7

Acids and bases

7.1 Brønsted–Lowry acids and bases

- According to the Brønsted–Lowry definition, an acid is a proton (H^+) donor and a base is a proton acceptor. An acid–base reaction involves a proton transfer.

- The oxonium ion (H_3O^+(aq)) is responsible for the acidic properties of aqueous solutions of acids.

- An acid–base reaction involves conjugate acid–base pairs. The conjugate base of an acid consists of the acid minus a proton, and the conjugate acid of a base consists of the base plus a proton.

? For a practice question on these topics, see question 1 at the end of this chapter (p.339).

7.2 The strengths of acids and bases

- The strength of an acid is measured by its acidity constant, K_a. For convenience, this is often quoted as pK_a, where $pK_a = -\log_{10} K_a$.
- The lower the value of pK_a, the stronger the acid, and the greater the value of K_a.
- The concentration of [H_3O^+(aq)] in solution is given by the pH, which is defined as $pH = -\log_{10}[H_3O^+(aq)]$.
- Pure water ionizes to a small extent, and this is quantified by the self-ionization constant of water, K_w. At 298 K, $K_w = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$, so the pH of pure water at 298 K is 7.00.
- The strength of a base is measured by its basicity constant, K_b, though it is often more convenient to provide the K_a value for the conjugate acid. These are related since $K_a \times K_b = K_w$.
- The lower the value of pK_b, the stronger the base, and the greater the value of K_b.
- A strong base has a low value of K_a for its conjugate acid, and a high value of pK_a.
- The stronger an acid, the weaker its conjugate base. The stronger a base, the weaker its conjugate acid.
- The position of equilibrium in an acid–base reaction depends on the relative strengths of the acids (or bases).
- For an acid–base reaction, $HA + B \rightleftharpoons A^- + BH^+$, the equilibrium constant for the reaction is found using $pK_c = pK_a(HA) - pK_a(BH^+)$.

? For practice questions on these topics, see questions 2–6 at the end of this chapter (p.339).

7.3 Buffer solutions

- A buffer solution is resistant to changes in pH on addition of small quantities of acid or base, and on dilution.

- Buffers consist of either a weak acid and its salt or a weak base and its salt.

- The pH of a buffer solution can be calculated using the Henderson–Hasselbalch equation (Equation 7.16).

? For a practice question on this topic, see question 7 at the end of this chapter (p.339).

OXFORD
UNIVERSITY PRESS

7.4   pH changes in acid–base titrations

- Acid–base reactions in solution can be carried out quantitatively using titrations.
- A titration curve shows how the pH of the solution changes during the titration.
- For the addition of a strong base to a strong acid, the pH starts low and increases slowly until very close to the equivalence point. It then rises sharply through the equivalence point before increasing slowly again at high pH. The equivalence point is at pH 7.00.
- For the addition of a strong base to a weak acid, the pH starts higher, and initially rises slowly as the system acts as a buffer. The equivalence point is at pH > 7.00 due to hydrolysis of the salt. At half-neutralization, pH = pK_a.
- For the addition of a strong acid to a weak base, the pH initially decreases slowly as the system acts as a buffer. The equivalence point is at pH < 7.00 due to hydrolysis of the salt.

? For a practice question on this topic, see question 8 at the end of this chapter (p.339).

7.5   Indicators

- Acid–base titrations can be followed easily by adding an indicator. An acid–base indicator is normally a combination of a weak acid with its conjugate base, or a weak base with its conjugate acid. The neutral and ionic forms have different colours.
- An indicator is chosen so that pK_{in} = pH at the equivalence point of a titration.
- The equivalence point occurs on the steep part of a titration curve. Indicators typically change colour over ~2 pH units, and at the steep part of a titration curve this occurs with addition of 1 or 2 drops of acid or base.

? For a practice question on this topic, see question 9 at the end of this chapter (p.339).

7.6   Oxoacids

- For an acid with more than one ionizable hydrogen atom (a polybasic acid), successive values of pK_a increase, as it is easier to remove a proton from a neutral molecule than from an anion.
- Oxoacids with the general formula H_mXO_n increase in strength with increasing value of $(n - m)$.
- The variation of the concentrations of the acid and associated anions with pH is shown using speciation curves.

? For practice questions on these topics, see questions 10–12 at the end of this chapter (p.340).

7.7   Acidic and basic oxides

- Oxides are often described as acidic or basic on the basis of their reactions with water, or their reactions with bases and acids.
- Compounds that react with both acids and bases, such as Al_2O_3, are described as amphoteric.

OXFORD
UNIVERSITY PRESS

7.8   Lewis acids and bases

- According to the Lewis theory, an acid is an electron-pair acceptor and a base is an electron-pair donor. These are generally referred to as Lewis acids and Lewis bases.

- The Lewis definition of acids and bases is broader than the Brønsted–Lowry definition. Brønsted–Lowry acids and bases are particular examples of Lewis acids and bases.

? For practice questions on this topic, see questions 13–14 at the end of this chapter (p.340).

» Concept review

By the end of this chapter, you should be able to do the following.

- Know the Arrhenius, Brønsted–Lowry, and Lewis definitions of acids and bases.

- Identify the conjugate acid and conjugate base for an acid–base reaction.

- Calculate the pH of a solution of a strong or weak acid and a strong or weak base.

- Manipulate logarithms to calculate pH from $[H_3O^+(aq)]$ and pK_a from K_a and carry out the reverse processes.

- Calculate K_b and K_a for a base.

- Determine the position of an acid–base equilibrium using K_a and K_b.

- Calculate the pH of a buffer solution and suggest an appropriate buffer solution for a given pH.

- Determine the pH at any point in the titration between a strong acid and a strong base.

- Sketch the titration curve for a titration between a strong acid and a strong base, a weak acid and a strong base, and a strong base and a weak acid.

- Suggest an appropriate indicator for a given acid–base reaction.

- Understand the factors involved in influencing the value of pK_{a1} for an oxoacid.

- Identify Lewis acids and Lewis bases.

⇄ Key equations

definition of K_a	$K_a = \dfrac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$ (units of K_a $mol\,dm^{-3}$)	(7.2)
definition of pK_a	$pK_a = -\log_{10} K_a$	(7.3)
definition of pH	$pH = -\log_{10}[H_3O^+(aq)]$	(7.5)
the self-ionization constant of water	$K_w = [H_3O^+(aq)][OH^-(aq)]$	(7.7)
definition of K_b	$K_b = \dfrac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$ (units of K_b $mol\,dm^{-3}$)	(7.10)
Henderson–Hasselbalch equation	$pH = pK_a + \log_{10}\dfrac{[\text{conjugate base}]}{[\text{acid}]}$	(7.16)

OXFORD
UNIVERSITY PRESS