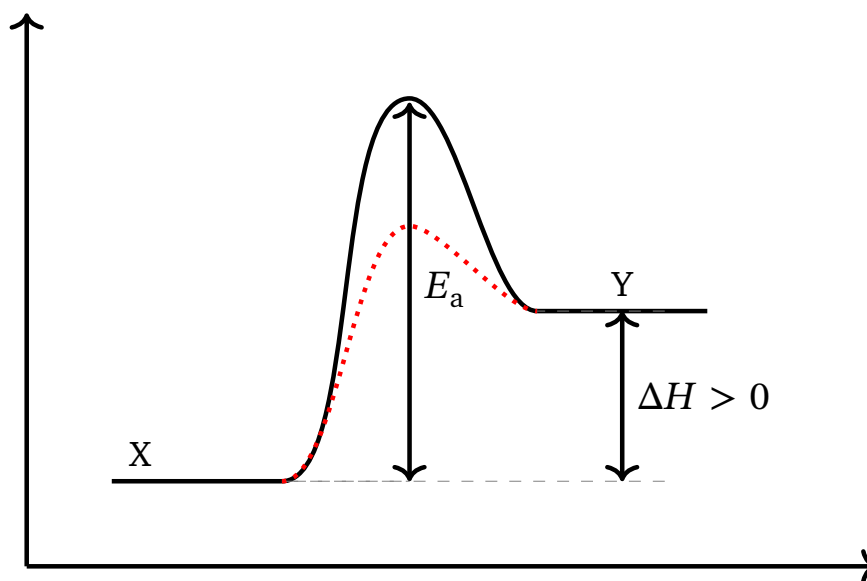


# Physical Chemistry



$$\Delta G = \Delta H - T \times \Delta S$$

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# Acid-Base Equilibrium

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## 1 Theory of Acids and Bases

### 1.1 Brønsted-Lowry

Fundamental to understanding this chapter is the Brønsted-Lowry theory of acids and bases... as the section header would lead you to conclude.

- Brønsted acids *donate* a proton ( $\text{H}^+$ ) to a base
- Brønsted bases correspondingly *accept* a proton ( $\text{H}^+$ ) from an acid.

Thus, there are some restrictions placed on each — acids must contain one or more atoms of H to donate, and bases must have one or more lone pairs in order to accept the  $\text{H}^+$  ion.

As such, acid-base reactions in the context of this theory involves the transfer of a proton from a Brønsted acid to a Brønsted base.

Note that, in the context of aqueous reactions,  $\text{H}^+$  can also be represented by  $\text{H}_3\text{O}^+$ , which is how it is currently theorised to exist in aqueous solutions.

### 1.2 Lewis

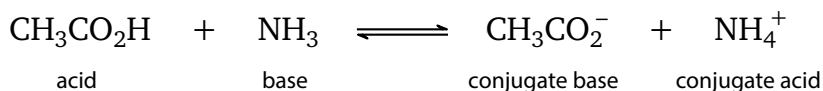
While Brønsted acids and bases are defined in terms of the transfer of protons, Lewis acids and bases are defined in terms of the transfer of electron pairs. Thus:

- Lewis acids *accept* an electron pair from a Lewis base donor.
- Lewis bases correspondingly *donate* an electron pair to a Lewis acid.

Further references to acids or bases implicitly refer to the *Brønsted* definition.

## 1.3 Conjugate Acid-Base Pairs

When an acid loses the  $\text{H}^+$  ion, an anion is naturally left — this is the conjugate base of the acid. Conversely, when a base accepts a proton, it forms the conjugate acid of the base.



In the forward reaction,  $\text{CH}_3\text{CO}_2\text{H}$  acts as the acid, donating a proton to the base,  $\text{NH}_3$ . In the reverse direction,  $\text{NH}_4^+$  is the acid, donating a proton to the base  $\text{CH}_3\text{CO}_2^-$ .

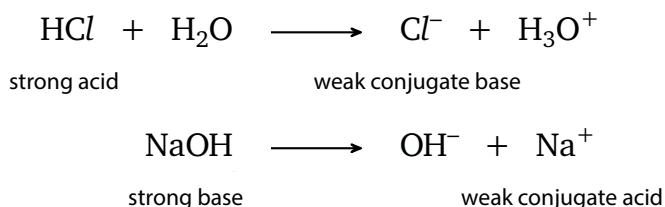
Furthermore,  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CO}_2^-$  are *conjugate pairs*, as are  $\text{NH}_3$  and  $\text{NH}_4^+$ . Conjugate pairs always differ by a proton, and in any given acid-base reaction, there are two such pairs.

## 1.4 Strength of Acids and Bases

Note that the *strength* of an acid or base is distinct from its *concentration* in solution.

### 1.4.1 Strong Acids and Bases

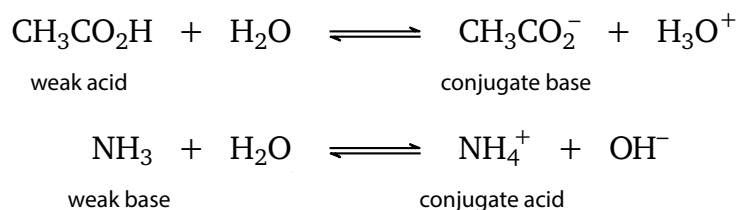
The strength of an acid or base is given as the degree of dissociation from the acid or base into ions, in solution. A strong acid or base is one that ionises *completely* in solution to give  $\text{H}^+$  or  $\text{OH}^-$  respectively.



Since they ionise *completely*, the reverse reaction is negligible. This is because the conjugate base  $\text{Cl}^-$ , in the case of  $\text{HCl}$ , has a low tendency to accept protons.

### 1.4.2 Weak Acids and Bases

Weak acids and bases, on the other hand, only dissociate *partially* in water to give  $\text{H}^+$  and  $\text{OH}^-$ . Thus, they are in an equilibrium with their conjugate:



A mixture of the undissociated acid or base, as well as its dissociated ions, will exist in solution.

## 1.5 Levelling Effect

When an acid (for example HCl) is dissolved in water, it forms the conjugate base ( $\text{Cl}^-$ ) and the hydronium ion,  $\text{H}_3\text{O}^+$  (which can be thought of as  $\text{H}^+$  (aq)).

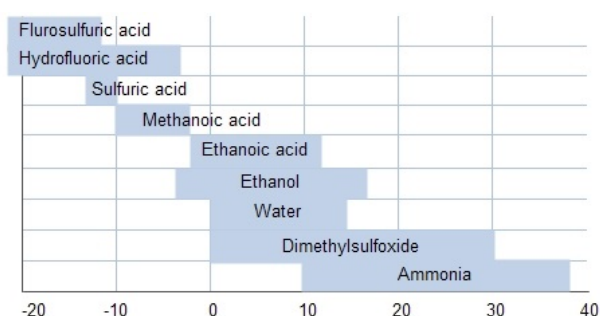
Since water already auto-ionises to form  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , any acid stronger than  $\text{H}_3\text{O}^+$  will simply continue to protonate water past its existing equilibrium, to create a large amount of  $\text{H}_3\text{O}^+$ . The reverse is true of strong bases, forming  $\text{OH}^-$ .

Because water is the solvent, it is in essentially unlimited supply, and any strong acid (or base) will ionise fully to form its conjugate, and a large supply of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  respectively. Thus, the overall effect is that the strength of the acid or base is 'levelled' by the solvent it is dissolved in; with water, any strong acid simply acts like a solution of  $\text{H}_3\text{O}^+$  (aq), and any strong base as  $\text{OH}^-$  (aq).

### 1.5.1 Discrimination Window

From the above, it should be implied that different solvents have different 'limits'; for water they are  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , for ammonia they are  $\text{NH}_4^+$  and  $\text{NH}_2^-$ , and so on.

Thus, each solvent has a *discrimination window* — acids or bases with strengths inside this window will exhibit different strengths, while those outside of it will be limited or *levelled*, and behave like the threshold species.



The discrimination windows of common solvents.

Since  $\text{NH}_4^+$  is a weaker acid than  $\text{H}_3\text{O}^+$ , almost all conventional strong acids will behave like a solution of  $\text{NH}_4^+$  when dissolved in  $\text{NH}_3$ . The primary purpose of using ammonia as a solvent is to experiment with strong bases, since  $\text{NH}_2^-$  is a stronger base than  $\text{OH}^-$ , so the levelling threshold is higher.

## 2 pH, pOH, and Other Such Constants

First, the general idea of  $p$  should be stated. In essence, it is this:

$$pX = -\lg X, \quad X = 10^{-pX}$$

So, it follows pH and pOH are, respectively,

$$\begin{aligned} \text{pH} &= -\lg [\text{H}^+], & [\text{H}^+] &= 10^{-\text{pH}} \\ \text{pOH} &= -\lg [\text{OH}^-], & [\text{OH}^-] &= 10^{-\text{pOH}} \end{aligned}$$

In other words, it is a measure of the concentration of either  $\text{H}^+$  or  $\text{OH}^-$  in the solution. As you might be aware, the lower the pH, the more  $\text{H}^+$  there is. pOH is similar, although it obviously measures the concentration of  $\text{OH}^-$ .

Note that neither pH nor pOH should be used to compare acid strengths — as previously mentioned, strength is independent of concentration. It can only be used as a comparison when both acids have the same initial concentration.

### 2.1 pH and pOH of Strong Acids and Bases

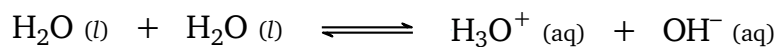
Given that strong acids and bases dissociate completely in water,  $[\text{H}^+]$  and  $[\text{OH}^-]$  simply become the initial concentration of the corresponding acid or base. If the acid in question is di- or even tri-protic, then the concentration of  $\text{H}^+$  will need to be multiplied by the appropriate ratio — the same applies for bases, of course.

If the initial concentration of the strong acid or base is smaller than  $1.0 \times 10^{-7} \text{ mol dm}^{-3}$ , the molecules of  $\text{H}^+$  or  $\text{OH}^-$  from the auto-ionisation of water must be taken into account — it is as simple as adding  $1.0 \times 10^{-7}$  to the concentration of the acid or base.



## 2.2 Ionic Product of Water, $K_w$

Pure water actually *auto-ionises* to a very slight degree, giving  $\text{H}^+_{(\text{aq})}$  and  $\text{OH}^-_{(\text{aq})}$ .



Since this is an equilibrium, the  $K_c$  value is as such:

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Given that the extent of ionisation is minuscule, the ‘concentration’ of  $\text{H}_2\text{O}$  is almost constant, and so

$$K_w = K_c \times [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$$

Thus,  $\text{p}K_w$  becomes relatively simple, taking  $\lg$  on both sides:

$$\text{p}K_w = \text{pH} + \text{pOH}$$

Experimentally, it is found that, at 25 °C,  $K_w = 1.0 \times 10^{-14} \text{ mol dm}^{-3}$ , so:

- $\text{p}K_w = 14$
- $\text{pH} + \text{pOH} = 14$ .

The value of  $K_w$ , and by extension,  $\text{p}K_w$ , is affected solely by temperature, just like  $K_c$ . Thus, only at 25 °C does  $\text{pH} + \text{pOH} = 14$  hold; at higher temperatures,  $K_w$  *increases*, so the sum is *greater than* 14.

Of course, the relationships  $\text{pH} + \text{pOH} = \text{p}K_w$  and  $K_w = [\text{H}^+][\text{OH}^-]$  always hold.

### 3 Dissociation of Acids and Bases

The acid and base dissociation constants,  $K_a$  and  $K_b$  respectively, are indicators of the degree of dissociation of the given acid or base.

Additionally, given the definitions of both  $K_a$  and  $K_b$ , the following relationships hold, for a given *conjugate acid-base pair*. Naturally it doesn't make sense to compare or relate two unrelated species.

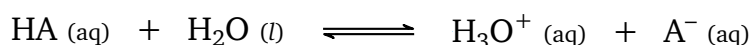
$$K_a \times K_b = K_w$$

$$\text{p}K_a + \text{p}K_b = \text{p}K_w$$

Thus, the weaker the acid, the stronger its conjugate base, and vice-versa.

#### 3.1 Acid Dissociation Constant, $K_a$

For some general weak acid HA, it dissociates partially in water:



In a dilute solution,  $[\text{H}_2\text{O}]$  is almost constant, so the equilibrium constant can be defined as such:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Naturally this is only true when the system is at equilibrium. Thus, the acid dissociation constant  $K_a$  is simply the equilibrium constant for the dissociation equilibrium, and indicates the *extent* to which the acid dissociates.

Additionally,  $\text{p}K_a$  is defined similarly to  $\text{p}K_w$ :

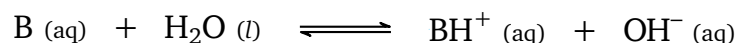
$$\text{p}K_a = -\lg K_a$$

The larger the value of  $K_a$  (and conversely, the smaller the value of  $\text{p}K_a$ ), the stronger the acid is. Thus,  $K_a$  values should be used as the basis for comparing the strength of weak acids. Naturally, the  $K_a$  values should be taken at the same temperature for a valid comparison.

Note that the  $K_a$  value for strong acids like HCl is very large, and is often irrelevant.

### 3.2 Base Dissociation Constant, $K_b$

The definitions of  $K_b$  and  $pK_b$  are essentially the mirror images of  $K_a$  and  $pK_a$ . For a given weak base B:



Thus, the base dissociation constant  $K_b$  can be defined:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$pK_b$  can also be defined similarly:

$$pK_b = -\lg K_b$$

As with acids, the larger the value of  $K_b$ , the stronger the base.

### 3.3 Degree of Dissociation, $\alpha$

The degree of dissociation of a given acid or base is the *ratio* of the number of moles of the substance that are ionised, to the number of unionised moles of acid or base.

$$\alpha = \frac{[\text{acid}]_{\text{dissoc}}}{[\text{acid}]_{\text{initial}}}$$

Thus, for a strong acid or base,  $\alpha$  is close to 1, while it is often much smaller than 1 for weak acids or bases.

### 3.4 Calculations involving $K_a$ and $K_b$

Calculations involving only  $K_a$  or  $K_b$  are fairly straightforward. Given the value of  $K_a$  for instance, it is trivial to find the concentration of  $\text{H}^+$  and hence pH, *assuming*:

- $[\text{H}^+] = [\text{A}^-]$ , ie. all the  $\text{H}^+$  and  $\text{A}^-$  comes from the acid
- $[\text{HA}]$  at equilibrium =  $[\text{HA}]$  initially

The first assumption will be *invalid* when there are *external sources* of  $\text{H}^+$  or  $\text{A}^-$ , as in a buffer system. The second assumption can be discarded to be more accurate, but should be used when  $[\text{H}^+] \ll 0.1$ .

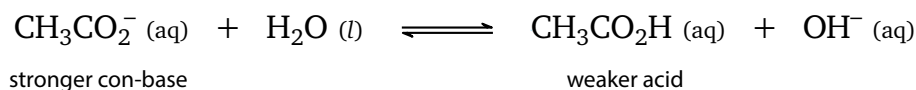
## 4 Salt Hydrolysis

Two main categories of salts undergo hydrolysis in water, forming  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions to give acidic or basic solutions respectively — ions of salts derived from weak acids or bases, and metal cations with a high charge density.

Ions of salts derived from strong acids and bases, eg.  $\text{NaCl}$  or  $\text{KNO}_3$ , will not hydrolyse, and will give a neutral solution.

### 4.1 Weak Acid, Strong Base

Examples of such salts include  $\text{CH}_3\text{CO}_2^-\text{Na}^+$ , which comes from the weak acid  $\text{CH}_3\text{CO}_2\text{H}$  and the strong base  $\text{NaOH}$ . The  $\text{Na}^+$  ion will not hydrolyse, while the  $\text{CH}_3\text{CO}_2^-$  ion will:

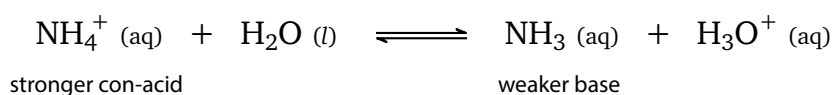


In this case, given that  $\text{CH}_3\text{CO}_2\text{H}$  is a weaker acid than water,  $\text{CH}_3\text{CO}_2^-$  is a stronger base than water; thus it is able to accept a proton — leaving  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{OH}^-$  as the products.

Since  $\text{OH}^-$  is present, the solution would be *alkaline*. However,  $\text{CH}_3\text{CO}_2^-$  is still an objectively weak base (water is a low benchmark), so the system exists in an equilibrium.

### 4.2 Strong Acid, Weak Base

$\text{NH}_4^+\text{Cl}^-$ , which comes from the weak base  $\text{NH}_3$  and the strong acid  $\text{HCl}$ , can have its  $\text{NH}_4^+$  ion undergo salt hydrolysis as well, in what is basically the mirror of the case with a strong base and weak acid:



Again,  $\text{NH}_4^+$  is a stronger acid than water, given that  $\text{NH}_3$  is weaker than water. Hence it donates a proton to  $\text{H}_2\text{O}$ , forming  $\text{H}_3\text{O}^+$  and giving an *acidic* solution that exists in an equilibrium.

## 4.3 Weak Acid and Weak Base

In this case, such as with the salt  $\text{CH}_3\text{CO}_2^-\text{NH}_4^+$ , both ions will hydrolyse — the final pH of the solution depends on the  $K_a$  and  $K_b$  values of the conjugate acid and base respectively. Generally speaking, the cation is the conjugate acid, and the anion is the conjugate base.

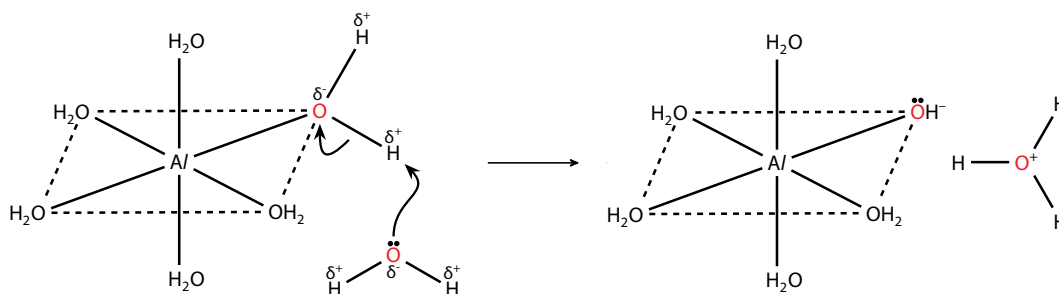
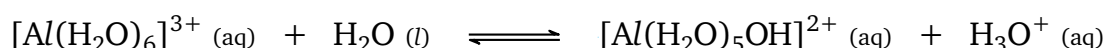
- $K_a > K_b$ ;  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$  — acidic solution
- $K_a = K_b$ ;  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  — neutral solution
- $K_a < K_b$ ;  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$  — basic solution

## 4.4 Metal Cation With High Charge Density

There are 3 main metal cations exhibiting this property —  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Fe}^{3+}$ . As will be covered later in the *Chemistry of Transition Metals*, these ions can form complexes with  $\text{H}_2\text{O}$  ligands in aqueous solution.

Due to their high charge density, they are able to sufficiently polarise and weaken an O—H bond in one of the ligands, allowing an external  $\text{H}_2\text{O}$  molecule to gain a proton. This of course requires breaking said O—H bond, hence hydrolysis.

The  $\text{H}_3\text{O}^+$  molecule is formed, so the solution becomes acidic.



The table below shows the  $K_a$  values for the 3 cations in question:

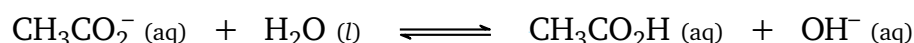
Ion	Hydrated Ion	$K_a / \text{mol dm}^{-3}$ at 25 °C
$\text{Fe}^{3+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$6.3 \times 10^{-3}$
$\text{Cr}^{3+}$	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$1.6 \times 10^{-4}$
$\text{Al}^{3+}$	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	$1.4 \times 10^{-5}$

## 4.5 pH of Hydrolysed Salt Solutions

Given the relevant  $K_a$  or  $K_b$  values, it is possible to find  $[H^+]$ , and hence pH, of the solution. However, if the  $K_a$  of the original weak acid is given, it is necessary to use the relationship  $K_w = K_a \times K_b$  to find the  $K_b$  value for the conjugate base.

$$K_b = \frac{K_w}{K_a} \quad K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]}$$

Note that, in the absence of external agents,  $[CH_3CO_2H]$  and  $[OH^-]$  are equal, given that the stoichiometric ratios are also equal, in the original hydrolysis equation:



## 5 Buffer Solutions

### 5.1 Overview

All of the situations above have operated with the assumption that there are no external agents supplying ions to the solution, ie. all the ions come from the dissociation of the weak acid or base.

In a buffer solution, there is a large supply of both the undissociated acid or base, and the conjugate ion. This allows the buffer solution to react with small amounts of *both*  $H^+$  and  $OH^-$  that might be added. This allows for the system to *resist* small changes in pH.

### 5.2 Method of Operation

Although the explanations below will use an acidic buffer as an example, the same principles apply for basic buffer using a weak base as a starting point.

Where an acidic buffer will have a large reservoir of the undissociated weak acid and its conjugate base, an alkaline buffer will have a large reservoir of the undissociated weak base and its conjugate acid.

## 5.2.1 Creation of Buffer

The weak acid  $\text{CH}_3\text{CO}_2\text{H}$  dissociates partially in water:



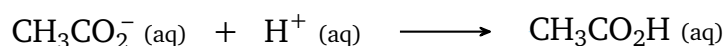
To create the buffer system, a large amount of  $\text{CH}_3\text{CO}_2^-$ , the conjugate base, is added — often using a soluble salt of that ion, for instance  $\text{CH}_3\text{CO}_2^-\text{Na}^+$ . This dissolves fully in water:



According to Le Châtelier's Principle, the position of equilibrium in the first equation (of the dissociation of the acid) shifts further to the left, suppressing the dissociation. Thus, the large supply of both  $\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CH}_3\text{CO}_2^-$  is achieved.

## 5.2.2 Reaction with $\text{H}^+$

When a small amount of  $\text{H}^+$  ions are added to the buffer solution, they react with the *large reservoir* of  $\text{CH}_3\text{CO}_2^-$  molecules, the conjugate base:



The  $\text{H}^+$  ions are removed, and thus a change to the pH of the solution is resisted. From the original dissociation equation:

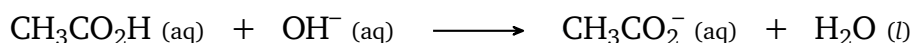
$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{CO}_2\text{H}]}{[\text{CH}_3\text{CO}_2^-]}$$

Thus, even though  $[\text{CH}_3\text{CO}_2\text{H}]$  increases slightly and  $[\text{CH}_3\text{CO}_2^-]$  decreases slightly to neutralise the  $\text{H}^+$ , compared to the large reservoir, the change is small, and so  $[\text{H}^+]$  remains *relatively constant*, and hence so does pH.

This is the reason why a *large reservoir* is needed for a buffer solution — the larger this supply, the larger the resistance to changes in pH (ie. the more  $\text{H}^+$  or  $\text{OH}^-$  can be added before the buffer fails).

### 5.2.3 Reaction with $\text{OH}^-$

Similarly, a buffer solution reacts with added  $\text{OH}^-$  ions using the large supply of the unionised weak acid present:



As evident, the added  $\text{OH}^-$  ions are removed, and the pH of the solution remains constant — the existing  $\text{H}^+$  ions in the equilibrium are not neutralised.

Note that the *action reactions* of the buffer system are written with a single-directional arrow, as it is not directly part of the equilibrium.

## 5.3 pH of Buffer Solutions

Since the dissociation of the weak acid or base is *not* the only source of  $\text{H}^+$  or  $\text{OH}^-$  ions in the solution, the calculation of the pH of a buffer solution becomes more complex. Of course, beginning with the basic (*pun intended*) equation, for the weak acid  $\text{CH}_3\text{CO}_2\text{H}$  and the weak base  $\text{NH}_3$ :

$$K_a = \frac{[\text{CH}_3\text{CO}_2^-]_{eqm}[\text{H}^+]_{eqm}}{[\text{CH}_3\text{CO}_2\text{H}]_{eqm}} \quad K_b = \frac{[\text{NH}_4^+]_{eqm}[\text{OH}^-]_{eqm}}{[\text{NH}_3]_{eqm}}$$

As stated above, adding the conjugate of the acid or base moves the position of equilibrium of the dissociation reaction to the left, reducing the amount of  $\text{CH}_3\text{CO}_2^-$  or  $\text{NH}_4^+$  that comes from the acid or base. Hence, the following approximations can be made:

- $[\text{CH}_3\text{CO}_2\text{H}]_{initial} = [\text{CH}_3\text{CO}_2\text{H}]_{eqm}$ , since very little  $\text{CH}_3\text{CO}_2\text{H}$  dissociates
- $[\text{CH}_3\text{CO}_2^-]_{salt} = [\text{CH}_3\text{CO}_2^-]_{eqm}$ , since almost all of the conjugate comes from the salt

Or, for the base:

- $[\text{NH}_3]_{initial} = [\text{NH}_3]_{eqm}$ , since very little  $\text{NH}_3$  dissociates
- $[\text{NH}_4^+]_{salt} = [\text{NH}_4^+]_{eqm}$ , since almost all of the conjugate comes from the salt

Hence, performing the appropriate replacements:

$$K_a = \frac{[\text{H}^+]_{eqm}[\text{salt}]}{[\text{acid}]} \quad K_b = \frac{[\text{OH}^-]_{eqm}[\text{salt}]}{[\text{base}]}$$

$$[\text{H}^+]_{eqm} = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \quad [\text{OH}^-]_{eqm} = K_b \times \frac{[\text{base}]}{[\text{salt}]}$$

Thus the pH and pOH can be found, given the concentrations of the acid and salt used to create the buffer solution.



### 5.3.1 Equation of Henderson and Hasselbalch

These two people made an equation apparently — simply perform a  $-lg$  on both sides of the equations above:

$$\text{pH} = \text{p}K_a + lg \frac{[\text{salt}]}{[\text{acid}]} \quad \text{pOH} = \text{p}K_b + lg \frac{[\text{salt}]}{[\text{base}]}$$

Note that the fraction inside the logarithm is *flipped*, because math works that way.

### 5.4 Buffer Capacity

The capacity of a buffer is determined by the initial concentration of [salt], and [acid] or [base]. Furthermore, the most effective buffer solution has equal concentration of the salt to the acid or base:

$$\frac{[\text{salt}]}{[\text{acid}]} = 1 \quad \frac{[\text{salt}]}{[\text{base}]} = 1$$

Thus, it can be shown that, at the maximum capacity:

$$\text{pH} = \text{p}K_a \quad \text{pOH} = \text{p}K_b$$

When a buffer is at maximum capacity, it is able to resist the greatest changes in pH, ie. the addition of  $\text{H}^+$  or  $\text{OH}^-$  ions. The further away it is from this maximum, the less effective it becomes.

### 5.5 Effective Buffer Range

As  $\text{H}^+$  ions are added, the capacity of the buffer is *used up*, so to speak, as the ions or molecules in the buffer are consumed. This causes a change in the ratio of [salt] to [acid] or [base], since one is consumed and the other is generated.

Since the maximum capacity exists when this ratio is 1, the further away it strays, the less effective the buffer becomes, and it is less able to resist the addition of  $\text{H}^+$  or  $\text{OH}^-$  ions.

In practice, these are the limits for the effectiveness of a buffer solution:

$$0.1 < \frac{[\text{salt}]}{[\text{acid}]} < 10$$

Or, in other words, the ratio between the acid or base and its conjugate must not deviate by more than a factor of 10. Alternatively, in terms of pH and pOH:

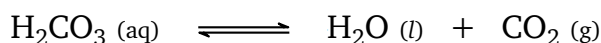
$$\text{pH range} = \text{p}K_a \pm 1 \quad \text{pOH range} = \text{p}K_b \pm 1$$

## 5.6 Biological Purpose of Buffer Systems

Curiously, chemistry seems to delve into the realms of physics and biology — *they are dark and full of terrors*. Anyway, one important function of buffers is in regulating the pH of human blood, to maintain the effectiveness of enzymes, and of course, preserve life.

In fact, blood contains a large reservoir of  $\text{H}_2\text{CO}_3$ , a weak acid which is actually dissolved aqueous  $\text{CO}_2$  and its conjugate base  $\text{HCO}_3^-$ .

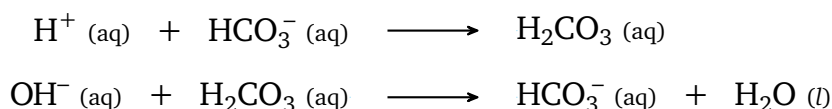
First,  $\text{H}_2\text{CO}_3$  exists in an equilibrium:



Since  $\text{H}_2\text{CO}_3$  is part of the buffer system in the blood, the following buffer equilibrium exists as well:



Thus, if the pH becomes too high, the excess  $\text{OH}^-$  will react with the  $\text{H}_2\text{CO}_3$ ; if pH becomes too low, the excess  $\text{H}^+$  reacts with the  $\text{HCO}_3^-$  in the buffer:



If the amount of  $\text{H}_2\text{CO}_3$  in the blood becomes too high, the lungs do the job of exhaling the  $\text{CO}_2$ :



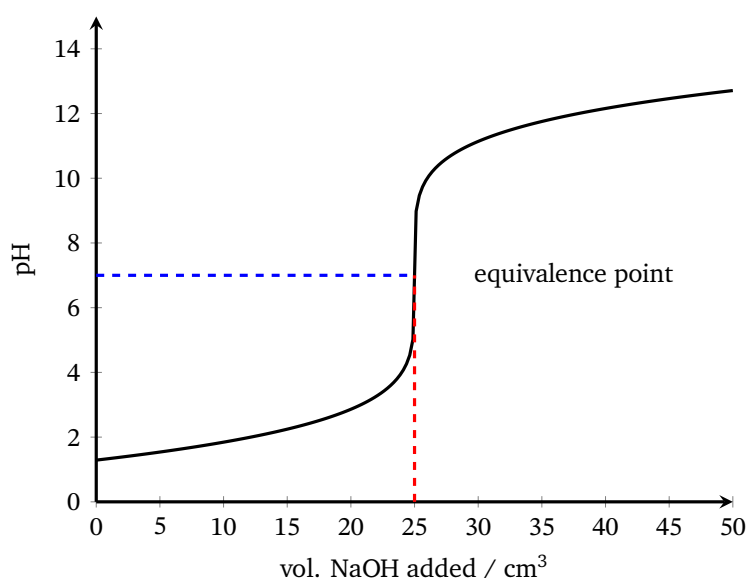
## 6 Titration of Weak Acids and Bases

In titrating acids and bases, there are  $2^2$  cases — strong acid against strong base, strong acid against weak base, weak acid against strong base, and weak acid against weak base.

Each of these cases will be covered below; all assume that the initial concentration of the acid and the base are identical, the acid is in the flask and the base in the burette, and  $25\text{ cm}^3$  of the acid is used.

### 6.1 Strong Acid and Strong Base

Here, the titration of  $\text{HCl}$  against  $\text{NaOH}$ .

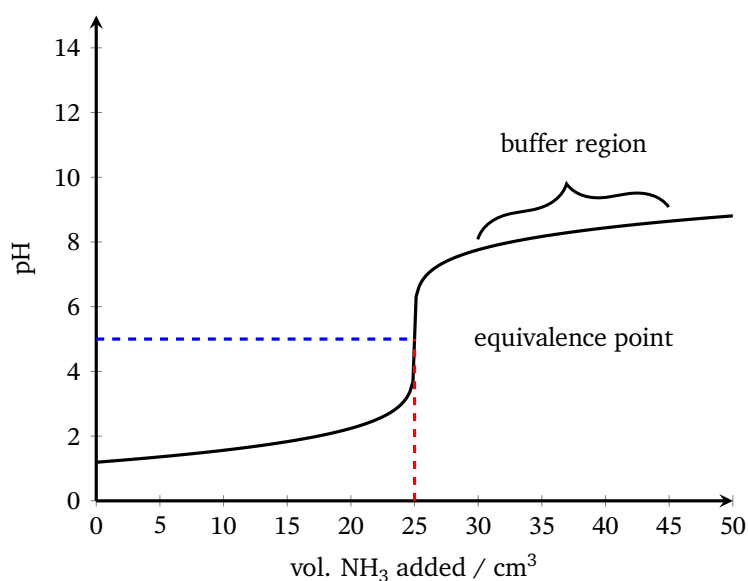


- $V = 0\text{ cm}^3$        $\text{pH} = [\text{acid}]$ , since only the strong acid exists.
- $V < 25\text{ cm}^3$        $\text{pH} < 7$ , but increases as more acid is neutralised.  
No salt hydrolysis or buffer, since there is no weak acid or base.
- $V = 25\text{ cm}^3$        $\text{pH} = 7$  at the equivalence point.  
No  $\text{H}^+$  or  $\text{OH}^-$  is present, so the solution is neutral.
- $V > 25\text{ cm}^3$        $\text{pH} > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more  $\text{NaOH}$ .

*Phenolphthalein*, *methyl orange* or *thymol blue* can be used as indicators. Of note is the sharp pH change at the equivalence point in the titration curve.

## 6.2 Strong Acid, Weak Base

Here, the titration of  $\text{HCl}$  against  $\text{NH}_3$ .

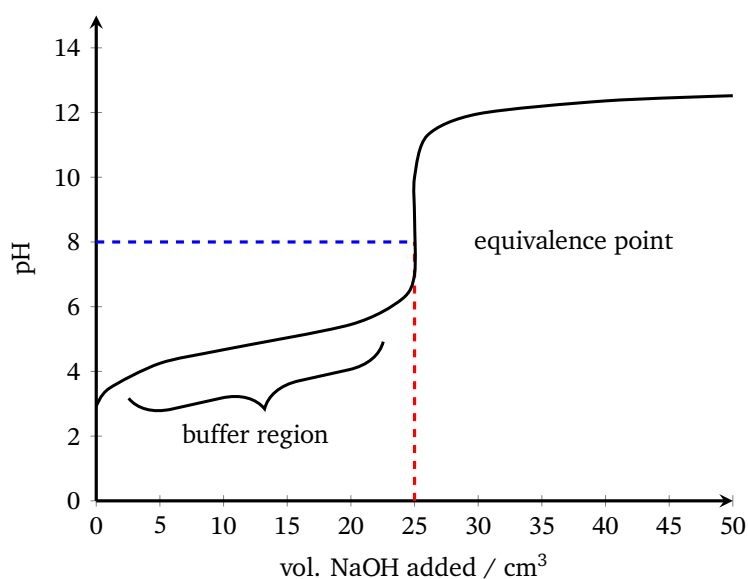


- $V = 0 \text{ cm}^3$        $\text{pH} = [\text{acid}]$ , since only the strong acid exists.
- $V < 25 \text{ cm}^3$        $\text{pH} < 7$ , but increases as more acid is neutralised.  
No salt hydrolysis or buffer, since there is no weak acid or base.
- $V = 25 \text{ cm}^3$        $\text{pH} < 7$  at the equivalence point.  
Even though no  $\text{H}^+$  or  $\text{OH}^-$  is present,  $\text{NH}_4^+$  in the salt hydrolyses, forming acid:  $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ .
- $V > 25 \text{ cm}^3$        $\text{pH} > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more base.  
A buffer forms, since there is  $\text{NH}_3$  and its conjugate acid  $\text{NH}_4^+$ .

*Methyl orange* can be used as the indicator, since its working range is within the sharp pH change.

## 6.3 Weak Acid, Strong Base

Here, the titration of  $\text{CH}_3\text{CO}_2\text{H}$  against  $\text{NaOH}$ .

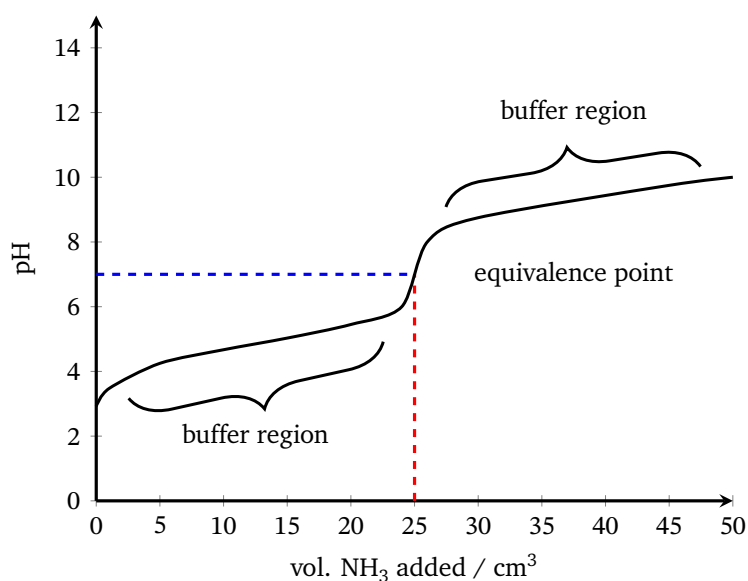


- $V = 0 \text{ cm}^3$       $\text{pH} > [\text{acid}]$ , since the acid is weak.
- $V < 25 \text{ cm}^3$       $\text{pH} < 7$ , but increases as more acid is neutralised.  
A buffer forms; there is  $\text{CH}_3\text{CO}_2\text{H}$  and its conjugate base  $\text{CH}_3\text{CO}_2^-$ .
- $V = 25 \text{ cm}^3$       $\text{pH} > 7$  at the equivalence point.  
Even though no  $\text{H}^+$  or  $\text{OH}^-$  is present,  $\text{CH}_3\text{CO}_2^-$  in the salt hydrolyses, forming base:  $\text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} + \text{OH}^-$ .
- $V > 25 \text{ cm}^3$       $\text{pH} > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more base.  
No buffer; there is no  $\text{CH}_3\text{CO}_2\text{H}$  left, only its conjugate  $\text{CH}_3\text{CO}_2^-$ .

*Phenolphthalein* or *thymol blue* can be used as the indicator, since their working ranges lie within the sharp pH change.

## 6.4 Weak Acid, Weak Base

Here, the titration of  $\text{CH}_3\text{CO}_2\text{H}$  against  $\text{NH}_3$ .



- $V = 0 \text{ cm}^3$        $\text{pH} > [\text{acid}]$ , since the acid is weak.
- $V < 25 \text{ cm}^3$        $\text{pH} < 7$ , but increases as more acid is neutralised.  
A buffer forms; there is  $\text{CH}_3\text{CO}_2\text{H}$  and its conjugate base  $\text{CH}_3\text{CO}_2^-$ .
- $V = 25 \text{ cm}^3$        $\text{pH} \approx 7$  at the equivalence point.  
Both the conjugate base and conjugate acid hydrolyse:  

$$\text{CH}_3\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2\text{H} + \text{OH}^-$$

$$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$$
The exact pH depends on the  $K_a$  and  $K_b$  values of the conjugates.
- $V > 25 \text{ cm}^3$        $\text{pH} > 7$  as  $[\text{OH}^-]$  increases, due to the addition of more base.  
A buffer forms; there is  $\text{NH}_3$  and its conjugate acid  $\text{NH}_4^+$ .

No suitable indicator can be used, since there is no sharp pH change at all. A pH meter can be used instead. Note that the pH at the equivalence point is not necessarily 7 — following the situation of simultaneous salt hydrolysis of a weak acid and base:

- $K_a > K_b$       —       $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ ;      acidic solution
- $K_a = K_b$       —       $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ ;      neutral solution
- $K_a < K_b$       —       $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ ;      basic solution

In this case, the  $K_a$  and  $K_b$  of  $\text{NH}_3^+$  and  $\text{CH}_3\text{CO}_2\text{H}$  are almost equal ( $1.8 \times 10^{-5} \text{ mol dm}^{-3}$ ), so the  $K_b$  and  $K_a$  of their conjugates will be as well.

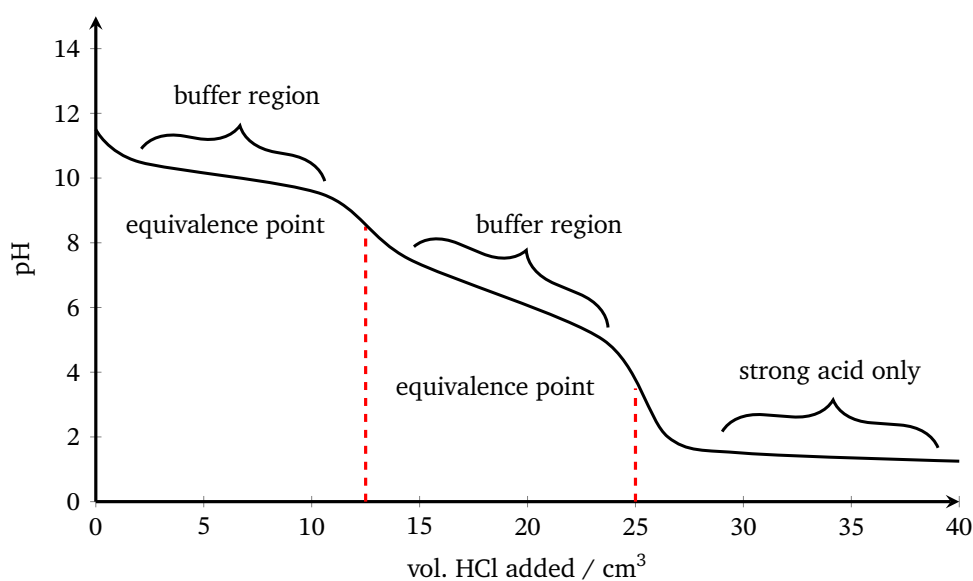
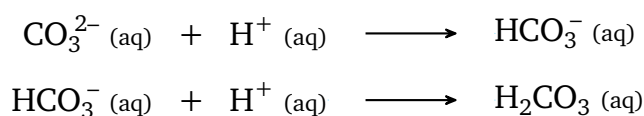
## 6.5 Titration of Polyprotic Acids or Bases

Polyprotic acids are acids with multiple ionisable protons; conversely polybasic bases are those that can accept more than one proton.

$\text{H}_2\text{CO}_3$  is a polyprotic acid with a weak second acid  $\text{HCO}_3^-$ , while  $\text{H}_2\text{SO}_4$  is a strong polyprotic acid with a strong first acid and a weak second acid  $\text{HSO}_4^-$ . Often times the  $K_a$  of the first proton is much larger than that of subsequent ones.

When analysing polyprotic things, it is often convenient and apt to assume that every molecule of acid will first lose one proton, before starting to lose the second.

Thus, a distinct titration curve can be seen, in this case using the example of  $\text{CO}_3^{2-}$ , which is the conjugate base of the weak acid polyprotic  $\text{H}_2\text{CO}_3$ :



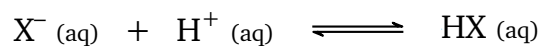
There are two distinct equivalence points here, and they should be observed separately with two indicators — *phenolphthalein* for the first equivalence point at  $\text{pH} = 8.5$ , and *methyl orange* for the second one at  $\text{pH} = 3.5$ .

*Methyl orange* should only be added to the solution after the first equivalence point is observed, if not the first point will be obscured since methyl orange exhibits no colour change at that point.

## 7 pH Indicators

### 7.1 Working Range

Indicators exist in an equilibrium with  $H^+$ ; the colour of the indicator depends on the ratio of the concentration of one ion to the other. For instance, taking an arbitrary indicator species  $X^-$  and its conjugate  $HX$ :



Following the general formula for  $K_a$ , and manipulating slightly:

$$K_X = \frac{[H^+][X^-]}{[HX]} \quad pH = pK_X + \lg \frac{[X^-]}{[HX]}$$

For the colour change to be visible, the concentration of the dominant ion must be greater than the less dominant one by a factor of 10, so the working range of an indicator is as such:

$$pH = pK_X \pm 1$$



## 7.2 Appropriate Indicator Selection

When selecting which indicator to use, the most obvious consideration is that the colour change will occur at the equivalence point of the reaction — if not it is pointless. For any indicator to be used at all, there should be a sharp change at said equivalence point; titrations involving at least one *strong* acid or base (or both) will exhibit such a sharp change.

The working pH ranges for a number of common indicators, and their uses, are summarised below:

Indicator	Working Range (pH)	Colour (Low/High)
methyl orange	3.1 to 4.4	red / yellow
phenolphthalein	8.0 to 9.6	colourless / pink
thymol blue	8.0 to 9.6	yellow / blue

Next, according to their working pH ranges, a summary of the suitable indicators for each kind of titration:

Situation	Sharp pH Change	Indicators
strong acid, strong base	3.0 to 11.0	any
strong acid, weak base	3.0 to 7.0	methyl orange
weak acid, strong base	7.0 to 11.0	phenolphthalein / thymol blue
weak acid, weak base	<i>none</i>	<i>none</i>