Chemical Foundations of Biology

By-

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pH

The concept of pH was first introduced by the Danish chemist Søren Peder Lauritz Sørensen at the Carlsberg Laboratory in 1909 and revised to the modern pH in 1924 to accommodate definitions and measurements in terms of electrochemical cells.

Introduction

1. Simply put, “*pH*” means “*potential of hydrogen”* or “*power of hydrogen*”.

2. It is a scale used to specify the acidity or basicity of an aqueous solution.

3. Acidic solutions (solutions with higher concentrations of H^+ ions) are measured to have lower pH values than basic or alkaline solutions.

4. The pH scale is logarithmic and inversely indicates the concentration of hydrogen ions in the solution. This is because the formula used to calculate pH approximates the negative of the base 10 logarithm of the molar concentration of hydrogen ions in the solution. More precisely, pH is the negative of the base 10 logarithm of the activity of the H^+ ion.

Definition and Measurement

1. pH is defined as the decimal logarithm of the reciprocal of the hydrogen ion activity, $a_{\mathrm{H+}}$, in a solution.

2. Simply put, the hydrogen ion activity is just like a regular number. It tells us of moles of hydrogen ions per liter of solution of the required substance in an aqueous solution.

$$pH = -\log_{10} a_{\mathrm{H+}} = \log_{10} \frac{1}{a_{\mathrm{H+}}}$$

$$\Longrightarrow 10^{pH} = \frac{1}{a_{\mathrm{H+}}}$$

3. Consequently we notice that,

$$pH \propto \frac{1}{a_{\mathrm{H+}}}$$

pH Indicators

Indicators may be used to measure pH, by making use of the fact that their color changes with pH. Visual comparison of the color of a test solution with a standard color chart provides a means to measure pH accurate to the nearest whole number. More precise measurements are possible if the color is measured spectrophotometrically, using a colorimeter or spectrophotometer. Universal indicator consists of a mixture of indicators such that there is a continuous color change from about pH 2 to pH 10. Universal indicator paper is made from absorbent paper that has been impregnated with universal indicator. Another method of measuring pH is using an electronic pH meter.

pH in non-aqueous solution

Hydrogen ion concentrations (activities) can be measured in non-aqueous solvents. pH values based on these measurements belong to a different scale from aqueous pH values, because activities relate to different standard states. Hydrogen ion activity, a_{H+}, can be defined as:

$$\boxed{a_{\mathrm{H}^+} = \exp\left(\frac{\mu_{\mathrm{H}^+} - \mu_{\mathrm{H}^+}^{\ominus}}{RT}\right)}$$

where μ_{H^+} is the chemical potential of the hydrogen ion,

$\mu_{\mathrm{H}^+}^{\ominus}$ is its chemical potential in the chosen standard state,

R is the gas constant and

T is the thermodynamic temperature.

Therefore, pH values on the different scales cannot be compared directly due to different solvated proton ions such as lyonium ions, requiring an inter-solvent scale which involves the transfer activity coefficient of hydronium/lyonium ion.

Applications of pH

Introduction

1. Pure water is neutral. When an acid is dissolved in water, the pH will be less than 7 (25 °C). When a base, or alkali, is dissolved in water, the pH will be greater than 7. A solution of a strong acid, such as hydrochloric acid, at concentration 1 mol dm^{-3} has a pH of 0. A solution of a strong alkali, such as sodium hydroxide, at concentration 1 mol dm^{-3}, has a pH of 14. Thus, measured pH values will lie mostly in the range 0 to 14, though negative pH values and values above 14 are entirely possible. Since pH is a logarithmic scale, a difference of one pH unit is equivalent to a tenfold difference in hydrogen ion concentration.

pH in living systems

Compartment	pH
Gastric acid	1.5 -3.5
Lysosomes	4.5
Human skin	4.7
Granules of chromaffin cells	5.5
Urine	6.0
Cytosol	7.2
Blood (natural pH)	7.34 – 7.45
Cerebrospinal fluid (CSF)	7.5
Mitochondrial matrix	7.5
Pancreas secretions	8.1

The pH of different cellular compartments, body fluids, and organs is usually tightly regulated in a process called acid-base homeostasis. The most common disorder in acid-base homeostasis is acidosis, which means an acid overload in the body, generally defined by pH falling below 7.35. Alkalosis is the opposite condition, with blood pH being excessively high.

The pH of blood is usually slightly basic with a value of pH 7.365. This value is often referred to as physiological pH in biology and medicine. Plaque can create a local acidic environment that can result in tooth decay by demineralization. Enzymes and other proteins have an optimum pH range and can become inactivated or denatured outside this range.

pK (Acid Dissociation Constant)

Introduction

An **acid dissociation constant**, K_a, (also known as **acidity constant**, or **acid-ionization constant**) is a quantitative measure of the strength of an acid in solution. It is the equilibrium constant for a chemical reaction

$$\mathrm{HA} \rightleftharpoons \mathrm{A}^- + \mathrm{H}^+$$

known as dissociation in the context of acid–base reactions. The chemical species HA is an acid that dissociates into A^-, the conjugate base of the acid and a hydrogen ion, H^+. The system is said to be in equilibrium when the concentrations of its components will not change with the passing of time, because both forward and backward reactions are occurring at the same rate.

Mathematical Interpretation of pK

The dissociation constant is defined by

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

$$pK_a = -\log_{10} K_a = \log_{10} \frac{[HA]}{[A^-][H^+]}$$

where quantities in square brackets represent the concentrations of the species at equilibrium.

Theoretical Background

The acid dissociation constant for an acid is a direct consequence of the underlying thermodynamics of the dissociation reaction; the pK_a value is directly proportional to the standard Gibbs free energy change for the reaction. The value of the pK_a changes with temperature and can be understood qualitatively based on Le Châtelier's principle: when the reaction is endothermic, K_a increases and pK_a decreases with increasing temperature; the opposite is true for exothermic reactions.

The value of pK_a also depends on molecular structure of the acid in many ways. For example, Pauling proposed two rules: one for successive pK_a of polyprotic acids, and one to estimate the pK_a of oxyacids based on the number of =O and -OH groups. Other structural factors that influence the magnitude of the acid dissociation constant include inductive effects, mesomeric effects, and hydrogen bonding.

Continuum

The quantitative behavior of acids and bases in solution can be understood only if their pK_a values are known. In particular, the pH of a solution can be predicted when the analytical concentration and pK_a values of all acids and bases are known; conversely, it is possible to calculate the equilibrium concentration of the acids and bases in solution when the pH is known. These calculations find application in many different areas of chemistry, biology, medicine, and geology. For example, many compounds used for medication are weak acids or bases, and a knowledge of the pK_a values, together with the octanol-water partition coefficient, can be

used for estimating the extent to which the compound enters the blood stream. Acid dissociation constants are also essential in aquatic chemistry and chemical oceanography, where the acidity of water plays a fundamental role. In living organisms, acid–base homeostasis and enzyme kinetics are dependent on the pK_a values of the many acids and bases present in the cell and in the body. In chemistry, a knowledge of pK_a values is necessary for the preparation of buffer solutions and is also a prerequisite for a quantitative understanding of the interaction between acids or bases and metal ions to form complexes. Experimentally, pK_a values can be determined by potentiometric (pH) titration, but for values of pK_a less than about 2 or more than about 11, spectrophotometric or NMR measurements may be required due to practical difficulties with pH measurements.

Acids

Introduction

1. An **acid** is a molecule or ion capable of donating a proton (hydrogen ion H+) (a Brønsted–Lowry acid), or, alternatively, capable of forming a covalent bond with an electron pair (a Lewis acid).

2. The first category of acids are the proton donors, or Brønsted–Lowry acids. In the special case of aqueous solutions, proton donors form the hydronium ion H3O+ and are known as Arrhenius acids. Brønsted and Lowry generalized the Arrhenius theory to include non-aqueous solvents. A Brønsted or Arrhenius acid usually contains a hydrogen atom bonded to a chemical structure that is still energetically favorable after loss of H^+.

Continuum

3. The second category of acids are Lewis acids, which form a covalent bond with an electron pair. An example is boron trifluoride (BF_3), whose boron atom has a vacant orbital which can form a covalent bond by sharing a lone pair of electrons on an atom in a base, for example the nitrogen atom in ammonia (NH_3). Lewis considered this as a generalization of the Brønsted definition, so that an acid is a chemical species that accepts electron pairs either directly *or* by releasing protons (H^+) into the solution, which then accept electron pairs.

However, hydrogen chloride, acetic acid, and most other Brønsted–Lowry acids cannot form a covalent bond with an electron pair and are therefore not Lewis acids. Conversely, many Lewis acids are not Arrhenius or Brønsted–Lowry acids. In modern terminology, an *acid* is implicitly a Brønsted acid and not a Lewis acid, since chemists almost always refer to a Lewis acid explicitly as *a Lewis acid*.

Modern Definitions

Modern definitions are concerned with the fundamental chemical reactions common to all acids.

Most acids encountered in everyday life are aqueous solutions, or can be dissolved in water, so the Arrhenius and Brønsted-Lowry definitions are the most relevant.

The Brønsted-Lowry definition is the most widely used definition; unless otherwise specified, acid-base reactions are assumed to involve the transfer of a proton (H+) from an acid to a base.

Hydronium ions are acids according to all three definitions. Although alcohols and amines can be BrønstedLowry acids, they can also function as Lewis bases due to the lone pairs of electrons on their oxygen and
nitrogen atoms.

Types of Acids

The Modern Interpretation of the subject matter states that there are three major categories of acids

The Three types of acids are:

1. Arrhenius Acids

2. Brønsted–Lowry acids

3. Lewis acids

1. Arrhenius Acids

1. Svante Arrhenius attributed the properties of acidity to hydrogen ions (H^+) or protons in 1884. An **Arrhenius acid** is a substance that, when added to water, increases the concentration of H^+ ions in the water. Note that chemists often write H^+(*aq*) and refer to the hydrogen ion when describing acid-base reactions but the free hydrogen nucleus, a proton, does not exist alone in water, it exists as the **hydronium ion** (H_3O^+) or other forms ($H_5O_2^+$, $H_9O_4^+$). Thus, an Arrhenius acid can also be described as a substance that increases the concentration of hydronium ions when added to water. Examples include molecular substances such as HCl and acetic acid.

2. An Arrhenius base, on the other hand, is a substance which increases the concentration of hydroxide (OH-) ions when dissolved in water. This decreases the concentration of hydronium because the ions react to form H2O molecules:

$$H_3O^{+}_{(aq)} + OH^{-}_{(aq)} \rightleftharpoons H_2O_{(l)} + H_2O_{(l)}$$

Continuum

3. Due to this equilibrium, any increase in the concentration of hydronium is accompanied by a decrease in the concentration of hydroxide. Thus, an Arrhenius acid could also be said to be one that decreases hydroxide concentration, while an Arrhenius base increases it.

In an acidic solution, the concentration of hydronium ions is greater than 10-7 moles per liter. Since pH is defined as the negative logarithm of the concentration of hydronium ions, acidic solutions thus have a pH of less than 7.

Brønsted–Lowry acids

1. While the Arrhenius concept is useful for describing many reactions, it is also quite limited in its scope. In 1923 chemists Johannes Nicolaus Brønsted and Thomas Martin Lowry independently recognized that acid-base reactions involve the transfer of a proton. A **Brønsted Lowry acid** (or simply Brønsted acid) is a species that donates a proton to a Brønsted Lowry base. Brønsted-Lowry acid-base theory has several advantages over Arrhenius theory. Consider the following reactions of acetic acid (CH_3COOH), the organic acid that gives vinegar its characteristic taste:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

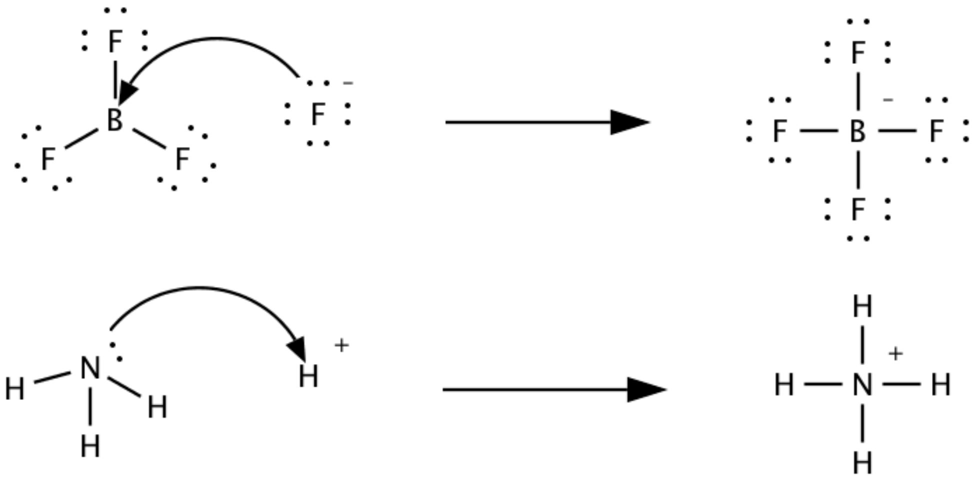
Continuum

Both theories easily describe the first reaction: CH_3COOH acts as an Arrhenius acid because it acts as a source of H_3O^+ when dissolved in water, and it acts as a Brønsted acid by donating a proton to water. In the second example CH3COOH undergoes the same transformation, in this case donating a proton to ammonia (NH_3), but does not relate to the Arrhenius definition of an acid because the reaction does not produce hydronium. Nevertheless, CH_3COOH is both an Arrhenius and a Brønsted-Lowry acid.

Brønsted-Lowry theory can be used to describe reactions of molecular compounds in non-aqueous solution or the gas phase. Hydrogen chloride (HCl) and ammonia combine under several different conditions to form ammonium chloride, NH_4Cl. In aqueous solution HCl behaves as hydrochloric acid and exists as hydronium and chloride ions.

Lewis Acids

A third, only marginally related concept was proposed in 1923 by Gilbert N. Lewis, which includes reactions with acid-base characteristics that do not involve a proton transfer. A **Lewis acid** is a species that accepts a pair of electrons from another species; in other words, it is an electron pair acceptor. Brønsted acid-base reactions are proton transfer reactions while Lewis acid-base reactions are electron pair transfers. Many Lewis acids are not Brønsted-Lowry acids. Contrast how the following reactions are described in terms of acid-base chemistry:



In the first reaction a fluoride ion, F-, gives up an electron pair to boron trifluoride to form the product tetrafluoroborate. Fluoride "loses" a pair of valence electrons because the electrons shared in the B—F bond are located in the region of space between the two atomic nuclei and are therefore more distant from the fluoride nucleus than they are in the lone fluoride ion. BF_3 is a Lewis acid because it accepts the electron pair from fluoride. This reaction cannot be described in terms of Brønsted theory because there is no proton transfer. The second reaction can be described using either theory. A proton is transferred from an unspecified Brønsted acid to ammonia, a Brønsted base; alternatively, ammonia acts as a Lewis base and transfers a lone pair of electrons to form a bond with a hydrogen ion. The species that gains the electron pair is the Lewis acid; for example, the oxygen atom in H_3O+ gains a pair of electrons when one of the H—O bonds is broken and the electrons shared in the bond become localized on oxygen. Depending on the context, a Lewis acid may also be described as an oxidizer or an electrophile. Organic Brønsted acids, such as acetic, citric, or oxalic acid, are not Lewis acids. They dissociate in water to produce a Lewis acid, H^+, but at the same time also yield an equal amount of a Lewis base (acetate, citrate, or oxalate, respectively, for the acids mentioned). Few, if any, of the acids discussed in the following are Lewis acids.

Base

Introduction

A **base** is a chemical species that donates electrons, accepts protons, or releases hydroxide (OH^-) ions in aqueous solution.

Bases and acids are seen as chemical opposites because the effect of an acid is to increase the hydronium (H_3O^+) concentration in water, whereas bases reduce this concentration. A reaction between aqueous solutions of an acid and a base is called neutralization, producing a solution of water and a salt in which the salt separates into its component ions. If the aqueous solution is saturated with a given salt solute, any additional such salt precipitates out of the solution.

Types of Bases

There are 3 types of bases. However all are merely different interpretations of the same thing

The Three types of bases are-

1. Arrhenius Base
2. Brønsted–Lowry Base
3. Lewis Base

Arrhenius Base.

1.Arrhenius proposed in 1884 that a base is a substance which dissociates in aqueous solution to form hydroxide ions OH^-. These ions can react with hydrogen ions (H^+ according to Arrhenius) from the dissociation of acids to form water in an acid-base reaction. A base was therefore a metal hydroxide such as NaOH or $Ca(OH)_2$. Such aqueous hydroxide solutions were also described by certain characteristic properties. They are slippery to the touch, can taste bitter and change the color of pH indicators (e.g., turn red litmus paper blue)

Continuum

In water, by altering the auto-ionization equilibrium, bases yield solutions in which the hydrogen ion activity is lower than it is in pure water, i.e., the water has a pH higher than 7.0 at standard conditions. A soluble base is called an **alkali** if it contains and releases OH^- ions quantitatively. Metal oxides, hydroxides, and especially alkoxides are basic, and conjugate bases of weak acids are weak bases.

Brønsted–Lowry Base

In the more general Brønsted–Lowry acid–base theory (1923), a base is a substance that can accept hydrogen cations (H^+)—otherwise known as protons. This does include aqueous hydroxides since OH- does react with H+ to form water, so that Arrhenius bases are a subset of Brønsted bases. However there are also other Brønsted bases which accept protons, such as aqueous solutions of ammonia (NH_3) or its organic derivatives (amines). These bases do not contain a hydroxide ion but nevertheless react with water, resulting in an increase in the concentration of hydroxide ion. Also, some non-aqueous solvents contain Brønsted bases which react with solvated protons. For example in liquid ammonia, NH_2^- is the basic ion species which accepts protons from NH_4^+, the acidic species in this solvent .

Lewis Base

G. N. Lewis realized that water, ammonia and other bases can form a bond with a proton due to the unshared pair of electrons that the bases possess. In the Lewis theory, a base is an electron pair donor which can share a pair of electrons with an electron acceptor which is described as a Lewis acid. The Lewis theory is more general than the Brønsted model because the Lewis acid is not necessarily a proton, but can be another molecule (or ion) with a vacant low-lying orbital which can accept a pair of electrons. One notable example is boron trifluoride (BF_3).

Properties of Bases

1. Concentrated or strong bases are caustic on organic matter and react violently with acidic substances.

2. Aqueous solutions or molten bases dissociate in ions and conduct electricity.

3. Reactions with indicators: bases turn red litmus paper blue, phenolphthalein pink, keep bromothymol blue in its natural colour of blue, and turn methyl orange-yellow.

4. The pH of a basic solution at standard conditions is greater than seven. Bases are bitter.

Buffer Solutions

Introduction

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.

Principles of Buffering

Buffer solutions achieve their resistance to pH change because of the presence of an equilibrium between the weak acid HA and its conjugate base A^-:

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

When some strong acid is added to an equilibrium mixture of the weak acid and its conjugate base, hydrogen ions (H^+) are added, and the equilibrium is shifted to the left, in accordance with Le Châtelier's principle. Because of this, the hydrogen ion concentration increases by less than the amount expected for the quantity of strong acid added. Similarly, if strong alkali is added to the mixture, the hydrogen ion concentration decreases by less than the amount expected for the quantity of alkali added. The effect is illustrated by the simulated titration of a weak acid with $pK_a = 4.7$.

The relative concentration of un-dissociated acid is shown in blue, and of its conjugate base in red. The pH changes relatively slowly in the buffer region, pH = pK_a ± 1, centered at pH = 4.7, where [HA] = [A^-]. The hydrogen ion concentration decreases by less than the amount expected because most of the added hydroxide ion is consumed in the reaction

$$OH^- + HA \rightarrow H_2O + A^-$$

and only a little is consumed in the neutralization reaction (which is the reaction that results in an increase in pH)

$$OH^- + H^+ \rightarrow H_2O.$$

Once the acid is more than 95% deprotonated, the pH rises rapidly because most of the added alkali is consumed in the neutralization reaction.

Applications

The pH of a solution containing a buffering agent can only vary within a narrow range, regardless of what else may be present in the solution. In biological systems this is an essential condition for enzymes to function correctly. For example, in human blood a mixture of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) is present in the plasma fraction; this constitutes the major mechanism for maintaining the pH of blood between 7.35 and 7.45. Outside this narrow range (7.40 ± 0.05 pH unit), acidosis and alkalosis metabolic conditions rapidly develop, ultimately leading to death if the correct buffering capacity is not rapidly restored. If the pH value of a solution rises or falls too much, the effectiveness of an enzyme decreases in a process, known as denaturation, which is usually irreversible. The majority of biological samples that are used in research are kept in a buffer solution, often phosphate buffered saline (PBS) at pH 7.4. In industry, buffering agents are used in fermentation processes and in setting the correct conditions for dyes used in coloring fabrics. They are also used in chemical analysis and calibration of pH meters.

Some Buffering Agents

Buffering agent	pK_a	Useful pH range
Citric acid	3.13, 4.76, 6.40	2.1 – 7.4
Acetic acid	4.8	3.8 – 5.8
KH_2PO_4	7.2	6.2 – 8.2
CHES	9.3	8.3 – 10.3
Borate	9.24	8.25 – 10.25

Free Energy

The basic definition of "energy" is a measure of a body's (in thermodynamics, the system's) ability to cause change. For example, when a person pushes a heavy box a few meters forward, that person exerts mechanical energy, also known as work, on the box over a distance of a few meters forward.

Definition

The **thermodynamic free energy** is a concept useful in the thermodynamics of chemical or thermal processes in engineering and science. The change in the free energy is the maximum amount of work that a thermodynamic system can perform in a process at constant temperature, and its sign indicates whether a process is thermodynamically favorable or forbidden. Since free energy usually contains potential energy, it is not absolute but depends on the choice of a zero point. Therefore, only relative free energy values, or changes in free energy, are physically meaningful. The free energy is a thermodynamic state function, like the internal energy, enthalpy, and entropy.

Overview

Free energy is that portion of any first-law energy that is **available** to perform thermodynamic work at constant temperature, *i.e.*, work mediated by thermal energy. Free energy is subject to irreversible loss in the course of such work. Since first-law energy is always conserved, it is evident that free energy is an expendable, second-law kind of energy. Several free energy functions may be formulated based on system criteria. Free energy functions are Legendre transforms of the internal energy.

The Gibbs free energy is given by $G = H - TS$, where H is the enthalpy, T is the absolute temperature, and S is the entropy. $H = U + pV$, where U is the internal energy, p is the pressure, and V is the volume. G is the most useful for processes involving a system at constant pressure p and temperature T, because, in addition to subsuming any entropy change due merely to heat, a change in G also excludes the $p\,dV$ work needed to "make space for additional molecules" produced by various processes. Gibbs free energy change therefore equals work not associated with system expansion or compression, at constant temperature and pressure. (Hence its utility to solution-phase chemists, including biochemists.)

The historically earlier Helmholtz free energy is defined as $A = U - TS$. Its change is equal to the amount of reversible work done on, or obtainable from, a system at constant T. Thus its appellation "work content", and the designation A from *Arbeit*, the German word for work. Since it makes no reference to any quantities involved in work (such as p and V), the Helmholtz function is completely general: its decrease is the maximum amount of work which can be done *by* a system at constant temperature, and it can increase at most by the amount of work done *on* a system isothermally.

The Helmholtz free energy has a special theoretical importance since it is proportional to the logarithm of the partition function for the canonical ensemble in statistical mechanics. (Hence its utility to physicists; and to gas-phase chemists and engineers, who do not want to ignore $p\,dV$ work.)

Historically, the term 'free energy' has been used for either quantity. In physics, *free energy* most often refers to the Helmholtz free energy, denoted by A (or F), while in chemistry, *free energy* most often refers to the Gibbs free energy. The values of the two free energies are usually quite similar and the intended free energy function is often implicit in manuscripts and presentations.

Applications of Free Energy

Just like the general concept of energy, free energy has a few definitions suitable for different conditions. In physics, chemistry, and biology, these conditions are thermodynamic parameters (temperature T, volume V, pressure p, etc.). Scientists have come up with several ways to define free energy. The mathematical expression of Helmholtz free energy is:

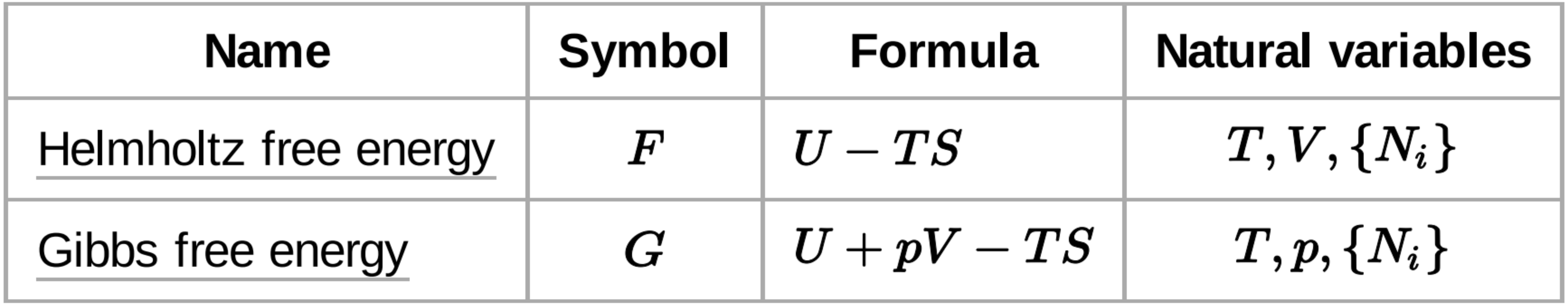
$$\boldsymbol{A = U - TS}$$

This definition of free energy is useful for gas-phase reactions or in physics when modeling the behavior of isolated systems kept at a constant volume. For example, if a researcher wanted to perform a combustion reaction in a bomb calorimeter, the volume is kept constant throughout the course of a reaction. Therefore, the heat of the reaction is a direct measure of the free energy change, $q = \Delta U$. In solution chemistry, on the other hand, most chemical reactions are kept at constant pressure. Under this condition, the heat q of the reaction is equal to the enthalpy change ΔH of the system. Under constant pressure and temperature, the free energy in a reaction is known as Gibbs free energy G.

$$\boldsymbol{G = H - TS}$$

These functions have a minimum in chemical equilibrium, as long as certain variables (T, and V or p) are held constant.

Types of Free Energy



Name	Symbol	Formula	Natural variables
Helmholtz free energy	F	$U - TS$	$T, V, \{N_i\}$
Gibbs free energy	G	$U + pV - TS$	$T, p, \{N_i\}$

N_i is the number of molecules (alternatively, moles) of type i in the system. If these quantities do not appear, it is impossible to describe compositional changes.

Gibbs Free Energy: Definition

In thermodynamics, the **Gibbs free energy** is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure. The Gibbs free energy ($\Delta G = \Delta H - T\Delta S$, measured in joules in SI) is the *maximum* amount of non-expansion work that can be extracted from a thermodynamically closed system (can exchange heat and work with its surroundings, but not matter).
This maximum can be attained only in a completely reversible process. When a system transforms reversibly from an initial state to a final state, the decrease in Gibbs free energy equals the work done by the system to its surroundings, minus the work of the pressure forces.

The Gibbs energy (symbol) is also the thermodynamic potential that is minimized when a system reaches chemical equilibrium at constant pressure and temperature. Its derivative with respect to the reaction coordinate of the system vanishes at the equilibrium point. As such, a reduction in is necessary for a reaction to be spontaneous at constant pressure and temperature.

Helmholtz Free Energy: Definition

In thermodynamics, the **Helmholtz free energy** is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume (isothermal, isochoric). The negative of the change in the Helmholtz energy during a process is equal to the maximum amount of work that the system can perform in a thermodynamic process in which volume is held constant. If the volume were not held constant, part of this work would be performed as boundary work. This makes the Helmholtz energy useful for systems held at constant volume. Furthermore, at constant temperature, the Helmholtz free energy is minimized at equilibrium.

Differences between G.F.E. and H.F.E.

In contrast, the Gibbs free energy or free enthalpy is most commonly used as a measure of thermodynamic potential (especially in chemistry) when it is convenient for applications that occur at constant *pressure*. For example, in explosives research Helmholtz free energy is often used, since explosive reactions by their nature induce pressure changes. It is also frequently used to define fundamental equations of state of pure substances.

Work and Free Energy Change

For a reversible isothermal process, $\Delta S = q_{rev}/T$ and therefore the definition of A results in

$$\Delta A = \Delta U - T\Delta S = \Delta U - q_{rev} = w_{rev} \text{ (at constant temperature)}$$

This tells us that the change in free energy equals the reversible or maximum work for a process performed at constant temperature .Under other conditions , free energy change is not equal to work ; for instance , for a reversible adiabatic expansion of an ideal gas, $A = wrev - S\Delta T$. Importantly, for a heat engine, including the Carnot cycle, the free energy change after a full cycle is zero, $\Delta_{cyc} A = 0$,

while the engine produces non-zero work. It is important to note that for heat engines and other thermal systems, the free energies do not offer convenient characterizations; internal energy and enthalpy are the preferred potentials for characterizing thermal systems

Free energy change and spontaneous processes

According to the second law of thermodynamics, for any process that occurs in a closed system, the inequality of Clausius, $\Delta S > q/T_{surr}$, applies. For a process at constant temperature and pressure without non-*PV* work, this inequality transforms into $\Delta G < 0$, Similarly, for a process at constant temperature and volume $\Delta A < 0$, Thus, a negative value of the change in free energy is a necessary condition for a process to be spontaneous; this is the most useful form of the second law of thermodynamics in chemistry. In chemical equilibrium at constant *T* and *p* without electrical work, $dG = 0$.

Isomerization

Introduction

Isomerization or **isomerisation** is the process in which a molecule, ion or molecular fragment is transformed into an isomer with a different chemical structure. Enolization is an example of isomerization, as is tautomerization. When the isomerization occurs intramolecularly it may be called a rearrangement reaction.

Examples of Isomerization

Alkanes:

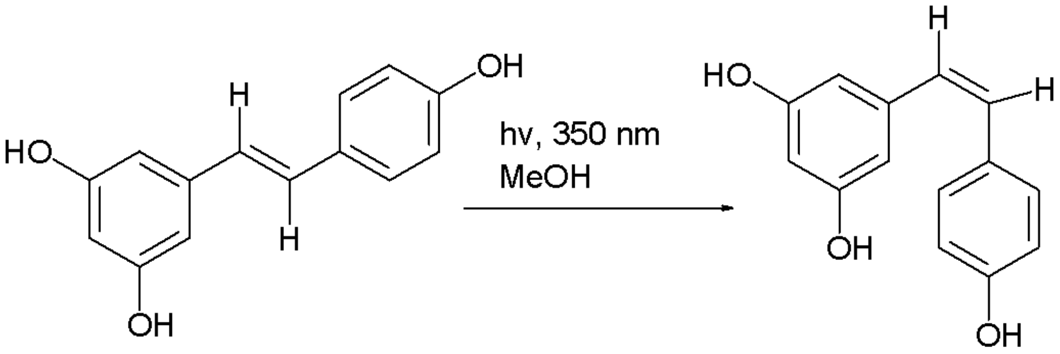
Skeletal isomerization occurs in the cracking process, used in the petrochemical industry. As well as reducing the average chain length, straight-chain hydrocarbons are converted to branched isomers in the process, as illustrated the following reaction.

$$CH_3CH_2CH_2CH_3 \text{ (n-butane)} \rightarrow CH_3CH(CH_3)CH_3 \text{ (i-butane)}$$

Alkenes:

Terminal alkenes isomerize to internal alkenes in the presence of metal catalysts. This process is employed in the Shell higher olefin process to convert alpha-olefins to internal olefins, which are subjected to olefin metathesis. In certain kinds of alkene polymerization reactions, chain walking is an isomerization process that introduces branches into growing polymers.

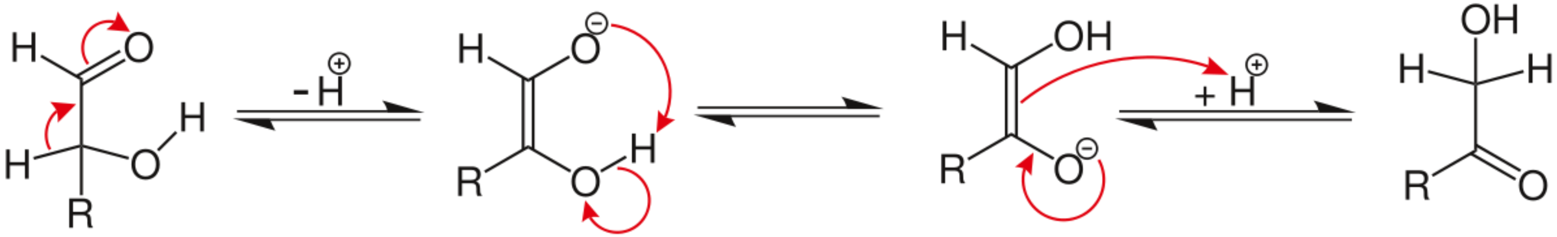
The *trans* isomer of resveratrol can be converted to the *cis* isomer in a photochemical reaction.



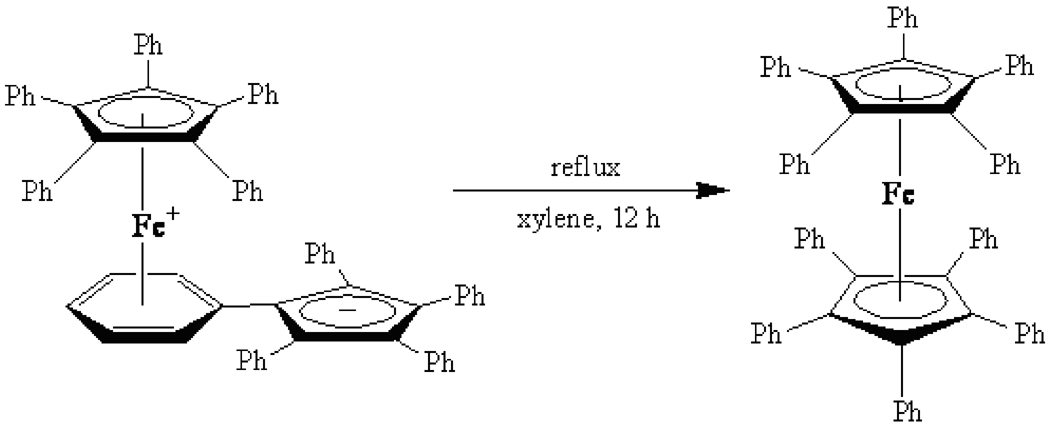
Thermal rearrangement of azulene to naphthalene has been observed

Other Examples

Aldose-ketose isomerism, aka Lobry de Bruyn–van Ekenstein transformation, provides an example in carbohydrate chemistry.



An example of an organometallic isomerization is the production of decaphenylferrocene, $[(\eta^5\text{-}C_5Ph_5)_2Fe]$ from its linkage isomer.



Thank You