1

General Chemistry Related to Textiles

1.1 Introduction

This chapter provides a background to the chemical principles involved in coloration processes, which will be beneficial to those with little working knowledge of dyeing chemistry. Chemistry has been classically divided into three branches: inorganic chemistry, organic chemistry and physical chemistry. Inorganic chemistry is the study of elements and their compounds. However carbon is so unique in the breadth of the compounds it forms (chiefly with hydrogen, oxygen, nitrogen and, to a lesser extent, sulphur) that it has its own branch – organic chemistry. Physical chemistry is concerned with the influence of process conditions such as temperature, pressure, concentration and electrical potential on aspects of chemical reactions, such as how fast they proceed and the extent to which they occur.

There are no clear distinctions between the three branches. For example, organometallic compounds are important substances that combine organic and inorganic chemistry, and the principles of physical chemistry apply to these two branches as well. Fundamental to all these branches of chemistry is an understanding of the structure of matter, so the chapter begins with this important aspect.

1.2 Atomic Structure

Modern chemistry is based on the belief that all matter is built from a combination of exceedingly minute particles (*atoms*) of the various chemical elements. Many different elements are found in nature, each possessing characteristic properties; the atoms of any one element are all chemically identical. An element is a substance made up of only one type of atom, for example, carbon is only made up of carbon atoms, and sodium is only made up of sodium atoms. Atoms combine together to form *molecules* of chemical compounds. A molecule is the smallest particle of a chemical element or compound that has the chemical properties of that element or compound.

A single atom consists of a very dense central core or *nucleus*, which contains numbers of positively charged particles called *protons* and uncharged particles, called *neutrons*. Protons and neutrons have equal mass and together they account for the atom's mass. A number of very small negatively charged particles, called *electrons*, circulate around the nucleus in fixed orbits or 'shells', each orbit corresponding to a certain level of energy: the bigger the shell (the further away from the nucleus it is), the greater the energy. These shells are labelled $n = 1$, 2, 3, etc., counting outwards from the nucleus, and each can hold a certain maximum number

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An Introduction to Textile Coloration: Principles and Practice, First Edition. Roger H. Wardman.

of electrons, given by $2n^2$. The movement of an electron from one energy level to another causes the absorption or emission of a definite amount of energy. Atoms are electrically neutral, so the number of electrons in an atom is exactly the same as the number of protons in its nucleus. The total number of electrons within an atom of a particular element is called the *atomic number* of the element. This is the same as the number of protons in its nucleus. It is the arrangement of the electrons around the nucleus of an atom that determines the chemical properties of an element, especially the electrons in the outermost shells.

It is possible that some of the atoms of an element have a different number of neutrons in their nucleus, but their numbers of protons and electrons are still the same. These atoms are called *isotopes*, and although they have the same chemical properties as the other atoms, their atomic masses are different. Also recent research into atomic structure has shown that the three subatomic particles are themselves made up of other smaller particles such as quarks, but for this book it is sufficient to only consider atoms in terms of protons, neutrons and electrons.

The simplest atom is that of hydrogen, which has a nucleus consisting of just one proton with one electron orbiting around it and has an atomic number of 1. In *deuterium*, an isotope of hydrogen, there is one neutron and one proton in its nucleus. So its atomic mass is 2, but its atomic number is still only 1. There are roughly 6400 atoms of ‘normal’ hydrogen for every atom of deuterium. Another example is chlorine, which has two stable isotopes – one with 18 neutrons and the other with 20 neutrons in the nucleus. Because each has 17 protons, their atomic weights (the combined weights of protons and neutrons) are 35 and 37, respectively. These two forms are labelled ^{35}Cl and ^{37}Cl. Approximately 75.8% of naturally occurring chlorine is ^{35}Cl and 24.2% is ^{37}Cl, and this is the reason why the periodic table of the elements shows the atomic weight of chlorine to be 35.45.

Within a shell there are *orbitals*, each of which can hold a maximum of two electrons. Within an orbital, the two electrons are distinguished by the fact that they are spinning around their own axis, but in opposite directions. In illustrating this diagrammatically the electrons in an orbital are often shown as upward and downward arrows ↑↓, for example, as in Figure 1.3. The orbital nearest the nucleus is called an s orbital, followed by p, d and f orbitals, which are occupied in the larger atoms. These orbital types have different shapes. The s orbitals are spherical, whilst the p orbitals have two lobes and are dumbbell shaped. The three p orbitals are all perpendicular to each other, in x, y, z directions around the nucleus, so are often labelled p_x, p_y and p_z (Figure 1.1). There are five d and seven f orbitals and these have more complex shapes.

The first shell ($n=1$) can accommodate only two electrons (according to the $2n^2$ rule) and there is just the s orbital. The next element, that of atomic number 2 (helium), has two electrons, both occupying the s orbital. In lithium (atomic number 3), its first shell contains two s electrons, but because that is now full, the third electron goes into the s orbital of the next shell. This second shell ($n=2$) now fills up, and after the s orbital is full, further electrons go into the p orbitals, as shown in Table 1.1. The p orbitals can hold a maximum of six electrons and after they are full the third shell ($n=3$) begins to fill.

Table 1.1 shows that once the three p orbitals of the third shell ($n=3$) are full in argon, the electron of the next element, potassium, goes into the fourth shell, instead of continuing to fill the third shell, which can hold a maximum of 18 electrons. However, after calcium, further electrons go into the third shell, into its d orbital, of which there are five, thus

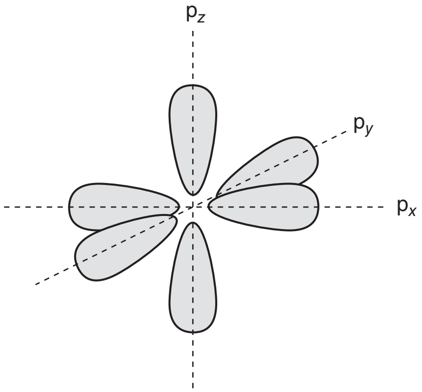


Figure 1.1 The three p orbitals.

Table 1.1 Filling of the shells by electrons in the first 30 elements.

		Orbit, *n*			
Atomic number	Element	1	2	3	4
1	Hydrogen	1s			
2	Helium	2s			
3	Lithium	2s	1s		
4	Beryllium	2s	2s		
5	Boron	2s	2s 1p		
6	Carbon	2s	2s 2p		
7	Nitrogen	2s	2s 3p		
8	Oxygen	2s	2s 4p		
9	Fluorine	2s	2s 5p		
10	Neon	2s	2s 6p		
11	Sodium	2s	2s 6p	1s	
12	Magnesium	2s	2s 6p	2s	
13	Aluminium	2s	2s 6p	2s 1p	
14	Silicon	2s	2s 6p	2s 2p	
15	Phosphorus	2s	2s 6p	2s 3p	
16	Sulphur	2s	2s 6p	2s 4p	
17	Chlorine	2s	2s 6p	2s 5p	
18	Argon	2s	2s 6p	2s 6p	
19	Potassium	2s	2s 6p	2s 6p	1s
20	Calcium	2s	2s 6p	2s 6p	2s
21	Scandium	2s	2s 6p	2s 6p 1d	2s
⋮					
30	Zinc	2s	2s 6p	2s 6p 10d	2s

holding a total of 10 electrons. After the d orbitals are all filled, at zinc, further electrons then fill up the 4p orbitals from gallium to krypton. Thereafter electrons go on to occupy the 5th orbit in a similar order, starting with the 5s orbital (rubidium and strontium).

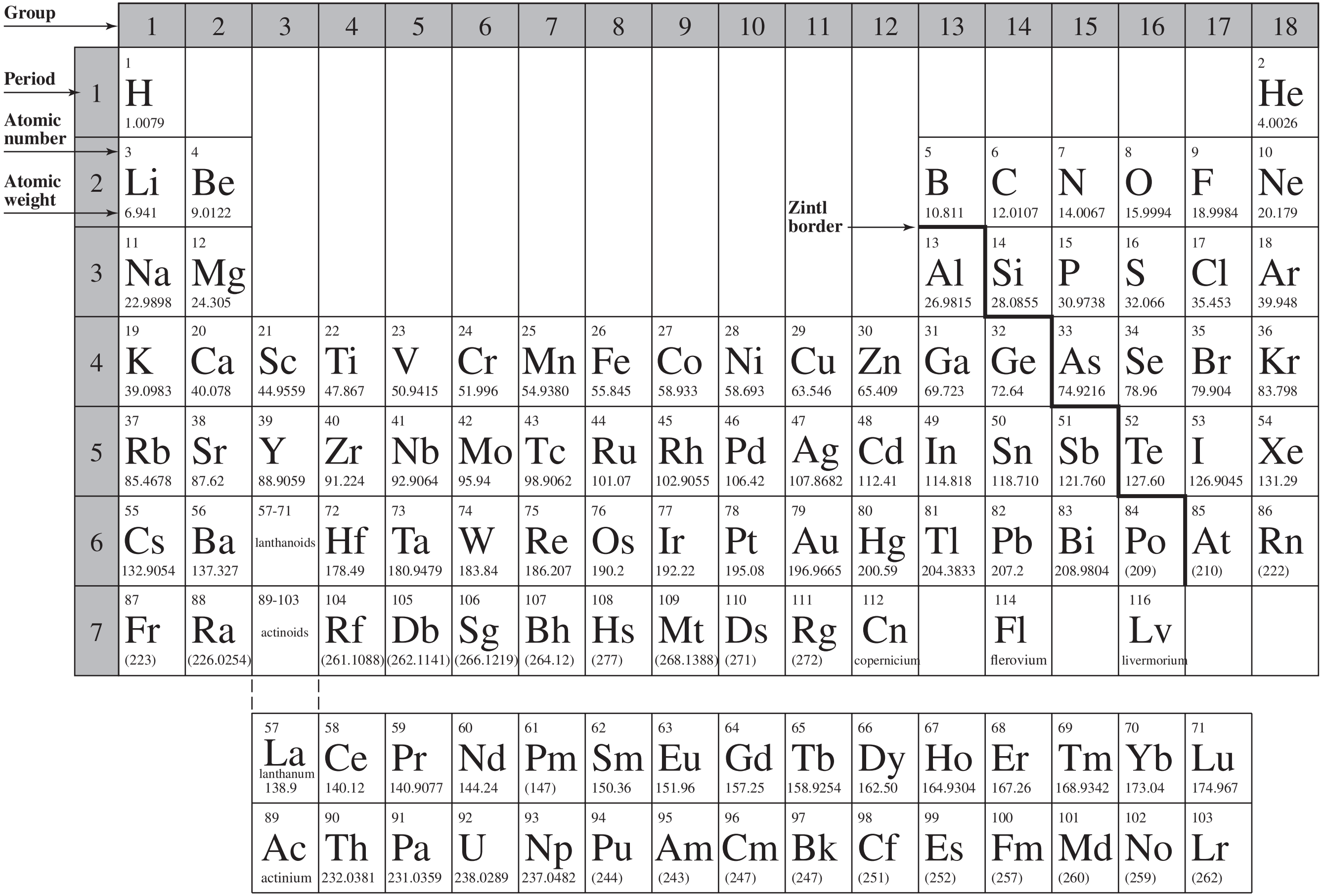
1.3 Periodic Table of the Elements

During the nineteenth century, as new elements were discovered, chemists attempted to classify them according to their properties, such as metals and non-metals, or on the basis of their atomic weights. One of the most important methods of classification was Newlands' law of octaves, which he developed in 1865. Newlands considered that elements with similar chemical characteristics differed by either seven or a multiple of seven and created a table comprising rows of the known elements, in sevens. Going down the columns of his table gave, for example, hydrogen (H), fluorine (F) and chlorine (Cl) with similar chemical properties in the first column, then lithium (Li), sodium (Na) and potassium (K) in the second and so on. However Newlands' table was not entirely correct, but his ideas were taken further by Mendeleev who developed what has become known as the *periodic table of elements*. Mendeleev, in focussing on arranging the elements into families with the same valencies (see Section 1.4), produced a more accurate table and left spaces in it for elements he considered had yet to be discovered. In the years since many new elements have indeed been discovered and a complete version of the periodic table is shown in Figure 1.2.

The periodic table lists the elements in columns called *groups* and rows called *periods*. Moving across the table from left to right, in any given period the atomic number increases incrementally, meaning the size of the atom increases. Moving down the table from top to bottom, in any given group the elements have the same number of electrons in their outer shells. In group 1 all the elements – hydrogen (H), lithium (Li), sodium (Na) and so on – have one electron in their outer shell and are all very chemically reactive and readily form ionic bonds (see Section 1.4.1). In group 2, the elements beryllium (Be), magnesium (Mg), calcium (Ca) and so on all have two electrons in their outer shell and, whilst chemically reactive, are not quite as reactive as the group 1 elements, but still form ionic bonds. The elements in group 17 (called the halogens) all have one electron short of a complete outer shell and readily form ionic bonds with elements of groups 1 and 2. The elements in group 16 are two electrons short of a complete outer shell and again readily form ionic bonds with elements of groups 1 and 2. The elements in groups 13, 14 and 15 do not gain (or lose) electrons easily, so they tend to form covalent bonds with other elements (see Section 1.4.2). The elements in group 18 have completely full outer shells and are unreactive. These elements – helium (He), neon (Ne), argon (Ar) and so on – are called inert gases.

The elements in groups 3–12 are the transition elements. Those in period 4 – scandium (Sc) to zinc (Zn) – involve the filling of the inner d orbitals with electrons, as described in Section 1.2. Those elements in period 5 – yttrium (Y) to cadmium (Cd) – involve the filling of f orbitals. In the higher periods (periods 6 and 7), many of the elements are unstable and gradually break down through radioactive decay.

The periodic table in Figure 1.2 shows a solid black line, labelled the Zintl border. This line represents the boundary between metals and non-metals: the elements to the left and below the line are metals, and those above it and to the right are non-metals.



Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.0079																	2 He 4.0026
2	3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.0107	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.179
3	11 Na 22.9898	12 Mg 24.305											13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.453	18 Ar 39.948
4	19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.867	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.409	31 Ga 69.723	32 Ge 72.64	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc 98.9062	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.41	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.9045	54 Xe 131.29
6	55 Cs 132.9054	56 Ba 137.327	57-71 lanthanoids	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226.0254)	89-103 actinoids	104 Rf (261.1088)	105 Db (262.1141)	106 Sg (266.1219)	107 Bh (264.12)	108 Hs (277)	109 Mt (268.1388)	110 Ds (271)	111 Rg (272)	112 Cn copernicium		114 Fl flerovium		116 Lv livermorium		

57 La lanthanum 138.9	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (147)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
89 Ac actinium	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.0482	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (260)	102 No (259)	103 Lr (262)

Based on information from IUPAC, the International Union of Pure and Applied Chemistry (version dated 1st May 2013).
For updates to this table, see http://www.iupac.org/reports/periodic_table.

Figure 1.2 Periodic table of elements.

1.4 Valency and Bonding

The number of electrons in the outermost shell considerably influences the chemical reactivity of the elements. For example, those elements with just one electron in their outermost shell (hydrogen, sodium, lithium, potassium) are very reactive, whilst those with eight electrons are very unreactive (the ‘inert’ gases helium, neon, argon, etc.), having what is termed *stable octets*. Although something of an oversimplification, it is convenient to assume that when bonds form between atoms of different elements, the atoms achieve an electronic configuration of a stable octet in their outermost shell. The achievement of a stable octet can be brought about either by atoms giving or receiving electrons or by the sharing of electrons.

1.4.1 Giving or Receiving of Electrons: Formation of Ionic Bonds

A good example of ionic bond formation is that of sodium chloride, formed by the reaction between sodium and chlorine atoms. As can be seen in Table 1.1, the sodium atom has an electronic configuration of 2.8.1, which means there are two (s) electrons in the first shell, eight (two s and six p) electrons in the second shell and a single (s) electron in its outermost shell. The chlorine atom has a configuration of 2.8.7 with seven (two s and five p) electrons in its outermost shell. Their electronic configurations are represented in Figure 1.3.

In the reaction between the two, one electron (the outermost) is transferred from the sodium atom to the chlorine atom. Sodium is then left with the configuration 2.8 and chlorine with 2.8.8, thus both having stable octets (Scheme 1.1).

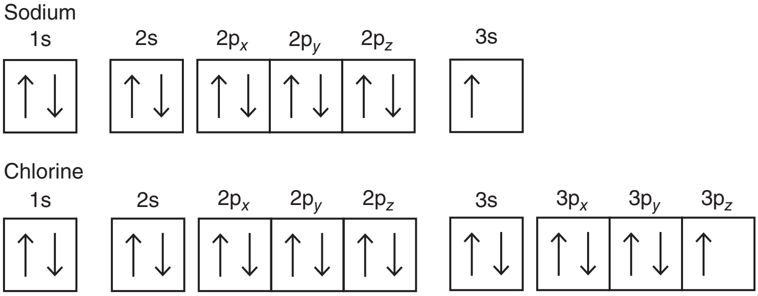
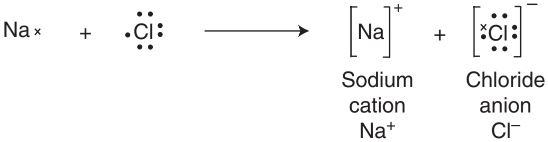


Figure 1.3 Electronic arrangements of the sodium and chlorine atoms (the ↑↓ arrows indicate electrons with opposite spins).

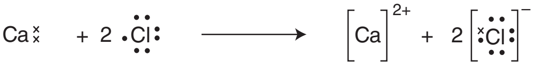


Scheme 1.1 Reaction between sodium and chlorine.

(The electron on the sodium atom represented by x is identical with those on the chlorine atom represented by •: they are only given different notations to show where the electrons come from.)

Since atoms started out electrically neutral, the loss of one electron in sodium leaves the atom positively charged (it is now a positive *ion*, or *cation*) and the gain of one electron leaves the chlorine atom negatively charged (a negative ion or *anion*). Crystals of sodium chloride are therefore made up of equal numbers of sodium and chloride ions. Since opposite charges attract each other, there is strong electrostatic attraction between the two kinds of ions, which makes sodium chloride a very stable compound. This type of bonding is called ionic bonding and is typical of compounds called *electrolytes*. When simple electrolytes of this type dissolve in water, they split up (*dissociate*) into their separate ions. It is for this reason that they allow an electric current to pass through water.

Sodium and chlorine react in equal numbers because they each have a *valency* of one, the sodium atom needing to lose one electron and the chlorine atom needing to gain one electron. In the case of atoms of an element with two electrons in their outermost shell, it is necessary for them to lose these two electrons to achieve a stable octet, so they have a valency of two. For example, a calcium atom needs to react with two atoms of chlorine, with the result that the ionic compound formed, calcium chloride, has the formula $CaCl_2$ (Scheme 1.2):

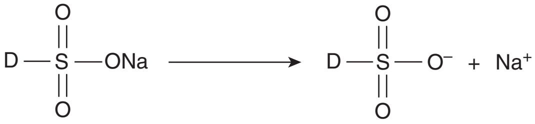


Scheme 1.2 Reaction between calcium and chlorine atoms.

It is reasonable to expect that atoms of elements with three or four electrons in their outermost shells will need to react with three or four atoms of chlorine, respectively. However, in these cases, the removal of so many electrons is less easy and such elements tend to form covalent bonds (Section 1.4.2) where electrons are shared instead.

There are many simple electrolytes and the two most commonly used in dyeing and printing are sodium chloride (NaCl) and sodium sulphate (Na_2SO_4), the latter being known as Glauber's salt. The reason why there are two ions of sodium to one sulphate ion in Glauber's salt is that the sulphate ion is a complex ion, but requires two electrons to achieve stability: it has a valency of 2. A sodium atom has one electron in its outer shell (a valency of 1) and so two sodium atoms are required to satisfy this valency requirement. However, because a calcium atom has two electrons in its outer shell (it also has a valency of 2), it can react with the sulphate on a 1 : 1 basis, so calcium sulphate has the formula $CaSO_4$.

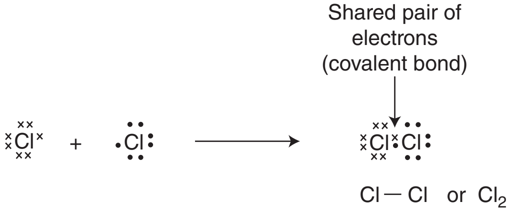
Water-soluble dyes are also electrolytes, but in this case the coloured part of the molecule is very large and usually an anion, whilst the cation, usually a sodium ion, is very small by comparison. In fact water-soluble dye molecules are all synthesised to contain at least one group of atoms known to confer water solubility on the dye molecule through the formation of ions. Very often this is the sulphonic acid (or sulphonate) group, $-SO_3H$, or the carboxylic acid group, $-COOH$, both of which form sodium salts that dissociate in water. In each case, their valency is one, so they form salts with sodium ions in a 1 : 1 ratio. The dissociation of a dye molecule with a sulphonate group is shown in Scheme 1.3, in which D represents the coloured part of the dye molecule.



Scheme 1.3 Dissociation of the sulphonate group.

1.4.2 Sharing of Electrons: Formation of Covalent Bonds

A covalent bond differs from the bonding in an ionic compound in that there is no transfer of electrons from one atom to another. Instead two atoms share two electrons, each atom providing one electron of the pair. Scheme 1.4 represents a covalent bond in the simple inorganic molecule of chlorine (Cl_2) as an example. As in Schemes 1.1 and 1.2, although electrons are given different symbols on the two atoms, this is just to show where they come from; in practice there is no difference between them.



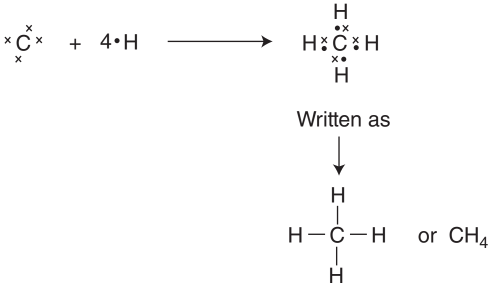
Scheme 1.4 Formation of the chlorine molecule.

By sharing a pair of electrons each of the chlorine atoms achieves a stable octet of electrons in their outer shells.

Elements whose atoms have four electrons in their outermost shells need to either gain or lose four electrons if they are to achieve a stable octet by forming ionic bonds. To do this requires too much energy and so instead they react with other atoms by forming covalent bonds instead, through the sharing of electron pairs. Such elements have a valency of 4. Typical of such an element is carbon, and the structures of all organic molecules, including dye molecules, are based on carbon atoms linked by covalent bonds.

The simplest organic compound is methane, CH_4 (Scheme 1.5). In methane there are four covalent bonds from the carbon atom, one to each hydrogen atom, arranged in the form of a symmetrical tetrahedron with the carbon atom in the middle (Figure 1.4).

The carbon atom has the electronic structure shown in Figure 1.5. There are only two unpaired electrons (in the p_x and p_y orbitals), so before the four covalent bonds can be formed, one of the 2s electrons must be promoted to the vacant p_z orbital, giving the electronic arrangement shown in Figure 1.6.



Scheme 1.5 Formation of methane (outer electrons only are shown); x electron from carbon, • electron from hydrogen.

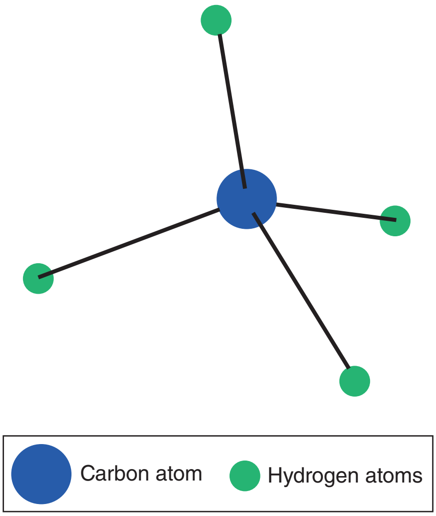


Figure 1.4 Tetrahedral molecular structure of the methane (CH_4) molecule.

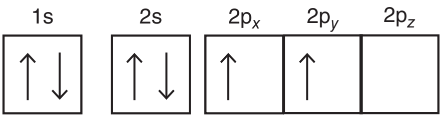


Figure 1.5 Electronic structure of the carbon atom.

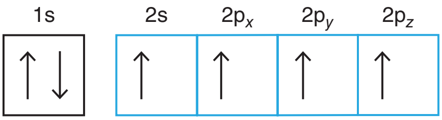
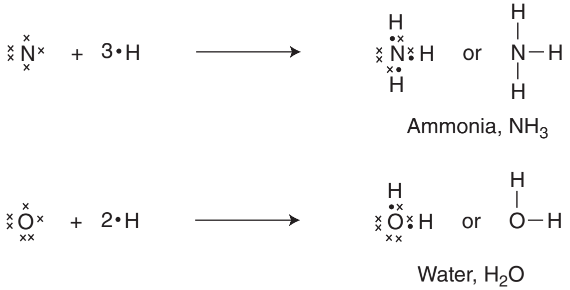


Figure 1.6 Electronic structure of the sp^3-hybridised carbon atom.

There are now four unpaired electrons, giving carbon a valency of four. The formation of the four orbitals, which now each contain one electron, is called *hybridisation*. The four sp^3 hybrid orbitals are equivalent and oriented tetrahedrally from the nucleus of the carbon atom. In methane the four bonds with hydrogen are formed by the overlap of the four sp^3 hybrid orbitals with the s orbitals of the hydrogen atoms.

On bonding with four hydrogen atoms, the carbon atom has eight electrons in its outermost shell and each hydrogen atom has two. The electronic requirements of both carbon and hydrogen atoms are satisfied and the compound is very stable. Such bonds do not dissociate in water; indeed most covalent compounds are insoluble in water and do not conduct electricity. Covalent bonds are the most stable of all chemical bonds and they cannot be broken easily. As indicated in Figure 1.4, the bonding is directional and covalent compounds therefore exist as molecules with a definite shape.

Organic chemistry is essentially the chemistry of carbon and the compounds it forms with atoms of other elements, most notably hydrogen, but also oxygen and nitrogen. Nitrogen with five electrons in its outermost shell and oxygen with six readily form covalent bonds, for example, with hydrogen to form ammonia and water, respectively (Scheme 1.6).



Scheme 1.6 Covalent bonding by nitrogen and oxygen atoms with hydrogen atoms.

Nitrogen and oxygen atoms (and also sulphur atoms) can also form covalent bonds readily with carbon atoms, so there is a vast range of organic compounds involving these elements. Dye and organic pigment molecules are comprised mainly of atoms of these elements covalently bound to each other. For all of these compounds, carbon has a valency of 4, so all C atoms can form four single bonds. The atoms of nitrogen, with a valency of 3, have three single bonds; of oxygen (valency 2) two single bonds, and of hydrogen (valency 1) one single bond. The classes of organic compounds are dealt with later in this chapter.

1.4.3 Secondary Forces of Attraction

Ionic and covalent bonds are referred to as primary forces. Most application classes of dyes are attracted to fibres by ionic bonds (e.g. acid dyes on wool and nylon, basic dyes on acrylics) and by covalent bonds (reactive dyes). In addition to these types of attractive forces between molecules, there exist other types called secondary forces because they are usually weaker than the primary forces. Although weaker, they have an important influence on the physical properties of organic compounds and indeed serve to enhance the attraction between dye molecules and fibres. The main types of secondary forces of attraction are dipolar forces, hydrogen bonding, π–H forces (pronounced 'pi–H') and dispersion forces. Collectively, these forces are often referred to as van der Waals forces.

Dipolar Forces

These forces occur between molecules that are *polar* in character. A molecule is polar if there exists some charge separation across it where some parts of the molecule are partially positive in character ($\delta+$) and other parts are partially negative ($\delta-$). Polarity in a molecule occurs when there is unequal sharing of the electrons of the covalent bond between two different atoms, because one has greater electronegativity than the other, the latter tending to pull the electron pair towards it from the other less electronegative atom. The polar molecules then attract each other, the slightly positive part of one molecule being attracted to the slightly negative end of the other (Figure 1.7).

Hydrogen Bonding

Hydrogen bonding can be regarded as a special case of dipole–dipole attraction. It is so named because it involves hydrogen and because hydrogen is such a small simple atom, when it is bound to another atom that is electronegative, such as oxygen, the shared electron pair forming the covalent bond between them is pulled so much more towards the oxygen that a strong charge separation occurs, creating polarity. The hydrogen atom then serves as a bridge, linking two other electronegative atoms. The most common example of a molecule that readily forms hydrogen bonds is water (Figure 1.8). Aside from forming between

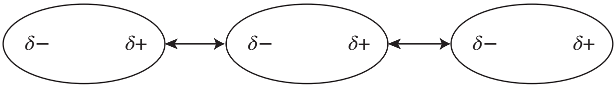


Figure 1.7 Dipole–dipole attraction between molecules.

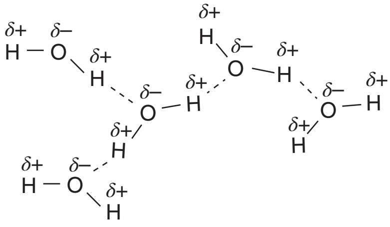


Figure 1.8 Hydrogen bonding in water (— covalent bond, ---- hydrogen bond).

neighbouring molecules (called intermolecular hydrogen bonds), these bonds can also occur between different functional groups of more complex organic molecules such as dyes and pigment molecules. This is called intramolecular hydrogen bonding and is often responsible for the good technical performance, especially the lightfastness, of many dyes and pigments.

π–H Bonding

This is a variation on hydrogen bonding in that it involves the interaction between the π-electron (pronounced 'pi' electron) system of an aromatic ring (see Section 1.8.1.2) that typically occurs in dye and pigment molecules and hydrogen donor groups such as the hydroxy (—OH) group. In the —OH group the O atom is slightly negatively charged and the H atom slightly positively charged. The π-electrons are attracted to the slightly positively charged hydrogen atom: this is called π–H bonding and is illustrated in Figure 1.9.

Dispersion Forces

These are very weak forces that exist between non-polar molecules, in which there is no charge separation in the molecule. They are explained by the fact that electrons in the orbits of the atoms that make up a molecule are in constant motion, so that at any instant small dipoles will be created. These transient dipoles will either induce oppositely oriented dipoles in neighbouring molecules or get into phase with the transient dipoles in them, creating an attractive force. Although these forces are very weak, they are considerable in number, so cumulatively can have an important effect.

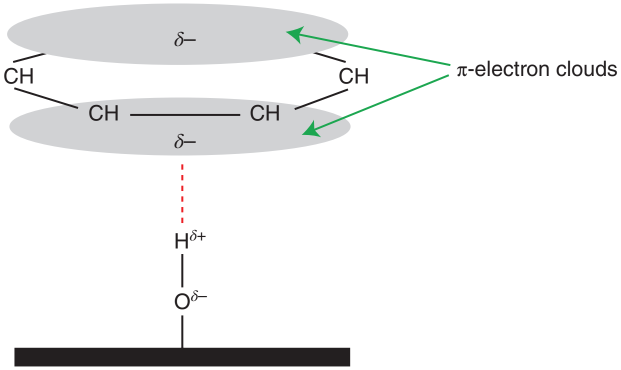


Figure 1.9 π–H bonding.

1.5 Chemical Reactions

1.5.1 Types of Chemical Reaction

Chemical reactions generally fall into three categories: synthesis, decomposition and displacement. In a *synthesis reaction*, two reactants combine to form a single product (Scheme 1.7).

$$A + B \rightarrow AB$$

Scheme 1.7 General formula representing a synthesis reaction.

The arrow → indicates that the reaction proceeds from left to right and is called the *forward reaction*. An example of a synthesis reaction is the formation of ammonia (NH_3) in the Haber process from nitrogen (N_2) and hydrogen (H_2), the equation for which is given in Scheme 1.8.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Scheme 1.8 Formation of ammonia from nitrogen and hydrogen.

When writing chemical equations it is important that they balance, that is, the number of atoms of each element is the same on each side of the arrow. Thus, in Scheme 1.8 the equation shows that two molecules of ammonia are formed and the equation balances because on each side of the arrow there are two atoms of nitrogen and six atoms of hydrogen. The equation is written in this way because it so happens that gases such as nitrogen, hydrogen and oxygen exist as diatomic molecules (N_2, H_2 and $O_{2,}$ respectively).

In a *decomposition* reaction a compound breaks down into two or more products, represented in Scheme 1.9.

$$AB \rightarrow A + B$$

Scheme 1.9 General formula representing a decomposition reaction.

An example of this type of reaction is the decomposition of calcium carbonate into calcium oxide and carbon dioxide (Scheme 1.10).

$$CaCO_3 \rightarrow CaO + CO_2\uparrow$$

Scheme 1.10 Decomposition of calcium carbonate.

The ↑ arrow next to the CO_2 indicates that carbon dioxide is evolved as a gas.

Displacement reactions can be single displacement or double displacement (Scheme 1.11).

$$\mathrm{A + BX \rightarrow AX + B} \qquad \mathrm{AX + BY \rightarrow AY + BX}$$

Single displacement — Double displacement

For example: $\mathrm{Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow}$ — $\mathrm{NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3}$

Scheme 1.11 Single and double displacement reactions.

The ↓ arrow next to AgCl indicates that silver chloride is precipitated from solution.

The → arrow in all of the above reactions indicates that they go to completion; for example, in the above single displacement reaction between zinc and sulphuric acid, the zinc reacts with the acid until it is all used up. However many reactions do not go to completion; for example, the reaction between hydrogen and nitrogen to form ammonia reaches an equilibrium, because ammonia itself can decompose back into hydrogen and nitrogen. This state of affairs is represented by a ⇌ sign. The reaction between nitrogen and hydrogen in the Haber process for synthesising ammonia shown above should be written as

$$\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3}$$

There are two aspects of chemical reactions that are important for practical reasons, especially in the case of industrial processes:

(1) The rate at which reactions take place (reaction kinetics)
(2) The driving forces of reactions and the extent to which they occur (thermodynamics)

These two aspects will be described in sections 1.5.2 to 1.5.5.

1.5.2 Rates of Chemical Reactions and Chemical Equilibria

For an industrial process to be commercially viable, a chemical reaction must proceed at a rate that produces the product in a reasonably quick time. The *law of mass action* states:

The rate of a chemical reaction is directly proportional to the active masses of the reactants.

For a reaction in which a reactant R gives a product P (Scheme 1.12), the active mass of the reactant is indicated by [R]. As the reaction progresses, [R] decreases. The rate of reaction, given by $-d\,[\mathrm{R}]/dt$, is the decrease in its concentration with respect to time, the negative sign indicating the decreasing rate of reaction. By law of mass action,

$$-\frac{d\left[\mathrm{R}\right]}{dt}\alpha\left[\mathrm{R}\right], \quad \text{or} \quad -\frac{d\left[\mathrm{R}\right]}{dt}=k\left[\mathrm{R}\right], \tag{1.1}$$

where k is the rate constant for the reaction.

$$\mathrm{R \rightarrow P}$$

Scheme 1.12 General formula representing a general reaction in which a reactant changes to a product.

For the general reversible reaction shown in Scheme 1.13,

$$\mathrm{A + B \rightleftharpoons C + D}$$

Scheme 1.13 General formula representing a reversible reaction.

The position of the equilibrium depends on the relative rates of the forward and reverse reactions and is established when they are equal. By law of mass action the rate (V_f) of the forward reaction between A and B is given by

$$V_f \propto [\mathrm{A}]\times[\mathrm{B}], \quad \text{or} \quad V_f = k_f[\mathrm{A}]\times[\mathrm{B}], \tag{1.2}$$

where [A] and [B] are the concentrations (active masses) of the reactants A and B and k_f is the rate constant. The corresponding equations for the rate of the backward reaction between C and D (V_b) are

$$V_b \propto [\mathrm{C}]\times[\mathrm{D}], \quad \text{or} \quad V_b = k_b[\mathrm{C}]\times[\mathrm{D}] \tag{1.3}$$

As reactants A and B react together, their concentrations gradually decrease, so V_f decreases. At the same time products C and D are formed, and as more of them are formed, their rate of reaction gradually increases (V_b increases). There then comes a point when $V_f = V_b$: this is the point at which equilibrium is reached. Then

$$k_f[\mathrm{A}]\times[\mathrm{B}] = k_b[\mathrm{C}]\times[\mathrm{D}] \tag{1.4}$$

or

$$\frac{k_f}{k_b} = K\frac{[\mathrm{C}]\times[\mathrm{D}]}{[\mathrm{A}]\times[\mathrm{B}]} \tag{1.5}$$

The term K is called *equilibrium constant*. It is the ratio of the forward and backward reaction rates, but its value indicates where the position of equilibrium lies, that is, if it is in favour of the products or the reactants. Thus, if its value is large, then the yield of the products is high, and conversely if its value is small, the yield of products is low.

Whilst Equations 1.2, 1.3, 1.4 and 1.5 apply to a general chemical reaction between two reactants, the same logic can be applied to the adsorption of dyes by fibres. This is a physical process whereby dye transfers from aqueous solution into the solid fibre, but because dye molecules can desorb from the fibre, an equilibrium is established. This concept is considered further in Chapter 6.

The position of equilibrium of a reversible chemical reaction varies with conditions such as pressure (in the case of reactions between gases) or temperature. The way in which the position of equilibrium is affected is given by application of *Le Chatelier's principle*:

> For a reaction at equilibrium, if one of the conditions changes, for example the temperature, the equilibrium shifts in a direction that nullifies the effect of the change.

If this principle is applied to the Haber process for synthesising ammonia, for example,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 - 92\,\text{kJ/mol}$$

heat is evolved in the forward reaction (the reaction is exothermic), so if heat is removed by lowering the temperature of the reaction, the equilibrium will compensate by producing more heat, that is, the equilibrium shifts in favour of the forward reaction and more ammonia is produced. Therefore it might be expected that the best yield of ammonia is produced at lower temperatures and indeed this is the case, but at lower temperatures, the rate at which ammonia is formed is very slow, so higher temperatures are preferred (about 400–450 °C) but at high pressure (about 200 atm). A very high pressure favours the forward reaction because 1 vol of nitrogen reacts with 3 vols of hydrogen (total 4 vols) to give 2 vols of ammonia. Thus ammonia occupies only half the volume of the reactants, and so its formation nullifies the effect of the high pressure.

Dyeing processes occurring in solution are unaffected by changes in atmospheric pressure but they are exothermic, so in principle, at equilibrium more dyes will be adsorbed by a fibre at lower temperatures. As with the Haber process though, the time taken to reach equilibrium at lower temperatures makes the dyeing process too long, so higher temperatures are preferred when diffusion of dye into the fibre is much quicker. Also, at higher dyeing temperatures, the fabric is wetted out more thoroughly.

1.5.3 Effect of Temperature on Rate of Reaction

The rate of reactions usually increases with temperature and the relationship between them is given by the *Arrhenius equation*:

$$k = Ae^{-E/RT} \tag{1.6}$$

where

k is the rate constant
A is the Arrhenius constant
e is the base of natural logarithms (for explanation of natural logarithms, see Section 1.5.5.4)
T is the absolute temperature
E is the *energy of activation*

This equation shows that the rate of reaction increases as the temperature increases. Typically the rate of a chemical reaction doubles for a 10 °C rise in temperature. Figure 1.10 shows the energy distribution of molecules at a low temperature and also at a higher temperature. It can be seen that at the higher temperature the energy of the molecules increases and that more molecules have energies in excess of the activation energy, E.

In any chemical reaction the reactants must possess sufficient energy so that when the molecules collide, a reaction between them occurs. The minimum energy required for a reaction to take place is the energy of activation, E, so that if reacting molecules possess less than this minimum energy collide, no reaction will occur. This is known as the *collision theory of reaction rates*.

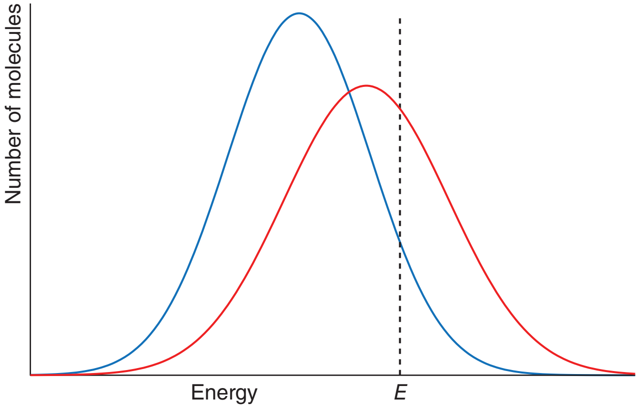


Figure 1.10 Effect of temperature on the energy of molecules: blue line low temperature; red line high temperature. *E* is the activation energy.

As the temperature increases, a greater number of molecules will possess more than this minimum energy and so achieve the necessary activated state for reaction to occur. The factor $e^{-E/RT}$ in the Arrhenius equation gives the proportion of collisions at a given temperature for which the colliding molecules have at least this minimum energy. Some reactions take place through the formation of an intermediate or *activated state* (the activated state in Figure 1.11), which exists for only a very short period of time, but its formation requires the additional energy given by E. This is the *activated state theory* of reaction rates.

1.5.4 Catalysts

A catalyst is a substance that increases the rate of a chemical reaction without changing itself chemically during the reaction. Although there are different mechanisms by which catalysts function, there are general characteristics that can be identified:

(1) The catalyst is chemically unchanged at the end of the reaction, and the same amount is present at the end of the reaction as at the beginning. But in some cases there can be a change in the physical form of the catalyst.
(2) Only a small amount of catalyst is required to considerably accelerate a reaction.
(3) In the case of reversible reactions, the catalyst does not alter the final position of equilibrium, but it only accelerates the rate at which equilibrium is established.
(4) The catalyst does not actually initiate a chemical reaction.

In the presence of a catalyst the same overall chemical process occurs, but by an alternative pathway, one that involves a smaller energy of activation. This means that under a given set of conditions, more of the reacting molecules will possess the minimum energy required for reaction to take place, so the process will take place more quickly. In Figure 1.11 this is the equivalent of the dotted line showing the activation energy being lower when the reaction is carried out in the presence of a catalyst.

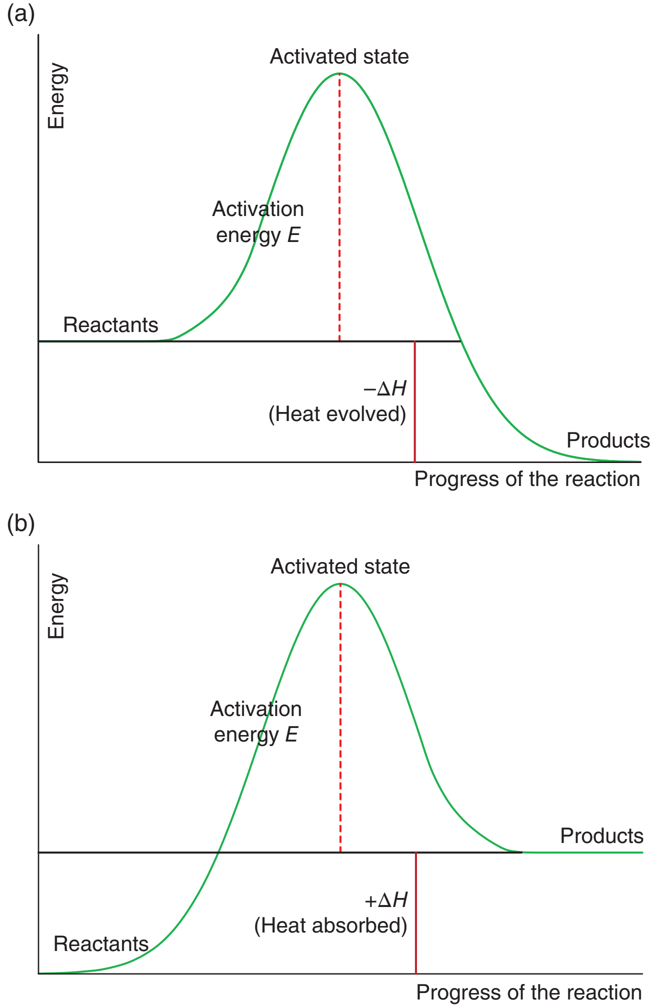


Figure 1.11 Energy pathway of a chemical reaction. (a) An exothermic reaction and (b) an endothermic reaction.

Catalysts can be classed as either *homogeneous* or *heterogeneous*. Homogeneous catalysts have the same phase as the reactants, for example, both may be gases (not all that common) or both may be liquids. An example of this is the use of concentrated sulphuric acid as a catalyst in the formation of esters (see Section 1.8.3.4). Heterogeneous catalysts are in a different phase from the reactants, usually a solid catalyst being used with gaseous or liquid reactants. Typical of this situation is the solid iron catalyst used in the reaction between the hydrogen and nitrogen gases in the Haber process.

Enzymes are an important class of catalyst, especially in textile fibre treatments, such as de-sizing (see Section 2.5.1.3) and bio-finishing, as well as in detergents generally. Unlike most other types of catalysts, they are highly specific in their action and are very sensitive to conditions of temperature and pH.

1.5.5 Thermodynamics of Reactions

Thermodynamic studies are concerned with the energetics of chemical reactions. They can be used to predict the outcome of reactions and calculate equilibrium constants of reversible reactions. Thermodynamic predictions are based only on the differences between the initial and final states, that is, once the system has reached its final equilibrium position. However they do not give any indication about the rate at which reactions occur, so although they may predict a reaction to give a good yield of a product, it may be that the rate at which the product forms takes such a long period of time that it is commercially unviable. Nevertheless, thermodynamic studies applied to dyeing processes can yield much useful information about the mechanism with which dye adsorption occurs and the influence of process conditions on (equilibrium) dye uptake.

The Sections 1.5.5.1–1.5.5.5 give a brief explanation of the laws of thermodynamics and their applications. Later, in Chapter 6, the relevance of thermodynamic studies to dyeing processes will be explained.

1.5.5.1 The First Law of Thermodynamics

The first law of thermodynamics is concerned with energy and the change of energy as systems move from one state to another, for example, when a chemical reaction takes place. It is also known as the *law of conservation of energy*, which states that energy cannot be created or destroyed.

In chemical thermodynamics the heat energy content of a system is called *enthalpy,* which has the symbol H. When a reaction takes place, the system may gain or lose heat energy, so it is the change in enthalpy, ΔH, that is of interest. ΔH is called the *heat of reaction*. It is positive if a chemical reaction is endothermic (absorbs heat) and negative if it is exothermic (liberates heat), as shown in Figure 1.11. A negative value for ΔH will favour a chemical reaction taking place.

The value of ΔH for a reaction can be determined from what are called the *standard enthalpies of formation* of the reactants and products involved. The standard enthalpy of formation, ΔH_f^o, of a compound is the change in enthalpy when it is formed from its elements in their most stable form at normal atmospheric pressure and a temperature of 298 K. (K is the temperature in *Kelvin*, measured on the absolute temperature scale. The units of Kelvin and centigrade temperature interval are identical. A temperature in centigrade is equal to the temperature in Kelvin minus 273.15.)

For example, when carbon reacts with oxygen to form carbon dioxide, the equation is represented as shown in Scheme 1.14.

$$\mathrm{C(graphite)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \qquad \Delta H_f^o = -393.5\ \mathrm{kJ/mol}$$

Scheme 1.14 Formation of carbon dioxide from carbon and oxygen.

The equation shows the carbon in its most stable form at normal atmospheric pressure and 298 K is solid graphite, whilst oxygen and carbon dioxide are gases. Values of the standard enthalpies of formation of compounds are available in tables in specialised textbooks. The values of ΔH_f^o for all elements are zero.

The standard enthalpy change for a chemical reaction, ΔH°, is given by

$$\Delta H^{\mathrm{o}} = \Delta H_{\mathrm{f}}^{\mathrm{o}}\left(\text{products}\right) - \Delta H_{\mathrm{f}}^{\mathrm{o}}\left(\text{reactants}\right) \tag{1.7}$$

For example, when methane burns in oxygen to give carbon dioxide and water (Scheme 1.15), the standard enthalpies of the formation of the reactants and products are as follows:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Scheme 1.15 Burning of methane in oxygen.

Products	Reactants
$CO_2(g)$ −393.5	$CH_4(g)$ −74.81
$H_2O(l)$ −285.8	$O_2(g)$ 0

Applying Equation 1.7 to obtain ΔH° for the reaction $= [-393.5 + 2(-285.8)] - (-74.8 + 0)$

$$= -965.1 + 74.8 \Rightarrow -890.3\ \mathrm{kJ/mol}$$

1.5.5.2 The Second Law of Thermodynamics

One of the driving forces that make naturally occurring processes such as chemical reactions occur is the minimisation of energy. It might be expected therefore that if a reaction is exothermic (enthalpy is decreased due to the liberated heat), it will occur spontaneously. This is usually the case if ΔH is large, but not necessarily if it is small. Conversely there are some endothermic reactions (enthalpy increases) that are also spontaneous. This apparent contradiction implies that there must be some other factor involved in governing whether or not a reaction proceeds and this factor is the *entropy*, which is given the symbol S. According to the second law of thermodynamics, the total entropy, that is, of a system and surroundings, increases during all naturally occurring processes.

Entropy is a measure of the randomness, or disorder, of a system. The tendency for entropy to increase is the second driving force of reactions. The concept of entropy can be difficult to understand but one way of imagining it is when liquid molecules vaporise into gaseous form. In doing so molecules move from a condition in which they are highly ordered to one where they have much more freedom to move. The opposite situation occurs during a dyeing process because the dye molecules move from a state of relatively high randomness when they are in solution to one where they are much more constrained once they have become adsorbed in the solid fibre. As with enthalpy changes, ΔH, it is the change in entropy, ΔS, as a chemical reaction takes place that is of interest. Depending on the reaction (or dyeing process), ΔS may be positive, negative or zero.

During a reversible process at a constant temperature, T, a small change in entropy dS is related to an infinitesimal amount of heat absorbed, q_{rev}, by the equation

$$dS = \frac{dq_{\text{rev}}}{T} \tag{1.8}$$

and for a finite change between the initial and final states

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{1.9}$$

Although the notion of a reversible change is required to obtain ΔS, it does not matter what path the process takes in transitioning from the initial to the final state or whether it is thermodynamically reversible or not. A positive value for ΔS will favour a reaction occurring.

1.5.5.3 The Third Law of Thermodynamics

The third law of thermodynamics states that all truly perfect crystals at absolute zero temperature have zero entropy. By using heat capacity data it is possible to calculate the entropy of a compound in its standard state, S^o. Values of S^o are available in tables in specialised textbooks.

1.5.5.4 Free Energy

In attempting to predict whether a chemical reaction will occur or not, it has been established above that the loss of enthalpy (i.e. a negative value of ΔH) and a gain in entropy (i.e. a positive value of ΔS) will each have a favourable influence. Conversely, if both are unfavourable (i.e. ΔH is positive and ΔS is negative), the reaction will not occur. However, if one is favourable and the other is not, a measurement is required that comprises two components of enthalpy and entropy changes. This measure is the *free energy*, G, also known as the *Gibbs free energy*, which is defined by the equation

$$G = H - T \cdot S \tag{1.10}$$

As with enthalpy and entropy, thermodynamics is only concerned with the change in free energy, ΔG, when a process takes place. For a reaction occurring at constant temperature T,

$$\Delta G = \Delta H - T \cdot \Delta S \tag{1.11}$$

If values for T, ΔH and ΔS are applied to Equation 1.11, the value of ΔG obtained indicates whether a reaction will take place. If ΔG has a negative value, the reaction will occur; if it is positive, the reverse reaction occurs; and if it is zero, equilibrium is attained. However, it should be remembered that the magnitude of ΔG is not related to the rate at which the reaction takes place; it only indicates the tendency for it to occur. In practice the reaction may be very slow or very fast – thermodynamics gives no indication of the rate.

It is convenient to determine the change in free energy under standard conditions (1 atm and 298 K), and this can be achieved using the equation

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \tag{1.12}$$

Often, it is necessary to know the value of ΔG^{o} at some other temperature. This can be done, but it involves knowledge of the heat capacities of the products and reactants, so that the enthalpy changes involved in heating (or cooling) the reactants and products and of the entropy values at the new temperature can be calculated.

Another important equation in thermodynamics is the relation between the Gibbs free energy and the equilibrium constant of a reaction:

$$\Delta G^{o} = -R \cdot T \cdot \ln K \tag{1.13}$$

where

R is the gas constant,
T is the absolute temperature,

ln is the symbol for natural logarithm, that is, logarithm to the base 'e', which has a value of 2.718. In the equation $a=b^n$, n is the logarithm of a. Common logarithms are to the base 10, so in $a=10^n$ n is the logarithm of a and is written '$\log_{10} a$' or often just 'log a'. In the case of natural logarithms $a=2.718^n$, n is now the natural logarithm of a and is written 'ln a'. The relationship between natural and common logarithms is: ln a=2.303 log a.

K is the equilibrium constant (see Equation 1.5).

Interpretation of this equation shows that for a reaction that has reached equilibrium, if $\Delta G^{o}<0$, then $K>1$, and vice versa. If $\Delta G^{o}=0$, then $K=1$ and the position of equilibrium is such that there are equal amounts of products and reactants.

1.5.5.5 Interpreting Thermodynamic Data

In Section 1.5.2 reference was made to Le Chatelier's principle and thermodynamic values can be used to provide quantitative evidence in support of it. If Equations 1.12 and 1.13 are combined,

$$-R \cdot T \cdot \ln K = \Delta H^{o} - T\Delta S^{o} \tag{1.14}$$

so

$$\ln K = -\frac{\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} \tag{1.15}$$

Entropy changes, ΔS^{o}, vary little over small changes in temperature, so $\Delta S^{o}/R$ can be regarded as constant, and

$$\ln K = -\frac{\Delta H^{o}}{R} \cdot \frac{1}{T} + C \tag{1.16}$$

Differentiating Equation 1.16 gives

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^{\circ}}{RT^2} \tag{1.17}$$

This equation, known as the Van't Hoff equation, indicates that if ΔH° is negative, then K will decrease with an increase in temperature, and vice versa. This is significant in dyeing processes for which ΔH° is negative, indicating that for dyeing processes at equilibrium, less dye will be adsorbed by the fibre at higher temperatures. This behaviour will be considered further in Chapter 6.

Equation 1.16 can be developed to form

$$\ln\frac{K_1}{K_2} = -\frac{\Delta H^{\circ}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{1.18}$$

This equation provides a useful method for determining the value of ΔH° of a dyeing process if the values of K_1 and K_2 at temperatures T_1 and T_2, respectively, are determined experimentally.

1.6 Acids, Bases and Salts

1.6.1 Acids and Bases

Acids are substances that dissociate in solution to liberate hydrogen ions, H^+. For example, hydrogen ions are formed when hydrogen chloride dissolves in water, forming hydrochloric acid:

$$\mathrm{HCl} \xrightarrow{\text{aq}} \mathrm{H^+} + \mathrm{Cl^-}$$

Acids are characterised by their sour taste and corrosive action. The most common inorganic acids are hydrochloric acid (HCl), sulphuric acid (H_2SO_4) and nitric acid (HNO_3). These acids are described as being 'strong' acids because they dissociate almost completely in water. There exist also acids, usually organic acids, that are described as being 'weak' acids because they only dissociate partially in water. These acids contain the carboxyl group —COOH, typical examples being methanoic acid (formic acid, HCOOH) and ethanoic acid (acetic acid, CH_3COOH).

Bases are substances that create hydroxyl ions (OH^-) in water. Typical of the bases are alkalis, which are the hydroxides of metals. A widely used alkali in preparation and dyeing processes is sodium hydroxide (caustic soda), NaOH. As with acids, bases can be described as being 'strong' or 'weak', for example, sodium hydroxide is a 'strong' alkali. Weaker alkalis are ammonium hydroxide (NH_4OH) and organic bases such as methylamine (CH_3NH_2) or ethylamine ($C_2H_5NH_2$).

1.6.2 The pH Scale

The pH scale is a convenient way of expressing the strength of solutions of acids or bases. A solution with a pH value of 7 is neutral. pH values of less than 7 represent acidity – the lower the value, the more acidic the solution. Values greater than 7 represent alkalinity (basicity) – the higher the value, the more alkaline the solution. The full scale ranges from 0 to 14.

These figures are not arbitrary. They are derived from the concentration of hydrogen ions in the solution, written $[H^+]$. Consider first the case of water, H_2O. Even liquid water undergoes dissociation to some extent: about one water molecule in every 10 million molecules dissociates:

$$H_2O \rightarrow H^+ + OH^-$$

Each positively charged hydrogen ion is accompanied by a negatively charged hydroxide ion, so that the numbers of positive and negative charges in the solution are balanced, and

$$\left[H^+\right] = \left[OH^-\right] = 10^{-7}$$

When $[H^+]$ and $[OH^-]$ are multiplied together, a constant value of 10^{-14} is obtained, that is:

$$\left[H^+\right] \times \left[OH^-\right] = 10^{-14}$$

An acidic solution contains more hydrogen ions than hydroxide ions. Even in solutions of weak acids, the number of hydrogen ions is very large, so the pH value expresses the concentration of hydrogen ions on a logarithmic scale:

$$\mathrm{pH} = -\log\left[H^+\right] \quad \text{or} \quad \mathrm{pH} = \log\left(\frac{1}{\left[H^+\right]}\right) \tag{1.19}$$

For pure water the $\mathrm{pH} = -\log(10^{-7})$, which is 7.

For acidic solutions $[H^+]$ is greater than 10^{-7}. For example, in a solution of 0.01 M hydrochloric acid, the $[H^+]$ is 10^{-2}, so the pH value will be 2.

In alkaline solutions the concentration of hydrogen ions is less than in neutral water, and the concentration of hydroxide ions is higher. For example, in a solution of 0.01 M sodium hydroxide, NaOH, the $[OH^-]$ will be 10^{-2}, so the $[H^+]$ will be 10^{-12}, in which case the solution has $\mathrm{pH} = 12$.

1.6.3 Salts and Salt Hydrolysis

When an acid is neutralised by a base, salt and water are formed. The hydrogen atoms of the acid are replaced by atoms of a metal. Typical examples are the reaction between hydrochloric acid and sodium hydroxide:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

and between sulphuric acid and sodium hydroxide:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

Note that in the second case, sulphuric acid has two hydrogen atoms that must be replaced, so two molecules of sodium hydroxide are required. The salts formed in each case, sodium chloride and sodium sulphate, are named according to the metal and the acid from which they were derived. These two salts are important as auxiliaries in dyeing processes. Sodium chloride is used in the application of anionic dyes (such as direct dyes, reactive dyes and vat dyes) to cotton, and sodium sulphate is used in the application of acid dyes to wool and nylon.

When salts are dissolved in water, they do not necessarily produce solutions with neutral pH; it just depends on the strengths of the acid and base from which they were formed. The salts in the two examples above were both produced from a strong base (sodium hydroxide, NaOH) and a strong acid (hydrochloric acid, HCl, and sulphuric acid, H_2SO_4). In solution both of these salts give neutral solutions.

However, a salt made from a strong base but a weak acid will give an alkaline solution ($pH > 7$). An example of this is sodium ethanoate (sodium acetate): the acid from which the salt is derived is ethanoic acid (acetic acid), which is a weak acid, but the base, sodium hydroxide, is, as noted above, a strong base.

Conversely, a salt made from a weak base and a strong acid will give an acidic solution ($pH < 7$). In this case an example is ammonium sulphate, $(NH_4)_2SO_4$, for which the weak base is ammonium hydroxide, NH_4OH, and the strong acid is sulphuric acid.

The last combination, that of salts produced from a weak base and a weak acid, such as ammonium ethanoate (ammonium acetate), CH_3COONH_4, is likely to be neutral, but may be slightly acidic or slightly alkaline, depending on the relative strengths of the acid and base.

Other important salts in dyeing processes are those of orthophosphoric acid, H_3PO_4. This acid is tribasic and three sodium salts of it are possible: sodium dihydrogen orthophosphate, NaH_2PO_4; disodium hydrogen orthophosphate, also called ‘sodium phosphate’, Na_2HPO_4; and trisodium orthophosphate, Na_3PO_4. Orthophosphoric acid is a weak acid and trisodium orthophosphate gives an alkaline solution. Disodium hydrogen orthophosphate is neutral in solution and sodium dihydrogen orthophosphate gives a slightly acidic solution.

This behaviour of salts is termed *salt hydrolysis*. Salts that give acidic or alkaline solutions are used in dyeing processes where conditions of pH that are not neutral are required. In some dyeing processes it is highly desirable that a certain pH is maintained throughout, and to ensure that this happens, a *buffer solution* is used. This is the subject of the next section.

1.6.4 Buffer Solutions

A buffer solution is capable of maintaining a constant pH value, even if a small quantity of acid or alkali is added to it. Such a solution usually consists of two components: a mixture of a weak acid and its salt, such as ethanoic (acetic) acid/sodium ethanoate (acetate), or of a weak base and its salt, such as ammonium hydroxide/ammonium sulphate. Buffer solutions of any desired pH can be made by appropriate formulation of the two components, though they do have what is called a *buffer capacity*, that is, there is a limit to the amount of acid or alkali that they can absorb without their pH changing.

1.7 Redox Reactions

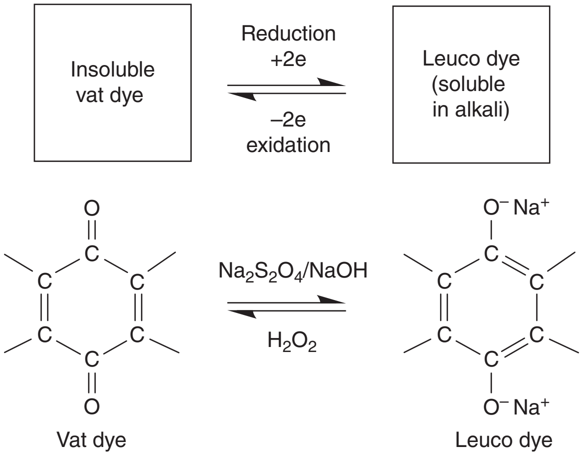
Oxidation–reduction reactions (*redox reactions*) are important in textile coloration because they are an essential part of the process of the application of vat and sulphur dyes. In rather oversimplified terms, when a compound is oxidised, it gains oxygen; when it is reduced, it loses oxygen.

Reduction of a substance can also be thought of as gaining hydrogen atoms and oxidation as losing hydrogen atoms. For example, when hydrogen reacts with oxygen to form water, hydrogen becomes oxidised and oxygen is reduced. In a redox reaction there is always a compound acting as a *reducing agent* (hydrogen in this example). The reducing agent becomes oxidised during the reaction by the compound that is being reduced, which is acting as an *oxidising agent* (in this case oxygen).

In the water molecule, each hydrogen atom shares the only electron it possesses by pairing with one of the six electrons of the oxygen atom to form a covalent bond (see Scheme 1.6). Thus the hydrogen atom has lost one electron to become oxidised and the oxygen atom is reduced by gaining electrons. This is a more general way of expressing the phenomena of oxidation and reduction:

- Oxidation entails the loss of electrons by the oxidised compound.
- Reduction entails a net gain of electrons by the reduced compound.

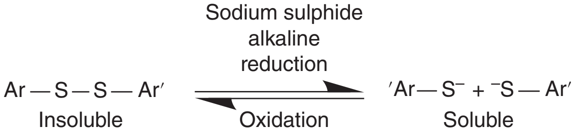
Vat dyes such as indigo and compounds derived from anthraquinone are applied after the temporary reduction of two carbonyl groups (C=O) in a conjugated chain (see Section 1.8.1); this converts the dye into a colourless water-soluble form. The conversion is carried out using a strong reducing agent such as sodium dithionite and sodium hydroxide. In the reaction (Scheme 1.16) the two oxygen atoms become reduced to $-O^-$.



Scheme 1.16 Reduction of vat dyes.

The reduced (soluble) form is called the *leuco* form and is applied from an alkaline solution. Once adsorbed on the fibre, the dye can be re-oxidised back to the insoluble carbonyl form by air or by the use of an oxidising agent.

Sulphur dyes are also applied using a redox reaction mechanism (Scheme 1.17), in which sodium sulphide is used as the reducing agent.



Scheme 1.17 Redox reactions of sulphur dyes.

1.8 Organic Chemistry

Organic chemistry is the study of compounds containing carbon. There are so many compounds containing carbon, well over one million, that a branch of chemistry different from inorganic chemistry (which deals with the chemistry of all the other elements) is justified. Carbon atoms have the ability to combine with themselves to form chains and these chains can have different lengths, be straight or branched. In addition, the ends of chains may join up at their ends to form closed rings.

Organic compounds that comprise carbon and hydrogen atoms are referred to as *hydrocarbons*. However, as noted in Section 1.1, carbon can also form compounds involving atoms of other elements, such as oxygen and nitrogen, which greatly extends the range and characteristics of organic compounds. Some organic molecules are highly complex in structure, containing small groups of atoms, known as functional groups. Examples of functional groups are alcohols ($-OH$), amines ($-NH_2$) and carboxylic acids ($-COOH$), which will be described in later sections. The properties of an organic compound depend on the properties of the individual functional groups that make up the molecule.

In simple terms, there are two classes of organic compounds: *aliphatic* and *aromatic*. Aromatic compounds are ring structures based on benzene and are so called because when they were first discovered they were considered to have pleasant aromas. The rest are aliphatic compounds, but many of these also have distinctive aromas.

The rules for naming organic compounds are now very formalised: as organic chemistry developed and new compounds discovered, trivial names were given to them, some of which are still used today. In the textile manufacturing, dyeing and finishing industries, some of these trivial names are still used, so it is necessary to be somewhat ‘bilingual’ and know the two names often used for the same chemical.

1.8.1 The Hydrocarbons

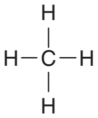
Hydrocarbons (compounds made up of just hydrogen and carbon atoms) can occur as straight (and branched) chain structures or as ring structures. The chain compounds are called *aliphatic* hydrocarbons, whilst the ring structures are called *aromatic* compounds.

1.8.1.1 Aliphatic Hydrocarbons

There are three families, called *homologous series*, of aliphatic hydrocarbons:

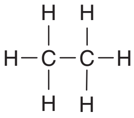
(1) Alkanes (paraffins)
(2) Alkenes (olefins)
(3) Alkynes (acetylenes)

Alkanes have the general formula C_nH_{2n+2}, where n is the number of carbon atoms in the molecule. The simplest compound is methane, CH_4 (**1.1**), where $n = 1$. The next member of the series is ethane, C_2H_6 (**1.2**), followed by propane, C_3H_8 (**1.3**), and then butane, C_4H_{10} (**1.4**). These alkanes have the following structures.



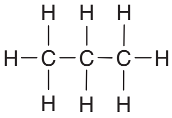
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

1.1



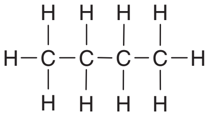
$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array}$$

1.2



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H \\ & | & | & | & \\ & H & H & H & \end{array}$$

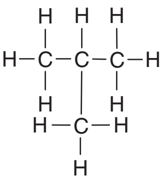
1.3



$$\begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C & -H \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$$

1.4

It can be seen that moving from one member to the next upwards in this homologous series adds a CH_2 group. These are all straight-chain hydrocarbons, but it is also possible to write the structure of butane with a branched chain (**1.5**), which is called an *isomer* of butane. This isomer is named 2-methylpropane (or isobutane).



1.5

Going up the homologous series further, there are greater possibilities for branched structures to be drawn.

An important structural feature of carbon chains is their zigzag form, illustrated in Figure 1.12.

As illustrated in Figure 1.4, the four bonds of a carbon atom are oriented tetrahedrally, and because the angles between single bonds are fixed, a chain of carbon atoms cannot lie flat in a straight line. Instead it is forced into a zigzag arrangement. This is important because it governs the three-dimensional shapes of organic molecules, which may in part determine their physical and chemical properties.

Alkanes are chemically unreactive, but burn readily in air to give carbon dioxide, CO_2, and water, H_2O. On ascending the series, the physical properties of the members gradually change, so the first four are all gases, those between pentane (C_5H_{12}) and heptadecane ($C_{17}H_{36}$) are all liquids, and those from $C_{18}H_{38}$ upwards are solids (waxes).

All the atoms of the compounds in the alkane series are joined by single covalent bonds and they are referred to as *saturated* compounds. This distinguishes them from similar

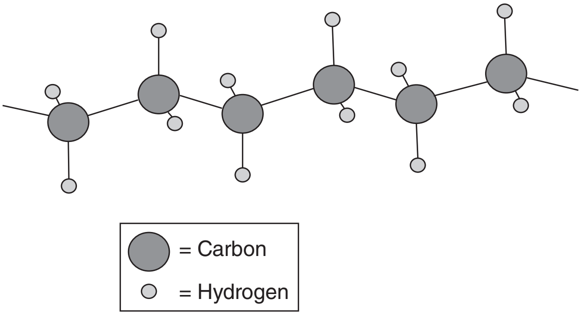
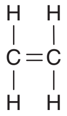


Figure 1.12 Zigzag form of hydrocarbon chains.

compounds in which some double bonds exist between the constituent atoms. Such compounds are known as *unsaturated* compounds.

Alkenes are the simplest homologous series of unsaturated hydrocarbons and have the general formula C_nH_{2n}. The first member of the series is ethene (ethylene), C_2H_4, (**1.6**), which contains two carbon atoms linked by a double bond.



$$\mathrm{H_2C{=}CH_2}$$

1.6

The presence of the double bond does not double the strength of the bonding between the two carbon atoms. The second bond is much less chemically stable than the first and is therefore more reactive. Each carbon atom undergoes hybridisation (see Section 1.4.2), but in this case hybridisation of an s orbital and two p orbitals occurs, giving three sp^2 hybrid orbitals (Figure 1.13).

These orbitals overlap with an sp^2 hybrid orbital of the other carbon atom and the s orbitals of two hydrogen atoms to form three sigma (σ) bonds. The remaining p orbital interacts with that on the other carbon atom, giving a pi (π) bond. The σ bonds between the carbon atoms and the hydrogen atoms are all in the same plane and the p orbitals are at right angles to this plane (Figure 1.14).

The σ bonds have true covalent character, but because the π bond is strained, it is easily broken. It is this reactive bond that is responsible for the characteristic chemical reactions

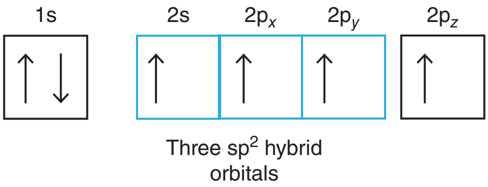


Figure 1.13 sp^2 hybridisation.

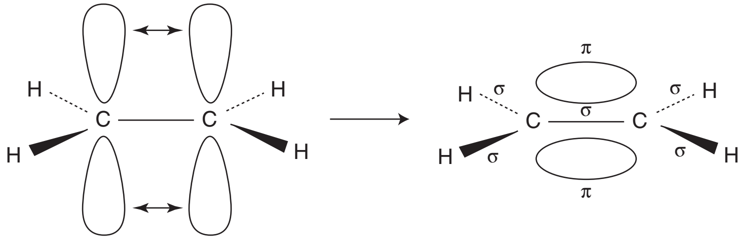
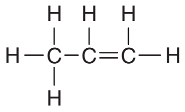


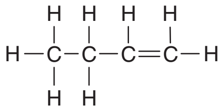
Figure 1.14 σ and π bonds in ethane.

of double-bonded hydrocarbon compounds. The next member of the alkene series is propene, C_3H_6 (**1.7**).



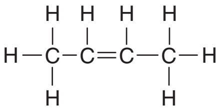
$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H}$

1.7



$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-H}$

1.8



$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-H}$

1.9

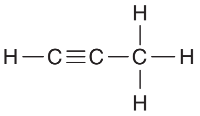
It does not matter where the double bond occurs in propene because the molecule is the same from whichever angle it is viewed. However, in the case of the next highest member of the series, butane (C_4H_8), two isomers are possible. If the double bond is located between the first and second carbon atoms, it is named 1-butene (**1.8**), but if it is located between the second and third carbon atoms, it is named 2-butene (**1.9**).

The reactions of these unsaturated compounds include the polymerisation reactions used in the formation of synthetic fibres such as acrylics and polyolefins (Chapter 2) and the dye–fibre reactions of certain dyes.

Alkynes contain triple bonds between carbon atoms. They have the general formula C_nH_{2n-2} and the simplest member is ethyne (acetylene), C_2H_2 (**1.10**), and the next member up the series is propyne, C_3H_4 (**1.11**). In the formation of alkynes, sp hybridisation occurs, so that between the two carbon atoms, in addition to the two σ bonds, there are two π bonds, both of which are highly strained, making them very chemically reactive gases.

$\mathrm{H-C\equiv C-H}$

1.10

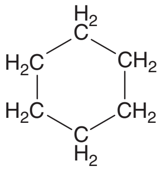


$\mathrm{H-C\equiv C-\overset{H}{\underset{H}{C}}-H}$

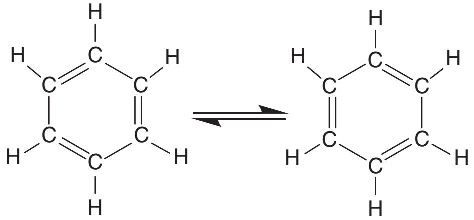
1.11

1.8.1.2 Aromatic Hydrocarbons

The molecules of aromatic compounds contain ring structures of a special kind. The structural formulae of aromatic rings may be drawn as if alternating single and double bonds existed between adjacent carbon atoms. Compare, for example, the six-carbon aliphatic cyclic compound cyclohexane, C_6H_{12} (**1.12**), with the six-carbon aromatic compound benzene, C_6H_6, (**1.13**).



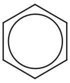
1.12



1.13

An arrangement of alternating single and double bonds (as in Structure **1.13**) is called a *conjugated system*, and it is very important in the molecular structure of dyes. In 1865 Kekulé proposed the closed ring structure for benzene with the three alternating single and double bonds. For this reason representing the structure of benzene in the way shown in **1.13** is called the Kekulé structure.

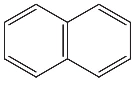
The bonds in the benzene ring are of a very special kind, however, and do not form a conjugated system. All six bonds in the ring are exactly alike and none of them undergo the characteristic reactions of double bonds in, say, alkenes; they are in fact much more stable (unreactive) than double bonds. The π electrons are distributed above and below the plane of the ring, forming diffuse clouds of negative charge: they are said to be *delocalised* and the phenomenon is known as *resonance*. The delocalising of electrons makes aromatic compounds different from aliphatic compounds. In recognition of the nature of the benzene ring, its structural formula is sometimes represented as a hexagon with a central circle (**1.14**) rather than with the alternating single and double bonds.



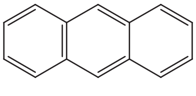
1.14

For simplicity's sake, the benzene ring is often drawn without showing the individual carbon and hydrogen atoms, as in **1.14**, their presence being implied by the notation.

All dye molecules contain aromatic ring structures, though it is more usual to find fused rings, such as naphthalene (**1.15**) (two rings fused together) or anthracene (**1.16**) (three rings fused together).



1.15



1.16

Where the rings join, they share two carbon atoms, and thus naphthalene with two rings has 10 carbon atoms, not 12. Similarly, anthracene with three rings has 14 carbon atoms rather than 18. As naphthalene and anthracene contain delocalised electrons *over all the rings,* it is inappropriate to use the delocalised symbol which is used for benzene on its own, for that would indicate, incorrectly, two or three separate delocalised systems. Thus in this book, *Kekule structures* are used.

Table 1.2 Common functional groups in organic compounds.

functional group	formula
Halide	F, Cl, Br, I
Alcohol	—OH
Carboxylic acid	—COOH
Ester	—COO—
Aldehyde	—CHO
Ketone	—CO—
Ether	—O—
Amine	$—NH_2$
Amide	$—CONH_2$
Cyano	—CN
Nitro	$—NO_2$
Sulphonic acid	$—SO_3H$

1.8.2 Functional Groups

One or more of the hydrogen atoms in hydrocarbons can be replaced by other atoms or, more commonly, groups of atoms, which gives rise to different homologous series. The most common functional groups are shown in Table 1.2.

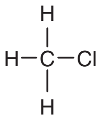
It is most usual for the functional groups shown in Table 1.2 to replace one of the hydrogen atoms in an alkane. When this is the case, the general formula becomes $C_nH_{2n+1}X$, where X is the functional group (—OH, —COOH, etc.). Often for convenience, the hydrocarbon part, C_nH_{2n+1}, called an *alkyl* group, is written R, so the general formula of an alcohol is represented as R—OH and a carboxylic acid as R—COOH. Alkyl groups are named by replacing the final letter *e* of the parent hydrocarbon (i.e. the hydrocarbon with the same number of carbon atoms) by 'y*l*', so the $CH_3—$ group is the *methyl* group, the $C_2H_5—$ group is the *ethyl* group and so on.

Just as a hydrogen atom of an alkane can be replaced by a functional group, so can one of the hydrogen atoms of an aromatic ring. In the case of benzene, the removal of one of the hydrogen atoms creates the *phenyl* group, $C_6H_5—$, and if this hydrogen atom is replaced by an alcohol group, the compound phenol, C_6H_5OH, is formed. The chemistry of the organic compounds with functional groups, relevant to fibres and dyes, is described in Sections 1.8.3 and 1.8.4.

1.8.3 Important Functional Groups of Aliphatic Compounds

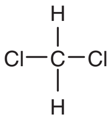
1.8.3.1 Halides

If one of the hydrogen atoms of an alkane is replaced by a halogen atom, an alkyl halide is formed. A typical example is monochloromethane, CH_3Cl (**1.17**), though fluorine, bromine and iodine derivatives are also known and are used as solvents. Chlorine derivatives tend to be mostly used because of their cheapness, such as di- (**1.18**), tri- (**1.19**) and tetra- (**1.20**) substituted chlorinated compounds of methane.



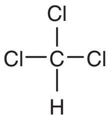
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H-C-Cl} \\ | \\ \mathrm{H} \end{array}$$

1.17



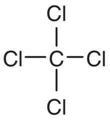
$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{Cl-C-Cl} \\ | \\ \mathrm{H} \end{array}$$

1.18



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl-C-Cl} \\ | \\ \mathrm{H} \end{array}$$

1.19



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Cl-C-Cl} \\ | \\ \mathrm{Cl} \end{array}$$

1.20

Dichloromethane (**1.18**) is used as a solvent in the dry spinning of cellulose triacetate fibre (see Section 2.7.4). Complex fluorinated hydrocarbon compounds are used in water-, oil- and soil-repellent finishes for fabrics.

1.8.3.2 Alcohols

If aliphatic hydrocarbons have just one of their hydrogen atoms replaced by an —OH group, in which case the general formula is $C_nH_{2n+1}OH$, they are called *monohydric* alcohols. The first two members of this series are methanol, CH_3OH (**1.21**), and ethanol, C_2H_5OH (**1.22**). Alcohols are named by replacing the final letter *e* of the parent hydrocarbon by *ol*. When the structural formulae of these alcohols are written, it is seen that for methanol and ethanol it does not matter which C atom the —OH group is located on – the structures will be the same. However, for the next members of the series, propanol and butanol, the —OH group can be placed at different positions on the carbon chain, giving rise to isomers. Thus propanol has two isomers, propan-1-ol (or *n*-propanol) (**1.23**) and propan-2-ol (or isopropanol) (**1.24**). In the case of butanol, four isomers are possible: butan-1-ol (**1.25**), butan-2-ol (**1.26**), 2-methyl-1-propanol (sometimes named isobutanol) (**1.27**) and 2-methyl-2-propanol (sometimes called *tert*-butanol) (**1.28**). For higher alcohols, such as pentanol, hexanol and so on, even greater numbers of isomers are possible.

CH_3-OH

1.21

CH_3-CH_2-OH

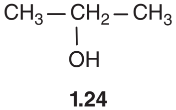
1.22

$CH_3-CH_2-CH_2-OH$

1.23

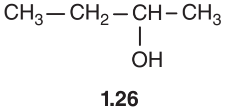
$CH_3-CH_2-CH_2-CH_2-OH$

1.25



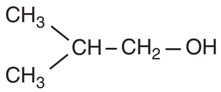
$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH_2}}-CH_3$$

1.24

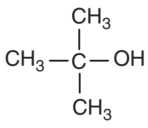


$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

1.26



1.27



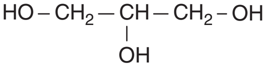
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$$

1.28

Alcohols containing two —OH groups are called *dihydric* alcohols, the most well known of which is ethane-1,2-diol (ethylene glycol, **1.29**), used in the manufacture of polyester (see Section 2.8.1.3). Propane-1,2,3-triol, better known as glycerol (**1.30**), is a *trihydric* alcohol.

$HO-CH_2-CH_2-OH$

1.29



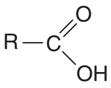
$HO-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-OH$

1.30

The lower members of the monohydric alcohols are liquids, and on ascending the homologous series, the boiling point rises. Methanol and ethanol boil at 64 and 78 °C, respectively. After decanol though, the higher members are solids. Methanol, ethanol and propanol all mix readily with water, but the greater hydrophobic character of the longer hydrocarbon chains of the higher members dominates and they become less miscible. Nevertheless, alcohols are a useful range of solvents for a variety of organic compounds.

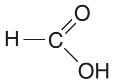
1.8.3.3 Carboxylic Acids

Carboxylic acids have the general formula R—COOH, in which the structure of the carboxylic acid group is shown in (**1.31**).

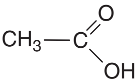


1.31

They are named by replacing the final letter *e* of the parent hydrocarbon by *oic acid*. The first member of the series is methanoic acid (formic acid, HCOOH, **1.32**) because there is one carbon atom, as in methane. The next member is ethanoic acid (acetic acid, CH_3COOH, **1.33**) because it has two carbon atoms, as does ethane. These two acids are used in textile wet processing operations. Ethanoic acid is also used in the manufacture of cellulose acetate fibres (see Section 2.7.4).

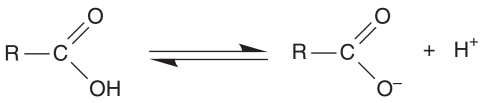


1.32



1.33

Pure anhydrous ethanoic acid is a colourless liquid. When it freezes at 16.7 °C, it is called *glacial* ethanoic acid because of its ice-like appearance. On ascending the series of carboxylic acids, the solubility in water decreases, and those where $R = C_8H_{17}—$ or longer are waxy solids. These organic acids are weak acids (see Section 1.6.1) because they only dissociate partially in water (Scheme 1.18).



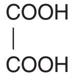
Scheme 1.18 Dissociation of carboxylic acids.

Methanoic and ethanoic acids readily form salts with alkalis, for example:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

The salt formed in this case is sodium acetate.

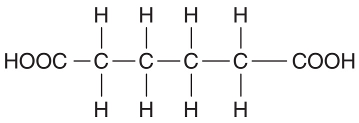
Carboxylic acids containing two acid groups are called dicarboxylic acids, the simplest being oxalic acid (**1.34**).



$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

1.34

The dicarboxylic acid 1,6-hexanedioic acid (**1.35**) is used in the manufacture of nylon 6.6 (see Section 2.8.1.1).



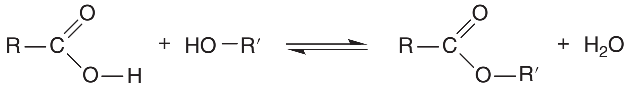
$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ HOOC & - & C & - & C & - & C & - & C & - & COOH \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

1.35

This acid is also called adipic acid and its formula is often written as $HOOC{-}(CH_2)_4{-}COOH$.

1.8.3.4 Esters

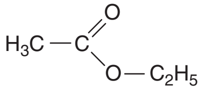
Aliphatic esters are produced by the reaction between a carboxylic acid and an alcohol (Scheme 1.19); in the presence of concentrated sulphuric acid, which acts as a catalyst,



Scheme 1.19 Formation of esters.

where the R and R′ groups may be the same or different. The formation of esters is a reversible reaction, and indeed esters can be hydrolysed back to their component carboxylic acid and alcohol.

Esters are named as though they are alkyl 'salts' of the acid, though they are not salts at all. The final letters *oic* of the carboxylic acid from which the ester is formed is replaced by the letters *oate*. For example, if the acid is ethanoic acid and the alcohol ethanol, the ester formed is ethyl ethanoate (**1.36**).



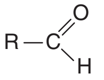
1.36

Lower members of the series are pleasant smelling volatile liquids, whilst higher members are oils, fats and waxes.

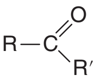
Esters are of interest in textile fibre chemistry because of the commercial importance of polyester fibres produced by the reaction between a dicarboxylic acid and a diol (see Section 2.8.1.3). Cellulose acetate fibres (acetate and triacetate) are also esters: in this case it is the —OH groups of cellulose that are esterified.

1.8.3.5 Aldehydes and Ketones

Aldehydes (**1.37**) and ketones (**1.38**) are closely related compounds in that both contain a carbonyl group and differ only in that aldehydes have a hydrogen atom bonded to it whereas ketones have a second alkyl group bonded to it.


Aldehyde

1.37


Ketone

1.38

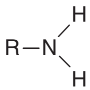
Aldehydes are named by replacing the final letter *e* of the parent hydrocarbon by ‘a*l*’. The most important aldehydes are methanal (formaldehyde, HCHO) and ethanal (acetaldehyde, CH_3CHO). Ketones are named by stating the names of the two alkyl groups, followed by ‘ketone’. Of the ketones, dimethylketone (acetone, CH_3COCH_3) is the most common, being widely used as a solvent. It is used in the manufacture of acetate fibre (see Section 2.7.4). It is also a good solvent for many disperse dyes.

1.8.3.6 Ethers

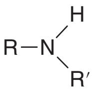
Ethers have the general formula R—O—R′, that is, two alkyl groups bonded to an oxygen atom. They are named in a similar way to the ketones by stating the names of the two alkyl groups, followed by ‘ether’. The most common ether is diethyl ether, $C_2H_5OC_2H_5$, often simply called ‘ether’. It is a dangerously inflammable liquid and often used as a solvent in organic synthesis.

1.8.3.7 Amines

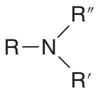
Amines can be regarded as derivatives of ammonia, NH_3, in which the hydrogen atoms are replaced by alkyl groups. One, two or all three of the hydrogen atoms can be replaced, giving primary (**1.39**), secondary (**1.40**) and tertiary (**1.41**) amines, respectively.


Primary amine

1.39


Secondary amine

1.40

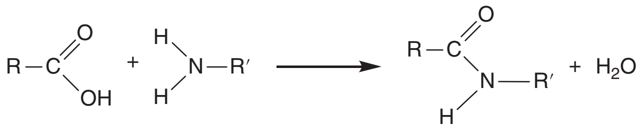

Tertiary amine

1.41

The R, R′ and R″ alkyl groups can be the same or different. Structure **1.39** contains only one alkyl group, and if R = —CH_3, then the amine has the formula CH_3NH_2 and is named methylamine. If R = —C_2H_5, the amine, $C_2H_5NH_2$, is named ethylamine. In the case of secondary amines (**1.40**), in which both R and R′ are —CH_3 groups, it is dimethylamine, $(CH_3)_2NH_2$, whilst if R = —CH_3 and R′ = —C_2H_5, the compound is named ethylmethylamine.

The tertiary amine (**1.41**) in which R, R′ and R″ are all $-CH_3$ groups is trimethylamine, $(CH_3)_3NH_2$. The lower members of primary amines smell strongly of ammonia and have many of the properties of ammonia, giving alkaline solutions in water.

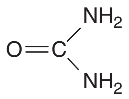
The amine functional group ($-NH_2$) is reactive and reacts with other types of functional groups. Of particular interest in textile chemistry is its reaction with a carboxylic acid to form an amide (Scheme 1.20).



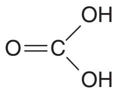
Scheme 1.20 Formation of amides.

The $-CONH-$ group is called the amide group and is an important structural feature of wool keratin and of nylons (polyamides). It has the ability to form hydrogen bonds with water, thereby providing these fibres with moisture absorbency properties.

An amide that is an important auxiliary chemical in dyeing and printing is a compound called urea (**1.42**). Urea is an amide of carbonic acid (**1.43**) and is used in textile printing. It is incorporated into print pastes to assist the solution of acid and direct dyes in the limited amount of water present in the paste. It also acts as a *humectant*, a substance that retains moisture, during steaming of print pastes (see Sections 5.2 and 5.7.2).

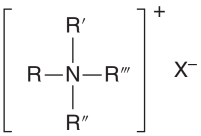


1.42



1.43

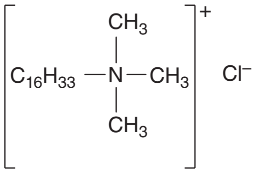
Quaternary ammonium compounds (**1.44**) are another important type of amine. These compounds have the following general formula:



$$\left[R-\overset{\displaystyle R'}{\underset{\displaystyle R''}{N}}-R''' \right]^+ X^-$$

1.44

where X^- is a halide ion (usually Cl^- or Br^-) and the four alkyl groups may be the same or different. These compounds are cationic surface-active agents (see Section 1.8.5.2), for example, cetyltrimethylammonium chloride (**1.45**), which is widely used in textile wet processing.



$$\left[C_{16}H_{33}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N}}-CH_3 \right]^+ Cl^-$$

1.45

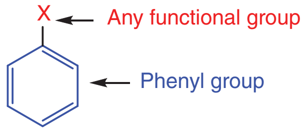
1.8.3.8 Cyano and Nitro Groups

Cyano (—CN) and nitro (—NO_2) groups are both important functional groups in organic synthesis, and both are extensively used in dyes and pigments where they act as auxochromes (see Section 3.3). They have an electron-attracting property that influences the colour of the dye or pigment molecules.

1.8.4 Important Functional Groups of Aromatic Compounds

In Section 1.8.3 examples were given of aliphatic organic compounds in which functional groups are bonded to alkyl groups. In a similar manner, one (or more) of the six hydrogen atoms on a benzene ring can be substituted by a functional group, and such compounds are widely used in the synthesis of dyes and pigments.

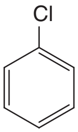
If just one of the six hydrogen atoms of a benzene ring is replaced by a functional group X, the C_6H_5— group to which the functional group is bonded is called the *phenyl* group, which is the simplest *aryl* group (**1.46**).



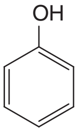
1.46

Aryl groups correspond to the alkyl groups of aliphatic chemistry and are all based on aromatic ring structures. The halogen derivatives are named as might be expected, for example, C_6H_5Cl (**1.47**) is called phenyl chloride (and also monochlorobenzene). However many aromatic compounds often have less obvious names. Thus, C_6H_5OH (**1.48**) is called phenol, $C_6H_5NH_2$ (**1.49**) is called aniline, C_6H_5COOH (**1.50**) is called benzoic acid, and C_6H_5CHO (**1.51**) is called benzaldehyde.

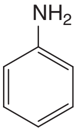
In general, the chemical reactivity of the functional groups bonded to aromatic rings is very similar to that of the groups when present in aliphatic compounds.



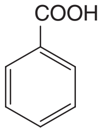
1.47



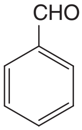
1.48



1.49



1.50

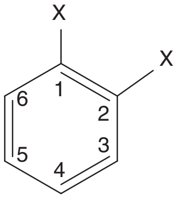


1.51

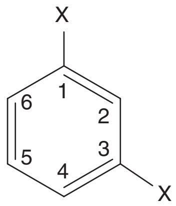
Difunctional compounds of benzene are very common and can exist in three isomeric forms depending on the relative positions on the ring of the two functional groups. The carbon atoms of the benzene ring are numbered 1–6. These six carbon atoms are equivalent, so positions 1,2- and 1,6- are equivalent, as are the 1,3- and 1,5-disubstituted positions.

If the two groups are in the 1,2- (or 1,6-) positions, the disubstituted compound is referred to as the *ortho*- (*o*-) compound. If they are in the 1,3- (or 1,5-) positions, they are referred to as the *meta*- (*m*-) compound. The last possible combination is the 1,4-disubstituted compound, referred to as *para*- (*p*-).

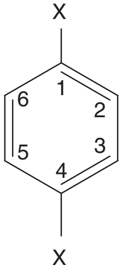
The aromatic ring of the disubstituted compounds (C_6H_4—) is now called the phenylene group.



ortho



meta



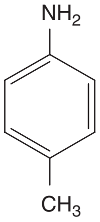
para

A feature of aromatic organic compounds is that the presence of a functional group in a ring has a direct influence on the position taken up by a second functional group. This is because they influence the electron density on the carbon atoms of the ring.

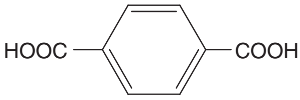
Groups that direct a second functional group to the *meta* position are electron attracting, such as —CN, —CHO, —COOH and —NO_2.

Groups that direct a second functional group to the *ortho* and *para* positions are electron donating, such as —NH_2, —OH and —CH_3.

Difunctional compounds are much used in the manufacture of dyes and pigments, typical of which is 4-methylaniline, more commonly known as *p*-toluidine (**1.52**). An important difunctional compound in the textile industry is benzene-1,4-dicarboxylic acid, more commonly known as terephthalic acid (**1.53**), which is used to manufacture polyester fibre (see Section 2.8.1.3).

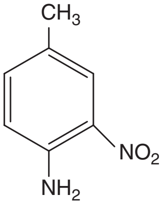


1.52



1.53

Trifunctional compounds are also important in the manufacture of dyes and pigments, and an example of such a compound is 4-amino-3-nitrotoluene, or 2-nitro-*p*-toluidine (**1.54**), widely used as a diazo component.



1.54

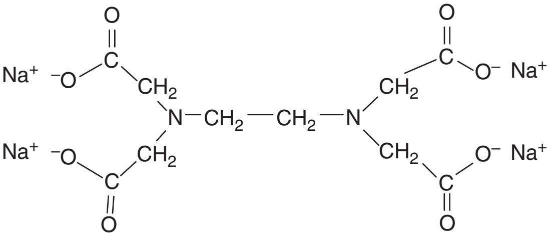
1.8.5 Important Compounds in Textile Dyeing

1.8.5.1 Sequestering Agents

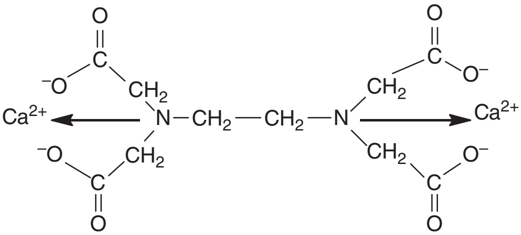
An important issue to be considered in dyehouses is the purity of its water supply. The presence of metal ions in water can adversely affect a number of operations by reacting with dyes or chemicals used in processing. For example, magnesium (Mg^{2+}) or calcium (Ca^{2+}) ions in hard water can form insoluble complexes with soaps, and if these complexes are deposited on textile substrates, they will create difficulties in subsequent dyeing processes. The presence of transition metal ions such as iron (Fe^{2+}) and copper (Cu^{2+}) can catalyse the decomposition of hydrogen peroxide in bleaching processes, and if these ions are already adsorbed into the substrate, then localised accelerated attack may occur.

Sequestering agents are compounds that are able to form soluble complexes with metal ions in what is termed a *chelation* reaction. For this reason, sequestering agents are also known as *chelating agents*. The soluble complex formed with the metal ions does not interfere with the process (such as bleaching or dyeing) and is washed out at the end of the operation with the exhaust liquors. Sequestering agents have structures that enable them to form closed rings with polyvalent metal ions by the sharing of a lone pair of electrons with them. In this way they 'lock up' the metal ions and prevent them from any further reaction.

The lone pairs of electrons that form the bonds with the metal ions come from electron-donating atoms in the sequestering agent, usually nitrogen (in amines) or oxygen (in phosphates). Typical of the former type is ethylenediaminetetraacetic acid (most usually known as EDTA, **1.55**), which forms complexes with metal ions (**1.56**).



1.55



1.56

Typical of the polyphosphate type is sodium hexametaphosphate, $Na_2(Na_4P_6O_{18})$, which forms the water-soluble complex anion $Na_2(Ca_2P_6O_{18})$ by an ion-exchange reaction.

1.8.5.2 Surface-Active Agents (Surfactants)

Surface-active agents are widely used in the manufacture of dyes, in dyeing processes and in preparatory processes for dyeing. Many types of surface-active agents exist and they have different names depending upon their function:

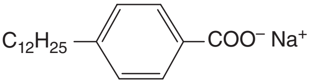
Detergents are used in washing and scouring processes. Some are called *wetting agents* and are incorporated into formulations of dye powders to aid wetting out when the powder is being dissolved in water and also to aid the wetting of fibres prior to dyeing operations.

Levelling and retarding agents are also surfactants, these types being used in the application of ionic dyes to fibres.

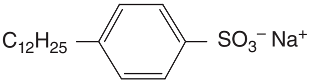
Dispersing agents are another type of surfactant and are used in the formulation of disperse dyes, whose function is to ensure a stable dispersion of the dyes in the dyebath during the dyeing process, aiding uniform uptake of dye by the fibre.

The molecules of surface-active agents comprise two components, a hydrophilic (water-loving) water-soluble head and a hydrophobic (water-hating) water-insoluble tail. This tail is usually a long-chain hydrocarbon. Surface-active agents may be anionic, cationic, amphoteric or non-ionic in nature.

Anionic surface-active agents are the most commonly used surface-active agents in dyeing systems, in which the hydrophilic head is usually a sulphonate ($—SO_3Na$) or a carboxyl group ($—COONa$). Examples of these types are sodium heptadecanoate (**1.57**) and sodium dodecylbenzenesulphonate (**1.58**), a widely used detergent in domestic washing powders.



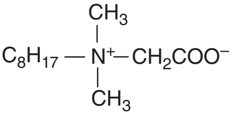
1.57



1.58

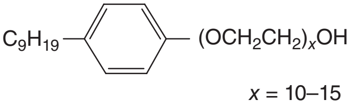
Cationic types of surface-active agent contain a positively charged group at the head. This positively charged group is usually a quaternary ammonium salt, and an example of such a structure is **1.45** in Section 1.8.3.7.

The amphoteric types contain both positively and negatively charged groups (e.g. betaines such as **1.59**), whilst the non-ionic types do not contain any charged groups at all: these instead contain a number of ethylene oxide groups to impart hydrophilic character, such as **1.60**.



$$C_8H_{17}—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}—CH_2COO^-$$

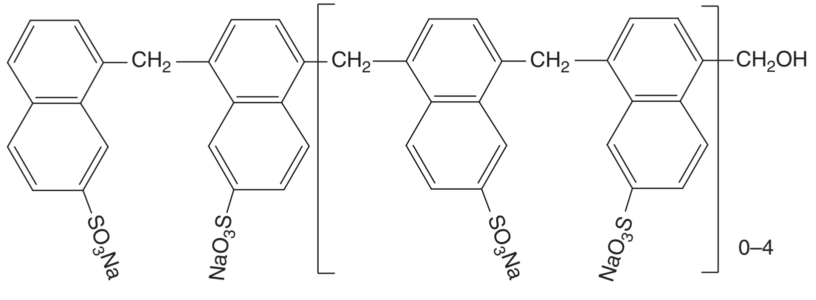
1.59



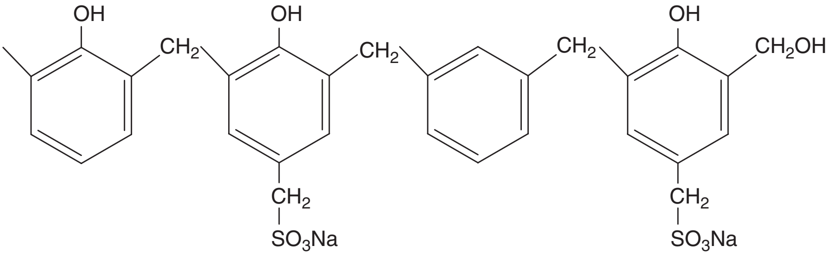
1.60

Surface-active agents used as dispersing agents are usually polyelectrolytes with complex structures, some of which are not known for certain. They fall into two classes:

(1) Condensation products of methanal (formaldehyde) with arylsulphonic acids, two examples of which are a condensate of naphthalene-2-sulphonic acid and methanal (**1.61**) and a condensation product of phenols with methanal and sodium sulphite (**1.62**)



1.61



1.62

(2) Lignin sulphonates, a group of compounds of very complex structure, probably mixtures of compounds, formed by the treatment of wood pulp with sulphite or bisulphite

1.8.5.3 Carriers

The dyeing of polyester fibres is problematic because the rate of diffusion of disperse dyes through the fibre is so low at temperatures where dye uptake is very low, making the process unfeasible. The problem is due to the high degree of crystallinity of polyester fibres (see Section 2.8.1.3) and its low glass transition temperature, T_g (see Section 2.2). Whilst dyeing can be carried out at temperatures above the T_g, that is, at about 130 °C, an alternative is to apply dyes at temperatures at the boil in the presence of a chemical called a *carrier*. The effect of the carrier on the polymer chains of the polyester fibres is similar to that of a raised temperature, allowing more rapid ingress of dye and the development of deep shades. Their smell is objectionable, however, and unless they are removed completely from the fibre, they can lower the lightfastness of the dyeing.

The types of chemicals used as carriers are non-ionic aromatic organic compounds of fairly low molecular weight (around 150–200). Typical of the carriers used fall into four main chemical groups:

(1) Phenols, such as *o*-phenylphenol
(2) Hydrocarbons, such as biphenyl

(3) Chlorinated hydrocarbons, such as dichlorobenzene
(4) Esters, such as butyl benzoate

Phenols and chlorinated hydrocarbons are no longer marketed due to concerns about aquatic toxicity. Indeed such is the concern about the use of carriers that they are now little used in polyester dyeing, the high-temperature method being preferred. An exception, however, is their use in the dyeing of polyester in its blends with wool, since wool is easily damaged above boiling temperature, especially at 130 °C.

1.9 The Use of Chemicals by Industry

1.9.1 REACH

A system for controlling the use of chemicals in Europe – Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) – became law in the United Kingdom in 2007. This legislation places controls on the supply and use of certain chemicals, especially those that can be harmful to human health or the environment. REACH applies to a wide range of chemical substances, including dyes and pigments, as well as chemicals used in dyeing and printing processes.

Under REACH, there are three groups of chemicals that are specifically controlled:

- A candidate list of substances of very high concern (SVHC). Suppliers of a chemical on this list have to give information about it and how to use it safely, for example, a safety data sheet.
- Priority SVHCs from the candidate list. These chemicals require authorisation by the European Chemicals Agency (ECHA) for their supply and use.
- Restricted substances, which are particularly hazardous, have controls on how they can be supplied or used. These chemicals are restricted to protect workers, consumers and the environment. The restriction may limit the concentration of a chemical for a particular use or ban a use entirely.

The ECHA has published lists of chemicals in the three groups. Chemicals that are classed as SVHCs are substances that the ECHA considers to have hazards that might be carcinogenic, mutagenic or toxic for reproduction. Substances that remain in the environment for a long time and are bioaccumulative and toxic are also included.

Since dyeing, printing and finishing companies use chemicals, not just dyes and pigments but also auxiliary chemicals necessary for the processes by which they are applied to textiles, they must ensure they meet the requirements of the REACH legislation. An example of the impact of REACH on the dyeing industry is the classification of chromium as an SVHC, requiring authorisation before it is used. As a result, the use of chrome dyeing in the United Kingdom has declined substantially to the point where it is very little used (see Section 3.5.1.2).

Some countries within the EU, such as Denmark and Sweden, together with France and Germany are urging the EU to move more quickly towards meeting its goal of a toxic-free environment. Outside the EU, some countries have started to implement regulations similar to those of EU REACH. For example, in 2010 *China REACH* came into force, though some countries, notably United States, have criticised the principle of REACH for harming global trade. The Toxic Substances Control Act (TSCA) in the United States regulates the introduction of new chemicals, though it does not categorise chemicals as toxic and non-toxic, and indeed when the law was introduced in 1976, all chemicals were considered to be safe. TSCA has been widely criticised over the years, and in 2016 a reform bill was passed, though it is still unlikely to be as rigorous as REACH in Europe.

A number of countries have adopted a framework to establish a more globalised system of chemicals registration under the Globally Harmonised System of Classification and Labelling of Chemicals (GHS). It was created by the United Nations in 1992 and designed to replace the various classification and labelling standards used in different countries by using consistent criteria on a global level. However it has not yet been fully implemented in many countries.

1.9.2 Effluent Disposal

In Europe, the Urban Waste Water Treatment Directive of the EU requires all member states to implement a control regime for trade effluent discharge. Within the United Kingdom, the Water Industry Act of 1991 meets this requirement. Trade effluent, the waste water produced by industry, can be disposed of to the public sewerage system in the United Kingdom, provided the prior consent of the local water authority is obtained. In granting consent, the water authority states the maximum permitted concentration of pollutant and in some cases states the load of a particular pollutant that can be discharged in a 24 hour period. The majority of water authorities specify the limits on parameters such as pH, biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids and temperature, in addition to pollutants such as heavy metals and colour.

As noted in Section 1.9.1, chrome dyeing is in significant decline. This is due to the restrictions not only on the use of dichromate under REACH legislation but also on the discharge of chromium to effluent. The methods developed to minimise the amount of hexavalent chromium being discharged into public sewers, outlined in Section 3.5.1.2, have varying degrees of effectiveness, so local water authorities impose the statutory limits governing the discharge of chromium in effluent. These limits, which vary from country to country and even between regions in a given country, are very strict, typically no more than 0.5 mg/l, often less. Because it is very difficult to analyse separately for trivalent and hexavalent chromium, limits are normally set for total chromium in effluent. In the United Kingdom, local water authorities state, under the conditions of their consent, the maximum permitted levels of chromium to be discharged. A similar situation pertains for the discharge of other hazardous chemicals, such as sulphides that are used in the dyeing of sulphur dyes (see Section 4.2.2.4). Whilst not especially hazardous chemicals, local authorities are also concerned about the discharge of high concentrations of electrolytes, such as sodium chloride and sodium sulphate, used in the dyeing of direct, reactive and acid dyes.

For example, it is recognised that sulphate can damage concrete structures, and a general guideline on sulphate is a limit of 1000 mg/l.

A group created by a number of clothing brands to limit hazardous wastewater discharges, the Zero Discharge of Hazardous Chemicals (ZDHC) Programme, was formed in 2011. Many leading brands have recognised the concern of the public concern and environmental lobby organisations for the need to limit hazardous wastewater discharges and are striving to move towards zero discharge by setting global guidelines. This is an example of manufacturing industry itself, rather than governments, taking action to ensure the textile and dyeing industries adopt more environmentally friendly processes.