TOPIC

ARRHENIUS THEORY

OF

IONISATION
Arrhenius theory of ionization and its factors

Arrhenius theory

One of the properties that acids and bases have in common is that they are electrolytes—they form ions when they dissolve in water. Svante Arrhenius, a Swedish chemist who received a Nobel prize in 1903 for his work on electrolytes, focused on what ions were formed when acids and bases dissolved in water. He came up with the concept or idea that acids dissociated in water to give hydrogen ions and that bases dissociated in water to give hydroxide ions. This definition is very useful when we talk about acids and bases as being electrolytes in solution.

These equations (also shown in example 12 in your workbook) serve as examples.

An acid, like HCl, is something that dissociates in water to give hydrogen ion.

A base, like NaOH, is something that dissociates in water to give hydroxide ion.

Acids and bases neutralize one another because the hydrogen ion and the hydroxide ion combine with one another to form water. The top equation shown here is the net-ionic version of acid-base neutralization. The complete-formula equation for this reaction (shown below) will depend on which acid and which base are reacting. In general, however, it will show that an acid and a base neutralize one another to form water and a salt. If the salt is soluble, it won’t show up in the net ionic equation, but the ions are there in solution as spectator ions.
Arrhenius focused on the idea that acids and bases split into ions when they dissolved in water. In a sense, the Arrhenius concept focuses on what the chemical contains or what is there in solution.

Two important features of acids and bases are readily explained using Arrhenius' approach. They are multiprotism and neutralization.

**Acid-base reactions**

An acid and base is a chemical reaction that occurs between an acid and a base. Several concepts exist which provide alternative definitions for the reaction mechanisms involved and their application in solving related problems. Despite several differences in definitions, their importance becomes apparent as different methods of analysis when applied to acid-base reactions for gaseous or liquid species, or when acid or base character may be somewhat less apparent. Historically, the first of these scientific concepts of acids and bases was provided by the French chemist Antoine Lavoisier, circa 1776.[1]

**Acid-Base Concepts**

Acids and bases are important in numerous chemical processes that occur around us, from industrial processes to biological ones, from reactions in the laboratory to those in our environment. There are several methods of defining acids and bases. While these definitions don't contradict each other, they do vary in how inclusive they are. The word acid comes from the Latin word acere, which means "sour." All acids taste sour. Well known from ancient times were vinegar, sour milk and lemon juice. Aspirin tastes sour if you don't swallow it fast enough. Its scientific name is acetosalicylic acid! Other languages derive their word for acid from the meaning of sour. So, in France, we have acide. In Germany, we have säure from saure and in Russia, kislota from kisly. The word "base" has a more complex history and its name is not related to taste. All bases taste bitter. Mustard tastes bitter. Many medicines, cough syrup is one, taste bitter. This is the reason cough syrups are advertised as having a "great grape taste."

The Arrhenius Concept of Acids and Bases

One of the first definitions of acids and bases was suggested by Arrhenius. The Arrhenius definition emphasizes the H+(aq) and OH−(aq) ions in water. According to Arrhenius, acids are substances that when dissolved in water increase the concentration of H+ ions. Likewise bases are substances that when dissolved in water
increase the concentration of OH⁻ ions. Because of the equilibrium in water, increasing the concentration of one of these ions decreases the concentration of the other. For Simplicity, chemists often use the notation H⁺(aq) for the H₃O⁺(aq) ion, and call it the hydrogen ion. Please keep in mind that it is really the hydronium ion, H₃O⁺(aq), that exists in water and not the hydrogen ion, H⁺(aq). The special role of the H₃O⁺ and the OH⁻ ions in aqueous solutions comes from the following equilibrium.

\[ 2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^- (aq) \text{ or less correctly } \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^- (aq) \]

In Arrhenius's theory a strong acid is a substance that is 100% ionized in water to give H₃O⁺(aq) and an anion. An example is nitric acid, HNO₃.

\[ \text{HNO}_3(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq) \]

A strong base is a substance that is 100% ionized in water to give OH⁻(aq) and a cation. An example is sodium hydroxide, NaOH.

\[ \text{NaOH (s)} \rightarrow \text{Na}^+(aq) + \text{OH}^- (aq) \]

The following is a list of the strong acids and strong bases (memorize it)

<table>
<thead>
<tr>
<th>Strong Acids</th>
<th>Strong Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄</td>
<td>LiOH</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>NaOH</td>
</tr>
<tr>
<td>HI</td>
<td>KOH</td>
</tr>
<tr>
<td>HBr</td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td>HCl</td>
<td>Sr(OH)₂</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Ba(OH)₂</td>
</tr>
</tbody>
</table>

**Ionization**, formation of electrically charged atom or molecules. Atoms are electrically neutral; the electrons that bear the negative charge are equal in number to the protons in the nucleus bearing the positive charge. When sodium combines with chlorine, for example, to form sodium chloride, each sodium atom transfers an electron to a chlorine atom, thus forming a sodium ion with a positive charge and a chloride ion with a negative charge. In a crystal of sodium chloride the strong electrostatic attraction between ions of opposite charge holds the ions firmly in place and close together.

When sodium chloride is melted, the ions tend to dissociate because of their thermal motion and can move about freely. If two electrodes (see Electrode) are placed in molten sodium chloride and an electric potential is applied, the sodium ions migrate to the negative electrode and the chloride ions migrate to the positive electrode, causing a current of electricity to flow. When sodium chloride is dissolved in water,
the ions are even more free to dissociate (because of the attraction between the ions and the solvent), and the solution is an excellent conductor of electricity.

Solutions of most inorganic acids, bases, and salts conduct electricity and are called electrolytes; solutions of sugar, alcohol, glycerine, and most other organic substances are poor conductors of electricity and are called nonelectrolytes. Electrolytes that give strongly conducting solutions are called strong electrolytes (for example, nitric acid, sodium chloride); electrolytes that give weakly conducting solutions are called weak electrolytes (for example, mercuric chloride, acetic acid).

IONIZATION RESEARCH

II

The Swedish chemist Svante August Arrhenius was the first to recognize that substances in solution are in the form of ions and not molecules, even when no electrical potential is applied. In the 1880s he stated the hypothesis that when an electrolyte goes into solution it is only partly dissociated into separate ions, and that the amount of dissociation depends on the nature of the electrolyte and the concentration of the solution. Thus, according to the Arrhenius theory, when a given quantity of sodium chloride is dissolved in a large amount of water, the ions dissociate to a greater degree than when the same quantity is dissolved in less water.

A different theory of the dissociation of electrolytes, developed by the Dutch physicist Peter Debye, has been generally accepted since 1923. The so-called Debye-Hückel theory assumes that electrolytes are completely dissociated in solution. The tendency of ions to migrate and thus conduct electricity is retarded by the electrostatic attraction between the oppositely charged ions and between the ions and the solvent. As the concentration of the solution is increased, this retarding effect is increased. Thus, according to this theory, a fixed amount of sodium chloride is a better conductor when dissolved in a large amount of water than when dissolved in a smaller amount, because the ions are farther apart and exert less attraction upon one another and upon the solvent molecules. The ions are not infinitely free to migrate, however. The dielectric constant of the solvent (see Dielectric) is also important in the conductance of a solution; ionization is most marked in a solvent such as water, with a high dielectric constant. See Atom; Electrochemistry.

IONIZATION IN GASES

III

When a rapidly moving particle, such as an electron, an alpha particle, or a quantum of radiant energy, collides with a gas atom, an electron is ejected from the atom, leaving a charged ion. The ions render the gas conductive (see Electricity). The amount of energy necessary to remove an electron from an atom is called the
ionization energy. The principle of ionization of gases by various types of radiation is used in the detection and measurement of radiation (see Particle Detectors) and in the separation and analysis of isotopes in the mass spectrometer. The atmosphere always contains ions that are produced by ultraviolet light and cosmic radiation (see Ionosphere).

A gas that is composed of nearly equal numbers of negative and positive ions is called a plasma. The atmospheres of most stars, the gas within the glass tubing of neon advertising signs, and the gases of the upper atmosphere of Earth are examples of plasmas. A gas becomes a plasma when the kinetic energy of the gas particles rises to equal the ionization energy of the gas. When this level is reached, collisions of the gas particles cause a rapid cascading ionization, resulting in a plasma. If the necessary energy is provided by heat, the threshold temperature is from 50,000 to 100,000 K and the temperatures for maintaining a plasma range up to hundreds of millions of degrees. Another way of changing a gas into a plasma is to pass high-energy electrons through the gas. See also Energy.

Nuclear physicists believe that a plasma contained within a closed magnetic field may enable them to harness the vast energy of thermonuclear fusion for peaceful purposes. Plasma-driven rocket motors are being designed that could propel vehicles in deep space. Ion-powered spacecraft have been used for a number of space missions, including SMART 1 to the Moon and Dawn to the asteroid belt. See Nuclear Energy; Space Exploration.

**Self ionization of water**

The self-ionization of water (also autoionization of water, and autodissociation of water) is the chemical reaction in which two water molecules react to produce a hydronium ion (H$_3$O$^+$) and a hydroxide ion (OH$^-$):

$$2 \text{H}_2\text{O} (l) \rightarrow \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq)$$

It is an example of autoprotolysis, and relies on the amphoteric nature of water.

Water, however pure, is not a simple collection of H$_2$O molecules. Even in "pure" water, sensitive equipment can detect a very slight electrical conductivity of 0.055 $\mu$S·cm$^{-1}$. According to the theories of Svante Arrhenius, this must be due to the presence of ions.

**Concentration and frequency**

The preceding reaction has a chemical equilibrium constant of $K_{eq} = ([\text{H}_3\text{O}^+] \cdot [\text{OH}^-]) / [\text{H}_2\text{O}]^2 = 3.23 \times 10^{-18}$. So the acidity constant which is $K_a = K_{eq} \cdot [\text{H}_2\text{O}] = ([\text{H}_3\text{O}^+] \cdot [\text{OH}^-]) / [\text{H}_2\text{O}] = 1.8 \times 10^{-16}$.[1] For reactions in water (or diluted aqueous solutions), the molarity (a unit of concentration) of water, [H$_2$O], is practically constant and is omitted.
from the acidity constant expression by convention. The resulting equilibrium constant is called the ionization constant, dissociation constant, or self-ionization constant, or ion product of water and is symbolized by $K_w$.

$$K_w = K_a [H_2O] = K_{eq} [H_2O]^2 = [H_3O^+] [OH^-]$$

where

$[H_3O^+]$ = molarity of hydrogen or hydronium ion, and
$[OH^-]$ = molarity of hydroxide ion.

At Standard Ambient Temperature and Pressure (SATP), about 25 °C (298 K), $K_w = [H_3O^+] [OH^-] = 1.0 \times 10^{-14}$. Pure water ionizes or dissociates into equal amounts of $H_3O^+$ and $OH^-$, so their molarities are equal:

$$[H_3O^+] = [OH^-].$$

At SATP, the concentrations of hydroxide and hydronium are both very low at 1.0 $\times$ $10^{-7}$ mol/L and the ions are rarely produced: a randomly selected water molecule will dissociate within approximately 10 hours. Since the concentration of water molecules in water is largely unaffected by dissociation and $[H_2O]$ equals approximately 56 mol/l, it follows that for every $5.6 \times 10^8$ water molecules, one pair will exist as ions. Any solution in which the $H_3O^+$ and $OH^-$ concentrations equal each other is considered a neutral solution. Absolutely pure water is neutral, although even trace amounts of impurities could affect these ion concentrations and the water may no longer be neutral. $K_w$ is sensitive to both pressure and temperature; it increases when either increases.

It should be noted that deionized water (also called DI water) is water that has had most impurity ions common in tap water or natural water sources (such as Na$^+$ and Cl$^-$) removed by means of distillation or some other water purification method. Removal of all ions from water is next to impossible, since water self-ionizes quickly to reach equilibrium.

**Dependence on temperature and pressure**

Temperature dependence of the water ionization constant at 25 MPa

Pressures dependence of the water ionization constant at 25 °C

By definition, $pK_w = -\log_{10} K_w$. At SATP, $pK_w = -\log_{10} (1.0 \times 10^{-14}) = 14.0$. The value of $pK_w$ varies with temperature. As temperature increases, $pK_w$ decreases; and as temperature decreases, $pK_w$ increases (for temperatures up to about 250 °C). This means that ionization of water typically increases with temperature.
There is also a (usually small) dependence on pressure (ionization increases with increasing pressure). The dependence of the water ionization on temperature and pressure has been well investigated and a standard formulation exists\[^3\].

## Acidity

pH is a logarithmic measure of the acidity (or alkalinity) of an aqueous solution. By definition, $\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$. Since $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ in a neutral solution, by mathematics, for a neutral aqueous solution pH = 7 at SATP.

Self-ionization is the process that determines the pH of water. Since the concentration of hydronium at SATP (approximately 25 °C) is $1.0 \times 10^{-7}$ mol/l, the pH of pure liquid water at this temperature is 7. Since $K_w$ increases as temperature increases, hot water has a higher concentration of hydronium than cold water, but this does not mean it is more acidic, as the hydroxide concentration is also higher by the same amount.

## Mechanism

Geissler et al. have determined that electric field fluctuations in liquid water cause molecular dissociation\[^4\]. They propose the following sequence of events that takes place in about 150 fs: the system begins in a neutral state; random fluctuations in molecular motions occasionally (about once every 10 hours per water molecule) produce an electric field strong enough to break an oxygen-hydrogen bond, resulting in a hydroxide (OH\(^-\)) and hydronium ion (H\(_3\)O\(^+\)); the proton of the hydronium ion travels along water molecules by the Grotthuss mechanism; and a change in the hydrogen bond network in the solvent isolates the two ions, which are stabilized by solvation.

Within 1 picosecond, however, a second reorganization of the hydrogen bond network allows rapid proton transfer down the electric potential difference and subsequent recombination of the ions. This timescale is consistent with the time it takes for hydrogen bonds to reorient themselves in water\[^5\][6][7].

## Isotope effects

Heavy water, D\(_2\)O, self-ionizes less than normal water, H\(_2\)O; oxygen forms a slightly stronger bond to deuterium because the larger mass of deuterium difference results in a lower zero-point energy, a quantum mechanical effect. The following table compares the values of $pK_w$ for H\(_2\)O and D\(_2\)O\[^8\].

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>H(_2)O</th>
<th>D(_2)O</th>
</tr>
</thead>
</table>

[3]: [Reference source for the standard formulation of water ionization.]
[4]: [Reference source for Geissler et al.'s mechanism.]
[5]: [Reference source for the consistent timescale of hydrogen bond reorientation.]
[6]: [Reference source for the timescale of hydrogen bond reorientation.]
[7]: [Reference source for the quantum mechanical effect of isotope difference.]
[8]: [Reference source for the comparison of $pK_w$ values.]
Aqueous solution

The first solvation shell of a sodium ion dissolved in water

An aqueous solution is a solution in which the solvent is water. It is usually shown in chemical equations by appending \((\text{aq})\) to the relevant formula. The word *aqueous* means pertaining to, related to, similar to, or dissolved in water. As water is an excellent solvent as well as naturally abundant, it is a ubiquitous solvent in chemistry.

Substances that do not dissolve well in water are called *hydrophobic* ('water fearing') whereas those that do are known as *hydrophilic* ('water-loving'). An example of a hydrophilic substance would be the sodium chloride (ordinary table salt). Acids and bases are aqueous solutions, as part of their Arrhenius definitions.

The ability of a substance to dissolve in water is determined by whether the substance can match or exceed the strong attractive forces that water molecules generate between themselves. If the substance lacks the ability to dissolve in water the molecules form a precipitate.

Aqueous solutions that conduct electric current efficiently contain strong electrolytes, while ones that conduct poorly are considered to have weak electrolytes. Those strong electrolytes are substances that are completely ionised in water, whereas the weak electrolytes exhibit only a small degree of ionisation in water.
Nonelectrolytes are substances that dissolve in water, but which maintain their molecular integrity (do not dissociate into ions). Examples include sugar, urea, glycerol, and methylsulfonylmethane (MSM).

When performing calculations regarding the reacting of one or more aqueous solutions, one generally must know the concentration, or molarity, of the aqueous solutions. Solution concentration is given in terms of the form of the solute prior to it dissolving.

**Aqueous solubility**

These are simple guidelines for determining solubility.

1. All compounds with Na\(^+\), K\(^+\), NH\(_4\)\(^+\) ions are soluble in water.
2. All nitrates (NO\(_3^-\)) and acetates (CH\(_3\)COO\(^-\)) are soluble in water.
3. Most chlorides (Cl\(^-\)) and sulfates (SO\(_4^{2-}\)) are soluble in water. Except the following: AgCl, PbCl\(_2\), Hg\(_2\)Cl\(_2\), BaSO\(_4\), PbSO\(_4\) and CaSO\(_4\).
4. Most carbonates (CO\(_3^{2-}\)), phosphates (PO\(_4^{3-}\)), sulfides (S\(^2-\)), and hydroxides (OH\(^-\)) are insoluble in water. Exceptions are LiOH, NaOH, KOH, NH\(_3\text{(aq)}\), Na\(_2\)HPO\(_4\) and NaH\(_2\)PO\(_4\).\([1]\)

**REFERENCE**

1. DARA S.S. 5\(^{th}\) EDITION
2. ENGINEERING CHEMISTRY
3. FROM WIKIPEDIA