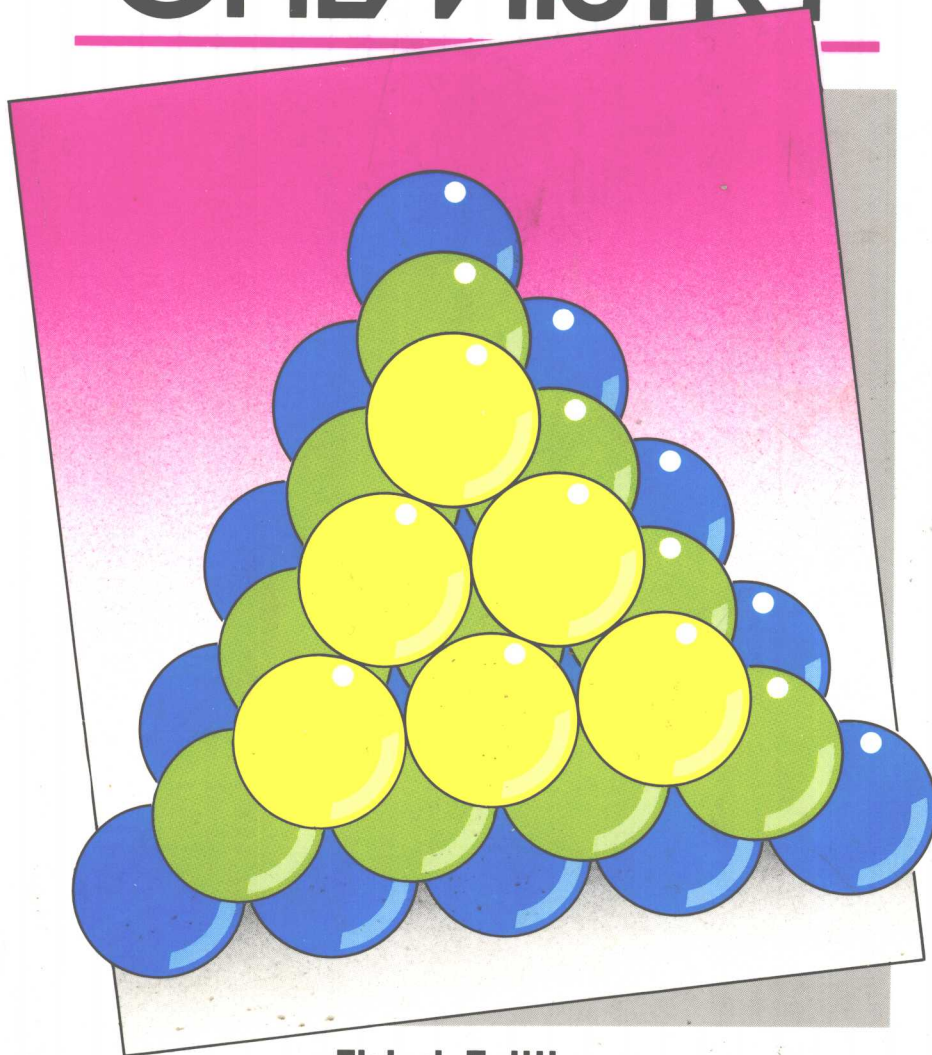


Bernard Moody

COMPARATIVE INORGANIC CHEMISTRY



Third Edition

Comparative Inorganic Chemistry

Third Edition

Bernard Moody, MA, CChem, FRSC



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The preparation of this 3rd edition led me to recall my many former students, however distinguished or otherwise they have become as chemists or biochemists (or other forms of life), in candid and grateful recognition of what they did for me by their efforts, albeit sometimes reluctantly, and their enterprising laboratory work which has made the study of chemistry such a stimulating discipline (yet an art in some of its preparatory aspects) and let me say, great fun.

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Preface to first edition

This book is an attempt to present in a systematic way the principles and facts needed to give a sound, coherent foundation to the study of Inorganic Chemistry. It has been written with the needs of students preparing for the Advanced Level Examinations of the General Certificate of Education in mind, and also for candidates attempting examinations for university and college Open Awards, and examinations for University Entrance. The treatment is comparative and reflects the shift in emphasis which has appeared in Inorganic Chemistry in recent years. The principal aim is to teach the generalizations, many of them subtle, which lie at the heart of Inorganic Chemistry. To do this properly and with intellectual honesty, factual detail must also be included. The amount of Physical Chemistry included has been cut to a minimum. It is hoped that the book will complement an experimental approach to the subject, both in the laboratory and lecture room.

Answers to the fundamental questions of classical chemistry—why we accept the existence of atoms and molecules—appear in the introductory chapter. Classification of the elements has been related to atomic structure. Evidence for the concept of energy levels has been included, a fundamental notion taken on trust without thought by so many of our pupils. Questions raised by the synthesis of the transuranic elements have been included to illustrate the way in which Seaborg and his co-workers have predicted the properties of elements in the best traditions of Mendeléeff. Valency has been developed in detail to show the evolution from its conception in the last century to the electronic theory, with a mention of the spin theory. Many bond diagrams are given and the transition from ionic to covalent bond type is emphasized and related both to physical properties and to the position of elements in the Period Table, the long form of which is preferred. This is

followed by an electronic treatment of certain aspects of oxidation and reduction to provide another unifying thread to the book, making the deduction of many equations possible.

Principles governing the extraction of elements and some details of the processes, to show the essential chemistry and give some idea of the magnitude and type of operation used, are grouped together. Metals of growing importance, such as beryllium, titanium and zirconium, are included. The general treatment followed removes a formidable quantity of detail out of chapters on families of elements, a barrier which reduces the stamina of so many readers of conventional books. Likewise, the usual odd collections of data about alloys have been grouped in one chapter and treated generally. Industrial processes linked with air, coal, water, salt and sulphuric acid have also been grouped together.

The study of each periodic group commences with an overall survey of the gradation of properties and of the bonding encountered. While the emphasis lies on the more important elements, other elements of the family and their compounds are introduced where a generalization is well illustrated. Compounds are given in the periodic order of the other principal element combining, and a cross-reference system avoids repetition. Each chapter includes qualitative tests, including those for elements showing anomalous behaviour. Enough detail is included to support generalizations made and to link the book with laboratory work, essential to the stimulating teaching of Inorganic Chemistry.

The treatment of transition elements is designed to bring out their similar, yet graded, properties. Short accounts of the chemistry of titanium, vanadium and cobalt and certain principal valency states are included not only for the benefit of the scholarship candidate but also to justify the general trends mentioned.

Many industrial organizations were most helpful. Their generous help is most gratefully acknowledged and if any are omitted from the following list, the author offers his sincere apologies:

Albright and Wilson Ltd
The Aluminium Development Association
The Associated Ethyl Company Ltd
The Association of British Chemical
Manufacturers
Borax Consolidated Ltd
BDH Chemicals Ltd
The British Iron and Steel Federation
The British Metal Corporation Ltd
The British Oxygen Company Ltd
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The Zinc Development Association

Care has been taken to include a wide range of questions from the various examination boards and scholarship groups. A full acknowledgement is given with the questions.

I offer my sincere thanks to Mr. F. P. Dunn who read the entire book and suggested numerous improvements in content and style and to Mrs. Pauline Woodhouse who most competently deciphered and typed a difficult manuscript. Finally, I wish to record my appreciation of the generous and patient help given to me by my Publishers.

1964

B.J.M.

Preface to second edition

This book was written to project a personal view of what Inorganic Chemistry should be like at about VIth form level. The motivation came, I like to think, from a genuine dissatisfaction with the books then available and not from a desire to burden the market. The contents are based on the chemistry which had been taught under the direction of the author at Latymer Upper School and later, at Bristol Grammar School. That the first printing sold out within 3–4 months was all the more gratifying because a conscious attempt had been made to present an individual approach, in the early infancy of the Nuffield developments. I would like to express my warmest thanks to the many chemists who have either written to me or sought me out to discuss what merit the book has, to offer criticisms and constructive advice, and if I have fallen short of their standards in this edition, the fault is entirely mine.

The 1960s have seen a rapid re-organization of some parts of the chemical and metallurgical industries, which in turn has required some reshaping of certain chapters in this book. Although the production of town gas from coal has almost completely disappeared in this country, the outline of the coal gas industry has been retained in this edition. The production of ammonia is now based on the steam re-forming of naphtha and will in the not too distant future, if the price is right, be based on North Sea gas. It is a pleasure to record the help given by the Agricultural Division of ICI Ltd at Billingham in supplying information and in answering my questions prior to the rewriting of this section. To Dr. M. J. Rhydderch for giving me permission to draw on his account of Spray Steelmaking in the July 1968 edition of *Science Journal*, and to the Editor of that journal, I extend my warmest thanks. I am also pleased to acknowledge the help given to me by my youngest brother, Stuart Moody, BSc, PhD, of the

University of Edinburgh, in keeping me abreast of certain recent developments.

The Stock Notation for nomenclature was a feature of the first edition and the underlying plan of the book was organized on it. In this edition the nomenclature has been completely revised to comply with the IUPAC recommendations (*The Nomenclature of Inorganic Chemistry* (1957), IUPAC, London: Butterworth Scientific Publications, 1959) and with the suggestions put forward by the Nuffield Foundation. A rationalized system of metric units, the *Système International d'Unités* (SI) is coming into international use and the units in this book are based on that system. But for both nomenclature and units the established, or *trivial*, names and units are also given where it seemed realistic and helpful to do so. Attention is drawn to the Royal Institute of Chemistry Monograph no. 15: *M. L. McGlashan, Physico-chemical Quantities and Units* (1968). In the first edition, values for ionic radii were based on those of V. M. Goldschmidt (1926). In the current edition the values adopted are those in the Nuffield Book of Data, and recommended by Ahrens and Yatsimirskii, to avoid confusion to those pursuing Nuffield courses, but it must be emphasized that while internuclear distances are often known precisely, how far each ion extends is arguable.

In addition to minor corrections and improvements, sections have been added on the shape of covalent molecules, based on simple theory of electrical repulsion, on the concept of lattice energy and its relation to the transition from ionic to covalent bonding and to the solubility of ionic compounds, and on the importance of co-ordination number. The terms ionic and co-ionic are still preferred to their alternatives (although these are given) largely for the reasons put forward by W. G. Palmer, my former Director of

Studies at Cambridge, in his book on *Valency* (Cambridge University Press) and used also in his university text, *Experimental Inorganic Chemistry* (Cambridge University Press).

Finally, I record my continued appreciation of the friendly and intelligent help given to me by my Publishers.

1969

B.J.M.

Preface to third edition

The experienced reader will see numerous alterations in this edition including the rearrangement of some of the early chapters. Units have been brought in line with current internationally accepted recommendations, some features of the text have been expanded and others modified. The alterations reflect changes in emphasis of the author's thinking and teaching, based on many years experience as a Chief Examiner at Advanced level in chemistry to two Examination Boards and are in turn a reflection of evolutionary change, or perhaps tidal change would be a more apposite metaphor, in the subject. In particular it is hoped that while the prime purpose of the book will be enhanced by the changes, the book will also fulfil another function: it will continue to act as a foundation for early college and university courses, being a reliable infill for those aspects of chemistry which have been glossed over fleetingly in some modern courses as the treasure-house of knowledge and achievement is plundered.

The opening chapters are historical in a double sense: the route passes some of the important landmarks of classical chemistry but more importantly, the chapters trace the development of thinking in the subject for they were written with many of the source papers to hand. Currently, and in the same vein, such books as Francis Crick's *What Mad Pursuit* (Basic Books, 1988), a personal view of scientific discovery by the Nobel Prize winner (with James Watson and Maurice Wilkins) who discovered the double helix structure of DNA, should be prescribed reading for all students. Therein lies the cultural value of science.

Two early chapters have been expanded and reorganized into four chapters. The properties of elements in relation to atomic structure has been separated from the matter of electronic configuration. Mass spectrometry has been promoted in this edition from being a side issue. While simple octet

theory is the springboard to what follows, the spin theory and the idea of electron-pairs is developed, and where it is helpful, molecular orbitals are not overlooked in the main text. In this edition there is greater emphasis on the quantitative aspects of ionization energies, electron affinity and exchange energy. As before, however, the criterion for inclusion of theory is strictly its relevance to the comparative theme of the book. Bonding and structure merits a separate chapter after the electronic theory of valency. Bonding found in complex ions involves hybridization, inner and outer orbital complexes, and a later discussion of the associated characteristic colours. Atomic, ionic, metallic and van der Waals' radii are dealt with in some detail and the significance of lattice energies, the theory, the relationship to oxidation states, solubility, interionic distance and physical properties, extended. Much of the foregoing is developed further in the introductory remarks at the beginning of each chapter on the respective Periodic families of elements. The treatment is always comparative, concerned with finding relationships for use as a teaching aid as much as anything else. Here, comparisons of ionization energies, various radii, electronegativities and standard electrode potentials are illustrated in simple graphical form. Crystallization and the crystalline state, formerly a middle order topic, has been promoted to support the opening chapters and now, in an expanded form to show the theoretical building up of close-packed (and not so close-packed) metal structures, it follows the critical examination of bonding, at the simple level. It remains the contention of the author that apparently quite simple concepts can be used to acquire a basic understanding and intuitive grasp of what happens during chemical reactions, and an insight into structural chemistry. The problem is age-old: to prepare the way for work at a higher level in such

a way that the subject unfolds like a flower, without implanting in the student the misunderstandings and old-fashioned prejudices of the teacher. The problem is well known and has to be accepted since it is inescapable.

While expanding the section on nuclear energy, the opportunity has been taken to discuss the hazards associated with the generation of nuclear power and the chemical processing of the products from nuclear reactors (and other sources). Current medical disquiet about the effects of radiation is discussed along with other related issues including politics and economics.

Redox processes are again considered from first principles but the use of equivalents has been omitted, with calculations in titrimetry (volumetric analysis) indicated along molarity lines. The *Stock Notation*, always a feature, has been extended as an alternative nomenclature for the oxoacids of the halogens, to avoid stress for students following the Nuffield courses. Here, and later, the perceptive reader will appreciate the experimental nature of the underlying scheme upon which this chapter, and later chapters is based.

The discussion of Gibbs' Free Energy has been taken further in looking at the principles governing the extraction of metals. In the associated chapters there are minor changes in emphasis and the Midrex process for iron is outlined. The retention of certain processes largely displaced in the United Kingdom is explained by the wider readership of the book.

The section on acids and bases, which already ranged from the initial concept right through to non-protonic systems has been enhanced by inclusion of the Lewis theory, with its link to electron-pairs and bonding. Perhaps it is appropriate here to mention that while extra headings have been introduced to facilitate reference, the temptation to subdivide various discourses has been resisted on the assumption that the student is quite capable of absorbing the study of (say) carbon dioxide, carbonic acid and its salts in one digestible whole.

There are a series of minor alterations to the main text and for up-to-date interest, short topics touching on such matters as metal clusters (for organometallic catalysis) and so-called one dimensional metals (replacing the silicon chip) are added, to give, it must be admitted, a whiff of current research. The text has been considerably enhanced by many illustrations of molecular and ionic structures, with a continuing emphasis on simple concepts like the electrical repulsion theory which accounts for (as an example) the octahedral structure from which the square planar shape of the nickel cyanide complex, $\text{Ni}(\text{CN})_4^{2-}$ may be derived. Certain aspects of pollution are also discussed in this edition including the contamination of water supplies from the excessive use of chemical fertilizers, the European concern over acid rain and the world problem of ozone depletion and the greenhouse effect.

Examination questions are included again but not for cramming! They have been vetted, pruned and extended, not primarily for examination preparation but as a useful and surprisingly interesting way of assessing how much of what has been read, has penetrated and been retained.

I would like to acknowledge David Kitchen (ICI, Billingham) and Geoff Daniels (ICI, Runcorn) for their help with Chapters 12 and 14, respectively. In addition to the organizations listed in the prefaces to the first and second editions, I would like to thank the following:

The Fertiliser Manufacturers Association
The National Sulphuric Acid Association
The Royal Mint
The Royal Society of Chemistry
The Science and Engineering Research Council

Finally I would like to acknowledge the help of my Publishers.

1991

B.J.M.

A Note of Prefixes for SI Units

The following are the approved decimal fractions or multiples of the basic SI Units or of the SI specially named derived units.

<i>Fraction</i>	<i>Prefix</i>	<i>Symbol</i>	<i>Multiple</i>	<i>Prefix</i>	<i>Symbol</i>
10^{-1}	deci	d	10	deka	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f			
10^{-18}	atto	a			

Example $\text{Mg km}^2 \mu\text{s}^{-2}$

$$\begin{aligned}
 &= (10^3 \text{ kg})(10^3 \text{ m})^2 (10^{-6} \text{ s})^{-2} \\
 &= 10^3 \text{ kg} \times 10^6 \text{ m}^2 \times 10^{12} \text{ s}^{-2} \\
 &= 10^{21} \text{ kg m}^2 \text{ s}^{-2}
 \end{aligned}$$

Note that the prefix must be written immediately adjacent to the unit, i.e. touching it in normal writing and separated from the next unit by a small space.

e.g. kg mm , Mg , nm but $\text{kg m}^2 \text{s}^{-2} \text{K}^{-1} \text{mol}^{-1}$ ($= \text{J K}^{-1} \text{mol}^{-1}$)

Further cm^2 always means $(0.01 \text{ m})^2$ and never 0.01 m^2 which may trap the unwary when faced with, say, km^2 or μs^{-2} as above.

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The development of fundamental ideas in 19th century chemistry

Science and chemistry

The Latin word *scientia* was Anglicized to 'science' and applied to any formal branch of knowledge until the beginning of the 17th century when its use became gradually restricted to the natural sciences. At the beginning of the last century the term philosophy was usually applied to all branches of knowledge, science having the same meaning. With the rapid advances in science as we know it, came a separation of the two terms. Philosophy was divided at first into moral philosophy and natural philosophy and science into moral science and natural science. Moral refers to man and his ways: thus, moral law is concerned with the requirements to which right action must conform, and moral sense, the power of distinguishing between right and wrong. Natural in this context has a diffuse meaning: it concerns everything external to man and his conduct. Thus, natural philosophy and natural science were equivalent in meaning but the former has declined in use and only survives in the 'Chairs of Natural Philosophy' at the older universities, philosophy being retained nowadays for the older branches of formal knowledge. The adjective, natural, is usually dropped from Natural Science although its use is retained in the 'Schools of Natural Science' serving to distinguish them from the 'Schools of Moral Science' of the older universities.

The divisions of Natural Science, or the Natural Sciences, are well known: fundamentally, Physics is the general study of matter, heat, light, electricity, etc., Chemistry involves the separation and detailed examination of selected kinds of matter, while Biology is the study of living organisms, Geology, the study of the Earth, and Astronomy, the Universe. However, it is extremely difficult to define science itself and the term is still sometimes used in its earlier sense, as in 'he is a scientific bowler', i.e. skilful. Scientists follow a highly

individual profession but it is generally agreed that any definition of science must indicate the methods by which scientific knowledge is obtained as well as the knowledge itself. Sir Richard Gregory defined science as organized and formulated knowledge of natural objects and phenomena derived from verifiable observations and experiments.

The concept of hypothesis and the crucial experiment lie at the heart of any understanding of science. Starting from the collection of verifiable observations, classification may lead to general statements called laws for which explanations are sought. To this end, hypotheses are formed. A hypothesis is the principal intellectual tool of the scientist. Hypotheses are intelligent guesses and require the possession of imaginative and intuitive powers. They enable the planning of observations and experiments so that predictions based on one or more rival hypotheses may be tested. Experiments are designed to ask specific questions of nature. A crucial experiment enables a choice to be made between rival hypotheses. Science advances by the formulation of hypotheses, with the prediction from them of results which may be tested by experiment. Theories to account for observed phenomena are then propounded. Hypotheses which seem well established become theories. But these must be modified or discarded as fresh evidence is uncovered which proves at variance with them. Of course, chance plays a role in scientific discovery and a clear sequence of events is not always apparent. Most hypotheses by their nature will prove wrong, but by the critical examination of such concepts, science progresses. With hypotheses established, an organized structure based on reason is erected.

In the study of Chemistry, the naturally occurring mixtures of the Earth's crust must be separated and purified so that an examination of the characteristic properties of the components of the mixtures and their relationships with each other

2 The development of fundamental ideas in 19th century chemistry

may be undertaken. During the interaction of different kinds of matter, the relative quantities of matter and associated energy are measured.

Chemistry may be roughly divided into the organic and inorganic branches. The former describes the chemistry of the countless compounds of carbon, although the behaviour of the element and a few simple compounds is left to Inorganic Chemistry, into which the study of all other elements and compounds falls. Inorganic Chemistry as a science may easily become choked by facts. After critical selection and examination of observations concerning the characteristics of elements and their compounds, a periodic pattern emerges. Order appears in the classification of the elements and the study of quantitative and qualitative trends. Physical Chemistry involves the study of chemical phenomena in general terms of Physics and of Chemistry. In what follows it will be assumed that much of the Physical Chemistry required to understand Inorganic Chemistry is known, or is readily available elsewhere.

The purification and identification of substances in the laboratory

Substance is a very vague term. The simplest forms of matter, which cannot be broken down any further, are termed chemical elements. By chemical action, involving the release or absorption of energy by the system, and described as exothermic or endothermic reactions accordingly, compounds are formed. A substance may be an element, a compound or any kind of physical mixture. The detection and identification of the element present in a compound is called analysis and the building up of the compound from simpler units, synthesis.

The details for purification techniques belong properly to laboratory manuals. Gases must be chemically separated into the constituents, dried and collected. This involves the use of wash bottles, absorption bulbs and U-tubes, with collection in air, over water or mercury, or into an evacuated vessel. Mixtures of gases are homogeneous; they consist of a single phase of uniform molecular distribution. Systems involving liquids or solids, and their vapour, consist of a number of phases, and are described as heterogeneous, each phase being of uniform composition and defined by boundary surfaces. Liquids may be separated by means of a separating funnel if immiscible, but their purification usually requires distillation. This may be accomplished generally under atmospheric

pressure, but where thermal decomposition would occur, distillation under reduced pressure may be used. The apparatus may consist of a simple retort or involve a condenser, which may be water- or air-cooled. Mixtures of liquids may require fractional distillation if they are miscible and their boiling-points are very similar. Liquids immiscible with water and otherwise difficult to isolate may be distilled in steam. Bromine, nitric acid, phosphorus trichloride and sulphuryl chloride require distillation, preferably in a glass-jointed apparatus. This is cleaner, easier to arrange and avoids the corrosion problems encountered with the use of corks. Hypochlorous acid and hydrogen peroxide are concentrated under reduced pressure. Hydrochloric acid requires fractionation. The separation of solids may require extraction with solvents. This will be followed by filtration and evaporation, possibly under reduced pressure. Filtration may be replaced by the use of a centrifuge, or in simple cases by decantation. Purification may depend on crystallization or fractional crystallization. Sometimes, solids may be sublimed. Drying may be accomplished in a desiccator, either at ordinary pressure or under reduced pressure in the presence of a desiccating agent, such as concentrated sulphuric acid.

For inorganic solids, crystallization is the most important process of purification and the formation of well-formed crystals from a given solvent may be sufficient to render identification possible. With the covalent solids of organic chemistry, their comparatively low melting-points make the practice of melting-point and mixed melting-point determination a major factor in their identification. Usually inorganic solids have comparatively high melting-points. But there are no homologous series to complicate matters and qualitative analysis may be used. The use of the flame test and spectroscope gives a ready means of identifying metals by their characteristic atomic spectra. The inert gases were identified by the spectra obtained by electrical discharge in them under reduced pressure.

Separation of mixtures may be accomplished by chromatographic techniques. They are of great importance in research and in the routine analytical work on complex mixtures in industry.

Atoms: classical arguments for their existence

Dalton's Atomic Theory was first described in Thomas Thomson's *System of Chemistry*, Volume

III (1807) and by John Dalton himself in *A New System of Chemical Philosophy* (1808). The concept that matter could not be divided indefinitely but would be left as ultimately indivisible particles was not new. It was apparent in Greek thought, as shown in the writings of Leukippos (480 B.C.?) and Demokritos of Abdera (468–370 B.C.). The word ‘atom’ comes from the Greek, *atomos*, meaning indivisible. The Roman, Lucretius, wrote about an atomic concept in his poem concerning *The Nature of the Universe*. Boyle, Newton and others revived the idea of ultimate particles. Dalton’s contribution was to create a working hypothesis out of speculation. He developed the idea that atoms of the same kind of matter would be alike, especially in weight and shape, and would differ from the atoms of other kinds of matter. However, the main step forward came with his explanation of chemical combination in terms of the rearrangement of atoms: ‘Chemical analysis and synthesis go no further than to the separation of particles from one another and to their union. No new creation or destruction of matter is within the reach of chemical agency.’

In the absence of evidence to the contrary, Dalton assumed that atoms united in the simplest ratios possible; for one compound, 1:1, and for more than one compound being formed between two elements, 1:1, 1:2, 2:1, etc. While the arbitrary assignment of combining ratios proved incorrect the hypothesis that chemical combination involved the regrouping of atoms into the same pattern for a given compound gave a simple explanation to the previously observed relationships between the (equivalent) combining weights of elements.

Dalton stressed the importance of the weight of atoms. Nowadays we distinguish between the mass of a body (the quantity of matter present) and its weight (the force of attraction exerted by gravity towards the earth). The quantity of matter in a body is the same wherever the body is while the weight may change. A popular example will be the weightless astronaut in space whose body (and therefore, his mass) is very much in evidence. Within the confines of a chemical balance, the directional pull of gravity on the unknown mass is compared, or balanced, against that of a known mass, the magnitude of the gravitational force cancelling so that masses are compared.

We now know that atoms of a given element may differ slightly in mass, the different kinds being called isotopes. It has been known since 1895 that

atoms are not indivisible and various sub-atomic particles have been described. Further, matter is not indestructible but its loss is associated with an enormous release of energy. But in the context of ‘chemical agency’, Dalton’s Atomic Theory is still substantially correct. As a hypothesis it was based on quantitative laws and tested by predicting another law, that of multiple proportions. **The Atomic Theory** may be summarized:

‘All matter is composed of very small discrete particles.

For elements the particles are called atoms and are indivisible and indestructible in chemical reactions.

The atoms of a given element are all identical and differ from the atoms of other elements. Dalton stressed weight as a property distinguishing atoms of different elements.

A chemical compound is formed from its elements by the combination of the different atoms in a fixed ratio for that compound.’

During the course of his researches into the role of oxygen in combustion, Lavoisier formulated the **Law of Conservation of Mass** (1774).

In a chemical reaction, the mass of the products is equal to the mass of the reactants.

He weighed a sealed retort containing tin and air, before and after heating. The experimental statement of the law is sometimes discarded for the statement that ‘matter is neither created nor destroyed in the course of a chemical reaction’. An accuracy of 1 in 10^7 was achieved by Landolt in further experiments during the period 1891–1908 and Morley in 1912 recorded an accuracy of 1 in 10^8 . Until 1801, the constancy of chemical composition of pure compounds had been assumed. Indeed, without it, chemistry would be very different. In that year the law, formally stated two years before by Proust, was challenged by Berthollet who drew the wrong conclusions from some experimental work on oxides of lead. However, Proust did further work and using compounds of copper he established the **Law of Constant Composition (or Definite Proportions)**.

All pure samples of a particular chemical compound contain the same elements combined in the same proportions by mass.

By 1808, after further work, the law was accepted. It will be seen later that elements usually contain a fixed proportion of isotopes or atoms of slightly different mass but where the formation of some specimens by radioactive decay has occurred a variation in composition by mass of certain compounds will be found. Interstitial compounds formed between the transition metals and the lighter elements (hydrogen, boron, carbon, nitrogen) and one or two sulphides and oxides show slight variations in composition. These are known as Berthollides as distinct from the much more usual Daltonide compounds. On the basis of the atomic hypothesis and these quantitative laws, Dalton predicted a relationship which would be found to hold where more than one compound was formed between two elements. This was then established experimentally and known as the **Law of Multiple Proportions**.

When two or more elements combine together to form more than one compound the several masses of one element combining with a fixed mass of the other element are in a simple ratio.

The concept that chemical interaction results in the regrouping of atoms in patterns peculiar to the compounds concerned, together with the notion that the mass of an atom is a characteristic property of the element of which it is the smallest particle explains the fourth quantitative law, the **Law of Equivalent (or Reciprocal) Proportions** established by Richter between 1791 and 1802.

The ratio of the mass of two elements which separately combine with a given mass of a third element is the ratio in which the two elements react with each other, or a simple multiple of this ratio.

A direct consequence of the laws of chemical combination and not depending on theory in any way is the importance attached to the idea of equivalent mass. This is the mass of the element which will combine with a standard mass of a standard element. Where direct combination does not occur, or difficulties arise, an indirect determination may be made by combination with an element of previously determined equivalent mass. The standard chosen will be that which proves most convenient, readily forming a wide range of compounds. The standard value should not be too cumbersome nor should values based on it be less than unity. Dalton chose hydrogen, which is the element with the lowest equivalent mass, as the

standard (equivalent = 1) but relatively few elements combine with it. Berzelius favoured oxygen and this is usually used today in the school laboratory. The value selected (equivalent = 8 exactly) makes the lowest equivalent mass, that of hydrogen, just greater than unity. Therefore, **the equivalent mass of an element is**

the number of parts by mass of that element which will combine with or displace, directly or indirectly, 8 parts by mass of oxygen exactly.

Dalton emphasized the importance of determining the relative mass of atoms and adopted arbitrary combination ratios for atoms uniting. The mass of individual atoms is very small indeed and it is much more convenient to define a scale in terms of the mass of one of the elements. Clearly, the scale should be based chemically on oxygen. The table of relative atomic masses so devised gives values near to whole numbers for most elements. When hydrogen and oxygen combine to form steam, the volumes uniting are in the ratio of 2 : 1. That the atoms of hydrogen and oxygen unite in groups of three, two of hydrogen to one of oxygen, will be deduced later. In round numbers, the equivalent mass of hydrogen = 1 when that of oxygen is defined as 8. Briefly, for steam the combining ratios of hydrogen and oxygen are: by atoms, $\frac{2}{1}$; by mass, $\frac{1}{8}$. By adopting the atomic mass standard based on 16 exactly as the value for oxygen, the atomic mass of hydrogen is equal to the equivalent mass and just greater than unity (1.0080): it has the smallest atomic mass. The atomic mass standard, and therefore the atomic mass scale for other elements, is arbitrary. **Until 1960, atomic masses were based on the scale showing the mass of an atom of oxygen as 16 exactly.** The masses of individual atoms may be calculated using Avogadro's constant (formerly Avogadro's Number), which determined experimentally, shows that there are 6.023×10^{23} atoms in one gram atom (i.e. the mole, p. 8).

The alchemists used a sort of shorthand to represent substances. Thus, silver was shown by a crescent moon, and silver nitrate is still sometimes called lunar caustic. Dalton first used symbols in a quantitative, as well as a qualitative way, in the development of the Atomic Theory. To him, a symbol represented a definite quantity of an element, namely, one atom. He pictured atoms as circles with shading and signs to distinguish different kinds of atoms so that a compound could be shown as a cluster of touching atoms, showing a definite

number of atoms of each of the combining elements. Berzelius invented the present system in 1811. He suggested that it was easier to write and print an abbreviated word than a diagram. He selected the initial letter of the Latin name of each element and where several had the same initial letter he added the next letter or if this failed, he used the first consonant not in common. He also stressed the need for a symbol to represent an atom of the element. It now represents that quantity of the element equal to the relative atomic mass measured in grams, to use the obsolescent definition.

The combining capacity of an atom of an element is called the valency, from the Latin, *valentia*, vigour or capacity. Because two elements may unite to form more than one compound, the valency may assume more than one value. Since equivalents are mass-combining ratios experimentally determined with atoms combining in small whole number ratios and atomic masses are ratios, both being based usually for our purposes on $O = 16$ exactly, there must be a simple relationship between the atomic mass and equivalent of an element referred to oxygen:

$$\frac{\text{Atomic mass}}{\text{Equivalent mass}} = \text{a small integer, which is the valency of the element in the compound in which it exhibits the equivalent mass shown.}$$

The valency of an element may be deduced in another way. This requires the use of test elements of indivisible valency, or univalency. The valency of an element equals the number of atoms of the test element with which one atom of the element unites. Hydrogen is accepted as the universal test element. The evidence in support of this will be given later. But this method is not so different from that used before. In counting the number of atoms of hydrogen uniting with the atom of the element, the number of gram atoms of hydrogen, or gram equivalents, combining with the gram atom of the element is being determined. The number of hydrogen atoms counted represents the number of gram equivalents in the gram atom of the element.

The **valency** of an element is equal to the number of hydrogen atoms with which one atom of the element will unite.

This classical view will be examined in detail again.

Until 1960, the standard for atomic mass was $O = 16$ exactly. Formerly, the term relative atomic mass was used, but nowadays the molar mass is preferred, which has the unit g mol^{-1} of the species quoted. The occurrence of isotopes, atoms of an element with different atomic masses, has been mentioned. The chemical scale of atomic masses was based on oxygen being, in this context, the ordinary mixture of isotopes. The nature of isotopes will be described in detail later. Atmospheric oxygen contains 99.758% of the isotope† ^{16}O , 0.0373% of ^{17}O , and 0.2039% of ^{18}O . The weighted mean is 16.004462. The physical scale of atomic masses was based on the most abundant isotope ^{16}O taken as 16. The prefixes refer to the mass number of each isotope, the integer nearest to the atomic mass. Atomic masses on the physical scale were larger by a factor of 1.000272 than those on the chemical scale. **A scale based on $^{12}\text{C} = 12.0000$ was proposed in 1960;** it differs from the chemical scale ($O = 16.0000$) by 42 p.p.m. and the physical scale ($^{16}\text{O} = 16.0000$) by 317 p.p.m.

The Table of relative atomic mass is given as Table 1.1, p. 6.

Molecules: classical arguments for their existence

In his conception of the Atomic Theory, Dalton postulated that atoms united in small whole numbers. A few months later in 1808, Gay-Lussac announced his **Law of Combining Volumes**:

Gases combine together in volumes which bear a simple ratio to each other and to the volume of the product if it be gaseous and all measurements are made under fixed conditions of temperature and pressure.

Three years before Gay-Lussac and von Humboldt had published *Experiments on the Ratio of the constituents of the Atmosphere*. One method of analysis for oxygen involved exploding measured volumes of air with hydrogen and measuring the volume of the product. Clearly, data for the combination of oxygen and hydrogen was required but there proved to be nothing reliable at hand. As a preliminary, they measured the combining ratio of hydrogen and oxygen by volume. As a mean of 24 experiments, they calculated that 100 parts of oxygen by volume reacted with 199.89 parts of

† spoken: oxygen-16

Table 1.1 Relative atomic masses of the elements
Based on the relative atomic mass of $^{12}\text{C} = 12$

The values for relative atomic mass given in the Table apply to elements as they exist in nature, without artificial alteration of their isotopic composition, and further to natural mixtures that do not include isotopes of radiogenic origin. If the term **molar mass** is preferred, the unit is g mol^{-1} .
 Alphabetical Order in English

Name	Symbol	Atomic number	Atomic mass	Name	Symbol	Atomic number	Atomic mass
Actinium	Ac	89	227.028	Mercury	Hg	80	200.59
Aluminium	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium*	Am	95	243.061	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.179 ^b
Argon	Ar	18	39.948	Neptunium*	Np	93	239.053
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine*	At	85	209.987	Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium*	Bk	97	247.070	Nobelium*	No	102	255.093
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994 ^a
Boron	B	5	10.811 ^a	Palladium	Pd	46	106.4
Bromine	Br	35	79.904 ^b	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Caesium	Cs	55	132.905	Plutonium*	Pu	94	239.052
Calcium	Ca	20	40.08	Polonium	Po	84	210.000
Californium*	Cf	98	252.082	Potassium	K	19	39.102
Carbon	C	6	12.01115 ^a	Praseodymium	Pr	59	140.907
Cerium	Ce	58	140.12	Promethium*	Pm	61	144.9126
Chlorine	Cl	17	35.453 ^b	Protactinium	Pa	91	231.036
Chromium	Cr	24	51.996	Radium	Ra	88	226.025
Cobalt	Co	27	58.9332	Radon	Rn	86	222.018
Copper	Cu	29	63.546 ^a	Rhenium	Re	75	186.2
Curium*	Cm	96	247.070	Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium*	Es	99	254.088	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Rutherfordium*	Rf	104	260
Europium	Eu	63	151.96	Samarium	Sm	62	150.35
Fermium*	Fm	100	253.086	Scandium	Sc	21	44.956
Fluorine	F	9	18.9984	Selenium	Se	34	78.96
Francium	Fr	87	223.020	Silicon	Si	14	28.086 ^a
Gadolinium	Gd	64	157.25	Silver	Ag	47	107.868 ^b
Gallium	Ga	31	69.72	Sodium	Na	11	22.9898
Germanium	Ge	32	72.59	Strontium	Sr	38	87.62
Gold	Au	79	196.967	Sulphur	S	16	32.064 ^a
Hafnium	Hf	72	178.49	Tantalum	Ta	73	180.948
Hahnium*	Ha	105	—	Technetium*	Tc	43	98.906
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797 ^a	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847 ^b	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lawrencium*	Lr	103	257	Vanadium	V	23	50.942
Lead	Pb	82	207.19	Xenon	Xe	54	131.30
Lithium	Li	3	6.939	Ytterbium	Yb	70	173.04
Lutetium	Lu	71	174.97	Yttrium	Y	39	88.905
Magnesium	Mg	12	24.305	Zinc	Zn	30	65.37
Manganese	Mn	25	54.9380	Zirconium	Zr	40	91.22
Mendelevium*	Md	101	257.096				

Rutherfordium, Rf, 104 is also called kurchatovium, Ku

^a Elements with a relative atomic mass so designated are known to be variable because of natural variations in isotopic composition. The observed ranges are:

Boron	± 0.003	Hydrogen	± 0.00001	Silicon	± 0.001
Carbon	± 0.00005	Oxygen	± 0.0001	Sulphur	± 0.003

^b Elements with a relative atomic mass so designated are believed to have the following experimental uncertainties:

Bromine	± 0.001	Copper	± 0.001	Neon	± 0.003
Chlorine	± 0.001	Iron	± 0.003	Silver	± 0.001

[Table adapted from Comptes Rendues of the XXIV Conference of IUPAC, Prague, September 1967, with additions]

*Not found naturally on Earth