

The Brønsted–Lowry Acid–Base Concept

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For a number of reasons the Brønsted–Lowry acid–base concept is a significant and integral part of the general chemistry course. Acids and bases are important classes of chemical substances, and the Brønsted–Lowry concept forms a practical and useful compromise between the classical but too restrictive Arrhenius concept (1) and the somewhat too general (for students, at least) Lewis (2) and Usanovich (3) concepts. Also, the approach outlined below, in which the Brønsted–Lowry concept is considered by analogy with the usually earlier discussed electromotive force (EMF) series, enables the student to learn new material by proceeding from an already mastered concept. Furthermore, the Brønsted–Lowry concept is a splendid example of simultaneous discovery, an occurrence in science that is much more prevalent than commonly believed.¹ Thus the Brønsted–Lowry concept takes a prominent place among the better known cases of virtually simultaneous independent discoveries—what the father of the sociology of science, Robert K. Merton, has christened “multiples” (4); e.g., in mathematics the calculus (Newton and Leibniz), in biology the theory of evolution (Darwin and Wallace), in physics the law of conservation of energy (Mayer, Joule, Colding, Helmholtz, etc., (5)), and in chemistry the tetravalence and self-linking of carbon atoms (Kekulé and Couper (6)) and the periodic table (de Chancourtois, Newlands, Odling, Hinrichs, Lothar Meyer, and Mendeleev (7)).

Brønsted

Johannes Nicolaus Brønsted (8) was born in Varde, Denmark, on February 22, 1879. He received his first degree in engineering (1899) from the Technical University of Denmark and his *Magister* degree in chemistry (1902) and his doctorate (1908) from the University of Copenhagen. He was appointed assistant in the university's chemical laboratory (1905) and professor of physical chemistry at the university (1908). He continued Julius Thomsen's idea of determining chemical affinity by measuring the maximum work of chemical reactions, but, instead of using calorimetric measurements, he measured EMF values for galvanic cells, resulting in a series of monographs on chemical affinity (1906–1921). He also determined specific heats and affinity constants and published a series of studies on solubilities (1921–1923), the specific interaction of ions (1921–1927), the protonic concept of acids and bases (1923) (9), and catalysis (1924–1933).

Brønsted's growing international reputation attracted foreign co-workers, especially from 1921 to 1935. For example, with György Hevesy he separated the isotopes of mercu-

ry and chlorine, and with Victor K. La Mer he related activity coefficients to the ionic strength of solutions, a relationship derived theoretically by Peter Debye and Erich Hückel at about the same time. Brønsted was unhappy with the classical formulation of the laws of thermodynamics, according to which heat is not directly comparable to other forms of energy. His formulations, especially those of work and heat, were not approved of by contemporary physicists, even by the time of his death. Brønsted died in Copenhagen on December 17, 1947.

Lowry

Thomas Martin Lowry (10) was born in Low Moor, Bradford, Yorkshire, England on October 26, 1874. He attended the Central Technical College, South Kensington and was awarded his DSc degree from the University of London in 1899. He was assistant to Henry E. Armstrong (1896–1913), Lecturer in Chemistry at the Westminster Training College (1904–1913), Head of the Chemical Department in Guy's Hospital Medical School (from 1913), and the first teacher of chemistry in a medical school to be made a professor at the University of London. In 1920 he was appointed to the newly established Chair of Physical Chemistry at Cambridge University. He died in Cambridge on November 2, 1936.

During his long service with Armstrong, Lowry became a master of organic technique, which gave him an advantage denied to many other physical chemists. He applied exact physical methods of measurement to the solution of chemical problems, and the vast amount of quantitative physical data collected by him and his co-workers provides useful



Johannes Nicolaus Brønsted (1879–1947) (left) and Thomas Martin Lowry (1874–1936) (right). Photos courtesy of the Oesper Collection, University of Cincinnati.

¹ A detailed history of this concept will be dealt with in a subsequent article.

working material for future generations of physical chemists.

Lowry laid the foundation of his lifelong study of optical rotatory power early in his career by discovering the mutarotation (a term which he introduced) of nitro-*d*-camphor and the stereoisomerism of a number of halogen derivatives of camphor. In 1923 he proposed an extended definition of acids and bases, which was advanced independently by Brønsted at the same time (11). In his work on the variation of optical rotatory power with wavelength, he realized that little progress could be made in the field until values were determined over the widest possible range of wavelengths instead of for a single arbitrarily selected point on a dispersion curve. He introduced the concept of induced dissymmetry (1924), and in later years he extended his work on rotatory dispersion from transparent to absorbing media, i.e., to a study of the Cotton effect. During World War I he investigated the production and use of amatol mixtures and the difficulties arising in shell filling caused by the polymorphism of ammonium nitrate. He also studied the chlorides of sulfur, phosphorus(V) chloride, valency, and the binary systems $N_2O_3-H_2O$ and $N_2O_4-H_2O$.

The following outline of the Brønsted-Lowry concept is adapted from a handout distributed to the author's students during the last three decades (12). The students have found it very helpful in supplementing the treatment in textbooks. Acid-base concepts are also discussed in articles and monographs (13-22).

The Brønsted-Lowry Concept

Acids are substances whose aqueous solutions taste sour, change the color of certain indicators, e.g., blue litmus to red, react with metals more active than hydrogen in the activity series to yield hydrogen gas, and neutralize bases to form salts. Bases are substances whose aqueous solutions are slippery to the touch and taste bitter, change the color of certain indicators, e.g., red litmus to blue, react with amphoteric elements such as aluminum or zinc to form hydrogen gas, and neutralize acids to form salts.

Of the several concepts proposed to explain the properties and reactions of acids and bases, the one originated independently in 1923 by the Dane, Johannes Nicolaus Brønsted, and the Englishman, Thomas Martin Lowry, is possibly the most useful. According to this approach, which, unlike the older Arrhenius approach, is not limited to aqueous solutions but is applicable to all proton (H^+)-containing systems, an acid is a proton donor, and a base is a proton acceptor; the strength of an acid or base is correlated with its tendency to donate or accept protons, respectively. Acids may be positive ions (cations), neutral molecules, or anions, while bases may be negative ions (anions) as well as neutral molecules.

A table of Brønsted acids and their conjugate bases (the acids from which one proton has been removed) in order of decreasing acid strength is very useful. The acid-base table is similar to the already familiar activity (EMF) series and can be used similarly. Just as the EMF table consists of couples, each consisting of a reduced and oxidized form, this acid-base table consists also of couples, each consisting of an acid and a base (conjugate acid-base pairs). Just as the EMF series is conventionally given in terms of tendency toward electron loss (oxidation), so the acid-base table is conventionally given in terms of tendency toward proton loss (acidity). Just as E^0 values give the tendency toward electron loss, so K_a values give the tendency toward proton loss. Just as the best reducing agents are found in the upper left-hand portion of the EMF table and the best oxidizing agents in the lower right-hand portion, so the strongest acids are found in the upper left-hand portion of the acid-base table and the strongest bases on the lower right-hand portion.

The analogy between the EMF series and the Brønsted-Lowry concept stems from the fact that both use half-reactions to store thermodynamic data, E^0 or K_a values, respectively. The procedure suggested here is based on the competition for a real or "imagined" ² intermediate, i.e., electrons

² The term "imagined" is important since these reactions are really two-step thermodynamic cycles, and no conclusions can be drawn about actual mechanisms. Indeed, many redox reactions in solution do not actually involve electron transfer but are the result of formal changes in oxidation state caused by atom transfer reactions.

Acid-Base Table

Acid		K_a		Base	
↑ Increasing Acid Strength "Strong" Acids ↑ Limits of Usefulness in Aq. Solution "Weak" Acids ↓	Perchloric Acid	—	$HClO_4 \rightleftharpoons (H^+) ClO_4^-$	Perchlorate Ion	↑ Increasing Basic Strength "Weak" Bases ↓ "Strong" Bases ↓
	Sulfuric Acid	—	$H_2SO_4 \rightleftharpoons (H^+) HSO_4^-$	Hydrosulfate Ion	
	Hydrochloric Acid	—	$HCl \rightleftharpoons (H^+) Cl^-$	Chloride Ion	
	Nitric Acid	^a	$HNO_3 \rightleftharpoons (H^+) NO_3^-$	Nitrate Ion	
	Hydronium Ion	^a	$H_3O^+ \rightleftharpoons (H^+) H_2O$	Water	
	Oxalic Acid	5.9×10^{-2}	$H_2C_2O_4 \rightleftharpoons (H^+) HC_2O_4^-$	Hydrogenoxalate Ion	
	Hydrosulfate Ion	1.2×10^{-2}	$HSO_4^- \rightleftharpoons (H^+) SO_4^{2-}$	Sulfate Ion	
	Hydrofluoric Acid	3.5×10^{-4}	$HF \rightleftharpoons (H^+) F^-$	Fluoride Ion	
	Hydrogenoxalate Ion	6.4×10^{-5}	$HC_2O_4^- \rightleftharpoons (H^+) C_2O_4^{2-}$	Oxalate Ion	
	Acetic Acid	1.8×10^{-5}	$HC_2H_3O_2 \rightleftharpoons (H^+) C_2H_3O_2^-$	Acetate Ion	
	Hexaaquaaluminum Ion	1.3×10^{-5}	$Al(H_2O)_6^{3+} \rightleftharpoons (H^+) Al(OH)(H_2O)_5^{2+}$	Pentaaquahydroxoaluminum Ion	
	Carbonic Acid	4.3×10^{-7}	$H_2CO_3 \rightleftharpoons (H^+) HCO_3^-$	Hydrogencarbonate Ion	
	Hydrogen Sulfide	1.1×10^{-7}	$H_2S \rightleftharpoons (H^+) HS^-$	Hydrosulfide Ion	
	Hypochlorous Acid	3.2×10^{-8}	$HClO \rightleftharpoons (H^+) ClO^-$	Hypochlorite Ion	
	Ammonium Ion	5.6×10^{-10}	$NH_4^+ \rightleftharpoons (H^+) NH_3$	Ammonia	
↓	Hydrocyanic Acid	4.9×10^{-10}	$HCN \rightleftharpoons (H^+) CN^-$	Cyanide Ion	
	Hydrogencarbonate Ion	5.6×10^{-11}	$HCO_3^- \rightleftharpoons (H^+) CO_3^{2-}$	Carbonate Ion	
	Water	1.0×10^{-14} ^a	$H_2O \rightleftharpoons (H^+) OH^-$	Hydroxide Ion	
	Hydrosulfide Ion	1.0×10^{-15}	$HS^- \rightleftharpoons (H^+) S^{2-}$	Sulfide Ion	
	Hydroxide Ion	—	$OH^- \rightleftharpoons (H^+) O^{2-}$	Oxide Ion	
	Ammonia	—	$NH_3 \rightleftharpoons (H^+) NH_2^-$	Amide Ion	
	Hydrogen	—	$H_2 \rightleftharpoons (H^+) H^-$	Hydride Ion	
	Methane	—	$CH_4 \rightleftharpoons (H^+) CH_3^-$	Methide Ion	

^a If the activity of water is considered to be 55 M rather than 1 M in dilute aqueous solution, K_a would be ≈ 50 for H_3O^+ , making it a stronger acid than HNO_3 ($K_a \approx 1$). Similar considerations would result in a K_a of $\approx 2 \times 10^{-16}$ for water, making H_2O a weaker acid than HS^- on a molar basis.

or protons, respectively. Thus this approach can similarly be applied to the Lux–Flood acid–base concept (Lux, H. Z. *Elektrochem.* 1939, 45, 303) or Ellingham diagrams, in which the intermediates are oxide ions or oxygen atoms, respectively. In our general chemistry course we discuss electrochemistry before acids and bases. For courses treating these topics in the opposite order the analogy still holds, but the procedure suggested should be reversed, i.e., the EMF series should be approached as analogous to the already discussed Brønsted–Lowry concept.

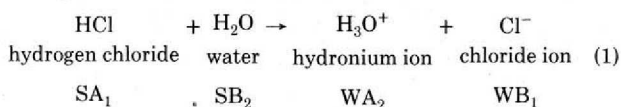
If we consider two given couples in the EMF table, the reducing agent of the couple higher in the table will reduce the oxidizing agent of the couple lower in the table, i.e., the “higher” reaction will go to the right, while the “lower” reaction goes to the left. Similarly, if we consider two given conjugate acid–base pairs in the acid–base table, the acid of the pair higher in the table will transfer a proton to the base of the pair lower in the table, i.e., the “higher” reaction goes to the right while the “lower” reaction goes to the left. In other words, in all acid–base reactions, stronger acids react to form weaker acids, while *simultaneously*, stronger bases react to form weaker bases.

A reduction must always accompany an oxidation, since while the reducing agent gives up its electrons (is oxidized), the oxidizing agent accepts these electrons (is reduced). Similarly, in any acid–base reaction, the stronger acid gives up its protons, while the stronger base *simultaneously* accepts them (a weaker acid and a weaker base thus being formed).

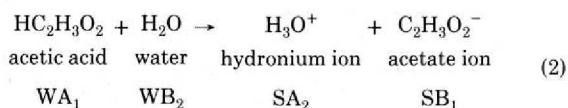
Note that the table is arranged so that *conjugate acid–base pairs are opposite each other*. Furthermore, *coming down the table acids become weaker, but bases become stronger*. Observe also that acid constants (K_a values) become numerically smaller coming down the table.

Because the stronger the Brønsted acid, the weaker the corresponding conjugate base, and vice versa, the strongest acids appear in the upper left-hand portion of the table, and the strongest bases appear in the lower right-hand portion. An acid–base reaction consists of the transfer of a proton from an acid to a base. The acid therefore forms its conjugate base, and the base forms its conjugate acid. A substance reacts as an acid only if a base is present to accept the proton of the acid, while a substance reacts as a base only if an acid is present to donate a proton to the base.

An acid–base reaction is therefore a competition between two bases for a proton. If the stronger (S) of the two acids and the stronger of the two bases are reactants (appear on the left side of the equation), the reaction is said to proceed to a *large* extent:



where the numerical subscripts are used to identify the corresponding conjugate acid–base pairs. If the weaker (W) of the two acids and the weaker of the two bases are reactants (appear on the left side of the equation), the reaction is said to proceed to only a *small* extent:

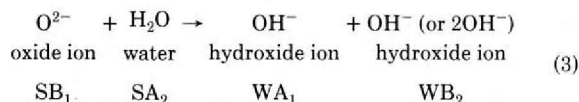


Equations (1) and (2) therefore agree with our common knowledge that in aqueous solution hydrochloric acid is a

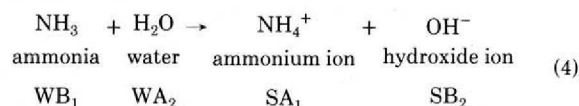
strong acid (completely dissociated), while acetic acid is a weak acid. (Its aqueous solution consists largely of undissociated molecules.)³

Since any acid stronger than hydronium ion will donate its proton to water to form the hydronium ion, these acids appear equally strong in water (the so-called leveling effect), that is, the hydronium ion is the strongest acid that can exist in aqueous solution. In order to differentiate between the strengths of different acids that are stronger than hydronium ion, a solvent that is a stronger acid than water must be used.

In eqs (1) and (2) in which acids react with water, the water molecule behaves as a base. When bases react with water, on the other hand, the water molecule behaves as an acid, as shown in the following two equations (A substance that can function as an acid in one reaction and as a base in a different reaction is said to be *amphiprotic*):



This reaction proceeds to a large extent, and therefore any metal oxide that dissolves in water gives a solution of the metal hydroxide.

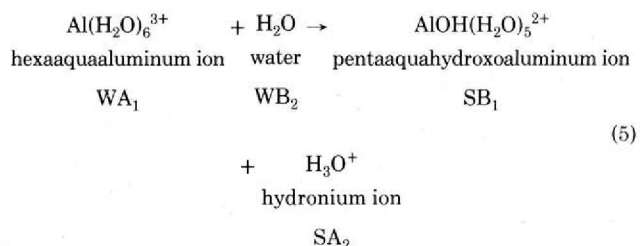


The fact that this reaction proceeds only to a small extent agrees with the well-known fact that ammonia is a weak base. (Its aqueous solution consists largely of undissociated molecules.)

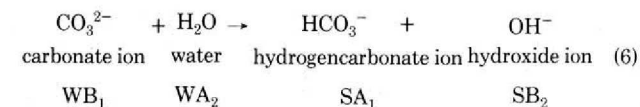
Since any base stronger than hydroxide ion will accept a proton from water to form the hydroxide ion, these bases appear equally strong in water (the leveling effect); i.e., the hydroxide ion is the strongest base that can exist in aqueous solution. In order to differentiate between the strengths of different bases that are stronger than hydroxide ion, a solvent that is a stronger base than water must be used.

Hydrolysis (reaction of an ion of a salt with water to produce either H_3O^+ or OH^- ion) is simply an acid–base reaction and is therefore readily accounted for according to the Brønsted–Lowry approach. A salt will hydrolyze to produce an acidic solution if it contains a cation that is a Brønsted acid; it will produce a basic solution if it contains an anion that is a Brønsted base. If the cation is stronger as a Brønsted acid than the anion is as a Brønsted base, the resulting solution will be acidic. If this situation is reversed, the solution will be basic. The following three equations summarize the possible cases:

Acidic Solution; Small Extent

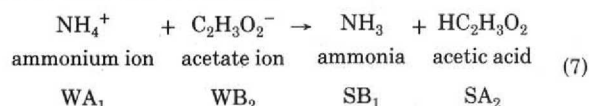


Basic Solution; Small Extent



³ Notice that “strong” and “weak” are *relative* rather than absolute terms. In common parlance the terms “strong” and “weak” are used for acids that are stronger or weaker, respectively, than the hydronium ion, i.e., the terms refer to strength in *aqueous* solution, as shown in eqs (1) and (2). In solvents other than water (17) hydrochloric acid and acetic acid may behave as weak and strong acids, respectively.

Neutral Solution; Small Extent



An aqueous solution of $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ is neutral even though it hydrolyzes because acetic acid is as strong an acid ($K_a = 1.8 \times 10^{-5}$) as ammonia is a base ($K_b = 1.8 \times 10^{-5}$).

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