

TOOLS OF TRADE

LABORATORY WORK IN LIFE SCIENCES



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Week 4

Acid-Base Chemistry, Buffers



21

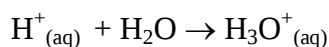
To understand the structure and activity relationship of biological molecules we should understand the acid-base chemistry. Because, many building blocks (e.g., amino acids, nucleotides) and the macromolecules (i.e., proteins and nucleic acids) built from these building blocks have acid or base characteristics and their activity is fine tuned in cell millieu which may have different acid-base chemistry. For example, while the internal (that is cytosol) pH in most cells is around 7.0, gastric cells in the stomach have an internal pH of 1-3. This shows that the cytoplasmic proteins or enzymes in most cells are active only near neutral pH (therefore, metabolism occurs in cells at pH values near neutrality), while in gastric cells they function under highly acidic conditions. More striking, while a cell may have a near alkali pH, its acidic organelle, lysosome, maintain an internal pH of 5.0. A number of mechanisms help accomplish this differential acid-base chemistry in different cells, including buffering by the mono- and di-basic forms of phosphate ion.

Given the properties of molecular constituents of cells, we need to know how an internal balance of acid-base chemistry maintains a microenvironment that leads to a "living cell".

Let's begin by asking one fundamental question about acids and bases: What are acids and bases?

Aqueous solution An aqueous solution is a solution in which the solvent is water. It is usually shown in chemical equations by appending (aq) to the relevant formula, such as NaCl (aq).

The first definition of acids and bases was made in 19th century by the Swedish chemist Swante Arrhenius who defined the acids as substances that produce H^+ ions in aqueous solution, and bases as substances that produce OH^- ions in aqueous solution. Today, however, we know that H^+ ions (a bare proton) cannot exist in water freely and it immediately combines with an H_2O molecules to give a hydronium ion, H_3O^+ :



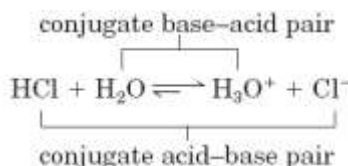
Although we know that acid aqueous solutions do not contain H^+ ions, we frequently use the terms “ H^+ ” or “proton” when in fact we mean H_3O^+ . Expect this minor modification, the Arrhenius definition of acids and bases is still valid today.

Another widely accepted definition of acids and bases is the one made by Johannes Brønsted and Thomas Lowry in 1923 and known as the Brønsted-Lowry theory. They both simultaneously proposed that “any proton donor is an acid, and a proton acceptor is a base”. For example, when HCl reacts with water:

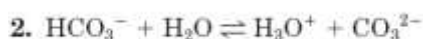
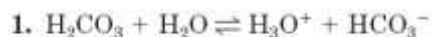


HCl is an *acid* and H_2O is a *base* because HCl donated a proton thereby becoming Cl^- , and water accepted a proton thereby becoming H_3O^+ . In the reverse reaction (from right to left) the H_3O^+ is an acid and Cl^- is a base. As the arrow indicates, the equilibrium in this reaction lies far to the right. That is, almost 100% of HCl molecules dissolved in water are converted to Cl^- and the released H^+ combines with water molecule. Although H_3O^+ (hydronium ion) is also an acid and can donate a proton to Cl^- and convert it to HCl, this indeed is impossible since HCl is a stronger acid than hydronium ion, and water is a stronger base than Cl^- .

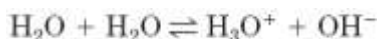
In the Brønsted-Lowry theory, every acid–base reaction creates its *conjugate acid–base pair*. In the above reaction HCl is an acid which, after giving up a proton, becomes a conjugate base, Cl^- . Similarly, water is a base which, after accepting a proton, becomes a conjugate acid, the hydronium ion.



Some acids can give up only one proton. These are *monoprotic* acids. Examples are HCl , HNO_3 , HCOOH , and CH_3COOH . The hydrogens squared are the ones donated. Other acids yield two or three protons. These are called *diprotic* or *triprotic* acids. Examples are H_2SO_4 , H_2CO_3 , and H_3PO_4 . However, in the Brønsted-Lowry theory, each acid is considered monoprotic, and a diprotic acid (such as carbonic acid) donates its protons in two distinct steps:



Thus the compound HCO_3^- is a conjugate base in the first reaction and an acid in the second reaction. A compound that can act either as an acid or a base is called *amphiprotic*. In the self-ionization reaction



one water acts as an acid (proton donor) and the other as a base (proton acceptor). In pure water, the equilibrium lies far to the left, that is, only very few hydronium and hydroxyl ions are formed. In fact, only 1×10^{-7} moles of hydronium ion and 1×10^{-7} moles of hydroxide ion are found in one liter of water. The dissociation constant for the self ionization of water is

$$K_d = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

This can be rewritten as

$$K_w = K_d [H_2O]^2 = [H_3O^+][OH^-]$$

K_w , the *ion product of water*, is still a constant because very few water molecules reacted to yield hydronium and hydroxide ions; hence the concentration of water essentially remained constant. At room temperature, the K_w has the value of

$$K_w = 1 \times 10^{-14} = [1 \times 10^{-7}] \times [1 \times 10^{-7}]$$

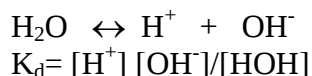
This value of the ion product of water applies not only to pure water but to any aqueous (water) solution. This is very convenient because if we know the concentration of the hydronium ion, we automatically know the concentration of the hydroxide ion and vice versa. For example, if in a 0.01 M HCl solution HCl dissociates completely, the hydronium ion concentration is $[H_3O^+] = 1 \times 10^{-2}$ M. This means that the $[OH^-]$ is

$$[OH^-] = K_w/[H_3O^+] = 1 \times 10^{-14}/1 \times 10^{-2} = 1 \times 10^{-12} \text{ M}$$

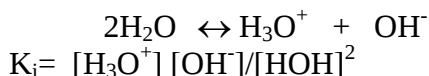
We can look at to ionization of water in two perspectives: with simple dissociation to H^+ ve OH^- or as conjugate acid-base pair. In both cases, it is seen that water behaves as an amfhoterik substance (i.e., it produces both acid and base ions). In other words, it can receive or donate hydrogen ions. As given below, the ionization of water can be defined in terms of dissociation constant (K_d), ionization constant (K_i) or a specific constant (K_w):

23

Simple dissociation



Conjuge acid-conjugate base



Note that water produces two conjuge acid-conjugate base pairs (HOH/OH^- and H_3O^+/HOH).

Thus, for every mole of H^+ (or H_3O^+), 1 mole of OH^- is produced. In pure water $[H^+] = 10^{-7}$ M and thus $[OH^-] = 10^{-7}$ M.

The molarity of water can be calculated as follow ($d_w = 1$ g/ml $MA_w = 18$ g/mol),

$$1 \text{ g/ml} \times 1000 \text{ ml/litre} \times 1 \text{ mol}/18 \text{ g} = 55.56 \text{ M}$$

Thus, K_d and K_i ,

$$K_d = (10^{-7})(10^{-7})/55.56 = 10^{-14}/55.56 = 1.8 \times 10^{-16} \quad K_i = (10^{-7})(10^{-7})/(55.56)^2 = 3.24 \times 10^{-18}$$

$$K_w = K_d \times [H_2O] \text{ or } K_w = K_i \times [H_2O]^2$$

$$K_w = 1 \times 10^{-14} = [H^+][OH^-]$$

In aqueous solutions, this equilibrium (i.e., $[H^+][OH^-] = 1 \times 10^{-14}$) is always satisfied. That is, if $[H^+]$ rises at a certain unit, $[OH^-]$ decreases in equal unit.

pH: the strength of an aqueous acidic or basic solution

In chemistry, pH is a measure of the activity of the (solvated) hydrogen ion. $p[H]$, which measures the hydrogen ion concentration is closely related to, and is often written as, pH. To measure the strength of an aqueous acidic or basic solution, P.L. Sorensen introduced the pH scale in 1909. It has been suggested that pH is derived from the Latin *pondus hydrogenii* (weight of hydrogen) or *potentia hydrogenii* (effectiveness of the hydrogen), while some suggest that the "p" in "pH" stands for "power" or "potential" and thus pH stands for "power of hydrogen".

	$[H^+]$	pH	Example
Acids	1×10^0	0	HCl
	1×10^{-1}	1	Stomach acid
	1×10^{-2}	2	Lemon juice
	1×10^{-3}	3	Vinegar
	1×10^{-4}	4	Soda
	1×10^{-5}	5	Rainwater
	1×10^{-6}	6	Milk
Neutral	1×10^{-7}	7	Pure water
Bases	1×10^{-8}	8	Egg whites
	1×10^{-9}	9	Baking soda
	1×10^{-10}	10	
	1×10^{-11}	11	Ammonia
	1×10^{-12}	12	
	1×10^{-13}	13	
	1×10^{-14}	14	NaOH

pH scale

pH is defined as the decimal logarithm of the reciprocal of the hydronium ion activity, $a_{H_3O^+}$, in a solution.

$$pH = -\log_{10}(a_{H^+}) = \log_{10}\left(\frac{1}{a_{H^+}}\right)$$

Because hydronium ion concentrations for most solutions are numbers with negative exponents, these concentrations are more conveniently expressed as pH, where

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad \text{or simply } \text{pH} = -\log [\text{H}^+]$$

while pOH designates the concentration of OH^- (i.e., $\text{pOH} = -\log [\text{OH}^-]$)

We know that, $K_w = 1 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$, by taking the minus logarithm of both sides:

$$14 = \text{pH} + \text{pOH}$$

Example: If the $[\text{OH}^-]$ of a strong base solution $2 \times 10^{-4} \text{ M}$, What are the pH and pOH of that solution?

$$\text{pOH} = -\log 2 \times 10^{-4} = 3.7, \text{ thus } \text{pH} = 14 - 3.7 = 10.3$$

You should remember that, since pH is a logarithmic scale, a decrease in one pH unit means 10 fold increase in the H^+ concentration. For instance, if you decrease the pH from 4 to 3, that means you have increased the H^+ concentration from 1×10^{-4} to 1×10^{-3} . Similarly, an increase in one pH unit means 10 fold decrease in the H^+ concentration. In other words, there is an inverse relation between pH and the H^+ concentration. The higher the pH, the lower the $[\text{H}^+]$, or vice versa.

Example. What is pH, pOH, $[\text{OH}^-]$ of 0.001 M HCl solution?

HCl is a strong acid and ionizes 100% : $\text{HCl} \leftrightarrow \text{H}^+ + \text{Cl}^-$

Thus 0.001 M HCl ionizes to 0.001 M H^+ and 0.001 M Cl^-

$$\text{pH} = -\log [\text{H}^+] = -\log 10^{-3} = 3$$

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = 1 \times 10^{-14} / 1 \times 10^{-3} = 1 \times 10^{-11}$$

$$\text{pOH} = -\log [\text{OH}^-] = 11$$

Or shortly since $\text{pH} + \text{pOH} = 14$

$$\text{pOH} = 14 - 3 = 11$$

Example. What is the pH of 0.04 M NaOH?

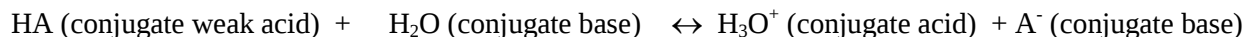
$$\text{pOH} = -\log 4 \times 10^{-2} = 1.4$$

$$\text{pH} = 14 - 1.4 = 12.6$$

Example. What is the pH of $1 \times 10^{-8} \text{ M}$ HCl?

Most students will answer this as $\text{pH} = 8$, simply taking the negative log of $[\text{H}^+]$. This, however, would be a wrong answer. Because, no matter how dilute an acid, when we add it to water it should bring its pH down not up (remember, the pH of pure water is 7.0). Thus, the pH of the given solution cannot be basic (i.e., pH 8.0) upon the addition of HCl. Thus, in this solution $x\text{M}$ $[\text{H}^+]$ will be from water while, 10^{-8}M will be contributed from HCl. *Try to solve this problem on your own...*

In living systems, most acids and base species are not strong type and thus they do not ionize 100%. Indeed, the ionization ratio of these weak acids and weak bases generally is less than 5%.



Given their resistivity to acid and base additions, most weak acids and weak bases could act as buffering systems. They have different ionization constants (K_a).

$K_a = [H^+][A^-]/[HA]$, $[H^+] = K_a ([HA]/[A^-])$, by taking the logarithm of both sides,

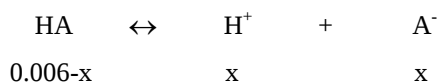
$\log [H^+] = \log K_a + \log ([HA]/[A^-])$, and multiplying both sides with -1 ,

$-\log [H^+] = -\log K_a - \log ([HA]/[A^-])$, $pH = pK_a - \log [HA]/[A^-]$,

$$pH = pK_a + \log [A^-]/[HA]$$

This last equation is known as Henderson-Hasselbalch equation. Using this useful formula, we can find out the pH of a solution of acid or base with known pK_a or vice versa.

Example. Acetic acid is one of the commonly known and used weak acids in biology. Its pK_a is 4.76. Find out the pH of 0.006 M acetic acid solution.



$$K_a = [H^+][A^-]/[HA]$$

$$K_a = x^2/0.006-x$$

For such an acid which has an about 10% ionization, the value of x in 0.006-x can be omitted (since it is substantially smaller than 0.006). Find the K_a value from acid's pK_a by taking the inverse (antilog) of 4.76.

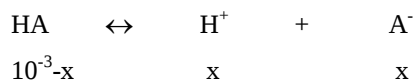
$$\text{Thus, } 1.74 \times 10^{-5} = x^2/0.006$$

$$x = [H^+] = 3.23 \times 10^{-4}$$

$$pH = -\log 3.23 \times 10^{-4} = 3.5$$

26

Example. What is the pH of a weak acid with a K_a value 1.6×10^{-6} . What would be the degree of ionization of this acid in a 10^{-3} M solution and calculate pK_a ve pK_b values?



$$K_a = [H^+][A^-]/[HA]$$

$$(x)(x)/10^{-3}-x = 1.6 \times 10^{-6}$$

$$x = [H^+] = 4 \times 10^{-5} \text{ M}$$

$$pH = 4.4$$

$$\% \text{ ionization} = [H^+]/[HA] = 4 \times 10^{-5}/10^{-3} = 0.04 = 4\%$$

Since pK_a is the negative logarithm of K_a

$$pK_a = -\log K_a = 5.8$$

$$pK_a + pK_b = 14$$

$$pK_b = 8.2$$

Example. If we add 0.16 M 25 ml NaOH solution to 0.34 M 10 ml NaOH solution, what would be the molarity of the new solution?

$$0.16 \text{ mol/L} \times 0.025 \text{ L} = 4 \times 10^{-3} \text{ mol} = 4 \text{ mmol}$$

$$0.34 \text{ mol/L} \times 0.010 \text{ L} = 3.4 \times 10^{-3} \text{ mol} = 3.4 \text{ mmol}$$

$$\text{Total} \quad 0.035 \text{ L (35 ml)} \quad = 7.4 \text{ mmol NaOH}$$

$$7.4 \text{ mmol}/35 \text{ ml} = 0.21 \text{ mmol/ml} = 0.21 \text{ mol/L} = 0.21 \text{ M}$$

Example. What is the pH of above mixture?

$$pOH = -\log [OH^-] = 0.68, \quad pH = 13.32$$

Example. Add 0.16 M 25 ml NaOH solution to 0.34 M 25 ml HCl solution. What is the pH of new solution?

$$\begin{array}{l} 0.16 \text{ mol/L} \times 0.025 \text{ L} = 4.0 \times 10^{-3} \text{ mol} = 4 \text{ mmol NaOH} \\ 0.34 \text{ mol/L} \times 0.025 \text{ L} = 8.5 \times 10^{-3} \text{ mol} = 8.5 \text{ mmol HCl} \\ \hline \text{Total} \quad 0.050 \text{ L (50 ml)} \quad = 4.5 \text{ mmol excess HCl} \end{array}$$

$$4.5 \text{ mmol}/50 \text{ ml} = 0.09 \text{ mmol/ml} = 0.09 \text{ mol/L} = 0.09 \text{ M HCl}, \text{ pH} = -\log [\text{H}^+] = 1.046$$

Example. How much NaOH should we add to 200 ml water so that the pH of solution is 11.5?

$$\text{pH} = 14 - \text{pOH}$$

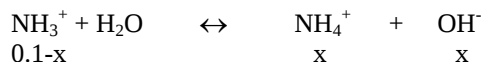
$$\text{pOH} = 2.5$$

To find out $[\text{OH}^-]$ take the antilog of 2.5

$$[\text{OH}^-] = 3.16 \times 10^{-3} \text{ M}$$

$$3.16 \times 10^{-3} \text{ mol/L} \times 0.2 \text{ L} \times 40 \text{ g/mol} = 0.025 \text{ g NaOH}$$

Example. NH_3^+ is one of the most widely used weak bases in biology and its K_a is 1.74×10^{-5} . What is the pH of its 0.1 M solution?



$$K_a = [\text{NH}_4^+][\text{OH}^-]/[\text{NH}_3^+]$$

$$1.74 \times 10^{-5} = x^2/0.1$$

$$x^2 = 1.74 \times 10^{-6}$$

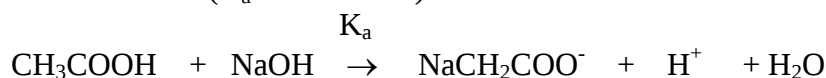
$$x = [\text{OH}^-] = 1.32 \times 10^{-3}$$

$$\text{pOH} = 2.88$$

$$\text{pH} = 14 - 2.88 = 11.12$$

27

Example. What is the pH of a solution containing acetic acid and sodium acetate each at 1 mol/l concentration? ($K_a = 1.74 \times 10^{-5}$).



$$K_a = [\text{NaCH}_2\text{COO}^-][\text{H}^+]/[\text{CH}_3\text{COOH}]$$

$$[\text{H}^+] = K_a ([\text{CH}_3\text{COOH}]/[\text{NaCH}_2\text{COO}^-]) = 1.74 \times 10^{-5} (1/1) = 1.74 \times 10^{-5}$$

$$\text{pH} = 4.76$$

or

$$\text{pH} = \text{p}K_a + \log (\text{salt}/\text{acid}) = 4.76 + \log (1/1) = 4.76$$

Example. If we add 0.1 mol HCl to above mixture what would be the pH of new solution?

$$\text{Total CH}_3\text{COOH} = 1 + 0.1 = 1.1 \text{ mol}$$

$$\text{Total NaCH}_2\text{COO}^- = 1 - 0.1 = 0.9 \text{ mol}$$

$$\text{pH} = \text{p}K_a + \log (\text{salt} / \text{acid}) = 4.76 + \log (1.1/0.9) = 4.67$$

Example. If we add 20 ml 0.2 M NaOH to 50 ml 0.1 M acetic acid, what is the new pH?

$$\text{pH} = \text{p}K_a + \log [\text{A}^-]/[\text{HA}]$$

$$\text{A}^- = 20 \text{ ml} \times 0.2 \text{ M} = 4 \text{ mmol conjugate base}$$

$$\text{HA} = 50 \text{ ml} \times 0.1 \text{ M} = 5 \text{ mmol conjugate acid (of 5 mmol acid, 4 mmol will be turned to base)}$$

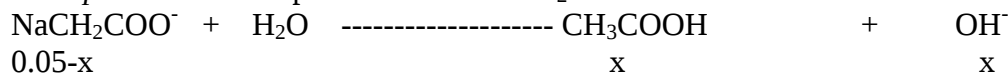
$$\text{Total} \quad 70 \text{ ml}, \quad 1 \text{ mmol excess acid}$$

$$\text{pH} = \text{p}K_a + \log (\text{base}/\text{acid}) = \text{p}K_a + \log [\text{A}^-]/[\text{HA}] = 4.76 + \log (4/1) = 5.36$$

Example. How much sodium acetate we must add to 250 ml 0.2 M acetic acid solution to have pH= 5.0? ($\text{NaCH}_2\text{COO}^- = 82 \text{ g/mol}$).

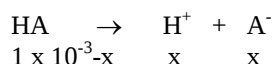
$$\begin{aligned} \text{pH} &= \text{pK}_a + \log [\text{A}^-] / [\text{HA}] \\ 5.0 &= 4.76 + \log [\text{A}^-] / [\text{HA}] \\ 0.24 &= \log [\text{A}^-] / [\text{HA}] \\ \text{by taking the inverse logarithm} \\ 1.74 &= [\text{A}^-] / [\text{HA}] \\ \text{HA} &= 0.2 \times 250 = 50 \text{ mmol} \\ 1.74 &= [\text{A}^-] / 50, \quad \text{A}^- = 87 \text{ mmol} \\ 87 \text{ mmol} / 250 \text{ ml} &= 0.348 \text{ M}, \\ 0.348 \text{ mol/L} \times 0.250 \text{ L} \times 82 \text{ g/mol} &= 7.13 \text{ g NaCH}_2\text{COO}^- \end{aligned}$$

Example. What is the pH of 0.05 M $\text{NaCH}_2\text{COO}^-$ salt soln?



$$\begin{aligned} K_b &= K_w / K_a = 1 \times 10^{-14} / 1.74 \times 10^{-5} = 5.75 \times 10^{-10} = x^2 / 0.05-x, \quad (\text{omit } x) \\ x^2 &= 2.88 \times 10^{-11} \\ x &= [\text{OH}^-] = 5.36 \times 10^{-6} \text{ M} \\ \text{pOH} &= 5.27 \\ \text{pH} &= 8.73 \end{aligned}$$

Example. Calculate the pH, % ionization, pK_a , and pK_b of a $1 \times 10^{-3} \text{ M}$ weak acid (K_a of weak acid 1.6×10^{-6}).

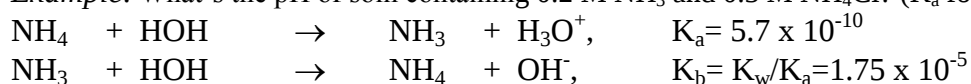


$$\begin{aligned} K_a &= x^2 / 1 \times 10^{-3}-x, \\ x &= [\text{H}^+] = 4 \times 10^{-5} \text{ M} \\ \text{pH} &= 4.4 \\ \% \text{ ionization} &= 4 \times 10^{-5} / 1 \times 10^{-3} = 0.04 = \% 4 \\ \text{pK}_a &= -\log K_a = 5.8, \\ \text{pK}_b &= 14 - 5.8 = 8.2 \end{aligned}$$

• Given these examples, we can summarize the pH of aqueous solutions as follow:

- for pure water, $\text{HOH} \leftrightarrow \text{H}^+ + \text{OH}^-$, $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$, $\text{pH} = 7.0$
- for strong acids, *Example* 10^{-3} M HCl , $[\text{H}^+] = 10^{-3} \text{ M}$, $\text{pH} = 3.0$
- for strong bases, *Example* 10^{-3} M NaOH , $[\text{OH}^-] = 1 \times 10^{-3} \text{ M}$, $\text{pOH} = 3.0$, $\text{pH} = 11.0$
- for weak acids, $\text{HA} \leftrightarrow \text{A}^- + \text{H}^+$, $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$, $[\text{H}^+] = K_a ([\text{HA}] / [\text{A}^-])$, by taking the negative log of the value found here, we can find the pH.
- for weak bases, $\text{B} + \text{HOH} \leftrightarrow \text{OH}^- + \text{BH}^+$, $K_b = [\text{BH}^+][\text{OH}^-] / [\text{B}]$, $[\text{OH}^-] = K_b ([\text{B}] / [\text{BH}^+])$, by taking the negative log of the value found here, we can find the pOH and subtracting it from 14 find the pH.
- weak acid and its salt or weak base and its salt,
 $\text{pH} = \text{pK}_a + \log (\text{base/acid})$, $\text{pOH} = \text{pK}_b + \log (\text{acid/base})$
- The hydrolysis of salt formed from weak acid and strong base. For instance, the hydrolysis of sodium acetate formed from the addition of NaOH to acetic acid:
 $\text{NaCH}_2\text{COO}^- + \text{HOH} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
 where $\text{CH}_3\text{COOH} = \text{OH}^-$, $K_b = [\text{OH}^-]^2 / \text{NaCH}_2\text{COO}^-$, $K_b = K_w / K_a$ and thus $K_b = 1 \times 10^{-14} / 1.74 \times 10^{-5} = 5.75 \times 10^{-10}$, if we know the conc of sodium acetate, we can calculate the $[\text{OH}^-]$ then pOH, and pH.
- The pH of salt soln formed from weak base and strong acid can be calculated similarly. The only thing here, we use pK_b in place of pK_a . For example, for an example like above pK_b value would be, $\text{pK}_b = K_w / K_a$.

Example. What's the pH of soln containing 0.2 M NH_3 and 0.3 M NH_4Cl ? (K_a for NH_4 , 5.7×10^{-10}).



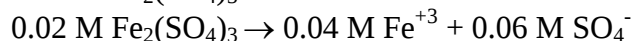
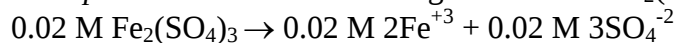
Since hydrogen ion conc ($[\text{H}_3\text{O}^+]$) is too small compared to hydroxyl ion conc ($[\text{OH}^-]$),
 $K_b = [\text{OH}^-][\text{NH}_4^+]/[\text{NH}_3]$, $[\text{OH}^-] = K_b[\text{NH}_3]/[\text{NH}_4^+] = 1.75 \times 10^{-5} (0.2)/0.3 = 1.17 \times 10^{-5} \text{ M}$
 $\text{pOH} = 4.93$, $\text{pH} = 9.07$

Ionic strength (μ), the ionic strength (activity) of a buffer may differ from its molar concn. Although, the activity of very dilute solutions may be the same with its concn, in concentrated solns this is not the case. As we have already seen in Lab #3, the ionic strength of a soln:

$$\mu = \frac{1}{2} \sum MZ^2$$

Where, M = is the true concn (molarity) of ions in the soln, Z = charge of the ions.

Example: What is the ionic strength of 0.02 M $\text{Fe}_2(\text{SO}_4)_3$?



$$\text{ionic strength} = \frac{1}{2} \sum [(0.04)(3)^2 + (0.06)(-2)^2] = \frac{1}{2} (0.60) = 0.30 \text{ M}$$

a soln containing solute with one +1 anion and one -1 cation (e.g., NaCl ,) μ is equal to M ($\mu=M$).

29

Example. What is the total ion concn and ionic strength of a mixture of 25 ml 0.12 M MnCl and 35 ml 0.06 M KCl solution?

$$\text{The concn of } \text{Mn}^{+2} = 25 \text{ ml} \times 0.12 \text{ M} / (25\text{ml} + 35\text{ml}) = 0.05 \text{ mol/l} = 0.05 \text{ M}$$

$$\text{The concn of } \text{K}^+ = 35 \times 0.06 \text{ M} / (25\text{ml} + 35\text{ml}) = 0.035 \text{ mol/l} = 0.035 \text{ M}$$

$$\text{The concn of } \text{Cl}^- = (25 \text{ ml} \times 0.24 \text{ M}) + (35 \times 0.06 \text{ M}) / (25\text{ml} + 35\text{ml}) = 0.135 \text{ M}$$

$$\begin{aligned} \text{Effective concn } (\mu) &= \frac{1}{2} (M_{\text{Mn}^{+2}} \times Z_{\text{Mn}^{+2}}^2 + M_{\text{K}^+} \times Z_{\text{K}^+}^2 + M_{\text{Cl}^-} \times Z_{\text{Cl}^-}^2) \\ &= \frac{1}{2} [0.05 \times (2)^2 + 0.035 \times (1)^2 + 0.135 \times (1)^2] = 0.185 \text{ M} \end{aligned}$$

Buffers

All life processes in cells, tissues, organs and organisms in general occur under defined hydrogen ion concentrations. The pH of cellular and extracellular milieu may differ from tissue to tissue even different organelles in the same cell may possess different pHs. These differences in pH balance are tightly regulated and are the main driving force behind the functioning of cells. For example, one pH unit difference in blood pH (7.4) level may result with serious consequences, including death.

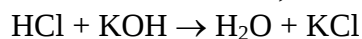
All organisms should maintain a balanced acid-base equilibrium in their cells and cell surroundings. This is done with buffering systems that all organisms naturally have. A buffer is a solution containing a weak acid and its conjugate base (i.e. CH_3COOH and CH_3COO^-) or a weak base and its conjugate acid (i.e. NH_3 and NH_4^+). Buffer solutions contain a base and an acid that can react with an added acid or base, respectively, and they maintain a pH very close to the original value. Two important buffer systems in organisms are *phosphate* and *carbonate*. For

example, when carbon dioxide enters blood cells (that are erythrocytes) it is rapidly converted to carbonic acid by the enzyme carbonic anhydrase.

Ornek 19. Plot the titration of 500 ml 0.01 N HCl with 0.01 N KOH (i.e., showing added base (y axis) vs. pH (x axis).

At the beginning (without adding KOH), the pH of HCl, $\text{pH} = -\log 0.01 = 2.0$

When KOH is added,



Up to the equivalence point (where acid and base ions are in equal concn), the pH level will be determined by the excess acid (the acid that is not titrated):

With addition of 100 ml KOH, the H^+ ion concn,

$$\text{H}^+ = \frac{[\text{HCl}]V_{\text{HCl}} - [\text{KOH}] V_{\text{KOH}}}{V_{\text{HCl}} + V_{\text{KOH}}} = 0.004 \text{ M}$$

$$\text{pH} = 2.18$$

Similarly,

At 200 ml KOH $\text{pH} = 2.39$

At 300 ml KOH $\text{pH} = 2.60$

At 400 ml KOH $\text{pH} = 2.95$

At equivalent base concn (500 ml 0.01 N),

$\text{pH} = 7.00$ ($[\text{H}^+] \times [\text{OH}] = 10^{-14}$, where $[\text{H}^+] = [\text{OH}]$) (remember HCl and KOH are strong acids and bases, respectively, and they ionizes almost 100% in aqueous solns).

When we continue to add KOH, there will be excess base,

In case of adding 600 ml KOH, the OH^- concn,

$$\text{OH}^- = \frac{[\text{KOH}] V_{\text{KOH}} - [\text{HCl}]V_{\text{HCl}}}{V_{\text{KOH}} + V_{\text{HCl}}} = 0.00091 \text{ M}$$

$$\text{pOH} = 3.04, \text{pH} = 10.96$$

At 700 ml KOH $\text{pH} = 11.22$

At 800 ml KOH $\text{pH} = 11.36$

At 900 ml KOH $\text{pH} = 11.46$

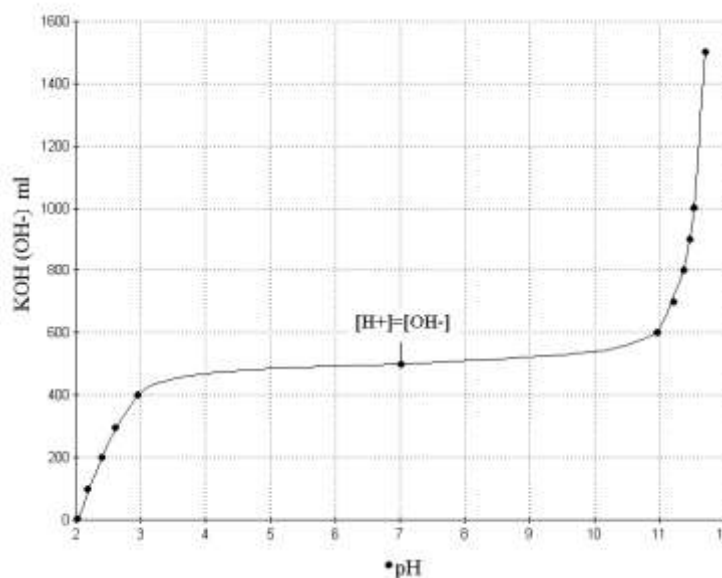
At 1000 ml KOH $\text{pH} = 11.52$

At 1500 ml KOH $\text{pH} = 11.70$

No matter how much further we add base at this concn (i.e., 0.01 M), the pH will not exceed 12.

Because, even in the presence of no acid the pH of 0.01 M KOH is 12. To have higher pHs than 12, we need to add more concentrated KOH.

The plot of strong acid and strong base titration given above is:



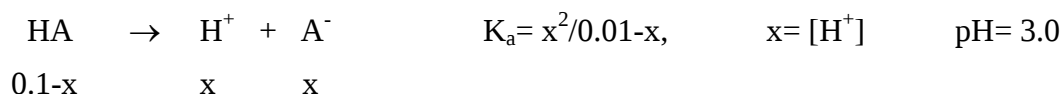
Titration curves are used to find the concn of acid (or base) in a solution and its pK_a . In general, an acid with known volume is diluted with a base with known concn. The volume of base to titrate acid to neutralization point is used to find out both the concn of acid and its pK_a .

Example. Now let us see how a 500 ml 0.1 M weak acid could be titrated with 0.1 M KOH ($pK_a = 5.0$).

31

As given above, titration of a weak acid with strong base have distinct 4 steps to find out the pH of titrated soln.

A. The step where no base is added yet:



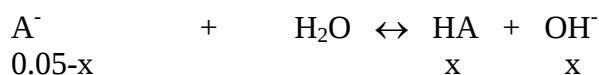
B. Up to the step where there is an equal mol of strong base addition:

The pH in this region is calculated by Henderson-Hasselbalch equation.

For example, with 100 ml KOH addition pH, $0.1 \text{ mol/L} \times 0.1 \text{ L} = 0.01 \text{ mol OH}^-$ is added, thus, 0.01 mol of weak acid will be neutralized and in the solution there will remain 0.04 mol acid ($0.1 \text{ mol acid/L} \times 0.5 \text{ L} - 0.01 \text{ mol} = 0.04$). Thus, $\text{pH} = 5 + \log (0.01/0.04) = 4.4$

C. The step where there is equal mol of strong base addition (equivalence point):

Theoretically, if we add 500 ml 0.1 M KOH all the acid in the soln will be neutralized (i.e., all HA will be converted to A^-). At this point, however, the pH of soln is not 7.0, contrary to strong acid and strong base titrations. Because, some salt or conjugated base (A^-) will ionize.



Thus, adding 1 mol KOH does not give 1 mol A^- ,

$$\text{A}^- = 500 \times 0.1 / 500 + 500 = 0.05 \text{ M}$$

$$K_b = K_w / K_a = 10^{-14} / 1 \times 10^{-5} = 1 \times 10^{-9}, \text{ at the same time } K_b = [\text{HA}][\text{OH}^-] / [\text{A}^-] = x^2 / 0.05 - x$$

$$1 \times 10^{-9} = x^2/0.05, \quad x = [\text{OH}^-] = 1.58 \times 10^{-6}, \quad \text{pOH} = 5.15, \quad \text{pH} = 8.85$$

D. The pH at equivalence point: The added KOH concn at this step exceeds the weak acid. For example, if we 600 ml KOH, $600 \text{ ml} \times 0.1 \text{ M} = 60 \text{ mmol OH}^-$

$$500 \text{ ml} \times 0.1 \text{ M} = 50 \text{ mmol HA}$$

So, there is an excess of 10 mmol OH^- . Given that the total volume is 1100 ml, $[\text{OH}^-] = 10 \text{ mmol} / 1100 \text{ ml} = 9.091 \times 10^{-3} \text{ M}$, $\text{pOH} = 2.04$, $\text{pH} = 11.96$

Exercises

1. If we dissolve 1.6 mg HX strong acid in 1.250 L water, the pH of soln becomes 5.0. What is the molecular weight of HX? ($H=1$).
2. If you add 10 M 100 μl to 100 ml water, what is the pH of new soln?
3. If you mix a strong acid with pH 2.0 with equal volume of strong base with pH 13.0, what will be the mixture's pH?
4. Find out the concn of all ionic species in the 0.02 M H_2SO_4 soln and its pH.
5. To prepare 200 ml buffer with pH 8.0, how much 0.5 M ammonium chloride and 0.5 M ammonia are required (ammonium chloride $K_b = 1.8 \times 10^{-5}$)?
6. What is the pH of solution made from 50 ml 0.2 M acetic acid and 150 ml 0.4 M NaOH? ($\text{pK}_a = 4.74$).
7. What is the molarity of acetic acid with pH 3.50? ($K_a = 1.76 \times 10^{-5}$).
8. To neutralize 50 ml acetic acid with pH 2.8, how much 0.0105 M NaOH should we use?
9. If you add 25 ml 0.2 M NaOH to 50 ml 0.1 M CH_3COOH soln, what will be the pH?
10. Construct a titration curve from titration of 0.02 M 100 ml acetic acid with 0.01 M NaOH.