Acid and Bases

1. Bronsted Concept

Johannes Bronsted in Denmark and Thomas Lowry in England proposed (in 1923) that the essential feature of an acid–base reaction is the transfer of a hydrogen ion, H^+ , from one species to another. In the context of this definition, a hydrogen ion is often referred to as a proton. They suggested that any substance that acts as a proton donor should be classified as an acid, and any substance that acts as a proton acceptor should be classified as a base. Substances that act in this way are now called 'Bronsted acids' and 'Bronsted bases', respectively.

An example of a Bronsted acid is hydrogen fluoride, HF, which can donate a proton to another molecule, such as H₂O, when it dissolves in water:

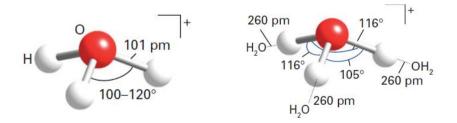
 $HF(g) + H_2O(l) \rightarrow H_3O^+(aq) + F(aq)$

An example of a Bronsted base is ammonia, NH3, which can accept a proton from a proton donor: $H_2O(1) + NH_3(aq) \rightarrow NH4^+(aq) + OH^-(aq)$

As these two examples show, water is an example of an **amphiprotic** substance, a substance that can act as both a Bronsted acid and a Bronsted base.

2. Structure of H⁺ ion

When an acid donates a proton to a water molecule, the latter is converted into a *hydronium ion*, H_3O^+ (as per the crystal structure of $H_3O^+ClO4^-$). However, the entity H_3O^+ is almost certainly an oversimplified description of the proton in water, for it participates in extensive hydrogen bonding, and a better representation is $H_9O_4^+(2)$.



3. Conjugate acids and bases

The form of the two forward and reverse reactions given above, both of which depend on the transfer of a proton from an acid to a base, is expressed by writing the general Bronsted equilibrium as $HF(g) + H_2O(l) \rightarrow H_3O^+(aq) + F^-(aq)$ Acid₁ + Base₂ \rightarrow Acid₂ + Base₁

The species Base₁ is called the **conjugate base** of Acid₁, and Acid₂ is the **conjugate acid** of Base₂. The conjugate base of an acid is the species that is left after a proton is lost. The conjugate acid of a base is the species formed when a proton is gained. Thus, F^- is the conjugate base of HF and H_3O^+ is the conjugate acid of H_2O . There is no *fundamental* distinction between an acid and a conjugate acid or a base and a conjugate base: a conjugate acid is just another acid and a conjugate base is just another base.

4. The strengths of Bronsted acids

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

More generally:

$$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq) \qquad K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

In this definition, $[X^-]$ denotes the numerical value of the molar concentration of the species X⁻ (so, if the molar concentration of HF molecules is 0.001 mol dm⁻³, then [HF] = 0.001).

A value $Ka \ll 1$ implies that [HX] is large with respect to [X⁻], and so proton retention by the acid is favoured. The experimental value of Ka for hydrogen fluoride in water is 3.5 x 10⁻⁴, indicating that under normal conditions only a very small fraction of HF molecules are deprotonated in water. The actual fraction deprotonated can be calculated as a function of acid concentration from the numerical value of Ka.

Numerical:

The pH of 0.145 M CH₃COOH(aq) is 2.80. Calculate Ka of ethanoic acid.

Answer: To calculate Ka we need to calculate the concentrations of H_3O^+ , $CH_3CO_2^-$, and CH_3COOH in the solution. The concentration of H_3O^+ is obtained from the pH by writing $[H_3O^+] = 10^{pH}$, so in a solution of pH = 2.80, the molar concentration of H_3O^+ is $1.6 \times 10^-$ ³ mol dm⁻³. Each deprotonation event produces one H_3O^+ ion and one $CH_3CO_2^-$ ion, so the concentration of $CH_3CO_2^-$ is the same as that of the H_3O^+ ions (provided the autoprotolysis of water can be neglected). The molar concentration of the remaining acid is 0.145 - 0.0016 mol dm⁻³ - 0.143 mol dm⁻³.

Therefore

$$K_{\rm a} = \frac{\left(1.6 \times 10^{-3}\right)^2}{0.143} = 1.8 \times 10^{-5}$$

This value corresponds to pKa = 4.75.

Self-test For hydrofluoric acid $Ka = 3.5 \times 10_{-4}$. Calculate the pH of 0.10 M HF(aq).