Appendix 2 Mathematical techniques

Basic procedures

A2.1 Logarithms and exponentials

The **natural logarithm** of a number x is denoted $\ln x$, and is defined as the power to which $e = 2.718\ldots$ must be raised for the result to be equal to x. It follows from the definition of logarithms that

$$\ln x + \ln y + \cdots = \ln xy \cdots \tag{A2.1}$$

$$\ln x - \ln y = \ln(x/y) \tag{A2.2}$$

$$a \ln x = \ln x^a \tag{A2.3}$$

We also encounter the **common logarithm** of a number, $\log x$, the logarithm compiled with 10 in place of e. Common logarithms follow the same rules of addition and subtraction as natural logarithms. Common and natural logarithms are related by

$$\ln x = \ln 10 \log x \approx 2.303 \log x \tag{A2.4}$$

The **exponential function**, e^x, plays a very special role in the mathematics of chemistry. The following properties are important:

$$e^x e^y e^z \ldots = e^{x+y+z+\cdots} \tag{A2.5}$$

$$e^x / e^y = e^{x-y} \tag{A2.6}$$

$$(e^x)^a = e^{ax} \tag{A2.7}$$

A2.2 Complex numbers and complex functions

Complex numbers have the form

$$z = x + iy \tag{A2.8}$$

where $i = (-1)^{1/2}$. The real numbers x and y are, respectively, the real and imaginary parts of z, denoted $\mathrm{Re}(z)$ and $\mathrm{Im}(z)$. We write the **complex conjugate** of z, denoted z^*, by replacing i by $-$i:

$$z^* = x - iy \tag{A2.9}$$

The **absolute value** or **modulus** of the complex number z is denoted $|z|$ and is given by:

$$|z| = (z^* z)^{1/2} = (x^2 + y^2)^{1/2} \tag{A2.10}$$

The following rules apply for arithmetic operations involving complex numbers:

1 Addition. If $z = x + iy$ and $z' = x' + iy'$, then

$$z \pm z' = (x \pm x') + i(y \pm y') \tag{A2.11}$$

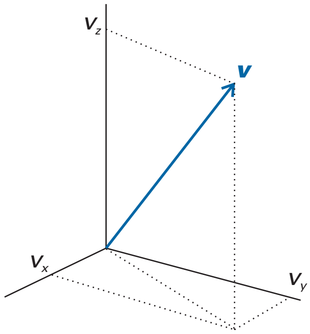

Fig. A2.1 The vector $\boldsymbol{v}$ has components v_x, v_y, and v_z on the x, y, and z axes with magnitudes v_x, v_y, and v_z, respectively.

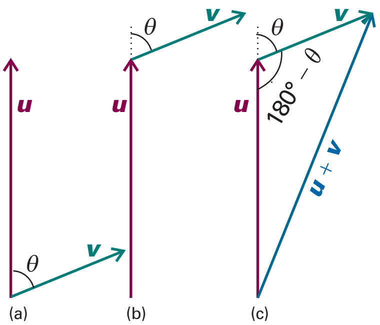

Fig. A2.2 (a) The vectors $\boldsymbol{v}$ and $\boldsymbol{u}$ make an angle θ. (b) To add $\boldsymbol{u}$ to $\boldsymbol{v}$, we first join the tail of $\boldsymbol{u}$ to the head of $\boldsymbol{v}$, making sure that the angle θ between the vectors remains unchanged. (c) To finish the process, we draw the resultant vector by joining the tail of $\boldsymbol{u}$ to the head of $\boldsymbol{v}$.

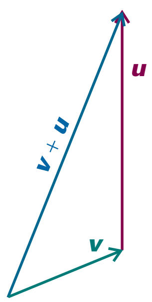

Fig. A2.3 The result of adding the vector $\boldsymbol{v}$ to the vector $\boldsymbol{u}$, with both vectors defined in Fig. A2.2a. Comparison with the result shown in Fig. A2.2c for the addition of $\boldsymbol{u}$ to $\boldsymbol{v}$ shows that reversing the order of vector addition does not affect the result.

2 Multiplication. For z and z' defined above,

$$z \times z' = (x + \mathrm{i}y)(x' + \mathrm{i}y') = (xx' - yy') + \mathrm{i}(xy' + yx') \tag{A2.12}$$

3 Division. For z and z' defined above,

$$\frac{z}{z'} = \frac{z(z')^*}{|z'|^2} \tag{A2.13}$$

Functions of complex arguments are useful in the discussion of wave equations (Chapter 8). We write the complex conjugate, f^*, of a complex function, f, by replacing i wherever it occurs by –i. For instance, the complex conjugate of $\mathrm{e}^{\mathrm{i}x}$ is $\mathrm{e}^{-\mathrm{i}x}$.

Complex exponential functions may be written in terms of trigonometric functions. For example,

$$\mathrm{e}^{\pm \mathrm{i}x} = \cos x \pm \mathrm{i} \sin x \tag{A2.14}$$

which implies that

$$\cos x = \tfrac{1}{2}(\mathrm{e}^{\mathrm{i}x} + \mathrm{e}^{-\mathrm{i}x}) \tag{A2.15}$$

$$\sin x = -\tfrac{1}{2}\mathrm{i}(\mathrm{e}^{\mathrm{i}x} - \mathrm{e}^{-\mathrm{i}x}) \tag{A2.16}$$

A2.3 Vectors

A vector quantity has both magnitude and direction. The vector shown in Fig. A2.1 has components on the x, y, and z axes with magnitudes v_x, v_y, and v_z, respectively. The vector may be represented as

$$\boldsymbol{v} = v_x\boldsymbol{i} + v_y\boldsymbol{j} + v_z\boldsymbol{k} \tag{A2.17}$$

where $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ are **unit vectors**, vectors of magnitude 1, pointing along the positive directions on the x, y, and z axes. The magnitude of the vector is denoted v or $|\boldsymbol{v}|$ and is given by

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2} \tag{A2.18}$$

Using this representation, we can define the following vector operations:

1 Addition and subtraction. If $\boldsymbol{v} = v_x\boldsymbol{i} + v_y\boldsymbol{j} + v_z\boldsymbol{k}$ and $\boldsymbol{u} = u_x\boldsymbol{i} + u_y\boldsymbol{j} + u_z\boldsymbol{k}$, then

$$\boldsymbol{v} \pm \boldsymbol{u} = (v_x \pm u_x)\boldsymbol{i} + (v_y \pm u_y)\boldsymbol{j} + (v_z \pm u_z)\boldsymbol{k} \tag{A2.19}$$

A graphical method for adding and subtracting vectors is sometimes desirable, as we saw in Chapters 10 and 18. Consider two vectors $\boldsymbol{v}$ and $\boldsymbol{u}$ making an angle θ (Fig. A2.2a). The first step in the addition of $\boldsymbol{u}$ to $\boldsymbol{v}$ consists of joining the tail of $\boldsymbol{u}$ to the head of $\boldsymbol{v}$, as shown in Fig. A2.2b. In the second step, we draw a vector $\boldsymbol{v}_{\mathrm{res}}$, the **resultant vector**, originating from the tail of $\boldsymbol{v}$ to the head of $\boldsymbol{u}$, as shown in Fig. A2.2c. Reversing the order of addition leads to the same result. That is, we obtain the same $\boldsymbol{v}_{\mathrm{res}}$ whether we add $\boldsymbol{u}$ to $\boldsymbol{v}$ (Fig. 2.2c) or $\boldsymbol{v}$ to $\boldsymbol{u}$ (Fig. 2.3).

To calculate the magnitude of $\boldsymbol{v}_{\mathrm{res}}$, we note that $\boldsymbol{v}$, $\boldsymbol{u}$, and $\boldsymbol{v}_{\mathrm{res}}$ form a triangle and that we know the magnitudes of two of its sides (v and u) and of the angle between them (180° – θ; see Fig. A2.2c). To calculate the magnitude of the third side, v_{res}, we make use of the *law of cosines*, which states that:

For a triangle with sides a, b, and c, and angle C facing side c:

$$c^2 = a^2 + b^2 - 2ab \cos C$$

This law is summarized graphically in Fig. A2.4 and its application to the case shown in Fig. A2.2c leads to the expression