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Solvents

Aqueous solvent

Since aqueous solutions are of particular importance in the laboratory and in the physiology of animals and plants, it is appropriate to consider them separately. The ion product of water, $K_w = [H_3O^+][OH^-]$, has the value 1.0×10^{-14} mole^{2}litre^{-2} at 25 °C, but it is strongly temperature-dependent, becoming 1.0×10^{-15} at 0 °C and 7×10^{-13} at 100 °C. In principle the value of K_w can be determined by measuring the electrical conductance of very pure water, in which $[H_3O^+] = [OH^-] = 10^{-7}$ at 25 °C, but in practice it is derived from other measurements—for example, measurements of the degree of hydrolysis of salts. For an uncharged acid, in this example acetic, the dissociation constant is given by the following expression:

$$\frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = K_a$$

For acetic acid, K_a has the value 1.76×10^{-5} at 25 °C. The dissociation constant may be expressed in terms of the degree of dissociation of the acid. This quantity, represented by the Greek letter alpha, α, is equal to the fraction of the acid that appears in dissociated form—in this case as the ions $CH_3CO_2^-$ and H_3O^+. If the initial concentration of acid is designated by c, then the concentrations of the ions are each equal to αc, or $[H_3O^+] = [CH_3CO_2^-] = \alpha c$, and the concentration of undissociated acid is equal to $c(1 - \alpha)$, or $[CH_3CO_2H] = c(1 - \alpha)$.

Substituting these expressions into the equation giving the value of the dissociation constant gives
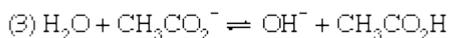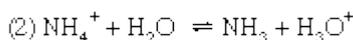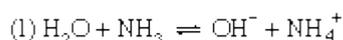
$$\alpha^2 c/(1-\alpha) = K_a.$$

From this equation it can be inferred that the degree of dissociation (α) increases with decreasing concentration (c). For small degrees of dissociation ($\alpha << 1$), the equation becomes

$$\alpha = K_a^{1/2}/c^{1/2} ;$$

whereas, at sufficiently low concentrations ($c << 1$), α tends to unity ($\alpha \rightarrow 1$).

Discussions exactly analogous to this apply to a number of other acid–base equilibria—for example, (1) the dissociation of ammonia in water, (2) the hydrolysis of ammonium salts, and (3) the hydrolysis of an acetate.

$$(1)\ H_2O + NH_3 \rightleftharpoons OH^- + NH_4^+$$

$$(2)\ NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

$$(3)\ H_2O + CH_3CO_2^- \rightleftharpoons OH^- + CH_3CO_2H$$

For reaction (1) α is the degree of dissociation of ammonia, and the dissociation constant is K_b, the basic dissociation constant. In reaction (2), the hydrolysis of an ammonium salt (for example, ammonium chloride), α would be termed the degree of hydrolysis and K the hydrolysis constant. In terms of the general definition of acids and bases, however, K could equally be called the acidity constant for the acid–base pair NH_4^+–NH_3, and this is a more rational way of describing the process. Finally, reaction (3) represents the hydrolysis of an acetate (for example, sodium acetate); the resulting equilibrium constant is termed the hydrolysis constant and can be seen to equal K_w/K_a, where K_w is the ion product of water and K_a the acidity constant for the acid–base pair CH_3CO_2H–$CH_3CO_2^-$ (i.e., the dissociation constant of acetic acid). The investigation of equilibria such as this is, in fact, one of the methods for determining the value of K_w .

The equilibria considered so far arise when one component of an acid–base pair is dissolved in water—if necessary, along with an ion, such as Na^+ or Cl^-, having negligible acid–base properties. The direct consequence of this is that the two new species produced (for example, those on the right-hand sides of the equations [1–3] above) have equal concentrations (αc), and hence the previously given equation

$$K = \frac{\alpha^2 c}{1 - \alpha}$$

is applicable.

A solution of a more generally useful type can be obtained by deliberately varying the proportions of acid and base present; such a solution is called a buffered solution or, somewhat more colloquially, a buffer. A buffered solution containing various concentrations of acetic acid and acetate ion, for example, can be prepared by mixing solutions of acetic acid and sodium acetate, by partially neutralizing a solution of acetic acid with sodium hydroxide, or by adding less than one equivalent of a strong acid to a solution of sodium acetate. Similarly, a buffer based on the pair NH_4^+–NH_3 can be prepared by mixing solutions of ammonia and an ammonium salt, by partially neutralizing a solution of ammonia with a strong acid, or by adding less than one equivalent of sodium hydroxide to a solution of an ammonium salt. The hydrogen ion concentration in a buffer solution is, of course, still given by the usual equation, which is conveniently written as

$$[H_3O^+] = K_a \frac{[A]}{[B]}.$$

Since hydrogen ion concentrations are usually less than unity and cover an extremely wide range, it is often convenient to use instead the negative logarithm of the actual concentration, a figure that varies usually only in the range 1–13. This figure is termed the pH, and its definition is expressed by the equation $pH = -\log_{10}[H_3O^+]$. For example, in pure water $[H_3O^+] = 1 \times 10^{-7}$, with the result that the pH = 7.0. The same term can be applied to alkaline solutions; thus, in 0.1 molar sodium hydroxide $[OH^-] = 0.1$, $[H_3O^+] = K_w/[OH^-] = 1 \times 10^{-14}/0.1 = 10^{-13}$, and pH = 13.0.

Applying the pH concept to buffered solutions gives the following equation:

$$\text{pH} = pK_a - \log_{10}\frac{[A]}{[B]},$$

known as the buffer ratio, can be calculated from the way in which the solution is prepared. According to this equation, the pH of the buffered solution depends only on the pK_a of the acid and on the buffer ratio. Most particularly it does not depend on the actual concentrations of A and B. Therefore, the pH of a buffered solution is little affected by dilution of the solution. It is also insensitive to the addition of acid or alkali, provided that the amounts added are much smaller than both [A] and [B]. This so-called buffering action will be impaired if either [A] or [B] becomes too small; hence, buffer ratios must not deviate too far from unity, and the effective buffering range of a given acid–base system is roughly from pH = pK_a + 1 to pH = pK_a − 1, corresponding to buffer ratios from 0.1 to 10.

Figure 1 shows the relation between pH and composition for a number of commonly used buffer systems. Effective buffer action is confined to the central, steep portion of each curve, where the pH is least sensitive to the composition. Figure 1 shows that an acid bearing several acidic hydrogens, such as phosphoric acid, can be used to prepare buffer solutions in several different pH ranges. Buffer action plays an important part in controlling the pH of many biological fluids; for example, the pH of the blood is controlled at about 7.4 by the carbonic acid–bicarbonate system shown in Figure 1. Buffers are widely used to control the pH in chemical or biological experiments. For the latter, the system $H_2PO_4^-$–HPO_4^{2-} is particularly useful, being effective in the physiological pH range, 6–8.
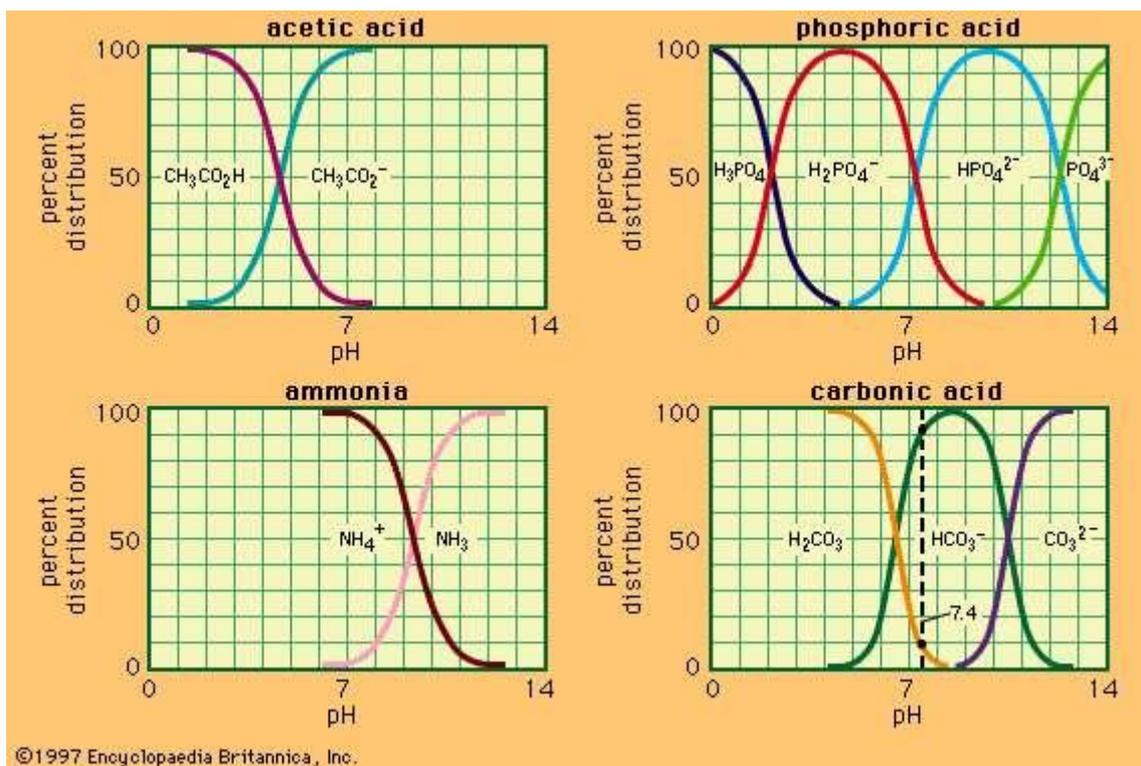
Figure 1: Relation between pH and composition for a number of commonly used buffer systems.*Encyclopædia Britannica, Inc.*

The same principles can be applied for the quantitative treatment of systems containing larger numbers of acid–base pairs; for example, in an aqueous solution of ammonium acetate, the following acid–base pairs must be considered: NH_4^+–NH_3, CH_3CO_2H–$CH_3CO_2^-$, H_3O–H_2O, and H_2O–OH^-. The situation is much more complicated in many solutions that are important in industry or in nature, but it is always possible to make a complete prediction of the state of the system in terms of the acidity constants K_a of each acid–base pair (provided, of course, that reactions other than proton transfers do not interfere).

Nonaqueous solvents

Although acid–base properties have been investigated most thoroughly in aqueous solutions, partly because of their practical importance, water is in many respects an abnormal solvent. In particular, it has a higher dielectric constant (a measure of the ability of the medium to reduce the force between two electric charges) than most other liquids, and it is able itself to act either as

an acid or as a [base](). The behaviour of acids and bases in several other solvents will be described briefly here.

The effect of the solvent on the [dissociation]() of acids or bases depends largely upon the basic or acidic properties of the solvent, respectively. Since many acid–base reactions involve an increase or decrease in the number of ions, they are also influenced by the dielectric constant of the solvent, for a higher dielectric constant favours the formation of ions. Finally, the specific [solvation]() (or close association with the solvent) of particular ions (excluding the solvation of the [proton]() to give SH_2^+, which is already included in the basicity of the solvent) may be important. It is usually not easy to separate these three effects and, in particular, the effects of dielectric constant and solvation merge into one another. These points are illustrated with examples of several of the more important solvents. In this discussion the solvents are classified as [amphoteric]() (both acidic and basic), acidic (in which the acidic properties are much more prominent than the basic), basic (in which the reverse is true), and aprotic (in which both acidic and basic properties are almost entirely absent). Finally, concentrated aqueous acids are mentioned as an example—a particularly important one—of mixed solvents.

Amphoteric solvents

The most important nonaqueous solvents of this class are the lower alcohols [methanol]() and [ethanol](). They resemble water in their acid–base properties but, because of their lower dielectric constants, facilitate processes producing ions to a much smaller extent. In particular, the ion products of these solvents are much smaller ($K_s = 10^{-17}$ for CH_3OH and 10^{-19} for C_2H_5OH, compared with 10^{-14} for water), and the dissociation constants of molecular acids and bases are uniformly lower than in water by four to five powers of 10. Nitric acid, for example, which is almost completely dissociated in water (K_a about 20), has $K_a = 2.5 \times 10^{-4}$ in methanol. On the other hand, the [equilibrium]() constants of processes such as $NH_4^+ + ROH \rightleftarrows NH_3 + ROH_2^+$ and $CH_3CO_2^- + ROH \rightleftarrows CH_3CO_2H + RO^-$ are similar in all three solvents, since they do not involve any change in the number of ions.

Acidic solvents

The most important strongly acidic solvent is [sulfuric acid](), which is able to protonate a wide variety of [compounds]() containing [oxygen]() or nitrogen. Thus, water, alcohols, [ethers](), ketones, nitro compounds, and sulfones all act as bases in sulfuric acid. This solvent must also possess some basic properties, because its ionic product is high ($[H_3SO_4^+]$ $[HSO_4^-]$ = 1.7 × 10^{-4}), but the basicity of the solvent is obscured normally by its very high acidity. For example, carboxylic acids behave as strong bases in sulfuric acid, reacting almost completely according to the equation $RCO_2H + H_2SO_4 \rightarrow RCO_2H_2^+ + HSO_4^-$. Many substances undergo reactions in sulfuric acid that are more complicated than simple proton transfers, often yielding species important because of their chemical reactivity. Thus, some alcohols produce carbonium ions in sulfuric acid; with triphenylcarbinol, for example, the reaction is $(C_6H_5)_3COH + 2H_2SO_4 \rightarrow (C_6H_5)_3 C^+ + H_3O^+ + 2HSO_4^-$. Nitric acid gives the nitronium ion, NO_2^+, according to the equation $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$. This ion frequently is the active agent in the nitration of organic compounds. Hydrogen fluoride has solvent properties resembling those of sulfuric acid but is less acidic and has negligible basic properties. [Acetic acid]() is another acidic solvent that has been extensively studied. Because of its low dielectric constant, ions exist in it largely in the form of ion pairs, and more complex associates are frequently formed. For this reason a quantitative interpretation of acid–base [equilibria]() in acetic acid is often difficult, but some general conclusions can be drawn. In particular, it can be seen that all substances more basic in water solution than aniline react completely with acetic acid according to the equation $B + CH_3CO_2H \rightarrow BH^+ + CH_3CO_2^-$. All such bases therefore give solutions with indistinguishable acid–base properties; this is often referred to as a levelling effect of the solvent. The converse is true for acids; for example, the strong mineral acids, nitric, hydrochloric, sulfuric, hydrobromic, and perchloric (HNO_3, HCl, H_2SO_4, HBr, and $HClO_4$) are "levelled" in aqueous solution by complete conversion to the hydronium ion, but in acetic acid they are [differentiated]() as weak acids with strengths in the approximate ratio 1:9:30:160:400.

Basic solvents

The only basic solvent that has been investigated in any detail is liquid [ammonia](), which has the very low ion product $[NH_4^+]$ $[NH_2^-]$

= 10^{-33}. As might be expected, this solvent has a marked levelling effect upon acids; thus, for example, acetic, benzoic, nitric, and hydrochloric acids all give solutions with identical acidic properties, owing to the ion NH_4^+, although, of course, in water they behave very differently.

Aprotic solvents

Strictly aprotic solvents include the hydrocarbons and their halogen derivatives, which undergo no reaction with added acids or bases. Acid–base equilibrium in these solvents can be investigated only when a second acid–base system is added; the usual reaction $A_1 + B_2 \rightleftarrows B_1 + A_2$ then takes place. Most such investigations have employed an indicator as one of the reacting systems, but the results are often difficult to interpret because of association of both ions and molecules in these media of low dielectric constant. The term *aprotic* has been extended recently to include solvents that are unable to lose a proton, although they may have weakly basic properties. Some of these aprotic solvents have high dielectric constants (for example, N, N-dimethylformamide, dimethyl sulfoxide, and nitrobenzene) and are good solvents for a variety of substances. They have a powerful differentiating effect on the properties of acids and bases. In particular, basic anions are poorly solvated in these solvents and thus behave as very strong bases; for example, it has been estimated that sodium methoxide dissolved in dimethyl sulfoxide gives a solution 10^9 times as basic as in methanol.

Concentrated aqueous acids

Dilute solutions of strong acids—for example, hydrochloric, sulfuric, and perchloric (HCl, H_2SO_4, $HClO_4$)—in water behave essentially as solutions of the ion H_3O^+, and their acidity increases in proportion to their concentration. At concentrations greater than about one molar (that is, one mole of acid per litre of solution), however, the acidity, as measured by action on indicators or by catalytic ability, increases much more rapidly than the concentration. For example, a 10 molar solution of any strong acid is about 1,000 times as acidic as a 1 molar solution. This behaviour is undoubtedly largely due to

the depletion of water with increasing concentration of acid; the hydronium ion, H_3O^+, is known to have a strong tendency to further hydration, probably mainly to the ion $H_3O^+(H_2O)_3$ (that is, $H_9O_4^+$), and a decrease in water content increases the proton-donating power of the solution. The acidity of these concentrated solutions is commonly measured by the acidity function, H_o, a quantity measured by the effect of the solvent on a basic indicator I. It is defined by $H_o + pK_{IH^+} - \log_{10} [IH^+]/[I]$ and becomes equal to the pH in dilute solution. The acidity function H_o frequently is found to be independent of the nature of the indicator and to give an approximate measure of the catalytic power of the acid solution. Mixtures of sulfuric acid and water ranging from 10 to 100 percent sulfuric acid have H_o values between −0.3 and −11.1, which corresponds to an acidity range of nearly 11 powers of 10.

Lewis acids

Much less information is available about Lewis acid–base equilibria than about ordinary acid–base equilibria, but it is clear that the situation is less simple for the former than for the latter. When a given Lewis acid reacts with a series of similarly constituted bases the equilibrium constants often vary in parallel with the conventional basic strengths. This is the case when a zinc halide, ZnX_2, for example, reacts with a series of amines. In general, however, it is not possible to arrange Lewis acids and bases in a unique order that will predict the extent to which a given pair will react. Thus, although the hydroxide ion (OH^-) is always a much stronger base than ammonia (NH_3) in reactions with proton acids, in reactions with the Lewis acid Ag^+, the complex $Ag(NH_3)_2^+$ is fairly stable, whereas AgOH is completely dissociated. Similarly, for some metal cations complex formation increases in the order fluoride < chloride < bromide < iodide, whereas for other metal cations the order is the reverse of this.

This kind of behaviour has led to a classification of Lewis acids and bases into "hard" and "soft" categories; as a rule, hard acids react preferentially with hard bases and, similarly, soft acids react with soft bases. The terms *hard* and *soft* are chosen to suggest that the atomic structures associated with hard acids and bases are rigid and impenetrable, whereas those associated with soft acids and bases are more readily deformable. Hard acids include the proton; sodium, calcium, and aluminum ions; and carbonium ions. The soft acids include cuprous, silver, mercurous, and the halogen cations.

Typical soft bases are iodide, thiocyanate, sulfide, and triphenylphosphine; whereas hard bases include hydroxide, fluoride, and many oxyanions. The dividing line between the hard and soft categories is not a sharp one, and its theoretical interpretation is obscure. Nevertheless, a surprising amount of factual information can be coordinated on the basis of preferential reactions of hard acids with hard bases and soft acids with soft bases.

The effect of molecular structure

Regularities and trends in the properties of the elements are best understood in terms of the periodic table, an orderly pattern seen when the elements are arranged in order of increasing atomic number. Comparing the hydrides of the various elements in the table reveals appreciable acidity only among those of the elements on the right-hand side of the table, especially the halogen elements—fluorine, chlorine, bromine, and iodine. This generalization is borne out when the elements across the first period of the table are examined in order; as the right-hand side of the table is approached, the elements encountered are carbon, nitrogen, oxygen, and fluorine. The hydrides of these elements show increasing acidity. Methane, CH_4, a hydride of carbon, has no detectable acidic properties, and the pK_a decreases sharply in the series ammonia (NH_3), 35; water (H_2O), 16; and hydrogen fluoride (HF), 4. In any given group of the periodic table, the acidity of the hydrides increases as the group is descended. For example, the two groups at the right-hand side of the table include, respectively and in descending order, the elements oxygen, sulfur, selenium, and tellurium; and fluorine, chlorine, bromine, and iodine. The pK_a's of the hydrides of the first group are as follows: water (H_2O), 16; hydrogen sulfide (H_2S), 7; hydrogen selenide (H_2Se), 4; and hydrogen telluride (H_2Te), 3. Similarly, hydrogen fluoride (HF) is a weak acid, whereas hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen iodide (HI) are all completely dissociated (are strong acids) in aqueous solution. These trends are due to variations in bond strength, electronegativity (attractive power of the atomic nucleus for electrons), and ionic solvation energy, of which the first is the most important. When a hydride is able to lose two or more protons, the loss of the second is always more difficult because of the increased negative charge on the base—e.g., $H_2S - HS^-$ (pK 7),

HS$^-$ – S^{2-} (pK 15); similarly, NH$_4^+$ – NH$_3$ (pK 9.5), NH$_3$ – NH$_2^-$ (pK 35).

A simple rule applies to the strengths of the [oxyacids](#), which can be given the general formula XOn(OH)m, in which X is any nonmetal. In these [compounds](#), the pK decreases with increasing n but does not depend significantly upon m. When $n = 0$ (e.g., ClOH, Si(OH)$_4$), pK_a is between 8 and 11; when $n = 1$ (e.g., HNO$_2$, H$_2$SO$_3$) gives pK_a 2–4; whereas with $n = 2$ or 3 (e.g., H$_2$SO$_4$, HClO$_4$) the acids are completely dissociated in water ($pK_a < 0$). These regularities are probably attributable to the sharing of the negative charge of the anion between $n + 1$ equivalent oxygen atoms; the more extensive the charge spread, the lower is the energy of the anion and hence the stronger the acid.

The most important groups of organic acids are the [alcohols](#) (including the [phenols](#)) and the [carboxylic acids](#). The simple alcohols are very weak acids (pK 16–19); the phenols are considerably stronger ($pK \sim 10$); and the carboxylic acids stronger still ($pK \sim 5$). The strength of the carboxylic acids is due to the sharing of the negative charge between two equivalent oxygen atoms in the ion RCO$_2^-$. The most important organic bases are the [amines](#), RNH$_2$, R$_2$NH, or R$_3$N. Most of these are stronger bases than ammonia; i.e., their cations are weaker acids than the ammonium ion.

The effect of substituents on the acid–base properties of organic molecules has been very extensively studied and is one of the main methods of investigating the nature of the electron displacements produced by substitution in these molecules. The simplest classification is into electron-attracting substituents (halogens, carbonyl, nitro, and positively charged groups) and electron-repelling groups (alkyl groups, negatively charged groups). The electron-attracting groups make acids stronger and bases weaker, whereas electron-repelling groups have the opposite effects. There are, however, often more specific electronic effects, especially in aromatic and unsaturated compounds, for which special explanations are needed.

Dissociation Constants In Aqueous Solution

The classical method for determining the <u>dissociation</u> constant of an <u>acid</u> or a <u>base</u> is to measure the electrical conductivity of solutions of varying concentrations. From these the degree of dissociation (α; *see above*) can be determined and K_a calculated from the equation

$$K_a = \frac{a^2 c}{1 - a}.$$

This method is unsuitable for acids with pK less than 2 because α is then close to unity and the value $1 - \alpha$ is therefore subject to error. It also is unsuitable for acids of $pK > 7$ because impurities in the solvent may affect the conductivity or displace the dissociation <u>equilibrium</u>.

It is often preferable to use a more specific method for determining the concentration of one of the species in the scheme $A + H_2\underline{O} \rightleftarrows B + H_3O^+$. For example, a <u>hydrogen electrode</u> (or more commonly a <u>glass electrode</u>, which responds in the same way) together with a reference electrode, commonly the calomel electrode, serves to measure the actual <u>hydrogen ion</u> concentration, or the pH, of the solution. If E is the <u>electromotive force</u> (in volts) observed by the electrode, the equation giving the pH is as follows:

$$E = E_0 + 0.059 \log_{10} \left[H_3O^+ \right] = E_0 - 0.059 \, pH.$$

In this equation, the value of E_0 depends on the nature of the reference electrode and is usually obtained by calibration with a solution of known pH. Measurements can be made on aqueous solutions of the acid, in which case $[B] = [H_3O^+]$, but it is better to use a series of <u>buffer</u> solutions with known ratios $[A]/[B]$, since these are less sensitive to the presence of impurities. Such a series is obtained by successive additions of <u>alkali</u> to a solution of the acid (or of a strong acid to a solution of the base) and the procedure is then often termed a pH titration.

If A and B have different optical properties—for example, if they differ in colour or in the absorption of ultraviolet light—this property can be used to measure the ratio $[A]/[B]$, commonly by

using an instrument called a [spectrophotometer](#). Since $[H_3O^+]$ must also be known, the commonest procedure is to measure $[A]/[B]$ in a solution made by adding a small quantity of A or B to a standard buffer solution. If A and B do not have convenient optical properties—as is commonly the case—an indicator, that is, an acid–base system that does show a difference in colour in changing from A to B, is used. If a small quantity of indicator A_I–B_I, with acidity constant K_I, is added to a buffer solution A–B, it is easily shown that the following relation holds:

$$K_A = K_I \frac{[B]}{[A]} \cdot \frac{[A_I]}{[B_I]},$$

in which $[A_I]/[B_I]$ is measured spectrophotometrically, and all the other quantities on the right-hand side of the equation are known. If accurate values of K are required, it is necessary in all the above methods to take into account the effect of interionic forces upon the equation and the quantities measured. This factor can induce a considerable degree of complexity into the problem.

Selected Values Of Acidity Constants

The table contains acidity constants for selected substances. These are listed as acids or bases according to the nature of the uncharged species, but in each case the value given is pK_a for the acid form (pK_a and pK_b for a conjugate acid–base pair being related by the equation

pK$_a$'s of representative acids and bases

Inorganic acids	
boric acid	9.1 (20 °C)
hypochlorous acid	7.53 (18 °C)
hydrogen sulfide	7.0, 11.9 (18 °C)
carbonic acid	6.4, 10.3
phosphoric acid	2.1, 7.2, 12.8
sulfurous acid	1.8, 6.9 (18 °C)
nitric acid	−1.6

pK$_a$'s of representative acids and bases

Inorganic acids

sulfuric acid	(−3), 1.9
hydrogen chloride	(−7)
perchloric acid	(−8)

Inorganic bases

ammonia	9.25
hydrazine	−0.9, 8.23 (20 °C)
hydroxylamine	6.03 (20 °C)

Alcohols and phenols

methanol	15.5
trifluoroethanol	12.37
phenol	9.89
o-nitrophenol	7.17
m-nitrophenol	8.28
p-nitrophenol	7.15
o-chlorophenol	8.49
m-chlorophenol	8.85
p-chlorophenol	9.18
picric acid	0.38

Carboxylic acids

formic	3.75 (20 °C)
acetic	4.75
chloroacetic	2.85
dichloroacetic	1.48

pK_a's of representative acids and bases

Inorganic acids

trichloroacetic	0.70
oxalic	1.23, 4.19
malonic	2.83, 5.69
benzoic	4.19

Nitrogen bases

methylamine	10.66
dimethylamine	10.73
trimethylamine	9.81
piperidine	11.12
aniline	4.63
pyridine	5.25
quinoline	4.90 (20 °C)
pyrrole	−0.27

$$pK_a + pK_b = pK_w = 14.00$$

for aqueous solutions at 25 °C). For instances in which several values of pK_a are given, these relate to successive dissociations; e.g., for phosphoric acid, they correspond to dissociations of H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-}. All values given refer to aqueous solutions at or near 25 °C; parentheses indicate values that have been estimated indirectly or are uncertain for other reasons.