Worked Problem 2.5

Q Use a graphical method to find the number of roots of the polynomial equations: (a) $x^3 - 7x + 6 = 0$; (b) $x^3 - 4x^2 - 2x - 3 = 0$.
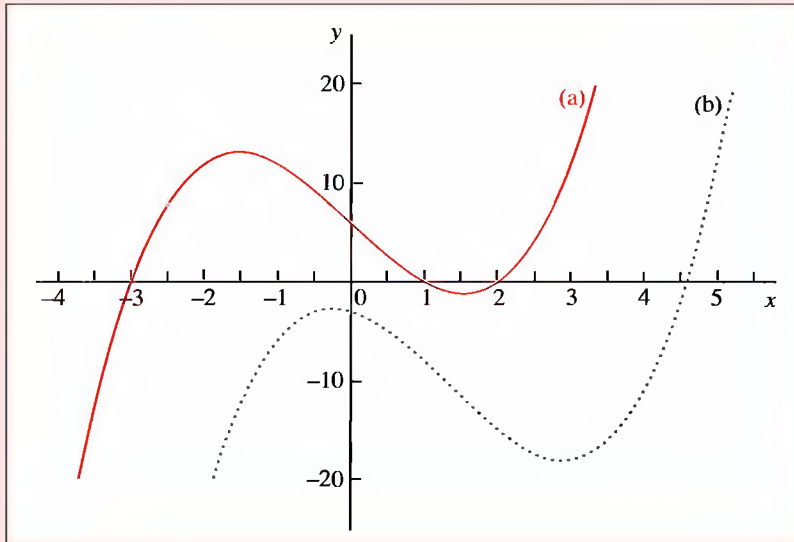
A (a) 3; (b) 1 (see Figure 2.24).

Figure 2.24 Plots of the polynomial functions (a) $x^3 - 7x + 6$, (b) $x^3 - 4x^2 - 2x - 3$

2.4.1 An Algebraic Method for Finding Roots of Polynomial Equations

For a given polynomial function $y = f(x)$, one (or more) roots of the polynomial equation $f(x) = 0$ can often be found by an algebraic method. Suppose the polynomial $f(x)$ is of degree n. If $x = \lambda$ is a root of the polynomial equation, then $f(\lambda) = 0$, and $(x - \lambda)$ is a factor of the polynomial:

$$f(x) = (x - \lambda)(c_1 x^{n-1} + c_2 x^{n-2} + \ldots + c_n) \qquad (2.46)$$

The truth of the previous statement follows by substituting $x = \lambda$ into the above equation, where we see that, irrespective of the value of the second expression in parentheses, which is a polynomial of degree $n-1$, the first term in parentheses is zero, thus implying that $f(\lambda) = 0$. If there is a root with integer value, then it can sometimes be found by trial and error, using $\lambda = \pm 1, \pm 2, \ldots$ the polynomial of degree $n-1$ can then be treated in the same way. If no further roots can be found algebraically, at any stage in the iterative procedure, then the current polynomial can be plotted to exhibit the existence, or otherwise, of remaining roots.

The key requirement is that, at each step, the coefficients c_i are found, in order to facilitate the recovery of another root. Once the polynomial of degree two is reached, it is easiest to use the formula given in equation (2.45) to test for the existence of a further two or zero roots.

Worked Problem 2.6

Q (a) Use the algebraic method to find the roots of the polynomial equation $f(x) = 0$, where $f(x) = 2x^3 + 11x^2 + 17x + 6 = 0$; (b) give the factored form of $f(x)$; (c) sketch a graph of the function $y = f(x)$.

A (a) Simple trial and error shows that $x = -2$ is a root of $f(x)$, since $f(-2) = 0$. The polynomial equation may now be written in the form:

$$(x + 2)(c_1 x^2 + c_2 x + c_3) = 0$$

On multiplying out the brackets, and collecting terms, we have:

$$c_1 x^3 + (c_2 + 2c_1)x^2 + (c_3 + 2c_2)x + 2c_3 = 0$$

Comparing coefficients of the powers of x with the given polynomial equation, we find:

$$c_1 = 2 \tag{2.47}$$

$$c_2 + 2c_1 = 11 \tag{2.48}$$

$$c_3 + 2c_2 = 17 \tag{2.49}$$

$$2c_3 = 6 \tag{2.50}$$

Equations (2.47) and (2.50) give the values $c_1 = 2$ and $c_3 = 3$, respectively. It then follows, by substituting the value of c_1 in equation (2.48), that $c_2 = 7$, and we then have:

$$(x + 2)(2x^2 + 7x + 3) = 0$$

(b) The solutions of $(2x^2 + 7x + 3) = 0$ are then found using equation (2.45):

$$x = -\frac{7}{4} \pm \frac{1}{4}\sqrt{49 - 24} = -\frac{7}{4} \pm \frac{5}{4} = -3 \text{ or } -\frac{1}{2}$$

Thus,

$$f(x) = (x + 2)\left(x + \frac{1}{2}\right)(x + 3).$$

(c) From (b) we know that the curve crosses the x-axis at $x = -2, -3,$ $-1/2$; in addition, for $x > -1/2$, all three brackets are positive and increase in value as x increases. Likewise, for $x < -3$, all brackets have increasing negative values, and therefore $f(x)$ is negative for these values. For $-3 < x < -2$, $(x + 3)$ is positive and $(x + 2)$ and $(x + 1/2)$ are both negative, and hence $f(x) > 0$. A similar argument shows that $f(x) < 0$ for $-2 < x < -1/2$, and it is then an easy matter to sketch the form of the cubic polynomial function (Figure 2.25).
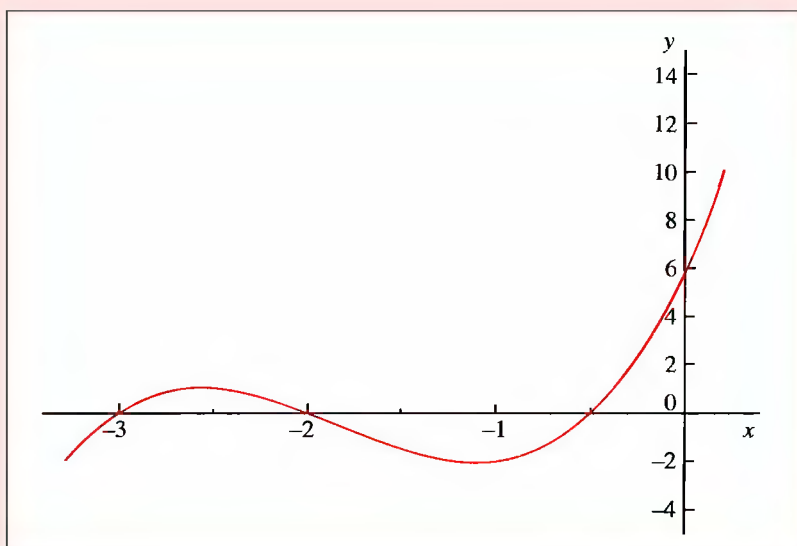

Figure 2.25 Plot of the function $f(x) = 2x^3 + 11x^2 + 17x + 6 = 0$

## 2.4.2 Solving Polynomial Equations in a Chemical Context

In practice, the solution of polynomial equations is problematic if no simple roots are found by trial and error. In such circumstances the graphical method may be used or, in the cases of a quadratic or cubic equation, there exist algebraic formulae for determining the roots. Alternatively, computer algebra software (such as Maple or Mathematica, for example) can be used to solve such equations

explicitly. In Worked Problem 2.7 we show how the calculation of the pH of 10^{-6} mol dm^{-3} HCl(aq) requires the solution of a quadratic equation.

Worked Problem 2.7

Q   Calculate the pH of 10^{-6} mol dm^{-3} HCl(aq), taking into account the hydronium (H_3O^+) ions from: (a) HCl alone; (b) HCl and the dissociation of water (equilibrium constant, $K_w = 10^{-14}$).

A   (a) The simple formula pH $= -\log([H_3O^+]/\text{mol dm}^{-3})$ leads to a value for the pH of 6, since $[H_3O^+] = 10^{-6}$ mol dm^{-3}. (b) As the concentration of HCl is so small, it is appropriate to take account of the dissociation of water in our calculation of the pH, and so we need to consider the concentration of hydronium ions produced from two sources, described by the following processes:

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$2H_2O \overset{K_w}{\rightleftharpoons} H_3O^+ + OH^-$$
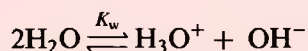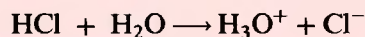
Thus, if $[H_3O^+]/\text{mol dm}^{-3} = h$, $[Cl^-]/\text{mol dm}^{-3} = c$ and $[OH^-]/\text{mol dm}^{-3} = b$, then charge conservation requires:

$$h = c + b \Rightarrow b = h - c$$

Charge conservation requires that there are the same number of cations as anions in the solution. Thus the sum of the concentrations of the OH$^-$ and Cl$^-$ ions must be the same as the hydronium ion concentration and so $h = c + b$.

where $c = 10^{-6}$. The equilibrium constant for the dissociation of water is given by $K_w = hb$, which we can now rewrite as:

$$K_w = hb = h(h - c) = h^2 - ch \Rightarrow h^2 - ch - K_w = 0 \qquad (2.51)$$

Equation (2.51) is a quadratic equation in h, and the two roots may be found using equation (2.45). Thus:

$$h = \frac{c}{2} \pm \frac{\sqrt{c^2 + 4K_w}}{2}$$

The logarithm of a negative number is a so-called complex number which we discuss in some detail in Chapter 1 of Volume 2.

and, on substituting for c and K_w, we find $h = 1.099 \times 10^{-6}$ or $h = -9.902 \times 10^{-9}$. The first solution yields pH $= 5.996$; the second solution, although mathematically required, does not correspond to a acceptable physical result, as the logarithm of a negative number is not defined as a real number and thus has no physical significance.

Problem 2.12

The radial function of the 3s atomic orbital for the hydrogen atom has the form given in equation (2.44).

(a) Calculate the value of R_{3s} at $r = 0$ and as r tends to infinity. Note that the exponential term will always dominate the term in parentheses (see Section 2.3.4) and so its limiting behaviour alone will determine the behaviour of the function as r tends to infinity (see also Chapter 3 for a more detailed discussion of limits).

(b) Calculate the values of r/a_0, and hence of r, for which $R_{3s} = 0$, by solving the quadratic polynomial equation $\{27 - 18(\frac{r}{a_0}) + 2(\frac{r}{a_0})^2\} = 0$.

(c) Sketch the form of R_{3s} for $0 \leqslant \frac{r}{a_0} \leqslant 12$, and then compare your result with that displayed in Figure 2.22.

Polynomial Equations of Higher Degree in Chemistry

Polynomial equations of degree three (cubic equations) arise in a number of areas of classical physical chemistry; however, such equations also arise in the modelling of:

- Electronic structures, through the determination of molecular orbitals, constructed as linear combinations of atomic orbitals (LCAO); thus, for example, the determination of the simplest σ-type molecular orbitals for HCN, in its linear configuration (as in the ground state), involves the use of the seven σ atomic orbitals $1s_H$, $1s_C$, $1s_N$, $2s_C$, $2s_N$, $2p\sigma_C$ and $2p\sigma_N$, and leads to the solution of a polynomial equation of degree seven for the molecular orbital energies.
- Characteristic frequencies of molecular vibrations. In the case of HCN, for example, there are four vibrational frequencies that may be calculated from a polynomial equation of degree four, by making appropriate assumptions about the stiffness of bond stretching and bond angle deformation.

Problem 2.13

Give the degree of the polynomial equation that arises in calculating the molecular orbitals for the following species in their ground states (σ or π bonding, as indicated): (a) carbon dioxide (σ only); (b) benzene (π bonds only).