## a.What is an acid and base?

An **acid** is a substance that donates protons (in the Brønsted-Lowry **definition**) or accepts a pair of valence electrons to form a bond (in the Lewis **definition**). A **base** is a substance that can accept protons or donate a pair of valence electrons to form a bond. **Bases** can be thought of as the chemical opposite of **acids**.

## b. What is a simple definition of an acid?

**An acid is a chemical species that donates protons or hydrogen ions and/or accepts electrons. ... The word acid comes from the Latin words acidus or acere, which mean "sour," since one of the characteristics of acids in water is a sour taste.**

## c.What is base and example?

**Examples of bases are sodium hydroxide, calcium carbonate and potassium oxide. A base is a substance that can neutralize the acid by reacting with hydrogen ions. ... Bases are defined as proton ($H^+$) acceptors. Common examples of bases include metal oxides and metal hydroxides and ammonium hydroxide**.

## d. What is modern definition of acid?

**Key Points. An acid is a substance that donates protons (in the Brønsted-Lowry definition) or accepts a pair of valence electrons to form a bond (in the Lewis definition). A base is a substance that can accept protons or donate a pair of valence electrons to form a bond.**

## e. What is Henderson Hasselbalch equation explain.

The Henderson–Hasselbalch equation relates the pH of a solution containing a mixture of the two components to the acid dissociation constant, $K_a$, and the concentrations of the species in solution. To derive the equation a number of simplifying assumptions have to be made.

## f. Calculation of Henderson Hassel Balch equation.

*Main article: Acid dissociation constant*

A simple buffer solution consists of a solution of an acid and a salt of the conjugate base of the acid. For example, the acid may be acetic acid and the salt may be sodium acetate. The Henderson–Hasselbalch equation relates the pH of a solution containing a mixture of the two components to the acid dissociation constant, $K_a$, and the concentrations of the species in solution.[3] To derive the equation a number of simplifying assumptions have to be made. The mixture has the ability to resist changes in pH when a small amount of acid or base is added, which is the defining property of a buffer solution.

**Assumption 1: The acid is monobasic and dissociates according to the equation**

**It is understood that the symbol H$^+$ stands for the hydrated hydronium ion. The Henderson–Hasselbalch equation can be applied to a polybasic acid only if its consecutive pK values differ by at least 3. Phosphoric acid is such an acid.**

**Assumption 2. The self-ionization of water can be ignored.**

**This assumption is not valid with pH values more than about 10. For such instances the mass-balance equation for hydrogen must be extended to take account of the self-ionization of water.**

$$C_H = [H^+] + K_a[H^+][A^-] - K_w/[H^+]$$
$$C_A = [A^-] + K_a[H^+][A^-]$$

and the pH will have to be found by solving the two mass-balance equations simultaneously for the two unknowns, [H$^+$] and [A$^-$].

Assumption 3: The salt MA is completely dissociated in solution. For example, with sodium acetate

$$Na(CH_3CO_2) \rightarrow Na^+ + CH_3CO_2^-$$
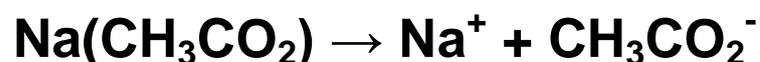
**Assumption 4: The quotient of activity coefficients, , is a constant under the experimental conditions covered by the calculations.**

The thermodynamic equilibrium constant, ,

is a product of a quotient of concentrations and a quotient, , of activity coefficients . In these expressions, the quantities in square brackets signify the concentration of the undissociated acid, HA, of the hydrogen ion $H^+$, and of the anion $A^-$; the quantities are the corresponding <u>activity coefficients</u>. If the quotient of activity coefficients can be assumed to be a constant which is independent of concentrations and pH, the dissociation constant, $K_a$ can be expressed as a quotient of concentrations.

Rearrangement of this expression and taking logarithms provides the Henderson–Hasselbalch equation

## Application

The Henderson–Hasselbalch equation can be used to calculate the pH of a solution containing the acid and one of its salts, that is, of a buffer solution. With bases, if the value of an equilibrium constant is known in the form of a base association constant, $K_b$ the dissociation constant of the conjugate acid may be calculated from

$pK_a + pK_b = pK_w$

where $K_w$ is the self-dissociation constant of water. $pK_w$ has a value of approximately 14 at 25°C.

If the "free acid" concentration, [HA], can be taken to be equal to the analytical concentration of the acid, $T_{AH}$ (sometimes denoted as $C_{AH}$) an approximation is possible, which is widely used in biochemistry; it is valid for very dilute solutions.

**The effect of this approximation is to introduce an error in the calculated pH, which becomes significant at low pH and high acid concentration. With bases the error becomes significant at high pH and high base concentration.**

## Henderson–Hasselbalch Equation

The Henderson–Hasselbalch equation was developed independently by the American biological chemist L. J. Henderson and the Swedish physiologist K. A. Hasselbalch, for relating the pH to the bicarbonate buffer system of the blood (see below). In its general form, the Henderson–Hasselbalch equation is a useful expression for buffer calculations. It can be derived from the equilibrium constant expression for a dissociation reaction of the general weak acid (HA) in Equation (1.3):

$$(1.4) \quad K = \frac{[H^+][A^-]}{[HA]}$$

where $K$ is the equilibrium constant at a given temperature. For a defined set of experimental conditions, this equilibrium constant is designated as $K'$ ($K$ prime) and referred to as an apparent dissociation constant. The higher the value of $K'$, the greater the number of $H^+$ ions liberated per mole of acid in solution and hence the stronger the acid. $K'$ is thus a measure of the strength of an acid. Rearrangement of Equation (1.4) yields

$$(1.5) \quad [H+] = K' \frac{[HA]}{A-}$$

Taking logarithms of both sides of Equation (1.5) and multiplying throughout by -1 gives

$$(1.6) \quad -\log[H+] = -\log K' - \log[HA] + \log[A-]$$

Substituting pH for $-\log[H^+]$ and pK′ for -log $K'$ yields

$$(1.7) \quad pH = pK' + \log\frac{[A-]}{[HA]}$$

or

$$(1.8) \quad pH = pK' + \log\frac{[conjucate\ base]}{[acid]}$$

This relationship is represented by the Henderson–Hasselbalch equation.

Since a buffer is intended to give only a small change in pH with added $H^+$ or $OH^-$, the best buffer for a given pH is the one that gives the smallest change. As may be seen from the Henderson–Hasselbalch equation, when the pH of the solution equals the pK′ of the buffer, [conjugate base] = [acid], and the buffer can therefore respond equally to both added acid and added base. It also follows from Equation (1.7) that when the pH of the solution is one pH unit above or below the pK′ value, the solution contains approximately 9% unprotonated or protonated species, respectively. Similarly, if the pH of the solution is two units above or below the pK′ value, the solution contains almost entirely (99%) unprotonated or protonated species, respectively. Table 1-3 provides percent unprotonated species and the corresponding unprotonated/protonated ratios for selected (pH-pK') values.

**Definition of Henderson Hassel Balch equation**

The **Henderson Hasselbalch equation** is an approximate equation that shows the relationship between the pH or pOH of a solution and the $pK_a$ or $pK_b$ and the ratio of the concentrations of the dissociated chemical species. In order to use

the equation, the acid dissociation constant must be known.

## Equation

There are multiple ways to write the equation. Two of the most common are:

$pH = pK_a + \log([\text{conjugate base}]/[\text{weak acid}])$

$pOH = pK_a + \log([\text{conjugate acid}]/[\text{weak base}])$

$$HA \rightleftharpoons [H^+] + [A^-]$$

$$\therefore \ K_a = \frac{[H^+][A^-]}{[HA]} \quad [\because \ Ka = \text{Dissociation}$$

constant]

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

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

on both sides].

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

ing sign on both sides]

# Prove that pKa + pKb = pKw

4. Prove that:

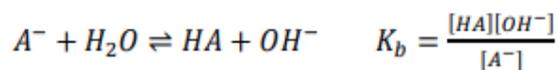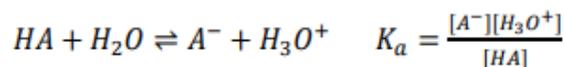$$K_a * K_b = K_w$$

and

$$pK_a + pK_b = 14$$

Using the equations below.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = [H_3O^+][OH^-] = 10^{-14}$$

## A Few More Relationships Between pKₐ, pK_b, and pK_w

$$pK_a + pK_b = pK_w$$

$$pK_w = -\log [K_w] = 14 \text{ (at } 25°C)$$

$$pK_a + pK_b = 14 \text{ (at } 25°C)$$

## Henderson-Hasselbalch Equation

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

$$pOH = pK_b + \log\left(\frac{[BH^+]}{[B]}\right) = pK_b + \log\left(\frac{[acid]}{[base]}\right)$$

This is an exceptionally powerful tool, and it's use will be emphasized in our problem solving.

# What is Buffer solution

**A buffer solution (more precisely, pH buffer or hydrogen ion buffer) is an aqueous solution consisting of a mixture of a weak acid and its conjugate base, or vice versa. Its pH changes very little when a small amount of strong acid or base is added to it. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. In nature, there are many systems that use buffering for pH regulation. For example, the bicarbonate buffering system is used to regulate the pH of blood.**

Solutions able to retain a constant pH regardless of small amounts of acids or bases added are called buffers. Classical buffer contains both a weak acid and its conjugate base. Small amounts of acids or bases added are absorbed by the buffer and the pH changes only slightly. In the case of high or low pH just solutions of strong acids

or bases are used - for example in the case of pH=1 acid concentration is relatively high (0.1 M) and small addition of acid or base doesn't change pH of such solution significantly.

How to calculate the pH of a buffer solution containing both acid and conjugate base? Dissociation constant definition 1.1 can be rearranged into

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$  15.1

or

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$  15.2

(note that due to sign change [A⁻] was moved to nominator).

This is so called **Henderson-Hasselbalch equation** (or a **buffer equation**). It can be used for pH calculation of a solution containing pair of acid and conjugate base - like HA/A⁻, HA⁻/A²⁻ or B⁺/BOH. For solutions of a weak bases sometimes it is more convenient to use equation in the form

$$pOH = pK_b + \log\left(\frac{[B^+]}{[BOH]}\right)$$  15.3

Both equations are perfectly equivalent and interchangeable.

The Henderson-Hasselbalch equation is used mostly to calculate pH of solutions created mixing known amounts of acids and conjugate bases (or neutralizing part of acid with a strong base). For example, what is the pH of a solution prepared mixing reagents so that it contains 0.1 M of acetic acid and 0.05 M NaOH? Half of the acid is neutralized, so concentrations of acid and conjugate base are identical, thus the quotient under logarithm is 1, the logarithm is 0 and pH=p$K_a$.

This approach - while perfectly justifiable in many cases - is dangerous, as it creates false conviction that the equation can be used this way always. That's not true.

The Henderson-Hasselbalch equation is valid when it contains equilibrium concentrations of an acid and a conjugate base. In the case of solutions containing not-so-weak acids (or not-so-weak bases) equilibrium concentrations can be far from those predicted by the neutralization stoichiometry.

Let's replace the acetic acid from our example with something stronger - e.g. dichloroacetic acid, with $pK_a$=1.5. Repeating the same resoning we used earlier we will arrive at pH=1.5 - which is wrong. The proper pH value can be calculated from the equation 11.13 or using the pH calculator - and it is 1.78. The reason is simple. The dichloroacetic acid is strong enough to dissociate on its own and equilibrium concentrations of the acid and conjugate base are not 0.05 M (as we expected from the neutralization reaction stoichiometry) but 0.0334 M and 0.0666 M respectively.

As a rule of thumb you may remember that acids with $pK_a$ below 2.5 dissociate too easily and use of the Henderson-Hasselbalch equation for pH prediction can give wrong results, especially in the case of diluted solutions. For solutions above 10 mM and acids weaker than $pK_a$ greater than equal to 2.5, the Henderson-Hasselbalch equation gives results with acceptable error. The same holds for bases with $pK_b$ greater than equal to 2.5. However, the same equation will work perfectly regardless of the $pK_a$ value if you are asked to calculate a

ratio of the acid to conjugate base in the solution with a known pH.

Similar problem is present in the calculation of pH of diluted buffers. Let's see what happens when you dilute acetic buffer 50/50:

\*\*\* wikipedia.