

3.4: Acid and base

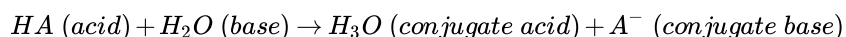
The definition of acid and base has changed over the course of time. This is not a problem of the orthodoxy of one definition but of the convenience of applying the concept to a particular chemical problem. Therefore, ranking the strength of acids and base also depends on the definition of acid and base used.

(a) Arrhenius's acid and base

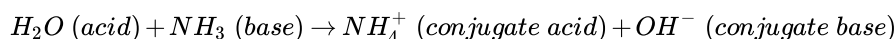
In 1884, Arrhenius defined that an **acid** is a substance that gives H^+ and a **base** one that gives OH^- . Namely, if an acid is HA and a base BOH , then $HA \rightarrow H^+ + A^-$ and $BOH \rightarrow B^+ + OH^-$. Therefore, when an acid and a base react, water is formed.

(b) Brønsted-Lowry's acid and base

In a new theory submitted in 1923 independently by Brønsted and Lowry, an acid is defined as a molecule or an ion which gives H^+ and a molecule or ion that receives H^+ from a partner is a base. A base is not only a molecule or an ion which gives OH^- but anything which receives H^+ . Since the acid HA gives H^+ to water in an aqueous solution and generates an **oxonium ion**, H_3O^+ , water is also a kind of base according to this definition.



Here H_3O^+ is called a conjugate acid and A^- a conjugate base. However, since water gives H^+ to ammonia and generates NH_4^+ , it is also an acid, as is shown below.



That is, water can be an acid or a base dependent on the co-reactant.

Although the definition of Brønsted-Lowry is not much different from that of Arrhenius for aqueous solutions, it is more useful because the theory was extended to non-aqueous acids and bases.

? Exercise 3.4.3

Write the molecular formulae of nitric acid, perchloric acid, sulfuric acid, and phosphoric acid as oxo acids together with the formal oxidation number of the central atom.

Answer

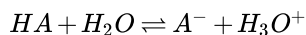
- Nitric acid $(HO)N^{5+}O_2$
- Perchloric acid $(HO)Cl^{7+}O_3$
- Sulfuric acid $(HO)_2S^{6+}O_2$
- and Phosphoric acid $(HO)_3P^{5+}O$.

Acid strength

A protonic acid gives H^+ to water and generates the oxonium ion H_3O^+ . The strength of an acid in a dilute aqueous solution is estimated from the equilibrium constant K_a

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

for the dissociation equilibrium,



but it is more convenient to use,

$$pK_a = -\log K_a \quad \text{or} \quad pH = -\log[H_3O^+]$$

An acid with $pK_a < 0$ is classified as a strong acid and one with $pK_a > 0$ a weak acid. The conjugate base of a strong acid is a weak base. The pK_a values of typical acids at 25 °C are shown in Table 3.4.2.

Table 3.4.2 Acidity constants for aqueous solutions of acids at 25 °C.

Acid	pK _a
HF	3.17
HCl	-8*
HBr	-9*
HI	-10*
H ₂ CO ₃	6.35
HClO ₄	< 0
HNO ₃	< 0
H ₃ PO ₃	1.5
H ₃ PO ₄	2.15
H ₂ SO ₄	< 0
CH ₃ COOH	4.56
C ₆ H ₅ COOH	4.00
NH ₄ ⁺	9.25
C ₅ H ₅ NH ⁺	5.25

* Estimated value

Since a solvent also works as an acid or a base, the acidity and its range depend on the solvent dissolving the acid. Full dissociation of an acid stronger than H₃O⁺ gives H⁺ to water, forming H₃O⁺ in an aqueous solution. For example, both HBr and HI dissociate completely to become H₃O⁺, and their acidities are similar. This kind of phenomenon is called the **leveling effect**, and all acidities become equal to that of H₃O⁺. In measuring the relative acidity of strong acids, it is necessary to use a solvent whose H⁺ affinity is smaller than that of water, such as acetic acid or ethanol.

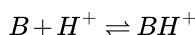
Binary halo acids HX, except for HF, are very strong acids. Although the H₃O⁺ concentration itself is also high in an aqueous solution of HF, the stronger hydrogen bond of F⁻ compared with that of other halide anions decreases the thermodynamic activity of H₃O⁺.

The acidity of oxo acids, such as phosphoric acid, sulfuric acid, nitric acid, and perchloric acid, is related to the formal oxidation number of P, S, N, and Cl. Namely, if the oxo acid H_nXO_m is denoted by (HO)_nXO_{m-n}, the positive charge on X becomes positive (2m - n), and the acidity is higher for larger value of this number. The number parallels the ease of dissociation of OH to give a proton. Acidity is higher in the following order: perchloric acid (HO)ClO₃ > sulfuric acid (HO)₂SO₂ > nitric acid (HO)NO₂ > phosphoric acid (HO)₃PO. Although phosphoric acid can be written as (HO)₃PO, phosphorous acid is not (HO)₃P but (HO)₂HPO, and has an acid strength comparable to phosphoric acid.

Hammett acidity function

Hydrogen ion concentration and pH are meaningful only in dilute aqueous solutions of acids. The acidity in nonaqueous and concentrated solutions is measured using the **Hammett acidity function**. This function makes it possible to measure the acidities of various acids in a non-aqueous solvent or of an acid in various non-aqueous solvents.

The Hammett acidity function in the equilibrium,



is defined by

$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$$

In a very dilute solution

$$K_{BH^+} = \frac{[B][H^+]}{[BH^+]}$$

and

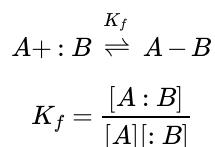
$$H_0 = -\log \frac{[B][H^+]}{[BH^+]} - \log \frac{[BH^+]}{[B]} = -\log[H^+] = pH$$

An acid with $-H_0$ over 6 is called a **superacid**. This is an acid that is 10^6 times stronger than a 1 molar solution of a strong acid. $-H_0$ for pure sulfuric acid is 12.1, 21.1 for a solution of HF in SbF_5 , and 26.5 for the combination of HSO_3F and SbF_5 .

Superacids have the ability to remove H^- from a hydrocarbon and perform H-D exchange and C-C bond scission, etc.

(c) Lewis acid and base

Whereas the concept of Brønsted acid and base is limited to the transfer of protons, a Lewis acid A is generally defined as an acceptor, and a Lewis base B a donor, of an electron pair. An acid A and a base :B bind together to form an adduct A:B. For example, a Lewis acid BF_3 and a Lewis base OEt_2 (diethylether) form an adduct $F_3B:OEt_2$. The stability increases by the completion of an octet around boron when such an adduct forms. The stability of an adduct is expressed by the equilibrium constant of the reaction



Therefore, the Lewis acidities of a series of acids are measured by comparing K_f against a common base :B. Since a proton is also an electron acceptor, Brønsted acids are the special case of the more general Lewis definition of acids. According to this definition, a co-ordinate bond in a transition metal complex is also an acid-base reaction of a ligand (Lewis base) with a metal center (Lewis acid).

V. Gutmann proposed the negative enthalpy of formation (kcal mol⁻¹ unit) of the adduct ($Cl_5Sb-Sol$) of Sol (solvent) with a standard acid ($SbCl_5$) in dichloroethane as a measure of the Lewis basicity of a solvent. This is called the **donor number** (D.N.) of a solvent. On the other hand, the ³¹P NMR chemical shift of Et_3P in a solvent is defined as the measure of the Lewis acidity of the solvent and is called the **acceptor number** (A.N.).

Hard and soft acids and bases

R. G. Pearson classified Lewis acids and bases according to their **hardness and softness**. This classification is an extension of the original theory of S. Ahlrand, J. Chatt, and N. R. Davies, who proposed that metal cations were classified in the order of the stability constants K_f of the formation of the complexes of the metal cations with halide anions. Namely, the order of K_f is $I < Br < Cl < F$ toward metal ions belonging to class a, and $F < Cl < Br < I$ toward those of class b. The class a type metal cations are hard acids, and class b type ones are soft acids. The metal cations which are not much dependent on the kind of halogens have **borderline** character.

What should be noticed here is that K_f tends to become large for the combination of a hard acid and a hard base, or a soft acid and a soft base. If the concept is extended from simple metal cations and halide anions to general Lewis acids and bases, they can similarly be classified in terms of the hard and soft acid-base affinity. Typical hard acids and bases, and soft acids and bases are shown in Table 3.4.3.

Table 3.4.3 The classification of Lewis acids and bases

	Hard	Borderline	Soft
Acids	H^+, Li^+, Na^+, K^+ $Be^{2+}, Mg^{2+}, Ca^{2+}$ $Al^{3+}, Ti^{4+}, Cr^{3+}$ Fe^{3+}, BF_3, Cl^{7+}	$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$ $Zn^{2+}, Sn^{2+}, Pb^{2+}$ Sb^{3+}, Bi^{3+}	Cu^+, Ag^+, Au^+ $Tl^+, Cd^{2+}, Hg^+, Hg^{2+}$ $Pd^{2+}, Pt^{2+}, Pt^{4+}$

	Hard	Borderline	Soft
Bases	$\text{NH}_3, \text{H}_2\text{O}, \text{R}_2\text{O}$ $\text{F}^-, \text{OH}^-, \text{O}^{2-}$ $\text{NO}_3^-, \text{SO}_4^{2-}, \text{PO}_4^{3-}$	$\text{N}_3^-, \text{N}_2, \text{NO}_2^-$ Br^- SO_3^{2-}	$\text{H}^-, \text{CN}^-, \text{R}^-$ I^- $\text{PR}_3, \text{SR}_2, \text{CO}$

The qualitative expression “softness” is a chemical paraphrasing of the ease of polarization and the larger contribution of covalency than ionicity in bonding. The cations of alkali and alkaline earth metals as well as aluminum are hard and the cations of mercury, copper, silver, and gold, etc. are soft. Whereas oxides are hard, sulfides and phosphorus compounds are soft. In the minerals of the Earth’s crust, aluminum, which is hard and oxophilic is found as an oxide, and cadmium, which is soft and chalcophilic is found as a sulfide.

? Exercise 3.4.4

Applying the concept of hard and soft acids for ferric and ferrous ions, what kind of minerals are expected in iron ores?

Answer

Fe^{3+} is a hard acid and Fe^{2+} is a borderline acid. Therefore, it is likely that the main iron ores are oxide minerals. Although the main ores are actually the oxides hematite Fe_2O_3 or magnetite Fe_3O_4 , a Fe^{2+} sulfide pyrite FeS_2 is also widely distributed.

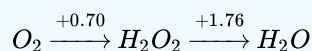
Acid-base and oxidation-reduction

Some people confuse acid-base and redox reactions. This confusion may be caused firstly by the similar terms originating from oxygen and secondly by misunderstanding about electron transfer. Historically, A. L. Lavoisier, who was one of the great founders of modern chemistry in the 18th century, considered that oxygen was the basis of all acids. He also defined oxidation as the formation of oxides from an element and oxygen. It then took a long time before the present definitions of acid-base and redox reactions were proposed and the old definitions were no longer satisfactory. Furthermore, the Lewis acid accepts an electron pair from a base forming a Lewis acid-base complex, and the oxidizing agent accepts electrons from a reducing agent and is reduced. The fact that acids and oxidizing agents are electron acceptors, and that bases and reducing agents are electron donors, is one of the causes of this confusion.

✓ Problems

3.1

The Latimer diagram of oxygen is shown below. Write the oxidation number of oxygen in each compound.



Calculate the reduction potential of the reaction which converts an oxygen molecule to water, and judge whether this reaction is a spontaneous reaction.

3.2

Which is the stronger base, ammonia or pyridine?

3.3

The order of the Lewis acidity of boron halides is $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$. Is this order reasonable from the standpoint of the electronegativities of halogens?

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