺ (NH₃) (b) CH₃COO⁻ (CH₃COOH) (c) HS⁻ (H₂S) (d) CN⁻ (HCN) and (H₂O / H₃O⁺) (b) (CH₃COO⁻ / CH₃COOH) and (HCl / Cl⁻) (c) (CO₃²⁻ / CN⁻) and (HNO₃ / NO₃⁻) and (OH⁻ / H₂O)

10.11 (a) HNO_{3(l)} + H₂O_(l) \rightleftharpoons NO_{3(aq)} + H₃O_(aq) (b) H₂O_(l) \rightleftharpoons HSO_{4(aq)} + H₃O_(aq)⁺ (c) HCl_(g) + H₂O_(l) \rightleftharpoons Cl_(aq)⁻ + H₃O_(aq)⁺ (d) NH_{3(g)} + H₂O_(l) OH_(aq)⁻

10.12 (a) CO₃²⁻_(aq) + HCN_(g) \rightleftharpoons HCO_{3(aq)}⁻ + CN_(aq)⁻ (b) HCO_{3(aq)}⁻ + HCN_(g) \rightleftharpoons CO_{3(aq)}²⁻ + OH_(aq)⁻

10.13 (a) 3.3 × 10⁻¹²M (b) 1.25 × 10⁻⁹M

10.14 (a) 0.027M (b) 4.57 × 10⁻¹¹M (c) 2.5 × 10⁻²M

10.15 [H⁺] = 1.5 × 10⁻⁴, [OH⁻] = 6.67 × 10⁻¹¹, [H⁺] = 4.9 × 10⁻¹², [OH⁻] = 2.0 × 10⁻³, basic; [H⁺] = 1.9 × 10⁻⁶, [OH⁻] = 5.3 × 10⁻⁹, Acidic, [OH⁻] = 1.0 × 10⁻⁷, neutral; **10.16** [H⁺] = 4.5 × 10⁻³, [OH⁻] = 2.2 × 10⁻¹², 2.3, 11.6; [OH⁻] = 3.2 × 10⁻⁷, 7.5, 6.5; [H⁺] = 7.1 × 10⁻⁶, [OH⁻] = 1.4 × 10⁻⁹, 5.1, 8.8; [H⁺] = 9.0 × 10⁻⁸, 7.1, 6.9; **10.17** [H⁺] = 3.5 × 10⁻¹, [OH⁻] = 2.8 × 10⁻¹⁴, 0.4, 13.5; [H⁺] = 1 × 10⁻¹², [OH⁻] = 2; **10.18** (a) 0.1M-H₂SO₄/0.1M-Na(SO₄)₂ (No buffer) (b) 0.01M-NH₃/0.01M-NH₄Cl (buffer) (c) NaNO₂ (buffer) **10.19** (a) 0.1M-H₂SO₄/0.1M-NaHSO₄ (No buffer) (b) 0.23M-HCl/0.20M-KCl (No buffer) HCN/0.22M-NaCN (buffer) **10.20** (a) KCl/HCl (No buffer) (b) H₂SO₄/NaHSO₄ (No buffer) (c) (buffer) **10.21** (a) H₃PO₄/NaH₂PO₃ (buffer) (b) Na₃PO₄/NaH₂PO₃ (buffer) (c) HNO₂/NaNO₂ (buffer) CH₃COOH and CH₃COONa **10.24** Only NH₃ and NH₄Cl **10.25** (a) 0.15 M-HCN/0.35M-NaCN, (PH=9.57) (b) 0.15 M-HCN/0.15M-NaCN, $K_a = 6.20 \times 10^{-10}$ (PH=9.21) (c) 0.25 M-HCN/0.620 × 10⁻¹⁰ (PH=9.98) **10.26** (a) 0.25 M-NH₃/0.45M-NH₄Cl, $K_b = 1.80 \times 10^{-5}$ (PH=9) (b) 0.1M-NaNO₂, $K_a = 5.60 \times 10^{-4}$ (PH=2.8) **10.27** (a) 0.02 M-C₆H₅NH₂/0.05M-C₆H₅NHCl, $K_b = 7.40 \times 10^{-10}$ (PH=3.5) (b) 0.4 M-HCNO/0.5M-NaCNO, $K_a = 3.50 \times 10^{-4}$ (PH=3.5) **10.28** 0.13 **10.29** (a) 0.13M (b) 0.02M **10.30** 0.02M **10.31** 0.2M **10.32** 333g/mol **10.33** 20g/mol