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ACID ANHYDRIDES

FIELDS OF STUDY

Organic Chemistry

SUMMARY

The characteristic properties and reactions of acid anhydrides are discussed. Acid anhydrides are useful compounds in organic synthesis reactions, helping to form complex molecular structures from simple starting materials.

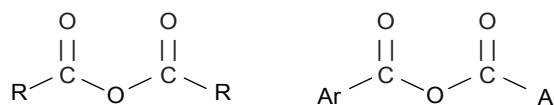
PRINCIPAL TERMS

- **acyl group:** a functional group with the formula RCO , where R is connected by a single bond to the carbon atom of the carbonyl ($\text{C}=\text{O}$) group.
- **carboxylic acid:** an organic compound containing a carboxyl functional group and having the general formula $\text{RC}(=\text{O})\text{OH}$.
- **functional group:** a specific group of atoms with a characteristic structure and corresponding chemical behavior within a molecule.
- **organic acid:** an acid derived from an organic compound.
- **R (generic placeholder):** a symbol used primarily in organic chemistry to represent a hydrocarbon side chain or other unspecified group of atoms in a molecule; can be used specifically for an alkyl group, with Ar used to represent an aryl group.

THE NATURE OF ACID ANHYDRIDES

The term “anhydride” indicates the absence of either water or its components, oxygen and hydrogen, from a molecular structure. Acid anhydrides are compounds in which a bond has been formed between two acid functional groups by the virtual elimination of -H from one acid group and -OH from the other. Most common acid anhydrides are formed from carboxylic acids, but they can also be formed from any organic acid and many inorganic acids. Mixed acid

anhydrides are also possible and are, in fact, essential components of certain biochemical cycles. Acid anhydrides can also be thought of as esters formed from an acyl group. Generally, acid anhydrides are represented as follows:

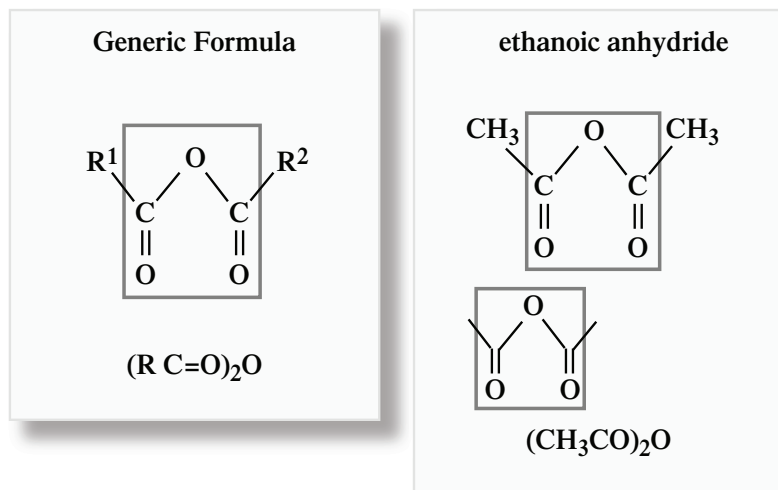


The generic placeholders R- and Ar- indicate an alkyl group substituent and an aryl group substituent, respectively.

Acid anhydrides of linear molecules are generally used to add single substituents to a molecular structure. Acid anhydride compounds with a cyclic structure are also commonly used in synthetic procedures to elaborate a molecular structure. In principle, an anhydride can be formed from any carboxylic acid. However, in practice, very few acid anhydrides are available, and other carboxylic-acid derivatives are more readily obtained for particular purposes. Thus, linear carboxylic acids are seldom prepared or utilized. Dicarboxylic acids, in which the formation of the anhydride produces a five- or six-membered ring structure, are more readily converted to their anhydride form and are generally more useful in synthetic methods.

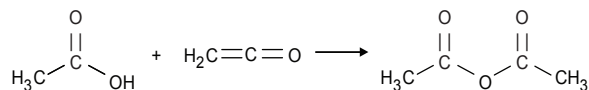
The most common acid anhydride is acetic anhydride. Because of its relative ease of handling and because it does not release hydrogen chloride (HCl) gas as a product of the reaction, it is the preferred reagent for forming acetate esters. In pure form, acetic acid tends to absorb atmospheric moisture. It is a common laboratory practice to add a small amount of acetic anhydride to pure acetic acid to counteract this effect, as any moisture consumed by the hydrolysis of acetic anhydride simply produces more acetic acid, which would not be a contaminant in the reagent.

ACID ANHYDRIDES



FORMATION OF ACID ANHYDRIDES

Simple acid anhydrides are never formed by dehydration reactions. Acetic anhydride is produced commercially by the reaction of acetic acid with ethenone in the gas phase, according to the following equation:



The anhydrides of larger linear carboxylic acids are more difficult to prepare, but in some cases, they can be formed by heating the acid in the presence of a strong dehydrating agent, such as phosphorus pentoxide (P_2O_5), and separating the anhydride from the reaction mixture as it forms. Cyclic anhydrides such as maleic anhydride and succinic anhydride form readily when their parent acids are heated. The process is assisted by the removal of water from the reaction as it is formed, which prevents the reverse reaction from occurring. Ring size is vitally important for this process: five- and six-membered rings are well suited to the geometric constraints of the electron orbitals in carbon and oxygen atoms, while seven-membered rings are more difficult to form because of the strain that the bond angles of such a ring impose on the molecule. Adipic acid, or 1,6-hexanedioic acid, does not form the corresponding cyclic anhydride; instead, it eliminates a molecule of both carbon

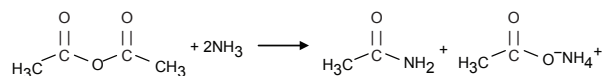
dioxide and water to produce the less strained compound cyclopentanone.

REACTIONS OF ACID ANHYDRIDES

Acid anhydrides are reactive compounds widely used for the formation of esters. By far the most common commercial use of acetic anhydride is in the formation of acetate esters of carbohydrate compounds such as sugars, starches, and celluloses. The carbonyl ($\text{C}=\text{O}$) groups of an acid anhydride readily interact with nucleophiles, which are chemical species that are attracted to positively charged species. This happens partly because the electronegative oxygen atoms of the carbonyl groups tend to draw electron density away from the carbon atoms, causing the carbon to behave

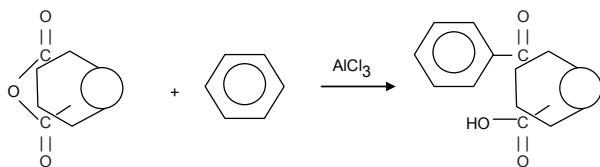
as though it were positively charged, and partly because the way the bonds are arranged around the carbon atoms makes it easier for nucleophiles to approach and interact. After the nucleophile is added and the leaving group is eliminated, the carbonyl groups re-form in the new molecule. This same basic mechanism permits acid anhydrides to be converted into different acid derivatives. Reaction with water reconverts the anhydride into its acid form, which allows other types of reactions to occur after an anhydride group has been added to a substrate molecule. For example, maleic anhydride is commonly used in a Diels-Alder reaction, which is a type of reaction that results in the addition of a six-membered ring structure to the substrate molecule. Hydrolysis of the resulting molecule produces two carboxylic acid functional groups ($-\text{COOH}$) that can be modified by other reactions to produce a desired product.

Acid anhydrides also react well with ammonia to produce the corresponding amide of one carboxylic acid group and the ammonium salt of the other. The reaction of acetic anhydride with ammonia, for example, would produce acetamide and ammonium acetate:



A reaction with a substituted amine such as ethylamine would produce the corresponding substituted amide compound.

Anhydrides are also able to act as acylating agents in the Friedel-Crafts acylation of benzene and benzene-like aromatic compounds. One half of the anhydride function bonds chemically to the aromatic ring as an acyl substituent, while the other half is reconverted into the acid. The reaction is typically catalyzed by a Lewis acid, such as aluminum trichloride (AlCl_3) or ferric chloride (FeCl_3). Phthalic anhydride, for example, can be used to acylate benzene, producing the corresponding benzoic acid derivative, according to the following equation:



Diels-Alder, Friedel-Crafts, and similar reactions are useful in organic synthetic chemistry because they allow the chemist to easily and quickly build a complex molecular structure from very simple starting materials. The reactions typically produce hydrogen chloride as well, but this is an inconsequential by-product and is seldom, if ever, shown in structural formula equations.

NOMENCLATURE OF ACID ANHYDRIDES

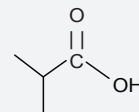
Acid anhydrides are named according to the parent acid from which they are formed, simply by adding “anhydride” to the name of the parent acid. Accordingly, the anhydride of butyric acid would be named butyric anhydride, while maleic acid and succinic acid readily form maleic anhydride and succinic anhydride. Mixed anhydrides, though uncommon, are also known. For a mixed anhydride, the names of the two parent acids are used, with the “higher” acid being named in second place. For example, the

SAMPLE PROBLEM

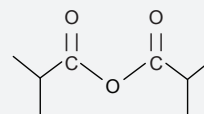
Given the chemical name isobutyric anhydride, draw the skeletal structure of the molecule.

Answer:

The name indicates that the material is the anhydride of isobutyric acid, which has the structure



Isobutyric anhydride must therefore have the structure



mixed anhydride of acetic acid and phosphoric acid would be named acetic phosphoric anhydride. Such mixed anhydrides sometimes appear in enzyme-mediated biochemical processes.

Richard M. Renneboog, MSc

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ACID CHLORIDES

FIELDS OF STUDY

Organic Chemistry; Inorganic Chemistry

SUMMARY

The characteristic properties and reactions of acid chlorides are discussed. Acid chlorides are useful compounds in both organic and inorganic synthesis reactions for the relatively easy formation of complex molecular structures from simple starting materials.

PRINCIPAL TERMS

- **acid derivative:** a compound formed by modifying the structure of an acid, such as an ester created by the reaction between a carboxylic acid and an alcohol.
- **functional group:** a specific group of atoms having a characteristic structure and corresponding chemical behavior within a molecule.
- **nucleophile:** a chemical species that tends to react with positively charged or electron-poor species.
- **reactivity:** the propensity of a chemical species to undergo a reaction under applied conditions.
- **R (generic placeholder):** a symbol used primarily in organic chemistry to represent a hydrocarbon side chain or other unspecified group of atoms in a molecule; can be used specifically for an alkyl group, with Ar used to represent an aryl group.

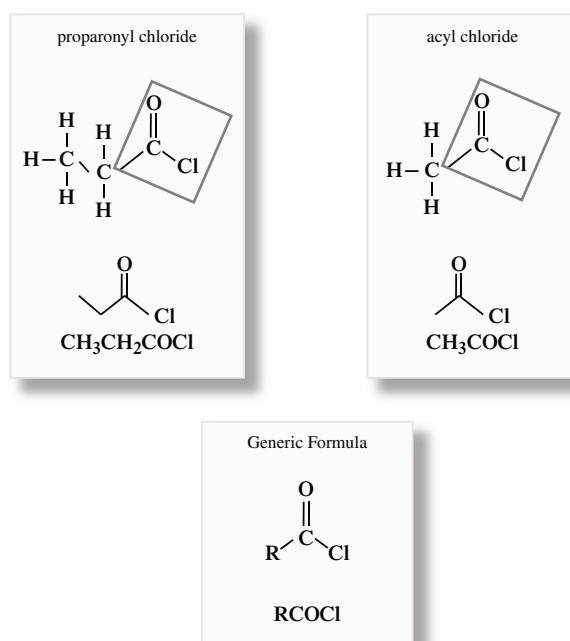
THE NATURE OF ACID CHLORIDES

The acid chlorides, also known as acyl chlorides, are characterized by the presence of a carbonyl functional group (C=O) connected by a single bond to a chlorine atom. Acid chlorides are acid derivatives of either alkyl or aryl carboxylic acids, and in fact the acid chloride functional group (-COCl) is essentially a carboxyl group (-COOH) in which the hydroxyl group (-OH) has been replaced by chlorine. The general formula of an acid chloride shows the acid chloride group attached to either an R- or an Ar- placeholder, where R indicates an alkyl group (a basic hydrocarbon) and Ar represents an aryl group (a hydrocarbon derived from an aromatic ring):



Acid chlorides are the most reactive derivatives of carboxylic acids. This relatively high reactivity and the ease with which acid chlorides can be prepared make them extremely versatile reagents in many applications. They are especially prone to reactions with nucleophiles, which typically replace the chlorine atom with another atom or group.

NOMENCLATURE OF ACID CHLORIDES ACID CHLORIDE



Acid chlorides are named by replacing the “-ic acid” ending of the parent acid name with “-yl chloride.” The acid chloride of benzoic acid, for example, is benzoyl chloride, while the acid chloride of oxalic acid is oxalyl chloride. The naming convention for acid chlorides of more complex acids, in which other functional groups take priority, uses the prefix “chlorocarbonyl-” ahead of the proper name of the parent acid.

PREPARATION OF ACID CHLORIDES

Acid chlorides can be readily prepared from essentially any carboxylic acid. The standard method of preparation is via reaction with thionyl chloride (SOCl_2), phosphorus trichloride (PCl_3), or phosphorus pentachloride (PCl_5). The reaction with thionyl chloride is generally preferred, as it is easier to obtain the acid chloride in a pure form using this reactant than with either of the phosphorus-based chlorinating agents. Any volatile thionyl chloride can be easily removed by distillation, whereas the phosphorus-based by-products are reactive solids that are not as readily eliminated from the reaction mixture.

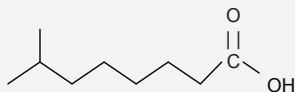
The inorganic chlorinating agents used to prepare acid chlorides are themselves acid chlorides of their corresponding acids. Thionyl chloride is the acid chloride of sulfurous acid (H_2SO_3), while phosphorus trichloride and phosphorus pentachloride are acid chlorides of phosphoric acid (H_3PO_4).

SAMPLE PROBLEM

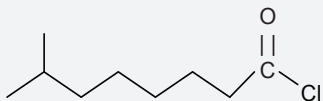
Given the chemical name 7-methyloctanoyl chloride, draw the skeletal structure of the molecule.

Answer:

The name indicates that the compound is a derivative of 7-methyloctanoic acid, which has the following structure:



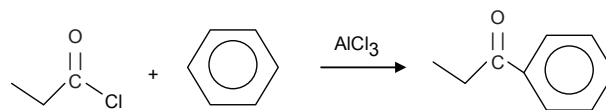
The acid chloride therefore has the following structure:

**REACTIONS OF ACID CHLORIDES**

Acid chlorides are the reagents of choice for acylation reactions, which add an acyl group ($\text{RCO}-$) to a compound. The reaction of an alcohol with an acid chloride can replace the hydrogen atom of the

alcohol's hydroxyl group with the acyl group to form the corresponding ester (RCOOR'), with hydrogen chloride (HCl) as a by-product. Similarly, the reaction of an acid chloride with ammonia (NH_3) or an amine will readily form the corresponding amide compounds. For example, the reaction of octanoyl chloride ($\text{C}_7\text{H}_{15}\text{COCl}$), a derivative of octanoic acid, with dimethylamine (CH_3NHCH_3) produces *N,N*-dimethyloctanamide ($\text{C}_7\text{H}_{15}\text{CON}(\text{CH}_3)_2$), where the *N,N* prefix indicates that the two methyl groups ($-\text{CH}_3$) are attached to the nitrogen atom.

Perhaps the most important use of acid chlorides is in the formation of ketones by the acylation of benzene and benzene-like aromatic compounds via Friedel-Crafts acylation reactions, which use a Lewis acid such as aluminum trichloride (AlCl_3) or ferric chloride (FeCl_3) to catalyze the reaction. The reaction between propanoyl chloride ($\text{C}_2\text{H}_5\text{COCl}$) and benzene (C_6H_6), for example, produces the ketone propiophenone, officially named 1-phenyl-1-propanone and also known as ethyl phenyl ketone, according to the following diagram:



The by-product of this reaction is again hydrogen chloride, which is usually given off as a gas. The by-products of such reactions are not a consideration and are seldom, if ever, included in the equations.

Richard M. Renneboog, MSc

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ACIDS AND BASES

FIELDS OF STUDY

Physical Chemistry; Biochemistry; Chemical Engineering

SUMMARY

The characteristics of acids and bases are discussed, and the progressive theories of Svante Arrhenius, Johannes Brønsted and Thomas Lowry, and Gilbert N. Lewis are described. The relationship of pH and acidity or basicity, and the technique of titration are presented in detail.

PRINCIPAL TERMS

- **Brønsted-Lowry acid-base theory:** definitions of acids and bases developed separately in 1923 by Danish chemist Johannes Nicolaus Brønsted and English chemist Martin Lowry; defines an acid as any compound that can release a hydrogen ion and a base as any compound that can accept a hydrogen ion.
- **dissociation:** the separation of a compound into simpler components.
- **equilibrium constant:** a numerical value characteristic of a particular equilibrium reaction, defined as the ratio of the equilibrium concentration of the products to that of the reactants..
- **Lewis acid-base theory:** definitions of acids and bases developed in 1923 by American chemist Gilbert N. Lewis; defines an acid as any chemical species that can accept an electron pair and a base as any chemical species that can donate an electron pair.
- **pH:** a numerical value that represents the acidity or basicity of a solution, with 0 being the most acidic, 14 being the most basic, and 7 being neutral.
- **protonation:** the addition of a proton, in the form of a hydrogen cation (H^+), to an atom, ion, or molecule.

THE NATURE OF ACIDS AND BASES

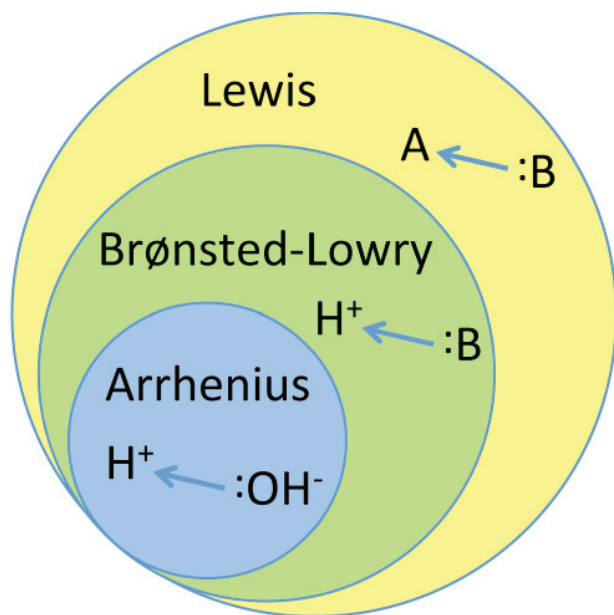
Acidity and basicity are concepts that refer to both the tactile nature of the respective solutions and the

nature of their chemical activity. Acidic solutions, such as vinegar and lemon juice, typically have a distinctly sour taste, an irritating smell, and a “sticky” feel between the fingers. Basic solutions, such as ammonia-based window cleaners and household bleach, typically have a bitter taste, pungent smell, and a “slippery-oily” feel between the fingers. While tasting, inhaling, and touching acidic and basic solutions is most definitely not recommended, historically this is precisely how early chemists experienced different materials before there was any workable theory of atomic structure to explain the properties and reactions of different compounds. In everyday life, some such experiences are unavoidable, especially with regard to foods. Indeed, many food flavors depend on the acidity or basicity of the particular condiment or other foodstuff. One cannot, for example, make pickles without vinegar (acetic acid) or fluffy pancakes without baking soda (sodium bicarbonate).

The essential differences between acidic and basic solutions have been recognized for centuries but could not be explained adequately before an understandable and workable model of atomic structure. In the 1880s, Svante Arrhenius (1859–1927) recognized that salts dissociate into charged ions in solution with water. In 1887, long before subatomic particles such as protons were discovered and identified, he defined an acid as a compound that could generate hydrogen ions in solution and a base as a compound that could generate hydroxide ions in solution. Arrhenius’s theory was the first to explain both acidity and basicity at the atomic level.

In 1923, Johannes Brønsted (1879–1947) and Thomas Lowry (1874–1936) simultaneously and independently defined acids as compounds that can donate hydrogen ions (H^+), or protons, and bases as compounds that can accept them. This is known as Brønsted-Lowry acid-base theory. Accordingly, a base that has accepted a hydrogen ion can then act as an acid by protonating another compound, and an acid that has donated a hydrogen ion can act as a base by accepting a hydrogen ion from another compound. This fact is the basis of conjugate acids and bases.

Also in 1923, American chemist Gilbert N. Lewis (1875–1946) published a more comprehensive definition of acids and bases that applied to both organic



The relationship between Arrhenius, Lewis, and Brønsted-Lowry acid-base theories. By Tem5psu via Wikimedia Commons

and inorganic chemistry. According to Lewis's definition, a base is a compound that has a lone pair of electrons that can be used to complete the valence group of another atom, and an acid is a compound that can use a lone pair of electrons from another atom to complete its own valence group. This Lewis acid-base theory was a direct result of Lewis's earlier work in valence theory and did much to unify the science of chemistry by providing a set of theoretical principles common to both organic and inorganic chemistry.

ACIDS, BASES, WATER, AND PH

Water is unique in its molecular structure, physical and chemical properties, and interaction with other materials. The water molecule has two hydrogen atoms bonded to an oxygen atom. As an element in the second period of group 16 of the periodic table, the oxygen atom has six electrons in its valence shell. The bonds to the two hydrogen atoms give the oxygen atom a filled valence-shell electron configuration of eight. According to the valence-shell electron-pair repulsion (VSEPR) principle, the $2s$ and $2p$ orbitals that contain those eight electrons, arranged in four pairs, hybridize to form four equivalent sp^3 hybrid atomic orbitals oriented to the four apexes of a tetrahedron. This arrangement of atomic orbitals

arises from the force of electrostatic repulsion experienced between the pairs of like-charged electrons. Two of these orbitals form the bonds to the hydrogen atoms; the other two orbitals are not involved in bonds, and each contains a pair of free electrons, often called a lone pair. This imparts a high degree of polarity to the water molecule, as the lone pairs create a region of high negative charge. In addition, the electrons from the hydrogen atoms are localized in the oxygen-hydrogen bonds, exposing the positive charge of the hydrogen nuclei. This charge separation in the molecule is known as a dipole moment. Water molecules can therefore act somewhat like bar magnets and stick to each other, positive charge to negative charge. The cohesion between the water molecules that results from dipole-dipole interaction gives water an extraordinarily high boiling point relative to its molecular weight.

In liquid water, water molecules undergo dissociation as described by the autolysis equilibrium equation:



The concentration of both the acid hydronium ions (H_3O^+) and the base hydroxide ions (OH^-) is exactly equal, as required by the balanced reaction equation, and liquid water is neither acidic nor basic but neutral. Experimental analysis has determined that the concentration of both is 10^{-7} moles per liter, or molar (M). The equilibrium dissociation constant for the reaction is determined as:

$$pK_{\text{eq}} = [\text{H}_3\text{O}^+][\text{OH}^-] = (10^{-7})(10^{-7}) = 10^{-14}$$

where $[x]$ is the concentration of x in molar. Since this is an equilibrium reaction, addition of any material that increases the concentration of one ion must decrease the concentration of the other ion while maintaining the value of the equilibrium constant (K_{eq}) at 10^{-14} . This is the foundational principle of the pH scale.

The pH of an aqueous solution is defined by the following equation:

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

(The notation $[\text{H}^+]$ is often used instead of $[\text{H}_3\text{O}^+]$, though the latter form is more accurate.) The pH

scale is a logarithmic scale, such that every increase of one unit of pH corresponds to a tenfold change in the concentration of hydronium ions. The use of logarithmic values greatly simplifies calculations of both acid and base concentrations. The logarithm, or log, of a value is the exponent, or power, to which a base number must be raised to produce that value. For example, the log of 10^3 is 3.

The ease of using logs comes from the power rules of mathematics. When multiplying two numbers, their respective powers are added together. For example, 100 multiplied by 1,000 is 100,000; in scientific notation, this is written as $10^2 \times 10^3 = 10^5$. Observe that the sum of the first two exponent values, 2 and 3, is equal to the third exponent value, 5. Conversely, when dividing two values, their exponents are subtracted from each other. Returning to the autolysis equilibrium of water, the logarithmic expression of the equation for the equilibrium constant of the process is as follows:

$$\log(10^{-14}) = \log(10^{-7})(10^{-7}) = (-7) + (-7)$$

By using the p-scale relationship, this becomes:

$$-\log(10^{-14}) = -\log(10^{-7})(10^{-7}) = -[(-7) + (-7)]$$

$$pK_{\text{eq}} = p[\text{H}_3\text{O}^+] + p[\text{OH}^-] = 7 + 7 = 14$$

Since the concentration of hydronium and hydroxide ions in water is in equilibrium, the pH and the pOH must always add up to the neutral value of 14. Adding any material that changes the concentration of either ion causes the concentration of the other ion to shift to compensate and restore the equilibrium condition. Thus, adding an acid material such as hydrochloric acid (HCl) increases the hydronium concentration and forces the hydroxide concentration to decrease by the same amount to maintain the equilibrium constant. Similarly, adding sodium hydroxide (NaOH) increases the hydroxide concentration and causes the hydronium concentration to decrease by the same amount.

TITRATION

Titration is an extremely useful technique for determining the concentration of a solution by comparing it to another solution of known concentration. The

SAMPLE PROBLEM

Rank the following aqueous solutions in order of increasing acidity:

- vinegar, pOH = 10.6
- beer, pH = 4.6
- grapefruit juice, pH = 3.2
- 0.05 M oxalic acid, pOH = 12.4
- 1 M sodium hydroxide, pOH = 0
- 1 M hydrochloric acid, pH = 0.1
- 0.01 M potassium hydroxide, $[\text{H}_3\text{O}^+] = 10^{-12}$ M
- blood plasma, $[\text{H}_3\text{O}^+] = 3.9 \times 10^{-8}$ M

Answer:

Using the relationship $\text{pH} + \text{pOH} = 14$, one can solve for the pH of a substance by subtracting its known pOH from 14. Thus, the pH of vinegar is 3.4, the pH of the oxalic acid solution is 1.6, and the pH of the sodium hydroxide solution is 14.

Using the definition of pH as $-\log[\text{H}_3\text{O}^+]$, the pH of the potassium hydroxide solution is 12, and the pH of blood plasma is 7.4.

Since the more acidic a solution is, the lower its pH is, then the above solutions are ranked from most acidic to least acidic as:

1. 1 M hydrochloric acid, pH = 0.1
2. 0.05 M oxalic acid, pH = 1.6
3. grapefruit juice, pH = 3.2
4. vinegar, pH = 3.4
5. beer, pH = 4.6
6. blood plasma, pH = 7.4
7. 0.01 M potassium hydroxide, pH = 12
8. 1 M sodium hydroxide, pH = 14

process entails a single, very controlled reaction that has a well-defined end point. First, a standard reference compound is weighed accurately and made up to a solution of precise volume. This solution, called the titrant, is then used to carefully neutralize a sample of an unknown solution of approximately the same concentration, called the analyte. The amount of titrant used to attain the precise end point of the acid-base neutralization reaction, along with its concentration, reveals the precise concentration of the analyte. Since most acid and base solutions are clear and colorless, the pH of the reacting solution is closely monitored either electronically or with an

indicator compound that changes color at a specific pH. The titrant is added to the analyte using a burette, a cylinder marked with a precise volumetric scale. The end of the burette is fitted with a stopcock and dropping tip, allowing the user to strictly control the amount of titrant that is meted out.

Richard M. Renneboog, MSc

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ACIDS AND BASES: BRØNSTED-LOWRY THEORY

FIELDS OF STUDY

Physical Chemistry; Inorganic Chemistry; Chemical Engineering

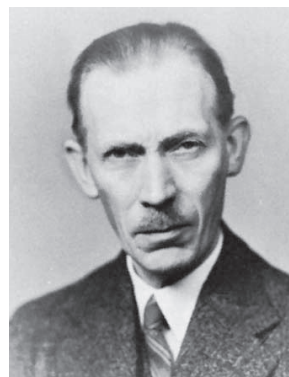
SUMMARY

The basic properties of acids and bases according to the Brønsted-Lowry theory are elaborated. Acidity and basicity (or alkalinity) are measured using the pH scale, which charts the concentration of H⁺ ions relative to pure water.

PRINCIPAL TERMS

- **amphoterism:** the ability of a compound to act as either an acid or a base, depending on its environment and the other materials present.
- **conjugate pair:** an acid and the conjugate base that is formed when it donates a proton, or a base and the conjugate acid that is formed when it accepts a proton.
- **hydronium ion:** a polyatomic ion with the formula H₃O⁺, formed by the addition of the hydrogen cation (H⁺) to a molecule of water; also called oxonium (IUPAC preference) or hydroxonium.
- **proton acceptor:** a compound or part of a chemical compound that has the ability to accept a proton (H⁺) from a suitably acidic material in a chemical reaction.

- **proton donor:** a compound or part of a chemical compound that has the ability to relinquish a proton (H⁺) to a suitably basic material in a chemical reaction.



Johannes Nicolaus Brønsted,
a Danish physical chemist.

Peter Elfelt via Wikimedia Commons

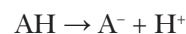


Thomas Martin Lowry

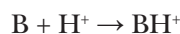
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THE NATURE OF THE BRØNSTED-LOWRY ACIDS AND BASES

In 1923, chemists Johannes Nicolaus Brønsted (1879–1947) and Thomas Martin Lowry (1874–1936) defined acids and bases in a straightforward way. Simply stated, an acid, a proton donor, is any compound that can release a proton from its molecular structure:

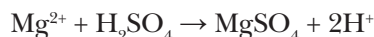


A base is a proton acceptor, any compound that can accept a proton from another compound:

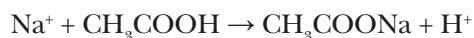


Acids that act in this way are termed “protic” acids, since the H^+ cation is identically a proton. For most practical purposes, this definition is sufficient, as most water-soluble acids are either protic or amphiprotic compounds. (Amphoterism is the ability of a compound to act as either an acid or a base, depending on its environment and the other materials present.)

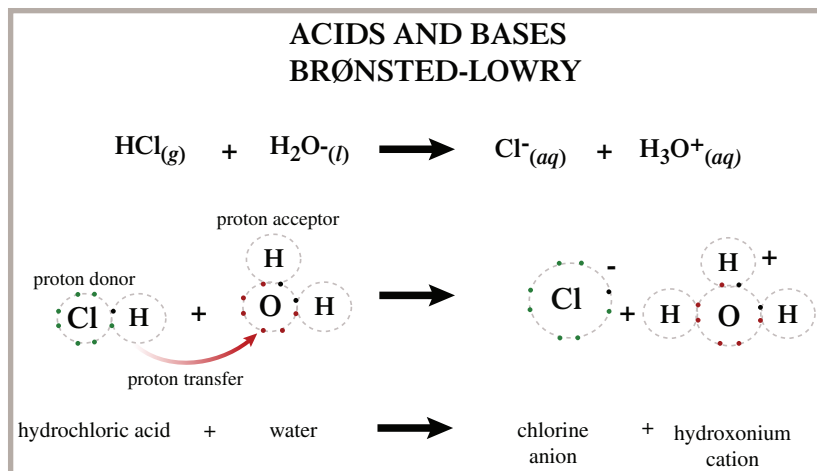
The Brønsted-Lowry definition refines those formulated before the development of the modern atomic theory. In 1838, Justus von Liebig (1803–73) described acids as materials containing hydrogen that could be replaced by a metal, which indeed they are. The acidic hydrogen atom on compounds such as the inorganic sulfuric acid and the organic acetic acid is easily replaced by metal ions such as magnesium to form magnesium sulfate ($MgSO_4$) or sodium to form sodium acetate ($C_2H_3NaO_2$). The corresponding equations are as follows:



and



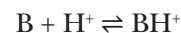
Svante Arrhenius (1859–1927) first elucidated the definition of acids and bases as specifically forming hydrogen ions and hydroxide ions in aqueous solutions. This statement seems to limit the identity of acids and bases to protic acids and hydroxide salts. The Brønsted-Lowry definition, however, recognizes that acidic and alkaline behaviors are complementary actions of the same fundamental molecular structure. That is, a compound that releases a proton in acting as an acid produces a corresponding anion as its conjugate base. An acid and its conjugate base are a conjugate pair and do not exist in isolation from each other in an equilibrium system. Accordingly,



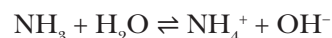
both the acid and base equations above should be properly written as follows:



and



These equations more clearly demonstrate the conjugate relationship of the various components, and they include such compounds as ammonia, which do not dissociate into ions in solution. When dissolved in water, ammonia accepts a proton from the water molecules, according to the following equation:



and so acts as a base without itself dissociating to release a hydroxide ion, as would be required by the Arrhenius definition.

MEASURING ACIDS AND BASES: THE pH SCALE

Equal molar quantities of different acids do not produce equally acidic solutions. The conjugate nature of the components of an acid dissociation equilibrium is an important factor in determining the acidity of the resulting solution. Hydrogen chloride and nitric acid, for example, are completely dissociated into ions in aqueous solutions, but acetic acid and other organic acids generally do not dissociate completely in solution. The resulting solutions all

SAMPLE PROBLEM

The material corresponding to the chemical formula AlH_3O_3 is an amphoteric compound and can act as either the base aluminum hydroxide, $\text{Al}(\text{OH})_3$, or the acid aluminic acid, H_3AlO_3 , both of which have the same molecular structure. Write the equations describing both modes of activity and identify the conjugate pairs in each case.

Answer:

As a base, the reaction releases OH^- from the compound by cleaving the $\text{Al}-\text{O}$ bond, as



The chemical species $\text{Al}(\text{OH})_2^+$ is the conjugate acid of the base $\text{Al}(\text{OH})_3$.

As an acid, the reaction releases a proton by cleaving an $\text{O}-\text{H}$ bond rather than an $\text{Al}-\text{O}$ bond, as



The chemical species $^-\text{OAl}(\text{OH})_2$ is the conjugate base of the acid $\text{Al}(\text{OH})_3$.

have different concentrations of H^+ ions and, thus, different acidities. As the most common material on the planet, water is the standard by which H^+ ion concentrations are measured. The structure of the water molecule allows it to dissociate into its component ions in solution without the participation of a second material (a process known as “autolysis”), according to the following equation:



In pure water, this equilibrium produces equal quantities of both H^+ and OH^- . The quantity of each has been determined experimentally to be 10^{-7} moles per liter (M). Solutions in which the concentration of H^+ , $[\text{H}^+]$, is greater than 10^{-7}M are acidic, while those in which $[\text{H}^+]$ is less than 10^{-7}M are alkaline. The pH scale was developed as a simple means of communicating the $[\text{H}^+]$ of an aqueous solution. The pH of an aqueous solution is defined as follows:

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

Because the $[\text{H}^+]$ of pure water is 10^{-7}M , the pH of pure water is defined as +7. A solution of HCl in water is hydrochloric acid, characterized by the complete dissociation of HCl into H^+ and Cl^- ions. Because hydrochloric acid has an $[\text{HCl}]$ of 0.01M , it also has a $[\text{H}^+]$ of 0.01M , or 10^{-2}M . Therefore, the corresponding pH is +2. Similarly, a solution in which the $[\text{H}^+]$ is 10^{-9}M , for example, has a pH of +9.

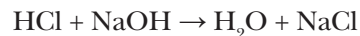
A complementary scale, the pOH scale, can be used for alkaline solutions, based on the following identical relationship:

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

Since the concentration of H_2O in pure water is always a strictly constant value, the relationship $[\text{H}^+][\text{OH}^-]$ must also be as strictly constant. In pure water, this p-scale value is the equilibrium constant of the autolysis reaction, with the value $(10^{-7})(10^{-7})$, or 10^{-14} . Therefore, in any aqueous solution the product $[\text{H}^+][\text{OH}^-]$ must also always be 10^{-14} . If the $[\text{H}^+]$ is greater than 10^{-7}M , the equilibrium of the autolysis reaction requires that the $[\text{OH}^-]$ be reduced by the corresponding amount. (When two numbers are multiplied together, their logarithmic values combine.) Thus, the value of the autolysis equilibrium is $7 + 7 = 14$ (the pH and the pOH of a solution must always add up to 14). Normally, aqueous acid solutions have pH between 1 and 7, corresponding to $[\text{H}^+]$ in the range of 10^{-1} to 10^{-7} . A pH with a value of 0 or less is also possible. A 10M solution of HCl, for example, has $[\text{H}^+]$ of 10^1M and a corresponding pH of -1 .

ACID-BASE NEUTRALIZATION REACTIONS

The goal of a neutralization reaction is to bring the pH of a particular solution to the neutral pH of 7. The product of any neutralization reaction is a salt. This is easily seen in the neutralization reaction of hydrochloric acid, HCl, with sodium hydroxide, NaOH:



By adding hydrochloric acid to a solution of sodium hydroxide to the point at which the pH is 7, one ends up with a solution of plain “salt water,” NaCl in H_2O . This process is called “titration” and is a common laboratory method for determining the precise $[\text{H}^+]$ of a solution. The technique can also be used to analyze many other materials by determining

the end point or equivalence point of a specific reaction. The technique depends on a means of monitoring the change in pH of the solution as acid or base is added. This has traditionally been done by using litmus paper or another indicator material that changes color according to the pH, but this method has been superseded by electronic devices that can measure the pH directly and display the measured values in graphic form.

Richard M. Renneboog, MSc

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ACTINIDES

FIELDS OF STUDY

Inorganic Chemistry; Nuclear Chemistry

SUMMARY

The basic properties and characteristics of the actinide elements are presented. The actinides are the elements with atomic numbers from 89 (actinium) to 103 (lawrencium) and are characterized by having an incomplete $5f$ shell as well as electrons in the $6d$ and $7s$ shells. All actinides are radioactive.

PRINCIPAL TERMS

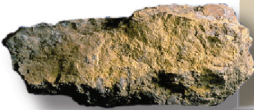
- **f-block:** the portion of the periodic table containing the elements with incompletely filled orbitals; includes all lanthanides (excluding lutetium) and actinides (excluding lawrencium).
- **oxidation state:** a number that indicates the degree to which an atom or ion in a chemical compound has been oxidized or reduced.
- **pyrophoricity:** a property of some solids and liquids that causes them to spontaneously combust when exposed to air.
- **radioactivity:** the emission of subatomic particles due to the spontaneous decay of an unstable atomic nucleus, the process ending with the formation of a stable atomic nucleus of lower mass.

THE NATURE OF THE ACTINIDES

All of the actinides reside in the f-block of the periodic table, though it is a matter of some debate whether one of the actinides, either actinium or lawrencium, should be considered a d-block element instead. The f-block elements are characterized by having their valence electrons in the f orbitals, with some of the outer d -orbitals being incompletely filled. This arrangement of electrons is responsible for the multivalent nature of actinides, enabling them to form compounds in which they have taken on different oxidation states; in other words, the atoms can lose or gain different numbers of electrons in order to form chemical bonds. Actinides characteristically lose electrons in order to form positively charged ions, or cations.

All of the actinides are scarce metals, with only thorium and uranium, and to a lesser extent plutonium, qualifying as primordial elements, meaning they have existed in the universe since before the earth was formed. All other actinides are trace elements that either occur in nature through radioactive decay or were synthesized in the laboratory through nuclear reactions in high-energy particle accelerators. All of the actinides are characterized by radioactivity. They also all display pyrophoricity, meaning that fine particles or shavings of them ignite on contact with air, appearing as a spark.

ACTINIDES

												<div style="border: 1px solid black; padding: 5px; background-color: #f0f0f0;"> <p style="margin: 0;">92 U uranium 238</p> </div>											
1 H hydrogen 1																	2 He helium 4						
3 Li lithium 7	4 Be beryllium 9																	5 B boron 11	6 C carbon 12	7 N nitrogen 14	8 O oxygen 16	9 F fluorine 19	10 Ne neon 20
11 Na sodium 23	12 Mg magnesium 24																	13 Al aluminum 27	14 Si silicon 28	15 P phosphorus 31	16 S sulfur 32	17 Cl chlorine 35	18 Ar argon 40
19 K potassium 39	20 Ca calcium 40	21 Sc scandium 45	22 Ti titanium 48	23 V vanadium 51	24 Cr chromium 52	25 Mn manganese 55	26 Fe iron 56	27 Co cobalt 59	28 Ni nickel 59	29 Cu copper 64	30 Zn zinc 65	31 Ga gallium 70	32 Ge germanium 73	33 As arsenic 75	34 Se selenium 79	35 Br bromine 80	36 Kr krypton 84						
37 Rb rubidium 85	38 Sr strontium 88	39 Y yttrium 89	40 Zr zirconium 91	41 Nb niobium 93	42 Mo molybdenum 96	43 Tc technetium 98	44 Ru ruthenium 101	45 Rh rhodium 103	46 Pd palladium 106	47 Ag silver 108	48 Cd cadmium 112	49 In indium 115	50 Sn tin 119	51 Sb antimony 122	52 Te tellurium 128	53 I iodine 127	54 Xe xenon 131						
55 Cs caesium 133	56 Ba barium 137	*	72 Hf hafnium 178	73 Ta tantalum 181	74 W tungsten 184	75 Re rhenium 186	76 Os osmium 190	77 Ir iridium 192	78 Pt platinum 195	79 Au gold 197	80 Hg mercury 201	81 Tl thallium 204	82 Pb lead 207	83 Bi bismuth 209	84 Po polonium 209	85 At astatine 210	86 Rn radon 222						
87 Fr francium 223	88 Ra radium 226	**	104 Rf rutherfordium 267	105 Db dubnium 268	106 Sg seaborgium 271	107 Bh bohrium 272	108 Hs hassium 270	109 Mt meitnerium 276	110 Ds darmstadtium 281	111 Rg roentgenium 280	112 Cn copernicium 285	113 Uut ununtrium 284	114 Fl flerovium 289	115 Uup ununpentium 288	116 Lv livermorium 293	117 Uus ununseptium 294	118 Uuo ununoctium 289						
57 * La lanthanum 139	58 Ce cerium 140	59 Pr praseodymium 141	60 Nd neodymium 144	61 Pm promethium 145	62 Sm samarium 150	63 Eu europium 152	64 Gd gadolinium 157	65 Tb terbium 159	66 Dy dysprosium 163	67 Ho holmium 165	68 Er erbium 167	69 Tm thulium 168	70 Yb ytterbium 173	71 Lu lutetium 175									
89 ** Ac actinium 227	90 Th thorium 232	91 Pa protactinium 231	92 U uranium 238	93 Np neptunium 237	94 Pu plutonium 244	95 Am americium 243	96 Cm curium 247	97 Bk berkelium 247	98 Cf californium 251	99 Es einsteinium 252	100 Fm fermium 257	101 Md mendelevium 258	102 No nobelium 259	103 Lr lawrencium 264									

ATOMIC STRUCTURE OF THE ACTINIDES

The f orbitals are presently the highest atomic orbitals in the known elements of the periodic table. When the atoms ionize, however, the $6d$ and $7s$ electrons are removed first. At this energy level, the $5f$, $6d$, and $7s$ levels are very similar in energy, and their distance from the atomic nucleus means that they have relatively low ionization energies and therefore easily form ions. This is because the farther an electron orbital is from the nucleus, the less force the positively charged protons exert on the negatively charged electrons to hold them in place.

The radioactive nature of the actinides and the scarcity of many of them make the study of these elements very difficult, and little is known about their chemical behavior. Of those that have been studied in some detail, the atoms have been observed to be

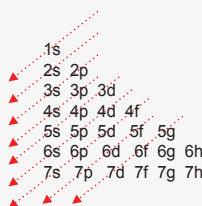
multivalent, with oxidation states ranging between +2 and +7. The +3 oxidation state is most common overall, having been observed in all of the actinides, but it is not always the most stable.

ACTINIDE COMPOUNDS

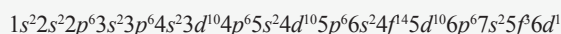
Of the actinide elements, only uranium and thorium occur in sufficient abundance to be economically useful. They are mined and smelted most commonly from the ore known as pitchblende (uraninite). Uranium occurs naturally in the form of various radioactive isotopes, or radioisotopes, with uranium-238 and uranium-235 being the most common. The small difference in atomic mass between the two isotopes is sufficient to permit their separation by physical means. Uranium forms various compounds with fluorine, all of which convert when heated to

SAMPLE PROBLEM

Use the chart below, which shows the order in which electron orbitals are filled, to determine the electron distribution of uranium (atomic number 92) and lawrencium (atomic number 103). Follow the arrows from top to bottom, keeping in mind that *s* orbitals can hold a maximum of two electrons, *p* orbitals hold six electrons, *d* orbitals hold ten electrons, and *f* orbitals hold fourteen electrons. Which electrons are the valence electrons?

**Answer:**

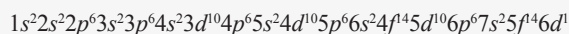
The total number of electrons in each element is equal to the atomic number of the element. Thus, uranium has ninety-two electrons, ordered as follows:



In this notation, the exponents tell how many electrons are in each orbital. One would expect the *5f* orbital to fill completely before any electrons appear in the *6d* orbital, but this is not the case for many actinides, which is what gives them the ability to take different oxidation states. Because the *5f* and *6d* orbitals are so far from the nucleus, at least on a subatomic scale, the difference in energy levels required to occupy each one is much smaller than in lower orbitals, so electrons can easily move between them as needed to make the atom more stable. There is no simple way to determine the exact distribution of valence electrons in these higher orbitals without additional information.

Uranium has six valence electrons, in the *5f*, *6d*, and *7s* orbitals. Atoms form ions in order to attain stable electron configurations, which are represented by the electron distributions of the noble gases (helium, neon, argon, krypton, xenon, and radon). The electron distributions of all elements apart from hydrogen can also be conveyed by putting the symbol of the noble gas immediately preceding the element in brackets, followed by the extra electrons not contained in the noble gas. For example, the last noble gas before uranium in the periodic table is radon, which has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6$, so the electron configuration of uranium can be written as $[\text{Rn}]7s^2 5f^6 6d^1$. For elements in the *f*-block, the valence electrons are the ones outside the noble gas configuration, as these are the electrons the uranium atom would have to lose to achieve a stable electron configuration.

Lawrencium has 103 electrons, ordered as follows:



Unlike uranium, lawrencium follows the expected pattern of filling the *5f* orbital completely before starting to fill the *6d* orbital. It has seventeen valence electrons, again in the *5f*, *6d*, and *7s* orbitals.

the compound uranium hexafluoride, UF_6 , which becomes a gas at 56.5 degrees Celsius (134 degrees Fahrenheit). Using differential diffusion in gas centrifuges, the uranium hexafluoride becomes enriched with the lighter isotope uranium-235. The enriched metal can then be recovered from the cooled "yellowcake" and used as the fuel of nuclear reactors. Further enrichment to increase the proportion

of uranium-235 produces so-called weapons-grade uranium, capable of undergoing the nuclear-fission chain reaction that produces a nuclear explosion.

In a nuclear reactor, a controlled fission process is maintained in which the nuclei of the uranium-235 atoms decay rapidly. The energy released is used indirectly to produce steam to drive turbines for electrical-power generation. The process gradually

depletes the amount of uranium-235 in the fuel rods until they are spent. At that point the rods must be replaced. The spent rods are still highly radioactive, however, and safe storage is problematic, as the natural half-life of uranium-235 is more than seven hundred million years.

One particular type of nuclear reactor, called a breeder reactor, uses both uranium-238 and thorium-232 in a fission process that results in the formation of the isotopes plutonium-239 and plutonium-233. The advantage of breeder reactors is that they can generate more fissionable fuel material than they consume. On the other hand, plutonium is far more toxic than uranium, and plutonium-239's half-life of around twenty-four thousand years poses a very serious environmental hazard.

ACTINIDES IN DAILY LIFE

The best-known applications of actinides are in nuclear power and nuclear weapons, which typically use uranium, plutonium, or to a lesser extent thorium. However, some of the rarer elements in this group, although highly radioactive and toxic, have a few practical uses as well. Some actinides are used in alloys and for components in high-end scientific instrumentation. Actinium (atomic number 89) and californium (atomic number 98) have uses in cancer treatment. Americium (atomic number 95) is perhaps the only actinide commonly found in households, as it is a component of some kinds of smoke detectors. Tiny amounts of curium (atomic number 96) have been

used to power cardiac pacemakers. Most of the other actinides have no known practical use outside of scientific research.

Richard M. Renneboog, MSc

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ACTIVATION ENERGY

FIELDS OF STUDY

Physical Chemistry; Inorganic Chemistry;
Biochemistry

SUMMARY

The activation energy of a process is defined, and its importance in chemical processes is elaborated. Activation energy is a widely variable quantity in different reactions but is nevertheless characteristic of any specific reaction process.

PRINCIPAL TERMS

- **Arrhenius equation:** a mathematical function that relates the rate of a reaction to the energy required to initiate the reaction and the absolute temperature at which it is carried out.
- **catalyst:** a chemical species that initiates or speeds up a chemical reaction but is not itself consumed in the reaction.
- **chemical reaction:** a process in which the molecules of two or more chemical species interact with each other in a way that causes the electrons in the bonds between atoms to be rearranged,