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.

GOALS

1. Identify acids and bases and its conjugate counterparts
2. Compare the strength of two acids or bases
3. Compute the PH of solutions of weak and strong acids and bases
4. Compute titration calculations
5. Compute buffer calculations

1.1 | The nature of acids & Bases

This first section of the chapter introduces some acid-base terminology. You will learn how to identify acids and bases, and the three different models that describe acidity. More importably, you will learn what makes an acid acidic and base basic: protons and hydroxyls.

�⚙ Discussion: You have two acids A and B of different concentration C_A and C_B. Given that the K_a of A is larger than the one for B, does this means that the PH of a solution of A is smaller than the PH of a solution of B? Elaborate.

How to differentiate acids and bases based on their formula

In general terms, we can identify acids and bases based on its formula. Let us consider these chemicals: HF, H_2SO_4 and HNO_3. All these named hydroflouric acid, sulfuric acid, and nitric acid are acidic. Hydro acids, and oxyacids will certainly be acidic. Acids are classified as monoprotic, diprotic and polyprotic. Monoprotic acids have only one acidic H on its 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). Hydroxides are basic and for example, NaOH and $Ca(OH)_2$ named sodium hydroxide and calcium hydroxide are well-known bases. At the same time, some covalent compounds such as ammonia (NH_3) are basic. However, not all covalent compounds containing hydrogen are basic and for example, CH_4 is not basic at all. Finally, organic acids are acidic and organic amines tends to be basic. For example, acetic acid CH_3COOH is an acid and CH_3NH_2 is a base.

> **Sample Problem 1**
>
> Identify the following chemicals as acids or bases and give their names: HCl, NH_3, 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. Bases are: NH_3 and KOH. Their names are: ammonia (common name) and potassium hydroxide.
>
> ◈ **STUDY CHECK**
>
> Identify the following chemicals as acids or bases and give their names: NaOH and H_2CO_3.
>
>   Answer: sodium hydroxide (base) and carbonic acid (acid).

✎ *Acids and bases* Acids and bases have very different properties. Acids are acidic, and this is characterized by a sour taste and often they sting to the touch. Bases are basic and that means they have a bitter–chalky–taste and they feel soapy–slippery–to the touch. 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 a food preservative. Acids are also used in the production of batteries. Car batteries contain corrosive sulphuric acid. Bases are extensively used in manufacturing. Sodium hydroxide is used in the manufacture of soap, medicines, and even paper. Calcium hydroxide–also known as slaked lime–is used to neutralize the acid in water supplies or as an antidote for food poisoning. Calcium hydroxide is also used in the construction industry, mixed with sand and water to make mortar. Potassium hydroxide (KOH) is also 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.

In the following, we will introduce the three different models used to describe acids and bases.

Arrhenius acid–base model Arrhenius claimed that acids are acidic because when dissolved in water they produce *protons*: H^+, also called hydronium ion written as H_3O^+. Differently, bases are basic because when you solve them in water they produce *hydroxyls*: OH^-. The reaction below described the process of dissociation of hydrogen chloride to produce chloride and a proton:

$$HCl_{(g)} \rightleftharpoons Cl^-_{(aq)} + H^+_{(aq)} \hspace{2cm} \text{(an acid)}$$

Based on this dissociation reaction we can say hydrogen chloride also know as hydrochloric acid is an Arrhenius acid, as it produces protons. Look now the dissociation of sodium hydroxide:

$$NaOH_{(s)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)} \hspace{2cm} \text{(a base)}$$

This chemical is an Arrhenius base as it produces hydroxyls. Based on the structure of the acid is easy to tell that HCl is an Arrhenius acid as it contains hydrogen on its structure and hence it can release it giving protons. However, this model does not explain neither why chemicals unsolved in water can also be acidic nor why chemicals such as NH_3 without OH on its structure can be basic.

Brönsted-Lowry acid-base model The second model describing acids and bases is the Brönsted-Lowry model. This more advanced model claims acids are chemicals that give away protons (H^+) whereas bases receive protons. Based on this mode, we can understand how acids can give away protons to water generating H_3O^+ and bases such as ammonia can receive protons from water leaving OH^- in solution:

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4{}^+{}_{(aq)} + OH^-_{(aq)}$$

Still, this models does not explain what structural particularity makes ammonia behave as a base and carbon dioxide (with no hydrogen on its structure) an acid.

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 bases are able to give way electron pairs. In other words, acids are electron-pair receiver and bases are electron-pair givers. In the example below you can see why ammonia acts as a base:

Lewis base

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 base receive and give away lone pairs. Lewis bases contain lone pairs and can give away electron density to an acid. Another example is presented below, in which the lone pairs of water make it a lewis base that can receive electron pairs from carbon dioxide, a lewis acid.

Lewis acid

In summary, the Arrhenius definition is based on what is on 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.

Model	Acid definition	Base definition
Arrhenius	H^+ producer	OH^- producer
Brönsted-Lowry	H^+ donnor	H^+ acceptor
Lewis	electron-pair acceptor	electron-pair giver

Sample Problem 2

Indicate whether the following chemicals are lewis acid or lewis bases: (a) BH_3 and (b) CH_3-O-CH_3.

SOLUTION

The lewis structure of the molecules are:

$$\begin{array}{c} H \\ | \\ H-B \\ | \\ H \end{array} \quad \text{and} \quad CH_3-\overline{O}-CH_3$$

BH_3 can receive a lone pair to complete the octet of Boron and hence it will be a Lewis acid. Differently, CH_3-O-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) AlH_3 and (b) OH^-.

(a) acid and (b) base.

1.2 Dissociation of acids & 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 an acids is a conjugate base. For example:

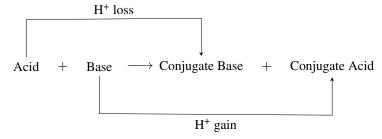$$\underset{\text{Acid}}{HI_{(l)}} + H_2O_{(l)} \longrightarrow \underset{\text{Conjugate Base}}{I^-_{(aq)}} + H_3O^+_{(aq)}$$

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

$$HI_{(l)} + \underset{\text{Base}}{H_2O_{(l)}} \longrightarrow I^-_{(aq)} + \underset{\text{Conjugate Acid}}{H_3O^+_{(aq)}}$$

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

$$\underset{\text{Acid}}{HI_{(l)}} + \underset{\text{Base}}{H_2O_{(l)}} \longrightarrow \underset{\text{Conjugate Base}}{I^-_{(aq)}} + \underset{\text{Conjugate Acid}}{HI_{(l)}}$$

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

H^+ loss

Acid $+$ Base $\longrightarrow$ Conjugate Base $+$ Conjugate Acid

H^+ gain

Sample Problem 3

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

$$NH_{3(g)} + H_2O_{(l)} \longrightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

SOLUTION

The trick is first identifying the acid and the base starting for the left side of the formula. In this case $NH_{3(g)}$ 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:

$$\underset{\text{Base}}{NH_{3(g)}} + \underset{\text{Acid}}{H_2O_{(l)}} \longrightarrow \underset{\text{Conjugate Acid}}{NH_4^+{}_{(aq)}} + \underset{\text{Conjugate Base}}{OH^-_{(aq)}}$$

◈ STUDY CHECK

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

$$CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + H_3O^+_{(aq)}$$

Answer: $\underset{\text{Base}}{CO_3^{2-}{}_{(aq)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Conjugate Acid}}{HCO_3^-{}_{(aq)}} + \underset{\text{Conjugate Base}}{H_3O^+_{(aq)}}$

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

$$H_2O_{(l)} + NH_{3(g)} \rightleftharpoons$$

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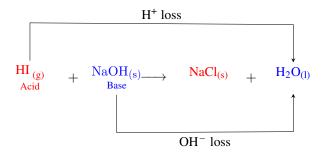

And that will give the dissociation equilibrium of ammonia.

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{Base}}{NH_{3(g)}} \rightleftharpoons \underset{\text{Conjugate Base}}{OH^-_{(aq)}} + \underset{\text{Conjugate Base}}{NH_4^+{}_{(l)}}$$

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

$$HI_{(g)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$$
Acid   Base

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

$$H^+ \text{ loss}$$

$$HI_{(g)} \quad + \quad NaOH_{(s)} \longrightarrow \quad NaCl_{(s)} \quad + \quad H_2O_{(l)}$$
Acid   Base

$$OH^- \text{ loss}$$

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

Sample Problem 4

Write down the following dissociation or acid-base reaction involving one proton: $H_2CO_{3(aq)} + H_2O_{(aq)} \longrightarrow$

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.

$$H_2CO_{3(aq)} + H_2O_{(aq)} \longrightarrow HCO_3{}^-{}_{(aq)} + H_3O^+_{(aq)}$$

As carbonic acid loses a proton to become hydrogencarbonate, its charge become 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: $HCl_{(g)} + NH_{3(g)} \longrightarrow$

Answer: $HCl_{(g)} + NH_{3(g)} \longrightarrow NH_4Cl_{(s)} + H_2O_{(l)}$

✎ *Dissociating organic acids and bases* Organic acids and bases often times contain numerous hydrogen atoms on its molecular structure. It is critical to dissociate these molecules using the acid and basic centers and not others. For example, acetic acid CH_3-COOH contains a methyl group and an carboxylic group. When dissociation this molecule, we need to remove the proton only from the acidic group, hence its name:

$$CH_3-COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3-COO^-_{(aq)} + H_3O^+_{(aq)}$$

Methylamine CH_3-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:

$$CH_3-NH_{2(l)} + H_2O_{(l)} \rightleftharpoons CH_3-NH_3{}^+{}_{(aq)} + OH^-_{(aq)}$$

✎ *Strength of acids and bases* Acids and bases are indeed electrolytes. Remember electrolytes can be weak or strong depending on the degree to what 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 acid or weak bases dissociate only partially and hence they produce less 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 the are strong electrolytes:

$$HCl(l) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq) \qquad \text{\textcolor{blue}{One arrow indicates strong acids or bases}}$$

Weak acids or basis that only dissociate partially are represented by a double arrow as the reaction is indeed an equilibrium. Examples of weak acids or bases are: NH_3 or HF.

$$HF(l) \xrightleftharpoons{H_2O} H^+(aq) + F^-(aq) \qquad \text{\textcolor{blue}{A double arrow indicates weak acids or bases}}$$

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

$$HF_{(l)} \xrightleftharpoons{H_2O} H^+_{(aq)} + F^-_{(aq)} \qquad K_a = \frac{\left[H^+\right] \cdot \left[F^-\right]}{\left[HF\right]}$$

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. For the case of ammonia:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)} \qquad K_b = \frac{\left[NH_4^+\right] \cdot \left[OH^-\right]}{\left[NH_3\right]}$$

remember liquid water can not be part of an equilibrium constant. As acids can also act as bases, there is relationship between the constant of acidity and the constant of basicity of an acid or base given by:

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

For example, if the constant of acidity of a given acid is 1.5×10^{-5}, the basicity constant of the same specie would be 6.6×10^{-10}.

In Table **??** you can find a list of some acidity and basicity constants. In general, there are some simple rules that predict the 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.

Table ?? Acidity and basicity constants at 25°C					
Name	Formula	K_a	Name	Formula	K_a
Hypoiodous acid	HIO	3.20×10^{-11}			⋮
Phenol	C_6H_5OH	1.00×10^{-10}	Fluoroacetic acid	CH_2FCO_2H	2.60×10^{-3}
Hydrocyanic acid	HCN	6.20×10^{-10}	Formic acid	CH_2O_2	1.80×10^{-4}
Hypobromous acid	HBrO	2.80×10^{-9}	Bromoacetic acid	CH_2BrCO_2H	1.30×10^{-3}
Hypochlorous acid	HClO	4.00×10^{-8}	Chloroacetic acid	CH_2ClCO_2H	1.30×10^{-3}
Benzoic acid	$C_6H_5CO_2H$	6.25×10^{-5}	Dichloroacetic acid	$CHCl_2CO_2H$	4.50×10^{-2}
Hydrazoic acid	HN_3	2.50×10^{-5}	Periodic acid	HIO_4	2.30×10^{-2}
Acetic acid	CH_3COOH	1.75×10^{-5}	Chlorous acid	$HClO_2$	1.10×10^{-2}
Iodoacetic acid	CH_2ICO_2H	6.60×10^{-4}	Trichloroacetic acid	CCl_3CO_2H	2.20×10^{-1}
Hydrofluoric acid	HF	6.30×10^{-4}	Trifluoroacetic acid	CF_3CO_2H	3.00×10^{-1}
Nitrous acid	HNO_2	5.60×10^{-4}	Iodic acid	HIO_3	1.70×10^{-1}
Cyanic acid	HCNO	3.50×10^{-4}	Chromic acid	$HCrO_4$	1.80×10^{-1}
⋮					

Name	Formula	K_b	Name	Formula	K_b
Aniline	$C_6H_5NH_2$	7.40×10^{-10}			⋮
Pyridine	C_5H_5N	1.70×10^{-9}	n-Butylamine	$C_4H_9NH_2$	4.00×10^{-4}
Hydroxylamine	NH_2OH	8.70×10^{-9}	Ethylamine	$C_2H_5NH_2$	4.50×10^{-4}
Hydrazine	N_2H_4	1.30×10^{-6}	Methylamine	CH_3NH_2	4.60×10^{-4}
Ammonia	NH_3	1.80×10^{-5}	tert-Butylamine	$(CH_3)_3CNH_2$	4.80×10^{-4}
Propylamine	$C_3H_7NH_2$	3.50×10^{-4}	Dimethylamine	$(CH_3)_2NH$	5.40×10^{-4}
⋮					

Sample Problem 5

Indicate the strongest acid from:

$$HF_{(aq)} \xrightarrow{H_2O} H^+_{(aq)} + F^-_{(aq)} \qquad K_a = 7.2 \cdot 10^{-4}$$

$$HNO_{2(aq)} \xrightarrow{H_2O} H^+_{(aq)} + NO_2^-{}_{(aq)} \qquad K_a = 4.5 \cdot 10^{-4}$$

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(HF)= $7.2 \cdot 10^{-4}$ and K_a(HNO$_2$)= $4.5 \cdot 10^{-4}$, HF is the stronger of both.

◈ **STUDY CHECK**

Indicate the strongest of the following acids:

$$H_2PH_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HPH_4^{2-}{}_{(aq)} \qquad K_a = 6.2 \cdot 10^{-8}$$

$$H^+_{(aq)} + HCO_3^{2-}{}_{(aq)} \rightleftharpoons H_2CO_{3(aq)} + H_2O_{(l)} \qquad K_b = 2.3 \cdot 10^{-8}$$

Answer: H_2CO_3 is the strongest.

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

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Conjugate Base}}{OH^-_{(aq)}} + \underset{\text{Conjugate Acid}}{H_3O^+_{(aq)}} \qquad K_w$$

We have that water, as well as many other chemicals, can acts as a base or an acid. We call these type of chemicals *amphoteric* or *amphiprotic*; the last two terms are synonyms, which means they have the same meaning. Other example of amphoteric chemicals are: HCO_3^- or HSO_4^-. The dissociation constant of water is called the ion-product of water K_w:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \qquad \left[H^+\right] \cdot \left[OH^-\right] = 1.0 \cdot 10^{-14}$$

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

$$\boxed{\left[H^+\right] \cdot \left[OH^-\right] = 1.0 \cdot 10^{-14}} \tag{1.2}$$

We will explore more the use of this constant in the following sections.

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:

$$HCl(l) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

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

$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

This way we explicitly represent the role of water as a proton receiver. Ultimately, both ways are correct and for some chemicals (e.g. NH_3) it is more convenient to use the role of water whereas for others it makes no difference.

Acid-base properties of salts Let us reming that strong acids (bases) produce weak conjugate bases (acids) and weak acids (bases) produce strong conjugate bases (acids). For example, HF is a weak acid and therefore its conjugate F^- acid would be strong. Similarly, NaOH is a strong base and its conjugate acid (Na^+) is therefore 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 Na^+ is a weak acid and F^- a strong base, a NaF solution would be basic. Similarly, we can predict that NH_4Cl would from an acidic solution, as ammonium (NH_4^+) is the conjugate acid of ammonia (a weak base) and Cl^- is the conjugate base of a strong acid (HCl).

Sample Problem 6

Write down the dissociation reaction using double arrows for the following chemicals: $H_3PO_{4(l)}$ and $NH_{3(g)}$.
SOLUTION
Phosphoric acid is a triprotic acid with three possible protons that can be given away:

$$H_3PO_{4(l)} \xrightleftharpoons{H_2O} 3\,H^+_{(aq)} + PO_4{}^{3-}{}_{(aq)}$$

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.

$$NH_{3(g)} + H_2O_{(l)} \rightleftharpoons NH_4{}^+{}_{(aq)} + OH^-_{(aq)}$$

◆ **STUDY CHECK**

Write down the dissociation reaction using double arrows for the following chemicals: $HI_{(g)}$ and $HClO_{2(l)}$.

$$\text{Answer: } HI_{(g)} \xrightleftharpoons{H_2O} H^+_{(aq)} + I^-_{(aq)} \text{ and } HClO_{2(l)} \xrightleftharpoons{H_2O} H^+_{(aq)} + ClO_2{}^-{}_{(aq)}.$$

1.3 The PH scale

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

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

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

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

Sample Problem 7

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

SOLUTION

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

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

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

◆ **STUDY CHECK**

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

$$\text{Answer: } [H^+] = 4.3 \cdot 10^{-9}\text{M}.$$

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

$$PH = -log\left[H^+\right] \tag{1.3}$$

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

$$POH = -log\left[OH^-\right] \tag{1.4}$$

The POH scale also ranges from 0 to 14. POH values lower than 7 correspond to this time to basic solutions, whereas POH values larger than 7 correspond to acidic solutions. Solutions with POH of 7 are neutral. The values of PH and POH are hence related by the following equation:

$$PH + POH = 14 \tag{1.5}$$

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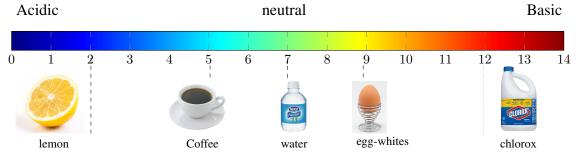

Figure 1.1: The PH scale

Sample Problem 8

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 **??**. Given is $\left[H^+\right] = 7.0 \cdot 10^{-5}$M and the problem ask for the PH. Solving for PH we have:

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

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

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

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

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

12

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

💎 STUDY CHECK

Calculate the PH for: (a) an acid 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.

Answer: 7.5; 5.3

📝 *PK of an acid or base* In the same way as we defined the PH and POH scale, we can also use the logarithmic notation to transform acidity and basicity constant into more manageable number. We define PK_a of an acid as:

$$PK_a = -log(K_a)$$ (1.6)

For example, as the acidity constant of acetic acid is 1.75×10^{-5} its PK_a would be 4.74. An equivalent definition exist for PK_b.

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

$$[H^+] = 10^{-PH}$$ (1.7)

In order to use the previous formula you need to use the power key in your calculator. For example if the PH is 3.3 and we need to calculate the proton concentration you will need to type: $10\boxed{\wedge}\boxed{-}3.3$, and the result is $5.0 \cdot 10^{-4}$M. Mind that: (a) in some calculators, sometime the power key looks like: $\boxed{10^x}$; (b) you need to use the negative key and not the minus key. Minus is used for substations, the negative key is used for number. An equivalent relation exist between the concentration of hydroxyls and the POH:

$$[OH^-] = 10^{-POH}$$ (1.8)

Sample Problem 9

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

SOLUTION

We will use Equation **??**, given PH and asking $[H^+]$.
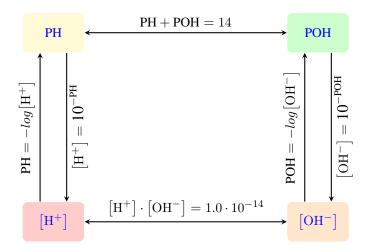
$$[H^+] = 10^{-PH} = 10^{-4.5}$$

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.

Answer: $3.16 \cdot 10^{-10}$M

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

✎ *PH of strong electrolyte 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:

$$PH = -log\big(n_{\text{H}} \cdot c_a\big)$$ (1.9)

where:

n_{H} is the number of protons in the acid (e.g. H_3PO_4 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:

$$POH = -log\big(n_{\text{OH}} \cdot c_b\big)$$ (1.10)

where:

n_{OH} is the number of hydroxyls in the base (e.g. $Ca(OH)_2$ 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 10

Calculate the PH of: (a) a 0.02M HNO_3 solution (b) a 0.02M $Ca(OH)_2$ solution.
SOLUTION
(a) We will use Equation **??** given that the molarity of the acid is 0.02M and the acid only has a single proton:

$$PH = -log\big(n_{\text{H}} \cdot c_a\big) = -log(0.02) = 1.69$$

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

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

Now, we will convert POH in PH using Equation **??**:

$$PH = 14 - POH = 12.61$$

✎ *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 by means of a 𝑒 *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:

$$\left[H^+\right]^2 + K_A \cdot \left[H^+\right] - K_a \cdot c_a = 0 \quad \text{with } \left[H^+\right] = x \qquad (1.11)$$

where:

$\left[H^+\right] = x$ is concentration of protons in equilibrium

K_a is 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:

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

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

$$\left[H^+\right] = 0.0076$$

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:

$$\left[OH^-\right]^2 + K_B \cdot \left[OH^-\right] - K_b \cdot c_b = 0 \quad \text{with } \left[OH^-\right] = x \qquad (1.12)$$

where:

$\left[OH^-\right] = x$ is concentration of hydroxyls in equilibrium

K_b is basicity constant of the base

c_b is the molarity of the base solution

Mind that in order to calculate the PH or POH you will need to employ Equations **??** and **??**. For example, the PH of a 0.1M NH_3 solution, given that ammonia is a weak base with $K_b = 1.8 \times 10^{-5}$, will be given by:

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

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

$$\left[OH^-\right] = 0.0013$$

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 11

Calculate the PH of a 0.02M CH_2O_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 **??** in order to calculate PH:

$$\left[H^+\right]^2 + K_A \cdot \left[H^+\right] - K_a \cdot c_a = 0$$

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

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

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

❖ **STUDY CHECK**

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

Answer: 8.08

✎ *PH of salt solutions* As well as hydracids or hydroxides, salts can exhibit acid or base character. For example, ammonium chloride (NH_4Cl) 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 (HCl) and has a weak character. Let us calculate the PH of a 0.1-M NH_4Cl solution. As the salt is acidic, we will use Equation **??** given that c_a=0.1M and $K_a = 5.5 \times 10^{-10}$ (mind for ammonia $K_b = 1.8 \times 10^{-5}$ and **??** related K_a and K_b):

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

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

Sample Problem 12

Calculate the PH of a 0.02M 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 **??** given that $K_b = 5.5 \times 10^{-11}$ and c_b=0.02M:

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

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

❖ **STUDY CHECK**

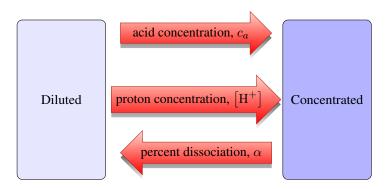Calculate the PH of a 0.01M sodium acetate (CH_3COONa). $K_a = 1.75 \times 10^{-5}$

✎ *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 ($[H^+]$) less than c_a. We define the percent dissociation α of an acid (or base) as:

$$\alpha = \frac{\text{amount dissociated}}{\text{initial amount}} \times 100 = \frac{[H^+]}{c_a} \times 100 \qquad (1.13)$$

where:

$[H^+]$ is concentration of protons in equilibrium

c_a is 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 13

Calculate the percent dissociation of CH_2O_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 **??**. 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: $[H^+]=1.25 \times 10^{-3}$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: $[H^+]=3.93 \times 10^{-3}$M. We can now calculate the degree of dissociation using Equation **??**. 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 CH_3NH_2 solution. $K_b = 4.4 \times 10^{-4}$

Answer: 9%

1.4 Buffer solutions

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

✎ *Buffers* Buffers are solutions of an acid and a base. But not any kind of acid and base. Buffers are solutions of an weak acid with its conjugate base, or weak bases and its conjugate acid. For example a mixture of 0.1M NH_3 and 0.1M NH_4Cl is a buffer. You can find acidic or basic buffer. For example, the previous example was a basic buffer, whereas a mixture of 0.1M CH_3COOH and 0.1M $NaCH_3COO$ is an acidic buffer. 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.

✎ *PH of a Buffer solution* A buffer solution consist of a solution containing both a weak electrolyte and its conjugate counterpart in the same of different concentration. For example, the PH of 5mL of a 0.01M CH_3COOH/0.1M $NaCH_3COO$ ($K_a = 1.75 \times 10^{-5}$) acidic buffer can be computed using the following formula:

$$PH = PK_a + \log\left(\frac{V_b \cdot c_b}{V_a \cdot c_a}\right) \tag{1.14}$$

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

V_a and V_b is the volume in which the buffer is contained, normally the same, and therefore they tend to cancel out in Equation **??**

This formula is called the Henderson-Hasselbalch equation. Using the date above, we have that: $PH = 4.76 + \log\left(\frac{0.1 \cdot 5}{0.01 \cdot 5}\right) = 5.75$. The following example will further demonstrate how to calculate the PH of buffer solutions.

> **Sample Problem 14**
>
> Calculate the PH of 20mL of a 0.1M NH$_4$Cl/0.2M NH$_3$ ($K_b = 1.80 \times 10^{-5}$).
> **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 5.5×10^{-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 ($K_a = 6.30 \times 10^{-4}$).
>
> Answer: 3.36

✎ *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$_3$COOH/0.1M NaCH$_3$COO ($K_a = 1.75 \times 10^{-5}$) after adding 1mL of NaOH 3M would be calculated with the following formula:

$$PH = PK_a + \log\left(\frac{V_b \cdot c_b + (V_b \cdot c_b)^{added} - (V_a \cdot c_a)^{added}}{V_a \cdot c_a + (V_a \cdot c_a)^{added} - (V_b \cdot c_b)^{added}}\right) \quad (1.15)$$

where most of the symbols of Equation **??** are the same as in Equation **??**:

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

The following example illustrates how to use Equation **??**.

> **Sample Problem 15**
>
> Calculate the PH of 20mL of a 0.1M NH$_4$Cl/0.2M NH$_3$ ($K_b = 1.80 \times 10^{-5}$) after adding 1mL of HCl 0.3M.
> **SOLUTION**
> In this example, we are adding an acid to a basic buffer. We have that $PK_a = 9.25$, $V_a = V_b = 20mL$, $c_a = 0.1M$ and $c_b = 0.2M$. As we are adding an acid we have $(V_b \cdot c_b)^{added} = 0$ and $(V_a \cdot c_a)^{added} = 1 \cdot 0.3 = 0.3$mM. Using Equation **??**:
>
> $$PH = 9.25 + \log\left(\frac{20 \cdot 0.2 - (1 \cdot 0.3)^{added}}{20 \cdot 0.1 + (1 \cdot 0.3)^{added}}\right) = 9.46$$
>
> We have that the original PH of the buffer is 9.56. After adding an acid, the PH remains close to the original buffer PH.
> ◈ **STUDY CHECK**
> Calculate the PH of 5mL of a 0.2M HF/0.3M KF ($K_a = 6.30 \times 10^{-4}$) after

adding 1mL of HCl 0.2M.

Answer: 3.23

1.5 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 tirate) by knowing the reacting amounts. A titration uses chemical equipment: a burette, erlenmeyers and an indicator. The unknown chemical is called the titrate and the known chemical is called the titrant. The goal of a titration is to calculate the volume of titrant needed to neutralize the titrate. We reach the endpoint of a titration when the titrant and titrate completely neutralize. At the en point the mixture of titrant and titrate has a specific PH. Even though the chemical procedure in the lab is similar when titrating strong of weak acids or bases, the calculations needed to calculate the PH at the endpoint differ. This section will cover the principles and calculations involved in titrations.

✎ *Neutralization Reactions* Titrations involves a neuralization reacion 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:

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \qquad \text{\textcolor{red}{Neutralization Reaction}}$$

In this reaction, one mole of HCl reacts with one mole of NaOH. The fact that one more reacts with one more can be used as a principle for an acid-base titration. We will have to use the stoichiometry of the reaction to calculate the volume of titrant needed to neutralize the titrate. Imagine you have an unknown sample of HCl and you need to know the amount of acid in the solution. If you know that this sample reacts with a specific amount of NaOH as you know that they react in a one-2-one ratio then you would know the acidic content. This is the idea behind a titration: a laboratory procedure in which an unknown sample is neutralized with a known solution. A chemical *indicator*, which changes color depending on the acidity of the medium, is used to visually reveal the moment in which the acid and the base are completely neutralized. The point at which the indicator changes color is called the *equivalency point* or the *endpoint*. At the endpoint, the acid and the base are neutralized.

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

$$\boxed{n_H \cdot c_a \cdot V_a = n_{OH} \cdot c_b \cdot V_b} \qquad (1.16)$$

where:

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

c_a and V_a is acid concentration and volume respectively

c_b and V_b is base concentration and volume respectively

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

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

Sample Problem 16

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 **??**, given: $c_b = 3M$, $V_b = 25mL$ and $V_a = 50mL$.

$$c_a \cdot 50mL = 3M \cdot 25mL$$

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.

Answer: 3M

Equation **??** 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 be before, after or at the endpoint? We have that in order to neutralize completely the titrant (H_2SO_4), and using Equation **??** we would need:

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

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

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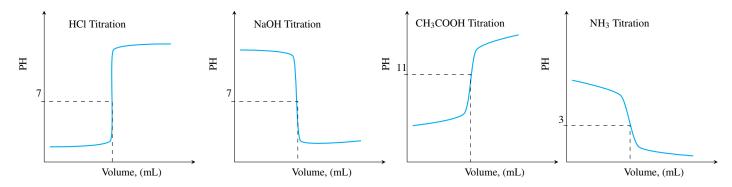

Figure ?? Different shapes of titration curves

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

✎ c_R *and* c_F First, c_R is the concentration of protons or hydroxyls remaining in solution. The formula for c_R is:

$$c_R = \frac{|n_H \cdot c_a \cdot V_a - n_{OH} \cdot c_b \cdot V_b|}{V_a + V_b} \tag{1.17}$$

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

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

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

$$c_F = \frac{min(n_H \cdot c_a \cdot V_a, n_{OH} \cdot c_b \cdot V_b)}{V_a + V_b} \tag{1.18}$$

where all variable refer to **??**. 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 $n_H \cdot c_a \cdot V_a = 8$mmol and $n_{OH} \cdot c_b \cdot V_b = 3$mmol. The smallest value is 3mmol, therefore $c_F = 0.6$M.

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

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 17

A 50mL sample of 3M HCl is titrated with with 25 mL of a NaOH 2M 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 **??** to calculate the PH (d) calculate the PH

SOLUTION

We have that HCl is the titrant and NaOH is the titrate. This is because the question indicates that you titrate HCl and therefore the chemical to be titrated is the titrant. 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 **??** and calculate the volume of titrant needed to neutralize the titrate. If the volume of titrant we have used is less than the endoint 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 =3M, $V_a = 50$mL, and n_H =1. We also have that c_b =2M, and n_{OH} =1. We will calculate V_b that fulfills **??**:

$$1 \cdot 3 \cdot 50 = 1 \cdot 2 \cdot V_b$$

Therefore, $V_b = 75$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: $[H^+] = c_R$. We can calculate c_R:

$$c_R = \frac{|n_H \cdot c_a \cdot V_a - n_{OH} \cdot c_b \cdot V_b|}{V_a + V_b} = \frac{|1 \cdot 3M \cdot 25mL - 1 \cdot 2M \cdot 25mL|}{(50 + 25)mL} =$$

$$= 0.33M$$

We have that PH=0.47.

◈ STUDY CHECK

A 5mL sample of 2M H_2SO_4 is titrated with with 25 mL of a NaOH 1M solution. (a) indicate whether you are before, after or at the endpoint (b) indicate whether the titrate is an acid or a base, and a weak or a strong electrolyte (c) indicate the formula that would need to be used from Table **??** to calculate the PH (d) calculate the PH

Answer: after, strong acid; $[OH^-] = c_R$; 13.22

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 **??-??**)

Sample Problem 18

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

SOLUTION

We have that CH$_3$COOH is the titrant and NaOH is the titrate. This is because the question indicates that you titrate CH$_3$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 **??** and calculate the volume of titrant needed to neutralize the titrate. If the volume of titrant we have used is less than the endoint 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 $c_a = 2$M, $V_a = 1$mL, and $n_H = 1$. We also have that $c_b = 3$M, and $n_{OH} = 1$. We will calculate V_b that fulfills **??**:

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

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

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

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

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

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

◈ STUDY CHECK

A 1mL sample of 2M NH_3 (1.80×10^{-5}) is titrated with with 2 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 from Table **??** to calculate the PH (d) calculate the PH

Answer: at the EP, weak base; $\left[H^+\right]^2 + K_a \cdot \left[H^+\right] - K_a \cdot c_f = 0$; 4.71

CHAPTER 1

THE NATURE OF ACIDS AND BASES

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

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

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

1.4 Classify the following species as Lewis acids or bases: (a) CO_2 (b) NH_3 (c) F^-

1.5 Classify the following species as Lewis acids or bases: (a) SO_2 (b) BCl_3 (c) I^-

DISSOCIATIONS OF ACIDS & BASES

1.6 Write down the formula of the conjugate bases: (a) H_2O (b) HCl (c) HNO_3 (d) H_2SO_4

1.7 Write down the formula of the conjugate bases: (a) HSO_4^- (b) H_2S (c) HCOOH (d) $H_2PO_4^-$

1.8 Write down the formula of the conjugate acids: (a) NH_4^+ (b) CH_3COO^- (c) HS^- (d) CN^-

1.9 Identify the conjugate acid-base pairs:

(a) $HCl_{(g)} + H_2O_{(l)} \rightleftharpoons Cl^-_{(aq)} + H_3O^+_{(aq)}$

(b) $CH_3COO^-_{(l)} + HCl_{(g)} \rightleftharpoons Cl^-_{(aq)} + CH_3COOH_{(aq)}$

(c) $CO_3^{2-}{}_{(aq)} + HCN_{(g)} \rightleftharpoons CN^-_{(aq)} + HCO_3^-{}_{(aq)}$

(d) $HNO_{3(aq)} + OH^-_{(aq)} \rightleftharpoons NO_3^-{}_{(aq)} + H_2O_{(aq)}$

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

(a) $HNO_{3(l)} + H_2O_{(l)} \rightleftharpoons$

(b) $H_2SO_{4(l)} + H_2O_{(l)} \rightleftharpoons$

(c) $HCl_{(g)} + H_2O_{(l)} \rightleftharpoons$

(d) $NH_{3(g)} + H_2O_{(l)} \rightleftharpoons$

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

(a) $CO_3^{2-}{}_{(aq)} + HCN_{(g)} \rightleftharpoons$

(b) $HCO_3^-{}_{(aq)} + HCN_{(g)} \rightleftharpoons$

(c) $HCO_3^-{}_{(aq)} + OH^-_{(aq)} \rightleftharpoons$

1.12 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 ($K_a = 4.3 \cdot 10^{-7}$)($K_a = 1.5 \cdot 10^{-2}$)

1.13 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) $H_2C_6H_5O^-$ ($K_a = 1.8 \cdot 10^{-5}$) or HCOOH ($K_a = 1.7 \cdot 10^{-4}$)

THE PH SCALE

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

1.15 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.

1.16 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.

1.17 Fill the table below:

$[H^+]$	$[OH^-]$	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}	

1.18 Fill the table below:

$[H^+]$	$[OH^-]$	**PH**	**POH**
4.5×10^{-3}		–	–
	3.2×10^{-7}	–	–
–	–	5.1	
–	–		6.9

1.19 Fill the table below:

$[H^+]$	$[OH^-]$	**PH**	**POH**
3.5×10^{-1}	–		–
–	–	–	2

1.20 Answer the following questions: (a) Calculate the PH of a 0.34M HCl solution (b) Calculate the PH of a 0.04M HNO_3 solution (c) Calculate the PH of a 0.08M NaOH solution

1.21 Answer the following questions: (a) Calculate the PH of a 0.27M H_2SO_4 solution (b) Calculate the PH of a 0.03M $Ba(OH)_2$ solution

1.22 Solve the following quadratic equations and select the positive root:

(a) $x^2 + 5.5 \times 10^{-11} \cdot x - 5.5 \times 10^{-12} = 0$

(b) $x^2 + 6.6 \times 10^{-5} \cdot x - 1.32 \times 10^{-5} = 0$

1.23 Answer the following questions: (a) Calculate the PH of a 0.23M C_6H_5COOH (benzoic acid, $K_a = 6.25 \times 10^{-5}$) solution (b) Calculate the PH of a 0.08M $C_6H_5NH_2$ (Aniline, $K_b = 7.40 \times 10^{-10}$) solution

1.24 Answer the following questions: (a) Calculate the PH of a 0.05M C_6H_5OH (phenol, $K_a = 1.00 \times 10^{-10}$) solution (b) Calculate the PH of a 0.09M C_5H_5N (pyridine, $K_b = 1.70 \times 10^{-9}$) solution

BUFFER SOLUTIONS

1.25 Which of the following mixtures of solutions can act as a buffer:

(a) 0.1M-H_2SO_4/0.1M-Na(SO_4)$_2$

(b) 0.01M-NH_3/0.01M-NH_4Cl

(c) 0.2M-HNO_2/0.2M-$NaNO_2$

1.26 Which of the following mixtures of solutions can act as a buffer:

(a) 0.4M-H_2SO_4/0.1M-$NaHSO_4$

(b) 0.23M-HCl/0.20M-KCl

(c) 0.56M-HCN/0.22M-NaCN

1.27 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, $K_a = 6.20 \times 10^{-10}$

1.28 Calculate the PH of the following buffers:

(a) 0.25 M-NH_3/0.45M-NH_4Cl, $K_b = 1.80 \times 10^{-5}$

(b) 0.15 M-HNO_2/0.05M-$NaNO_2$, $K_a = 5.60 \times 10^{-4}$

1.29 Calculate the PH of the following buffers:

(a) 0.02 M-$C_6H_5NH_2$/0.05M-C_6H_5NHCl, $K_b = 7.40 \times 10^{-10}$

(b) 0.4 M-HCNO/0.5M-NaCNO, $K_a = 3.50 \times 10^{-4}$

1.30 The PH of a $C_6H_5NH_2$/C_6H_5NHCl ($K_b = 7.40 \times 10^{-10}$) buffer is 4.0. Calculate the ratio of [$C_6H_5NH_2$]/[C_6H_5NHCl].

1.31 Calculate the PH for the following scenarios: (a) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer (b) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer after adding 3mL of 0.1HCl into 5mL of the buffer (c) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer after adding 3mL of 0.1NaOH into 5mL of the buffer (d) A 0.3 M-HCNO/0.4M-NaCNO, $K_a = 3.50 \times 10^{-4}$ buffer after adding 1mL of 0.1NaOH into 5mL of the buffer

1.32 Calculate the PH for the following scenarios: (a) A 0.8 M-HF/0.1M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer (b) A 0.8 M-HF/0.1M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1HCl into 2mL of the buffer (c) A 0.8 M-HF/0.1M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1NaOH into 2mL of the buffer (d) Is the buffer more resistant to acids or bases, and why?

1.33 Calculate the PH for the following scenarios: (a) A 0.1 M-HF/0.9M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer (b) A 0.1 M-HF/0.9M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1HCl into 2mL of the buffer (c) A 0.1 M-HF/0.9M-NaF, $K_a = 6.30 \times 10^{-4}$ buffer after adding 1mL of 0.1NaOH into 2mL of the buffer (d) Is the buffer more resistant to acids or bases, and why?

TITRATIONS

1.34 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 H$_2$SO$_4$ neutralize 8.4 mL of Ca(OH)$_2$. What is the concentration of the base solution?

1.35 A 15 mL solution of 0.2 M HCl is titrated with a 0.3 M KOH solution. Calculate the pH after the following additions of the base solution: (a) 0mL (b) 5mL (c) 10mL (d) 15mL

1.36 A 25 mL solution of 0.1 M HNO$_2$ ($K_a = 5.60 \times 10^{-4}$) is titrated with a 0.05 M KOH solution. Calculate the pH after the following additions of the base solution: (a) 0mL (b) 25mL (c) 50mL (d) 65mL

1.37 A 20 mL solution of 0.1 M KOH is titrated with a 0.5 M HCl solution. Calculate the pH after the following additions of the acid solution: (a) 0mL (b) 2mL (c) 4mL (d) 5mL

1.38 A 10 mL solution of 0.2 M NH$_3$ ($K_b = 2.50 \times 10^{-5}$) is titrated with a 0.1 M HCl solution. Calculate the pH after the following additions of the base solution: (a) 0mL (b) 10mL (c) 20mL (d) 30mL

Answers **1.1** (a) H_2SO_4 (acid) (b) NaOH (base) (c) HNO_3 (acid) (d) HCl (acid) (e) $Ca(OH)_2$ (base) **1.3** (a) HCO_3^- (both) (b) HI (acid) (c) HCN (acid) (d) HSO_4^- (both) (e) HCOONa (base) **1.5** (a) SO_2 (Lewis acid) (b) BCl_3 (Lewis acid) (c) I^- (Lewis base) **1.7** (a) HSO_4^- (SO_4^{2-}) (b) H_2S (HS^-) (c) HCOOH ($HCOO^-$) (d) $H_2PO_4^-$ (HPO_4^{2-}) **1.9** (a) (HCl / Cl^-) and (H_2O / H_3O^+) (b) (CH_3COO^- / CH_3COOH) and (HCl / Cl^-) (c) (CO_3^{2-} / CN^-) and (HCN / HCO_3^-) (d) (HNO_3 / NO_3^-) and (OH^- / H_2O) **1.11** (a) $CO_3^{2-}{}_{(aq)} + HCN_{(g)} \rightleftharpoons HCO_3^-{}_{(aq)} + CN^-_{(aq)}$ (b) $HCO_3^-{}_{(aq)} + HCN_{(g)} \rightleftharpoons H_2CO_{3(aq)} + CN^-_{(aq)}$ (c) $HCO_3^-{}_{(aq)} + OH^-_{(aq)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$ **1.13** (a) CN^- (b) HCOOH **1.15** (a) 12.66 (b) 12 **1.17**

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

1.19

$[H^+]$	$[OH^-]$	**PH**	**POH**
3.5×10^{-1}	2.8×10^{-14}	0.4	13.5
1×10^{-12}	1.0×10^{-2}	12	2

1.21 (a) 0.27 (b) 12.77 **1.23** (a) Calculate the PH of a 0.23M C_6H_5COOH (benzoic acid, $K_a = 6.25 \times 10^{-5}$) solution (b) Calculate the PH of a 0.08M $C_6H_5NH_2$ (Aniline, $K_b = 7.40 \times 10^{-10}$) solution **1.25** (a) 0.1M-H_2SO_4/0.1M-$Na(SO_4)_2$ (No buffer) (b) 0.01M-NH_3/0.01M-NH_4Cl (buffer) (c) 0.2M-HNO_2/0.2M-$NaNO_2$ (buffer) **1.27** (a) 0.15 M-HCN/0.35M-NaCN, $K_a = 6.20 \times 10^{-10}$ (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/0.15M-NaCN, $K_a = 6.20 \times 10^{-10}$ (PH=9.98) **1.29** (a) 0.02 M-$C_6H_5NH_2$/0.05M-C_6H_5NHCl, $K_b = 7.40 \times 10^{-10}$ (PH=4.47) (b) 0.4 M-HCNO/0.5M-NaCNO, $K_a = 3.50 \times 10^{-4}$ (PH=3.5) **1.31** (a) PH=3.58 (b) PH=3.43 (c) PH=3.73 (d) PH=3.63 **1.33** (a) PH=4.15 (b) PH=3.95 (c) PH=4.48 (d) acids **1.35** (a) PH=0.70 (b) PH=1.12 (c) PH=7 (d) PH=12.70 **1.37** (a) PH=13 (b) PH=12.65 (c) PH=7 (d) PH=1.69