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Mathematics and Sciences

**J. Brockington &  
P. J. Stamper**

# **Inorganic chemistry for higher education**

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# **Inorganic chemistry for higher education**



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# Preface

This is one of a series of three textbooks that we have prepared primarily to meet the needs of students on the first year of TEC courses leading to higher awards in physical science and technology. Students on the first year of single or general honours degree courses which include chemistry should also find it useful.

In the course of preparing this book we studied numerous Level IV units from various colleges. Because of the wide disparity of topics that they contained, it was clear that we could not hope to accommodate all aspects of every syllabus in a book of modest length. We were therefore obliged to concentrate on the principal units, namely the TEC Level IV Standard Unit and that produced by the Committee of Heads of Polytechnic Chemistry Departments. However, we have not hesitated to extend these units wherever we felt that, by so doing, we could provide a better understanding of the subject matter. It is for this reason that we have introduced a chapter on chemical bonding, based on a simplified molecular orbital approach and in which all references to hybridisation have been omitted. We have also selected some additional material, including a considerable amount of descriptive chemistry, intended to give students a wider appreciation of inorganic chemistry.

Throughout this book we have adhered to IUPAC nomenclature and presented data in SI units. The former has been taken from *Nomenclature of Inorganic Chemistry* (Butterworths), and the latter from *Chemistry Data Book* by J.G. Stark and H.G. Wallace (John Murray).

We are particularly grateful to David Browning of Bristol Polytechnic who has edited the book and made many constructive criticisms. Also, we should like to express our gratitude to Longman's editorial staff and the typesetters for their painstaking assistance in producing this book.

John Brockington and Peter Stamper  
May 1983

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# Contents

<i>Preface</i>	vii	
<i>Acknowledgements</i>	viii	
<hr/>		
<b>Chapter 1</b>	<b>Nomenclature</b>	<b>1</b>
<b>Chapter 2</b>	<b>Electronic structure of atoms</b>	<b>10</b>
<b>Chapter 3</b>	<b>The periodic table</b>	<b>32</b>
<b>Chapter 4</b>	<b>Chemical bonding and intermolecular attraction</b>	<b>45</b>
<b>Chapter 5</b>	<b>Oxidation and reduction</b>	<b>101</b>
<b>Chapter 6</b>	<b>Hydrogen</b>	<b>136</b>
<b>Chapter 7</b>	<b>Groups 1A and 2A</b>	<b>146</b>
<b>Chapter 8</b>	<b>Group 3B</b>	<b>164</b>
<b>Chapter 9</b>	<b>Group 4B</b>	<b>179</b>
<b>Chapter 10</b>	<b>Group 5B</b>	<b>206</b>
<b>Chapter 11</b>	<b>Group 6B</b>	<b>235</b>
<b>Chapter 12</b>	<b>Group 7B</b>	<b>266</b>
<b>Chapter 13</b>	<b>The noble gases</b>	<b>294</b>
<b>Chapter 14</b>	<b>d-Block transition elements</b>	<b>299</b>
<hr/>		
<i>Index</i>		369

# Chapter 1

## Nomenclature

Chemical substances are named in accordance with the recommendations of the International Union of Pure and Applied Chemistry (IUPAC), which are subject to occasional revision. The most recent edition of *Nomenclature of Inorganic Chemistry* was published in 1970 by Butterworths. The underlying philosophy is that for many simple substances *trivial names* should be retained if they are well established and unambiguous; other substances are given *systematic names* based on a series of well defined rules.

### 1.1 Elements

All the isotopes of an element, except hydrogen, bear the same name. For allotropes, IUPAC allows trivial names but also gives systematic names based on the structure of the molecule. Examples are as follows.

Allotrope	Trivial name	Systematic name
O <sub>2</sub>	oxygen	dioxygen
O <sub>3</sub>	ozone	trioxygen
S <sub>8</sub>	λ-sulphur	cyclo-octasulphur
P <sub>4</sub>	white phosphorus	tetrahedro-tetraphosphorus



## 1.2 Binary compounds

There are two systematic ways of naming such compounds.

- (i) By means of *stoichiometric names*, in which the proportions of the constituent elements are indicated by prefixes of Greek origin, e.g. mono, di, tri, tetra, penta and hexa. In practice, the prefix 'mono' is usually omitted. Oxides, sulphides and halides of non-metals, together with certain metal oxides, are conveniently named in this way, e.g.

$N_2O$	dinitrogen oxide	$S_2Cl_2$	disulphur dichloride
$NO_2$	nitrogen dioxide	$MnO_2$	manganese dioxide
$N_2O_4$	dinitrogen tetroxide	$Fe_3O_4$	triiron tetroxide
$N_4S_4$	tetranitrogen tetrasulphide	$Pb_3O_4$	trilead tetroxide

- (ii) Alternatively, *Stock's system* may be used, in which the oxidation number of an element is shown by a roman numeral enclosed in parentheses immediately after the name. This system is becoming increasingly favoured. With only a few exceptions, all metallic oxides, sulphides and halides, together with the oxides of phosphorus, are now named in this way. Examples:

$SnCl_2$	tin(II) chloride	$MnO_2$	manganese(IV) oxide
$SnCl_4$	tin(IV) chloride	$Fe_3O_4$	iron(II) diiron(III) oxide
$CrO$	chromium(II) oxide	$Pb_3O_4$	dilead(II) lead(IV) oxide
$Cr_2O_3$	chromium(III) oxide	$P_4O_6$	phosphorus(III) oxide
$CrO_3$	chromium(VI) oxide	$P_4O_{10}$	phosphorus(V) oxide

Hydrides constitute a special case. They may be named in accordance with the above rules, e.g. sodium hydride for  $NaH$ , but many of them have well established trivial names whose continued use is recommended. Common examples are water and ammonia; others are as follows:

$B_2H_6$	diborane	$N_2H_4$	hydrazine
$CH_4$	methane	$PH_3$	phosphine
$SiH_4$	silane	$P_2H_4$	diphosphane
$GeH_4$	germane	$AsH_3$	arsine
$SnH_4$	stannane	$SbH_3$	stibine
$PbH_4$	plumbane	$BiH_3$	bismuthine

## 1.3 Cations

Monoatomic cations derived from elements of variable valency are given the name of the element with its appropriate oxidation number, e.g.

$Fe^{2+}$  iron(II) ion       $Fe^{3+}$  iron(III) ion

In the naming of cations derived from elements of constant valency, IUPAC recommends that the oxidation number is omitted, e.g.

$\text{Na}^+$	sodium ion
$\text{Ca}^{2+}$	calcium ion
$\text{Al}^{3+}$	aluminium ion

The common polyatomic cations are named as follows:

$\text{H}_3\text{O}^+$	oxonium ion	$\text{PH}_4^+$	phosphonium ion
$\text{NH}_4^+$	ammonium ion	$\text{NO}^+$	nitrosyl cation
$\text{HONH}_2^+$	hydroxylammonium ion	$\text{NO}_2^+$	nitryl cation
$\text{NH}_2\text{NH}_2^+$	hydrazinium(1+) ion		

## 1.4 Anions

The name of a monoatomic anion is derived from that of the element and has the termination '-ide', e.g.

$\text{H}^-$	hydride	$\text{N}^{3-}$	nitride
$\text{Cl}^-$	chloride	$\text{P}^{3-}$	phosphide
$\text{O}^{2-}$	oxide	$\text{C}^{4-}$	carbide
$\text{S}^{2-}$	sulphide	$\text{Si}^{4-}$	silicide

Polyatomic anions may have names that end in '-ide', '-ate' or '-ite'. The commonest ones which end in '-ide' are as follows:

$\text{HO}^-$	hydroxide	$\text{HF}_2^-$	hydrogendifluoride
$\text{O}_2^{2-}$	peroxide	$\text{N}_3^-$	azide
$\text{O}_2^-$	superoxide	$\text{NH}_2^-$	amide
$\text{HS}^-$	hydrogensulphide	$\text{NHOH}^-$	hydroxylamide
$\text{S}_2^{2-}$	disulphide	$\text{CN}^-$	cyanide
$\text{I}_3^-$	triiodide	$\text{C}_2^{2-}$	acetylide

The names of most oxoanions consist of the root of the name of the characteristic element, followed by the suffix '-ate', e.g. sulphate for  $\text{SO}_4^{2-}$ . Although it is permissible to name such anions systematically as though they were complex anions (§1.10), e.g. tetraoxosulphate(VI) for  $\text{SO}_4^{2-}$ , IUPAC does not advise this except for less well known and newly discovered ions. Other examples are as follows.

$\text{NO}_3^-$	nitrate	$\text{SiO}_3^{2-}$	metasilicate
$\text{CO}_3^{2-}$	carbonate	$\text{ClO}_3^-$	chlorate
$\text{PO}_4^{3-}$	phosphate or orthophosphate	$\text{OCN}^-$	cyanate
$\text{PHO}_3^{2-}$	phosphonate	$\text{CrO}_4^{2-}$	chromate
$\text{PH}_2\text{O}_2^-$	phosphinate	$\text{MnO}_4^-$	permanganate
$\text{BO}_3^{3-}$	borate or orthoborate		

Certain oxoanions, containing an element in a low oxidation state, have long-established trivial names that end in '-ite'. They are as follows.

$\text{NO}_2^-$	nitrite	$\text{SO}_3^{2-}$	sulphite	$\text{ClO}_2^-$	chlorite
$\text{N}_2\text{O}_2^{2-}$	hyponitrite	$\text{S}_2\text{O}_3^{2-}$	disulphite	$\text{ClO}^-$	hypochlorite
$\text{NOO}_2^-$	peroxonitrite	$\text{S}_2\text{O}_4^{2-}$	dithionite	$\text{BrO}^-$	hypobromite
$\text{AsO}_3^{3-}$	arsenite	$\text{S}_2\text{O}_5^{2-}$	thiosulphite	$\text{IO}^-$	hypoiodite
		$\text{SeO}_3^{2-}$	selenite		

The use of these, *but no other names ending in '-ite'*, is permitted by IUPAC. Note particularly that  $\text{PHO}_3^{2-}$ , formerly known as the phosphite ion, is now called the phosphonate ion.

## 1.5 Isopolyanions

IUPAC recommends two systems for naming isopolyanions, i.e. anions which contain more than one atom of the characteristic element.

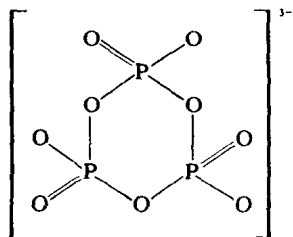
- If structural information is unavailable, the ion is given a stoichiometric name; e.g.  $\text{S}_2\text{O}_7^{2-}$  could be named in this way as the heptaaxodisulphate ion.
- If structural information is available, and if it is known that the characteristic element is in an oxidation state corresponding to the number of its group in the periodic table, the number of oxygen atoms can be omitted. The number of atoms of the characteristic element must still be indicated, by means of a numerical prefix, and the charge on the anion is placed in parentheses immediately after the name, e.g.

$\text{S}_2\text{O}_7^{2-}$	disulphate(2-)
$\text{P}_2\text{O}_7^{4-}$	diphosphate(4-)
$\text{H}_2\text{P}_2\text{O}_7^{2-}$	dihydrogendiphosphate(2-)

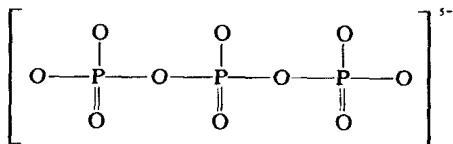
It is customary to omit the ionic charge from the name, a practice recognised by IUPAC in recommending the name dichromate ion for  $\text{Cr}_2\text{O}_7^{2-}$ . (The ionic charge must never be omitted from the formula.)

If the characteristic element is in a lower oxidation state than its periodic table group number, a Stock number must be included to show that oxidation state, e.g. disulphate(IV)(2-) ion for  $\text{S}_2\text{O}_4^{2-}$ .

Cyclic and chain structures are denoted by means of the prefixes *cyclo* and *catena* respectively, although the latter is usually omitted, e.g.



*cyclo*-triphosphate



(*catena*)-triphosphate

## 1.6 Radicals

For purposes of nomenclature, the term 'radical' is defined by IUPAC as a group of atoms that occurs repeatedly in a number of different compounds. The names of the commonest radicals are as follows. Note that the names bismuthyl and antimonyl, formerly used in naming such compounds as  $\text{BiClO}$  and  $\text{SbClO}$ , are no longer approved. (The naming of basic salts is described in §1.9.)

HO	hydroxyl	PO	phosphoryl
CO	carbonyl	SO	sulphinyl or thionyl
NO	nitrosyl	SO <sub>2</sub>	sulphonyl or sulphuryl
NO <sub>2</sub>	nitryl	CrO <sub>2</sub>	chromyl

These radicals are always regarded as forming the positive part of any compound in which they occur. They are therefore written first in the formula, and referred to first in the name, e.g.

COCl <sub>2</sub>	carbonyl chloride
NOCl	nitrosyl chloride
SOCl <sub>2</sub>	sulphinyl chloride or thionyl chloride
SO <sub>2</sub> Cl <sub>2</sub>	sulphonyl chloride or sulphuryl chloride

## 1.7 Acids

Acids are named after the anions to which they give rise. If the name of the anion ends in '-ide', the acid is named as hydrogen -ide, e.g.

HCl	hydrogen chloride
H <sub>2</sub> S	hydrogen sulphide
HCN	hydrogen cyanide

Note that  $\text{HN}_3$  is named as hydrogen azide; not hydrazoic acid.

If the IUPAC name of the anion ends in '-ite' or '-ate', that of the acid ends in '-ous acid' or '-ic acid' respectively, e.g.

HNO <sub>2</sub>	nitrous acid	HNO <sub>3</sub>	nitric acid
H <sub>2</sub> SO <sub>3</sub>	sulphurous acid	H <sub>2</sub> SO <sub>4</sub>	sulphuric acid
HClO <sub>2</sub>	chlorous acid	HClO <sub>3</sub>	chloric acid

An '-ous acid' thus contains the characteristic element in a low oxidation state, while an '-ic acid' contains the element in a high oxidation state. A name of the kind 'hypo-ous acid' is used to show that the element is in a particularly low oxidation state, e.g.

HClO	hypochlorous acid	(oxidation state of Cl = +1)
H <sub>2</sub> N <sub>2</sub> O <sub>2</sub>	hyponitrous acid	(oxidation state of N = +1)

It should be noted that  $\text{HPH}_2\text{O}_2$ , a compound formerly known as hypophosphorous acid, is now called phosphinic acid.

Until recently, the prefix 'per-' (not to be confused with 'peroxo-')

was used for naming certain acids containing an element in a particularly high oxidation state. This prefix is now used only for  $\text{HMnO}_4$ , permanganic acid,  $\text{HClO}_4$ , perchloric acid, and the corresponding acids of bromine and iodine.

Isopolyacids, i.e. oxoacids containing more than one atom of the characteristic element, are named, like simple acids, after the anions to which they give rise. For example,  $\text{H}_4\text{P}_2\text{O}_7$  is called diphosphoric acid. The trivial name of pyrophosphoric acid is not recommended; indeed, the prefix 'pyro-' is no longer in common use. Nevertheless, the prefixes 'ortho-' and 'meta-' are permitted by IUPAC to distinguish between acids of differing water content, e.g.

$\text{H}_3\text{BO}_3$	orthoboric acid	$(\text{HBO}_2)_n$	metaboric acid
$\text{H}_4\text{SiO}_4$	orthosilicic acid	$(\text{H}_2\text{SiO}_3)_n$	metasilicic acid
$\text{H}_3\text{PO}_4$	orthophosphoric acid	$(\text{HPO}_3)_n$	metaphosphoric acid

The prefix 'peroxo-' is used to indicate the substitution of  $\text{—O—}$  by  $\text{—O—O—}$ , e.g.

$\text{HNO}_4$	peroxonitric acid
$\text{H}_2\text{SO}_5$	peroxomonosulphuric acid
$\text{H}_2\text{S}_2\text{O}_8$	peroxodisulphuric acid

Acids in which an atom of oxygen has been substituted by one of sulphur are known as thioacids, e.g.

$\text{H}_2\text{S}_2\text{O}_3$	thiosulphuric acid	$\text{HSCN}$	thiocyanic acid
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## 1.8 Acid derivatives

Acid chlorides, i.e. those compounds in which the HO groups of the acid have been replaced by atoms of chlorine, are named by IUPAC in accordance with the acid radicals they contain, e.g. nitrosyl chloride for  $\text{NOCl}$  (see §1.6).

Amides, in which the HO groups of the acid have been replaced by  $\text{NH}_2$  groups, may be named either by replacing the word 'acid' by 'amide', 'diamide', etc, or by utilising the name of the acid radical. For example, the compound  $\text{SO}_2(\text{NH}_2)_2$ , derived from sulphuric acid, may be called either sulphuric diamide or sulphonyl diamide.

If not all the HO groups have been replaced by  $\text{NH}_2$  groups, the compound may be named as either an 'amido- acid' or an '-amidic acid', e.g.

$\text{NH}_2\text{SO}_3\text{H}$	amidosulphuric acid or sulphamidic acid
----------------------------------	---

(The abbreviated name, sulphamic acid, is not recommended.)

## 1.9 Salts

Simple salts are named according to Stock's system for binary compounds; see §1.2.

Acid salts, i.e. those containing acid hydrogen, are named by introducing the prefix 'hydrogen-', with di, tri, etc, if necessary, to the name of the anion, e.g.

$\text{NaHCO}_3$       sodium hydrogencarbonate  
 $\text{NaH}_2\text{PO}_4$     sodium dihydrogenphosphate

When naming double salts, the cations should be cited in alphabetical order in both formulae and names. (This may cause the cation order in a formula to differ from that in the name.) Acidic hydrogen is always placed last, e.g.

$\text{KNaCO}_3$             potassium sodium carbonate  
 $\text{MgNH}_4\text{PO}_4$        ammonium magnesium phosphate  
 $\text{NaNH}_4\text{HPO}_4$      ammonium sodium hydrogenphosphate

For salt hydrates, two systems may be followed.

- (i) In the absence of structural information, the extent of hydration may be indicated by writing 'monohydrate', 'dihydrate', etc, after the name, e.g.

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$     aluminium chloride hexahydrate

Alternatively, the number of water molecules may be represented by an arabic numeral, e.g.

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$             aluminium chloride 6-water  
 $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$     aluminium potassium sulphate 12-water

- (ii) If the mode of hydration is known, both the formula and the name of the salt may be modified accordingly. For example, in aluminium chloride hexahydrate the six water molecules are coordinated to the aluminium ion. The compound is effectively a complex salt,  $[\text{Al}(\text{H}_2\text{O})_6]\text{Cl}_3$ , and may be named as such, i.e. hexaaquaaluminium(III) chloride.

Basic salts, better known as oxide and hydroxide salts, are regarded as double salts containing two or more anions, one of which is  $\text{O}^{2-}$  or  $\text{HO}^-$ . When naming them, the anions should be cited in alphabetical order, e.g.

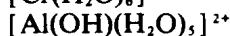
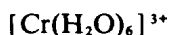
$\text{MgCl}(\text{OH})$     magnesium chloride hydroxide  
 $\text{BiClO}$         bismuth chloride oxide  
 $\text{VO}(\text{SO}_4)$      vanadium(IV) oxide sulphate

## 1.10 Complex salts

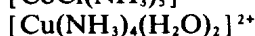
The following IUPAC rules apply to the formulae and names of all complex ions and certain other complexes.

### *Formulae of complex ions*

The symbol for the central atom is written first, followed by anionic ligands and neutral ligands in that order. Within each ligand class the order should be alphabetical in terms of the symbol for the donor atom of the ligand. Polyatomic ligands, but not monoatomic ligands, are enclosed in curved brackets, and the formula of the whole complex is enclosed in square brackets, e.g.



NH<sub>3</sub> in parentheses, but not Cl



### *Naming of complex ions*

Ligands are cited first, followed by the metal.

### *Ligand names*

Some common ligands, with the names used for complex nomenclature, are as follows.

Neutral ligands		Anionic ligands			
H <sub>2</sub> O	aqua	F <sup>-</sup>	fluoro	HO <sup>-</sup>	hydroxo
NH <sub>3</sub>	ammine	Cl <sup>-</sup>	chloro	CN <sup>-</sup>	cyano
CO	carbonyl	Br <sup>-</sup>	bromo	NO <sub>2</sub> <sup>-</sup>	nitro
NO	nitrosyl	I <sup>-</sup>	iodo	H <sup>-</sup>	hydrido†

† The term 'hydro' is used in complexes of boron.

### *Ligand numbers*

A Greek prefix: di, tri, tetra, penta or hexa, is used to denote the number of each type of ligand. 'Mono' is not normally used.

### *Order of citation of ligands*

Ligands are listed in alphabetical order, the multiplying prefix being ignored. Thus, pentaqua is cited before dicyano.

### *Central metal*

For all complex ions, the name of the metal follows the names of the ligands. In the case of complex anions the metal name is modified to end in '-ate'. In general, for elements ending in '-ium', the anionic name is obtained by replacing this ending by '-ate', e.g. *chromium* to

chromate. Other examples are as follows:

Element	Name in complex	Element	Name in complex
Ti	titanate	Ag	argentate†
V	vanadate	Au	aurate†
Mn	manganate	Hg	mercurate
Fe	ferrate†	B	borate
Co	cobaltate	Al	aluminate
Ni	niccolate†	Ge	germanate
Cu	cuprate†	Sn	stannate†
Zn	zincate	Pb	plumbate†

† Based on the Latin names of the elements.

### Oxidation state of the central atom

In the Stock notation the oxidation state of the central atom, i.e. the formal charge on the central ion, is indicated by a roman numeral in parentheses after the name of the complex.

A few examples should help to clarify the above rules. Notice that complex names are written as one word, with no hyphens, and no spacing between the name and the oxidation state of the central atom.

$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	hexaaquachromium(III) ion
$[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$	pentaaquahydroxoaluminium(III) ion pentaqua before hydroxo
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	pentaamminechlorocobalt(III) ion
$[\text{Fe}(\text{CN})_6]^{4-}$	hexacyanoferrate(II) ion
$[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$	pentacyanonitrosylferrate(III) ion
$[\text{AlH}_4]^-$	tetrahydridoaluminate(III) ion
$[\text{BH}_4]^-$	tetrahydroborate(III) ion

The salts of these and other complex ions are named accordingly, e.g.

$[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$	pentaamminechlorocobalt(III) chloride
$\text{K}_4[\text{Fe}(\text{CN})_6]$	potassium hexacyanoferrate(II)

Metal carbonyls are named in a similar manner to complex ions, e.g.

$[\text{Ni}(\text{CO})_4]$	tetracarbonylnickel(0)
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The oxidation state of nickel in this complex is zero.



# Chapter 2

## Electronic structure of atoms

### 2.1 The hydrogen spectrum

Much of our knowledge concerning the electronic structure of atoms originates from atomic spectra, and of particular importance in this respect is the *hydrogen spectrum*. Before discussing this spectrum, let us see how spectra are obtained from radiation in general by considering a simple example.

If light comprising, say, three different wavelengths is passed through a slit and then a prism we observe three different lines of light on a suitably placed screen (Fig. 2.1). The prism separates the incident light by refracting (i.e. bending) radiation of different wavelengths unequally. The shorter the wavelength of the radiation the greater is the angle through which it is refracted. The wavelengths of radiation after refraction constitute the *spectrum* of the incident radiation.

(Wavelength ( $\lambda$ ) and frequency ( $\nu$ ) are both used in descriptions of spectra.) In Fig. 2.1 each line on the screen represents radiation of a single frequency, with wavelengths in the order  $A < B < C$ . The lines A, B and C can be photographed so as to provide a permanent record of the spectrum. Similar results are obtained if a diffraction grating is used in place of a prism.

When an electric discharge is passed through hydrogen gas at low pressure, many of the molecules absorb energy by collision with electrons (cathode rays) and break up into atoms which then absorb energy and emit radiation (§2.3). By means of a prism the emitted radiation