An Introduction to Textile Coloration
Titles in the Society of Dyers and Colourists – John Wiley Series

*An Introduction to Textile Coloration: Principles and Practice*  
Roger H. Wardman

*Physico-chemical Aspects of Textile Coloration*  
Stephen M. Burkinshaw

*Standard Colorimetry: Definitions, Algorithms and Software*  
Claudio Oleari

*The Coloration of Wool and Other Keratin Fibres*  
David M. Lewis and John A. Rippon (Eds)
An Introduction to Textile Coloration
Principles and Practice

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### Society of Dyers and Colourists

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Society of Dyers and Colourists

Society of Dyers and Colourists (SDC) is the world’s leading independent educational charity dedicated to advancing the science and technology of colour. Our mission is to educate the changing world in the science of colour.

SDC was established in 1884 and became a registered educational charity in 1962. SDC was granted a Royal Charter in 1963 and is the only organisation in the world that can award the Chartered Colourist status, which remains the pinnacle of achievement for coloration professionals.

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For further information please email: info@sdc.org.uk or visit www.sdc.org.uk.
Preface

In 1993 the Society of Dyers and Colourists published the book *Colour for Textiles: A User’s Handbook* by Dr Wilfred Ingamells, which covered the basic science and technology of textile coloration. Dr Ingamells wrote the book at a level at which those without a detailed scientific background could understand the fundamental principles underlying dyeing and printing processes and it proved to be a very successful publication.

During the 25 years since the publication of the book, there have been a considerable number of developments in the dyeing and printing industry, not least of which have been the challenges imposed by the drive towards environmentally friendly processes and restrictions on the use of certain chemicals. In response, the Publications Committee of the Society of Dyers and Colourists (SDC) considered it necessary to produce an updated version of the book, and I, together with Dr Matthew Clark, agreed to take on the task. Unfortunately Dr Clark had to withdraw from the project at an early stage, but did complete Chapter 5 on textile printing, and I gratefully acknowledge his contribution.

One of the aims of rewriting Dr Ingamells’ book was to create a supporting textbook for the course ‘Textile Coloration Certificate’, which had been developed by Dr Clark and Mr Filarowski at the SDC and introduced in 2011. This course is aimed at personnel working in textile dyeing or printing companies, but who do not have a strong scientific background, so that they may attain a good understanding of the chemical principles involved in the processes with which they are involved. Accordingly, given the slightly different aim of this book, there is slightly more technical detail than in Dr Ingamells’ book.

It is the intention that candidates who successfully complete this course will be very well prepared to continue their studies to enter the Society’s examinations for Associateship, an honours degree level qualification. It is hoped therefore that this book additionally will provide a sound basis for students preparing for the ASDC qualification, though of course it is expected that they will also consult books available on the specialised topics related to textile coloration. At the introductory level of this book, it has not been possible to cover the dyeing of all the variants of textile fibre types. For example, there are many different types of polyester fibres and numerous types of fibre blends, and it is unrealistic to detail the processes involved in all these cases.

It was necessary for me to make some decisions about nomenclature in writing the book. In the teaching of organic chemistry in schools, the names of chemicals established by the rules of the International Union of Pure and Applied Chemistry (IUPAC) are used. In industry the original (trivial) names are still widely used, so to avoid confusion I have used these names also. Thus, for example, I have used ‘ethanoic (acetic) acid’, instead of just ‘ethanoic acid’. Another issue to address was that of commercial names for products. I have tried to avoid giving commercial names as much as possible, so, for example, all dye structures are labelled with their Colour Index numbers.

Finally, in preparing the book, I am grateful to Dr Ingamells for allowing me to use, where I considered it appropriate, parts of his text and diagrams. I gratefully acknowledge
the help of the library staff at the Scottish Borders campus of Heriot-Watt University, especially Mr Peter Sandison, Mr Jamie MacIntyre and Mrs Alison Morrison. I am particularly indebted to Mr Andrew Filarowski at the Society of Dyers and Colourists for so carefully going through the manuscripts of Chapters 1–6 and suggesting countless, yet very pertinent, modifications. His advice, support and links with the dyeing companies have been invaluable in the preparation of the book. Dr Jim Nobbs, formerly of Leeds University, very carefully scrutinised Chapter 7 and similarly provided many useful comments. Finally, I would like to thank Mr Alan Ross of High Street Textile Testing Services Ltd for carrying out very thoroughly a similar task on Chapter 8 and for making many useful corrections.

Roger H. Wardman
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 \( n = 1, 2, 3, \text{ etc.} \), counting outwards from the nucleus, and each can hold a certain maximum number...
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 \(^{35}\text{Cl}\) and \(^{37}\text{Cl}\). Approximately 75.8\% of naturally occurring chlorine is \(^{35}\text{Cl}\) and 24.2\% is \(^{37}\text{Cl}\), 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
## General Chemistry Related to Textiles

**Figure 1.1** The three p orbitals.

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Element</th>
<th>Orbit, $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydrogen</td>
<td>1s</td>
</tr>
<tr>
<td>2</td>
<td>Helium</td>
<td>2s</td>
</tr>
<tr>
<td>3</td>
<td>Lithium</td>
<td>2s 1s</td>
</tr>
<tr>
<td>4</td>
<td>Beryllium</td>
<td>2s 2s</td>
</tr>
<tr>
<td>5</td>
<td>Boron</td>
<td>2s 2s 1p</td>
</tr>
<tr>
<td>6</td>
<td>Carbon</td>
<td>2s 2s 2p</td>
</tr>
<tr>
<td>7</td>
<td>Nitrogen</td>
<td>2s 2s 3p</td>
</tr>
<tr>
<td>8</td>
<td>Oxygen</td>
<td>2s 2s 4p</td>
</tr>
<tr>
<td>9</td>
<td>Fluorine</td>
<td>2s 2s 5p</td>
</tr>
<tr>
<td>10</td>
<td>Neon</td>
<td>2s 2s 6p</td>
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<tr>
<td>11</td>
<td>Sodium</td>
<td>2s 2s 6p 1s</td>
</tr>
<tr>
<td>12</td>
<td>Magnesium</td>
<td>2s 2s 6p 2s</td>
</tr>
<tr>
<td>13</td>
<td>Aluminium</td>
<td>2s 2s 6p 2s 1p</td>
</tr>
<tr>
<td>14</td>
<td>Silicon</td>
<td>2s 2s 6p 2s 2p</td>
</tr>
<tr>
<td>15</td>
<td>Phosphorus</td>
<td>2s 2s 6p 2s 3p</td>
</tr>
<tr>
<td>16</td>
<td>Sulphur</td>
<td>2s 2s 6p 2s 4p</td>
</tr>
<tr>
<td>17</td>
<td>Chlorine</td>
<td>2s 2s 6p 2s 5p</td>
</tr>
<tr>
<td>18</td>
<td>Argon</td>
<td>2s 2s 6p 2s 6p</td>
</tr>
<tr>
<td>19</td>
<td>Potassium</td>
<td>2s 2s 6p 2s 6p 1s</td>
</tr>
<tr>
<td>20</td>
<td>Calcium</td>
<td>2s 2s 6p 2s 6p 2s</td>
</tr>
<tr>
<td>21</td>
<td>Scandium</td>
<td>2s 2s 6p 2s 6p 1d 2s</td>
</tr>
<tr>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Zinc</td>
<td>2s 2s 6p 2s 6p 10d 2s</td>
</tr>
</tbody>
</table>
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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 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.
<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
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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).

\[ \text{Na}^+ + \text{Cl}^- \rightarrow \left[ \text{Na} \right]^+ + \left[ \text{Cl}^- \right] \]

**Scheme 1.1** Reaction between sodium and chlorine.
Since atoms started out electrically neutral, the loss of one electron in sodium leaves the atom positively charged (it is now a positive ionic, 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 CaCl₂ (Scheme 1.2):

\[ \text{Ca}^{2+} + 2 \text{Cl}^- \rightarrow [\text{Ca}^{2+}] + 2 [\text{Cl}^-] \]

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 (Na₂SO₄), 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 CaSO₄.

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 sulphonate group, —SO₃H, 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.

(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.)
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 (Cl₂) 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.

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, CH₄ (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 pₓ and pᵧ orbitals), so before the four covalent bonds can be formed, one of the 2s electrons must be promoted to the vacant pₓ orbital, giving the electronic arrangement shown in Figure 1.6.
Scheme 1.5  Formation of methane (outer electrons only are shown); \(\times\) electron from carbon, \(\bullet\) 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).

\[
\begin{align*}
\text{\(\text{NH}_3\)} & \quad \text{Ammonia, NH}_3 \\
\text{\(\text{H}_2\text{O}\)} & \quad \text{Water, H}_2\text{O}
\end{align*}
\]

**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, $\pi$–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

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**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](image_url)  
**Figure 1.9** π–H bonding.