Henderson-Hasselbalch Equation

The Henderson-Hasselbalch equation provides a relationship between the pH of acids (in aqueous solutions) and their pK_a (acid dissociation constant). The pH of a buffer solution can be estimated with the help of this equation when the concentration of the acid and its conjugate base, or the base and the corresponding conjugate acid, are known.

Equation of Henderson-Hasselbalch

The Henderson-Hasselbalch equation can be written as:

$pH = pK_a + \log_{10} ([A^-]/[HA])$

Where $[A^-]$ denotes the molar concentration of the conjugate base (of the acid) and [HA] denotes the molar concentration of the weak acid. Therefore, the Henderson-Hasselbalch equation can also be written as:

$$pH = pKa + \log \frac{[\text{ conjugate base }]}{[\text{ acid}]}$$

An equation that could calculate the pH value of a given buffer solution was first derived by the American chemist Lawrence Joseph Henderson. This equation was then re-expressed in logarithmic terms by the Danish chemist Karl Albert Hasselbalch. The resulting equation was named the Henderson-Hasselbalch Equation.

Derivation of the Henderson-Hasselbalch Equation

The ionization constants of strong acids and strong bases can be easily calculated with the help of direct methods. However, the same methods cannot be used with weak acids and bases since the extent of ionization of these acids and bases is very low (weak acids and bases hardly ionize). Therefore, in order to approximate the pH of these types of solutions, the Henderson-Hasselbalch Equation is used.

Let us take an example of ionization of weak acid HA:

$HA + H_2O \leftrightharpoons H^+ + A^-$

Acid dissociation constant, K_a can be given as:

$Ka=[H+][A-][HA]$

Taking, negative log of RHS and LHS:

$-\log Ka=-\log [H+][A-][HA]$
$\Rightarrow -\log Ka=-\log [H+]-\log [A-][HA]$

As we know,

$-\log [H+]=pH and -\log Ka=pKa$

The equation above can also be written as,

$pKa=pH-\log [A-][HA]$

Rearranging the equation,

$\Rightarrow pH=pKa + \log[A-][HA]$

The above equation is known as Henderson-Hasselbalch equation, popularly known as Henderson equation. It is very useful for estimating the pH of a buffer solution and finding the equilibrium pH in acid-base reactions. From the equation, we can infer when

$pH=pKa$
$\log [A-][HA]=0$
$[A-]=[HA]$

That is, when

$pH=pKa$
, concentration of both the species are same or in other words, acid will be half dissociated.

Similarly, for a weak base B:

$B + H2O \leftrightharpoons OH- + HB+$

Base dissociation constant, Kb, of the base can be given as,

$Kb=[BH+][OH-][B]$

Taking the negative log of RHS and LHS

$-\log Kb=-\log[BH+][OH-][B]$
$\Rightarrow -\log Kb=-\log [OH-]-\log[BH+][B]$

As we know,

$-\log [OH-]=pOH and -\log Kb=pKb$
,

The above equation can be written as,

$pKb=pOH - \log[BH+][B]$

Rearranging the equation,

⇒pOH=pKb+log [BH+][B]

Important Points to Remember

- When exactly half of the acid undergoes dissociation, the value of [A]/[HA] becomes 1, implying that the pK_a of the acid is equal to the pH of the solution at this point. ($pH = pK_a + \log_{10}(1) = pK_a$).
- For every unit change in the pH to pK_a ratio, a tenfold change occurs in the ratio of the associated acid to the dissociated acid. For example, when the pK_a of the acid is 7 and the pH of the solution is 6, the value of $[A^-]/[HA]$ is 0.1 but when the pH of the solution becomes 5, the value of $[A^-]/[HA]$ becomes 0.01.
- The value of $[A^-]/[HA]$ is dependent on the value of the pH and pK_a. When $pH < pK_a$; $[A^-]/[HA] < 1$. When $pH > pK_a$; $[A^-]/[HA] > 1$.

Limitations of the Henderson-Hasselbalch Equation

The Henderson-Hasselbalch equation fails to predict accurate values for the strong acids and strong bases because it assumes that the concentration of the acid and its conjugate base at chemical equilibrium will remain the same as the formal concentration (the binding of protons to the base is neglected).

Since the Henderson-Hasselbalch equation does not consider the self-dissociation undergone by water, it fails to offer accurate pH values for extremely dilute buffer solutions.

Solved Example

A buffer solution is made from 0.4M CH_3COOH and 0.6M CH_3COO^-. If the acid dissociation constant of CH_3COOH is $1.8*10^{-5}$, what is the pH of the buffer solution?

As per the Henderson-Hasselbalch equation, $pH = pK_a + \log([CH_3COO^-]/[CH_3COOH])$

Here, $K_a = 1.8*10^{-5} \Rightarrow pK_a= -\log(1.8*10^{-5}) = 4.7$ (approx.).

Substituting the values, we get:

$pH = 4.7 + \log(0.6M /0.4M) = 4.7 + \log(1.5) = 4.7 + 0.17 = 4.87$

Therefore, the pH of the solution is 4.87.

What are Van der Waals Forces?

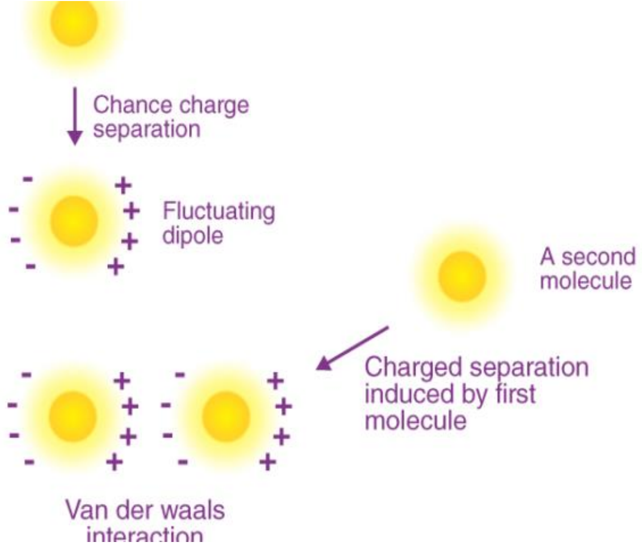
Van der Waals forces are weak intermolecular forces that are dependent on the distance between atoms or molecules. These forces arise from the interactions between uncharged atoms/molecules.

For example, Van der Waals forces can arise from the fluctuation in the polarizations of two particles that are close to each other.

In the group of forces that fall under the category of '***weak chemical forces'***, Van der Waals forces are the weakest. They are known to rapidly vanish when the distance between the interacting molecules increases. The strengths of Van der Waals forces typically ***range from 0.4 kJ.mol^{-1} to 4 kJ.mol^{-1}.***

When the electron density around the nucleus of an atom undergoes a transient shift, it is common for Van der Waals forces arising. For example, when the electron density increases in one side of the nucleus, the resulting transient charge may attract or repel a neighbouring atom. The nature of these forces is dependent on the distance between the atoms:

- When the distance between the atoms is greater than 0.6 nanometres, the forces are extremely weak and cannot be observed.
- When the distance between the atoms ranges from 0.6 to 0.4 nanometres, the forces are attractive.
- If the interatomic distance is smaller than 0.4 nanometres, the forces are repulsive in nature.



An illustration detailing the induced formation of a dipole in an atom/molecule due to a fluctuating dipole in another atom/molecule is provided above. The adsorption of gaseous molecules to the surface of an adsorbent and the cohesion of condensed phases can be accounted for by Van der Waals forces.

Characteristics of Van der Waals Forces

- Covalent bonds and ionic bonds are significantly stronger than Van der Waals forces
- These forces are additive in nature, they are made up of several individual interactions
- These forces cannot be saturated
- No directional characteristic can be attributed to these forces
- They are not dependent on temperature (except dipole-dipole interactions)
- Van der Waals forces are short-range forces. Their magnitude is high when the atoms/molecules in question are close to each other.

Types of Van der Waals Forces

1. Keesom Interactions

Keesom interactions can arise due to the following interactions (all of which are electrostatic in nature):

- The electrostatic interaction between the charges in ionic molecules.
- Interaction between dipoles in polar molecules.
- Quadrupole interactions in the molecules whose symmetry is lower than cubic.
- Interaction between permanent multipoles.

These forces are named after the Dutch physicist Willem Hendrik Keesom. It is important to note that Keesom interactions only originate from the interactions between two permanent dipoles and are temperature dependent.

2. Debye Forces

Debye forces are caused by the interactions between permanent dipoles and other atoms/molecules, which results in the formation of induced dipoles. For example, an induced dipole can be formed from the repulsive forces between electrons (belonging to a molecule) and a permanent dipole.

Unlike Keesom interactions, Debye forces are not dependent on temperature. These forces are named after the Dutch-American physical chemist Peter Debye.

3. London Dispersion Forces

London dispersion forces arise due to the interactions between an instantaneous dipole and an atom/molecule. These forces are named after the German physicist Fritz London and are also known as instantaneous dipole – induced dipole forces.

These forces are believed to be the weakest of all Van der Waals forces. The strength of the London dispersion force between two atoms/molecules depends entirely on the polarizability of the atom/molecule.

Factors Affecting Van der Waals Forces

1. Number of Electrons Held by the Atoms/Molecules

While traversing down a group in the modern periodic table, the atomic radii of the elements increase along with the number of electrons held by their respective nuclei. The presence of a relatively large number of electrons (along with the additional space for these electrons to disperse over) contributes to the formation of temporary dipoles. The greater the number of (instantaneous) dipoles formed, the greater the strength of the Van der Waals force.

An example of this relationship can be observed in the significantly different boiling points of xenon and neon – the boiling point of xenon is -108°C whereas the boiling point of neon is -246°C. The lower boiling point of xenon can be explained by the stronger dispersion forces experienced by its atoms.

2. Shape of the Molecule

Long, unbranched molecules tend to feature stronger dispersion forces than branched, short-chain molecules. For example, the structural isomers butane and isobutane (2-methyl propane) have different boiling points despite having the same chemical formulae. The boiling point of butane is -0.5°C and that of isobutane is -11.7°C.

The difference in the boiling points of these isomers can be accounted for by the stronger Van der Waals forces in the unbranched butane molecules (and the weaker Van der Waals forces in the short, branched isobutane molecules).

Applications of Van der Waals Forces

- It is widely believed that Geckos exploit Van der Waals forces hanging on to smooth surfaces with only their toes.
- The attractive forces that arise between the spatulae of the Gecko’s footpads and the smooth surface enable the lizard to effectively climb these surfaces. Similar biological designs can be observed in some spiders.