

Introduction to Chemical Nomenclature

Fifth Edition

**Cahn
Dermer**

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R. S. Cahn, MA, Dr Phil nat, FRIC, CC

*Formerly Editor to the Chemical Society and member of
the IUPAC Committee of Nomenclature of Organic Chemistry*

O. C. Dermer, BSc, PhD, ScD

*Regents Service Professor Emeritus of Chemistry,
Oklahoma State University*



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Preface

Since the previous edition of this 'Introduction to Chemical Nomenclature', not only has the International Union of Pure and Applied Chemistry (IUPAC) continued its publication of varied recommendations on nomenclature, but also Chemical Abstracts Service (CAS) has set out great changes which it has introduced into its indexing procedures. Bringing this 'Introduction' up to date would have been impossible for me had I not secured the collaboration of Professor O.C. Dermer of Oklahoma State University, Stillwater, Oklahoma, U.S.A., whose long experience of research and its publication and as section editor of *Chemical Abstracts (CA)* enabled the text to be modernized, corrected, and expanded so as to show the divergences between the recommendations of IUPAC and the indexing practices of *CA*. My indebtedness and thanks to him are boundless.

The principal expansions have been in the treatment of stereochemistry, natural products, and organometallic compounds.

It is a feature of many IUPAC recommendations that a choice of names is permitted; insofar as *CA* selects for its indexes and its computer services any one of the IUPAC offerings, it may be expected that a large body of chemists, particularly the younger members, will follow the more systematic *CA* usages; but when *CA* adopts completely new methods a more permanent conflict due to divergent loyalties may result. Professor Dermer and I agreed that the present book should merely set out the main differences between *CA* and IUPAC practices, only rarely stating a preference; this accords with the intention of previous editions, retained here, to explain the reasons rather than to dictate; and it is hoped that this will help the individual chemist who must know *CA* nomenclature as used in its indexes and information services as well as the IUPAC nomenclature that is seen in a great mass of current and past publications.

Professor Dermer and I are extremely grateful to S.P. Klesney (Secretary of the IUPAC Commission of Nomenclature of Organic Chemistry and in charge of the Central Report Index of Dow Chemical, U.S.A.) and Dr. W.H. Powell (of CAS and member of the above-mentioned IUPAC Commission), each of whom read the manuscript and made very many valuable corrections and additions. We are grateful

also to IUPAC, Pergamon Press, and CAS for permission to quote from their publications, although unfortunately the IUPAC revised 1979 edition of Sections A, B, C, D, E, F and H of the organic nomenclature rules were not available when our manuscript went to press. Finally, we thank Mrs. Verne Allen Ospovat who with great efficiency typed the whole manuscript.

R.S. Cahn

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1

The Development of Chemical Nomenclature

Nomenclature — the way that names are given to things — is one main point of difference between the language of chemistry, as of other sciences, and natural languages. The other is the importance of the written language compared with the spoken one. In chemistry there are several nomenclatures; not only elements and compounds must be named, but also reactions, methods, pieces of apparatus, and theoretical concepts. However, the vast numbers of compounds to be distinguished present the main problem, and this one addressed in the following pages.

Many things are designated by means other than names, and chemical compounds can be precisely represented by, for example, formulas, linear ciphers abbreviating formulas, or merely registry numbers. Such assemblies of symbols, not being words, are literally 'unspeakable' and are little discussed in this book. Even among words, chemists have some choice in referring to a compound; according to the occasion, '2-chloronaphthalene', 'that substance', or 'compound 2' may be the most suitable designation. Specific names, however, will continue to be needed for lists and legislation, as well as for abstracts, indexes, and lexicons. Of course names are essential, too, for most research papers or reports, for textbooks, and for chemical conversation whether written or oral.

The picturesque old appellations based on sources or properties of substances, or the name of the discoverer — spirits of hartshorn, muriatic acid, liver of sulfur, Glauber's salt, etc. — have long since disappeared from the chemist's language; and, as in any evolving language, the abandonment of old terms goes on. The need for reform was emphasized by Bergmann (ca. 1760), and it was met by the system of Guyton de Morveau, Lavoisier, and others (1787), based on the then novel idea that a name should indicate *composition*. This proved so very useful

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that before long it was widely accepted; but of course virtually all the well-characterized compounds of the time were inorganic, and relatively simple. Each such compound was later named by Berzelius as made up of an electropositive and an electronegative part, and two-word names of the kind he popularized are still familiar in inorganic nomenclature. (Berzelius also devised letter chemical symbols for the elements in much the form we use them today.) The success of the Berzelius names and philosophy, however, impeded the development of the concept of substitution in organic compounds (which it could not describe), and consequently that of substitutive nomenclature.

The rapid growth of organic chemistry in the latter part of the nineteenth century produced a need for new systematization, especially for classification and indexing of compounds. This was undertaken by the Geneva Conference (1892). The rules developed there were seriously incomplete, but sound in principle, and are still used in the current edition of *Beilsteins Handbuch der organischen Chemie*. Since that time there have grown up two parallel efforts to improve and standardize chemical nomenclature, one by the International Union of Pure and Applied Chemistry (IUPAC) and the other by *Chemical Abstracts (CA)*. IUPAC Commissions for nomenclature of inorganic, organic, and biological chemistry were organized in 1922, and in other fields later; over the years, the first two have been most active in issuing recommendations. The need of *CA* to improve its indexes has led it to develop and publish rules, modified from time to time, by which it assigns index names, especially to chemical compounds.

It is the aim of systematic chemical nomenclature to describe the composition, and insofar as practicable the structure, of compounds. To the extent that this is achieved, chemists are fortunate; biologists, geologists, and astronomers have no such convenient way of associating scientific names with the things, or classes of thing, that they describe. However, no system of nomenclature can start afresh, abandoning all previous names. As a result, present practices are a patchwork, as diverse, specialized, and involved as the compounds they describe. Over the great complexities and illogicalities of current nomenclature hangs the shadow of the computer; the marshalling of four million structures and their attendant properties is increasingly admitted to be a computer responsibility. Because computers depend on logic, their use promotes systematic nomenclature. The groups of symbols best suited to computer programs to represent compounds, however, are mostly not names. Thus it does not appear that a computer language will soon displace the often arbitrary and sometimes inconsistent current usage. The origins of many common chemical names have been compiled in dictionary form¹.

A major shift to more structure-descriptive names has been made in

recent subject indexes of *Chemical Abstracts* (CA), but there have been objections to replacing familiar names (such as *p*-benzoquinone) with longer ones (such as 2,5-cyclohexadiene-1,4-dione) that are not used in journals and books. Thus both the colloquial language, full of alternatives and irregularities, and the new one, with its complexities, will for many years, at least, still have to be read and understood. Nomenclature is thus worth study; every chemist should know its principles and its correct use.

The nomenclature that is today regarded as 'correct' is defined by the consensus of users' opinions. As in all linguistics, there is a struggle between the pragmatists, who regard as satisfactory any word that conveys the intended meaning, and the purists, who insist that rules ought to be followed, with the pragmatists having the advantage. Thus the Commissions of the International Union of Pure and Applied Chemistry (IUPAC) and of the International Union of Biochemistry (IUB) try to see nomenclature as a whole, codifying existing usage into rules and occasionally suggesting novelties; they accept the useful practices of specialists within their own fields but reject what they consider to be unnecessary aberrations from general principles. Since chemists differ widely in native language, and (as has been noted) the written language is more important to the chemist than the spoken, little attention is given to standardization of pronunciation.

While there are a very few problems in oral communication because two names have virtually the same sound (e.g., fluorine, fluorene), there are few of consequence that arise because two substances have the same written chemical name. It would be correspondingly simpler if there were only one 'correct' name for a substance, as in botany and zoology there is only one internationally authorized Latin name for a species of plant or animal. In chemistry, particularly organic chemistry, this is not so. The only exception is in indexes to collected works, where it is essential to place all entries under one name to save the user's time. Aside from the variations caused by differing natural languages, there are two reasons for the diversity. First, large compilations such as Beilstein's *Handbuch* and CA often use differing principles, and for them to introduce fundamental changes would bring chaos into their indexes; equally, a single rule is not always practicable, as when two or more large sections of chemists steadfastly maintain different customs. It is, however, noteworthy that CA, on the whole, conforms to the rules of the International Commissions, and conversely that those who formulate rules pay much attention to the practices of CA. There is one other feature that must be emphasized in a book such as this, devoted mainly to rules, namely that rules are a tool and not a master. Like other tools they can be used in different ways, or even set aside, or, better, modified when the science or its exposition is thereby

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improved or made easier to understand. This echoes Lavoisier's advice² of nearly 200 years ago: 'If languages are really instruments fashioned by men to make their thinking easier, they ought to be of the best kind possible; and to try to perfect them is actually to work for the advancement of science'.

Because, as just explained, it is not always possible for chemists to agree on the most desirable type of name, there are cases where alternative names are prescribed as equally 'correct' in the international rules. Then one country, Society, journal, or compendium may exercise its own preference. Within reason, each individual chemist has the same choice, though in practice he may be limited by his Society, editor, or publisher, and he is expected to be consistent in his choices. In most cases there is one name that is correct for a particular purpose: an author may use one of the alternatives, or even an unauthorized name, if it is essential for his theoretical arguments, but not just because of his personal preference; the authorized version will, with a little ingenuity, suffice for almost all purposes.

Now a systematic name for a complex compound is usually itself complex, and some thought will be needed to understand it. It is therefore misuse of nomenclature to scatter long chemical names indiscriminately into a cursive explanation of ideas. It is better to choose carefully a phrase such as 'the unsaturated alcohol', 'the derived acid', 'the starting material', or simply 'compound 5' (which has already been described by structure or name) than to bespatter one's prose with names such as 3-hydroxy-5-oxo-D-nor-5,6-secocholest-9(11)-en-6-oic acid or 5-(4-diethylamino-1-methylbutyl)dibenz[*a*]acridine.

A more common misuse, which has produced some names now solidly entrenched, is false analogy in naming new types of compound, e.g., silicones (R_2SiO)_x and sulfones (R_2SO_2) are very little like ketones (R_2CO) either structurally or chemically, but usage has made these names familiar. It is very hard to lay down precise rules for avoiding inappropriate names of this kind. Selection depends on a wide knowledge of previous practice: it is only too easy to mislead — and the overriding criterion for a name is that it shall be unambiguous. The advice of the national expert or editor is here essential.

Difficulties notwithstanding, chemists should, if they wish to be clearly understood, learn to describe accurately the compounds they are writing or talking about — and a definite act of learning is needed. Nomenclature, particularly in its modern developments, is not merely an arbitrary collection of names. It combines past practice with general principles, which it is the object of the following pages to explain. Tampering with it merely makes life harder for the reader and for the searcher in indexes. It is rarely good to call a spade a shovel, with or without a prefix.

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1. FLOOD, W.E., *The Origins of Chemical Names*, Oldbourne, London (1963)
2. LAVOISIER, A.L., *quoted by* SAVORY, T.H., *The Language of Science*, 2nd Ed., Deutsch, London (1966), p. 67

2

Inorganic

General

The greater part of inorganic nomenclature was for many years handled with reasonable ease by means of the endings '-ic', '-ous', '-ium', '-ide', '-ite', and '-ate'. When these did not suffice, help was sought mainly in prefixes of the type 'pyro-', 'hypo-', 'meta-', 'ortho-', 'per-', and 'sub-', and in endings such as '-oxylic', '-yl', and '-osyl'. There was, however, little consistency in the use of these adjuncts, and the resulting confusion was made worse when later studies of structure disclosed irrationalities in place of some of the supposed analogies. The Stock notation helped in many cases, and Werner's nomenclature was invaluable for coordination compounds.

There have been four international attempts in recent decades to devise a general system for inorganic nomenclature. A comprehensive set of rules was issued¹ by the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Chemistry* in 1940, but because of the war it received no outside comment before publication. A revision was published in 1953 as 'Tentative Rules'²; independent comment and further consideration led to 'Definitive'† Rules³ resulting from the Paris Conference of 1957. Some revisions were published in 1965⁴. Finally, in 1971 a new set of Definitive Rules⁵ was published by IUPAC that amalgamates, revises, and greatly extends previous versions, providing principles, rules, and examples over a very wide range. It is on this last set, which has recently been summarized⁶, that the present chapter is based. Among the chief features are acceptance of the well-known '-ide' nomenclature for binary compounds, recommendations for use of either the Stock or the Ewens-Bassett

*The older title, International Union of Pure and Applied Chemistry (IUPAC), was re-assumed in 1949.

† 'Definitive' here means 'as accepted, or revised after being laid open to criticism by chemists'. It does not mean 'final, unalterable'.

notation, and extension of Werner's system for coordination compounds to a large part of general inorganic chemistry. Exceptions are still made for very common names such as water or ammonia and for a long list of acids, though the Commission doubtless hopes that these exceptions also will in time be superseded. Much that is familiar remains; and the extensions often lead to easily recognizable names such as potassium tetrachloroaurate(III) $K[AuCl_4]$, hydrogen difluorodihydroxoborate $H[B(OH)_2F_2]$, and potassium tetrafluorooxochromate(V) $K[CrOF_4]$; the extensions would, systematically, give disodium tetraoxosulfate for Na_2SO_4 though, of course, sodium sulfate is included among the permitted exceptions. The main virtue of the extension and revision is the replacement of personal or national preference by system and the provisions of unambiguous principles for naming new compounds, including many organometallic compounds of great complexity. It is unfortunate, however, that so many alternatives are left available.

Elements

Names and symbols for the elements are given in *Table 2.1* (pp. 8-9). The names in parentheses are those to be used with affixes, e.g., cupric, ferrate. A few specific points may be noted. Tungsten is now accepted, after an earlier attempt to replace it by wolfram. The symbol for argon is Ar (not A), usage in different countries having become confused and the other noble gases having two-letter symbols. Some compounds of sulfur and antimony are named by use of syllables from the Greek (*thion*) or Latin (*stibium*); occasionally old French usage persists in English, as in azide from the French usage of *azote* for nitrogen. Use of wolframate and niccolate in place of tungstate and nickelate has been recommended [but *Chemical Abstracts* (CA) uses the latter older names]. Sulfur, not sulphur, should be used; the English use of sulphur is based on a mistaken belief that sulfur had a Greek origin, in which case *ph* would replace the Greek *phi* (ϕ). The American spellings cesium and aluminum may also be noted.

Naming of elements of atomic number greater than 105 on the basis of such numbers is recommended in tentative rules recently proposed by IUPAC⁷. This produces names such as unnilhexium (un-nil-hex-ium) for No. 106 and ununtrium for No. 113. It remains to be seen whether this unfamiliar system will replace naming new elements by scientists according to their personal preferences.

Some collective names now receive international sanction: noble gases; halogens (F, Cl, Br, I, At); chalcogens (O, S, Se, Te, Po); alkali metals (Li to Fr); alkaline-earth metals (Ca to Ra); lanthanoids for elements 57-71 (La to Lu inclusive) (lanthanides before 1965);

Table 2.1 IUPAC NAMES AND SYMBOLS OF THE ELEMENTS

<i>Name</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Name</i>	<i>Symbol</i>	<i>Atomic number</i>
Actinium	Ac	89	Lead (Plumbum)	Pb	82
Aluminum*	Al	13	Lithium	Li	3
Americium	Am	95	Lutetium	Lu	71
Antimony	Sb	51	Magnesium	Mg	12
Argon	Ar	18	Manganese	Mn	25
Arsenic	As	33	Mendelevium	Md	101
Astatine	At	85	Mercury	Hg	80
Barium	Ba	56	Molybdenum	Mo	42
Berkelium	Bk	97	Neodymium	Nd	60
Beryllium	Be	4	Neon	Ne	10
Bismuth	Bi	83	Neptunium	Np	93
Boron	B	5	Nickel	Ni	28
Bromine	Br	35	Niobium	Nb	41
Cadmium	Cd	48	Nitrogen	N	7
Calcium	Ca	20	Nobelium	No	102
Californium	Cf	98	Osmium	Os	76
Carbon	C	6	Oxygen	O	8
Cerium	Ce	58	Palladium	Pd	46
Cesium†	Cs	55	Phosphorus	P	15
Chlorine	Cl	17	Platinum	Pt	78
Chromium	Cr	24	Plutonium	Pu	94
Cobalt	Co	27	Polonium	Po	84
Copper	Cu	29	Potassium	K	19
(Cuprum)			*Praseodymium	Pr	59
Curium	Cm	96	Promethium	Pm	61
Dysprosium	Dy	66	Protactinium	Pa	91
Einsteinium	Es	99	Radium	Ra	88
Erbium	Er	68	Radon	Rn	86
Europium	Eu	63	Rhenium	Re	75
Fermium	Fm	100	Rhodium	Rh	45
Fluorine	F	9	Rubidium	Rb	37
Francium	Fr	87	Ruthenium	Ru	44
Gadolinium	Gd	64	Samarium	Sm	62
Gallium	Ga	31	Scandium	Sc	21
Germanium	Ge	32	Selenium	Se	34
Gold (Aurum)	Au	79	Silicon	Si	14
Hafnium	Hf	72	Silver		
Helium	He	2	(Argentum)	Ag	47
Holmium	Ho	67	Sodium	Na	11
Hydrogen	H	1	Strontium	Sr	38
Indium	In	49	Sulfur	S	16
Iodine	I	53	Tantalum	Ta	73
Iridium	Ir	77	Technetium	Tc	43
Iron (Ferrum)	Fe	26	Tellurium	Te	52
Krypton	Kr	36	Terbium	Tb	65
Lanthanum	La	57	Thallium	Tl	81
Lawrencium	Lr†	103	Thorium	Th	90

Table 2.1 continued

<i>Name</i>	<i>Symbol</i>	<i>Atomic number</i>	<i>Name</i>	<i>Symbol</i>	<i>Atomic number</i>
Thulium	Tm	69	Vanadium	V	23
Tin (Stannum)	Sn	50	Xenon	Xe	54
Titanium	Ti	22	Ytterbium	Yb	70
Tungsten	W	74	Yttrium	Y	39
(Wolfram)			Zinc	Zn	30
Uranium	U	92	Zirconium	Zr	40

*Aluminium is nevertheless still current in British publications and is in accord with the '-ium' ending adopted for all newly discovered elements.

†The spelling caesium or caesium is generally used by British authors.

‡Not Lw as sometimes seen.

actinoids, uranoids, and curoids analogously. A transition element is defined as an element whose atoms have an incomplete *d* subshell or which gives rise to a cation or cations with an incomplete *d* subshell. The term metalloid is vetoed: it is stated that elements should be classified as metallic, semimetallic, or nonmetallic.

Protium, deuterium, and tritium are retained as names for the hydrogen isotopes ^1H , ^2H , and ^3H , respectively, but other isotopes should be distinguished by citing mass numbers, e.g., oxygen-18 or ^{18}O . The prefixes are 'deuterio-' and 'tritio-' (not deutero-).

Indexes to be used with atomic symbols are:

left upper	.	.	mass number
left lower	.	.	atomic number
right upper	.	.	ionic charge
right lower	.	.	number of atoms

For example, $^{32}_{16}\text{S}_2^{2+}$ is a doubly charged molecule containing two atoms of sulfur, each atom having the atomic number 16 and mass number 32. The atomic number is obviously redundant and often omitted. Others of these indexes may also be unnecessary; for instance, Ca^{2+} is a doubly charged calcium ion (with natural abundance of isotopes), ^{15}N an uncharged atom of nitrogen-15, $^{40}\text{K}^+$ a singly charged ion of potassium-40. Although physicists formerly wrote the mass number as upper right index, and many still do, the newer preference is for the positions given above.

Radioactivity is often indicated by an asterisk, $^*\text{K}$; it is rarely necessary to give both the mass number and the asterisk ($^{*40}\text{K}$).

Ionic charge must be given as, e.g., superscript $2+$, and not superscript $+2$.

For allotropic forms of elements a very simple numerical system is recommended: monohydrogen, dioxygen, tetraphosphorus, etc. Trioxxygen is then recommended by IUPAC for O_3 , though this can hardly be held to exclude use of the familiar name *ozone* since *ozonide* is listed among the recognized names of polyatomic anions.

Table 2.2 IUPAC DESCRIPTION OF SUBGROUPS

1A	2A	3A	4A	5A	6A	7A
K	Ca	Sc	Ti	V	Cr	Mn
Rb	Sr	Y	Zr	Nb	Mo	Tc
Cs	Pa	La*	Hf	Ta	W	Re
Fr	Ra	Ac†				
1B	2B	3B	4B	5B	6B	7B
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg	Tl	Pb	Bi	Po	At

*Including the lanthanoids.

†Including the actinoids, but thorium, protactinium, and uranium may also be placed in groups 4, 5, and 6.

Ring and chain structures can be designated by prefixes *cyclo-* and *catena-*, e.g., *cyclo-octasulfur* (or *octasulfur*; for λ -sulfur), *catena-sulfur* (or *polysulfur*; for μ -sulfur). The prefix *cyclo-* is now specified for italics by IUPAC in inorganic chemistry (not in organic chemistry).

The description of subgroups of the Periodic Table has been settled by the IUPAC 1965 revision as shown in Table 2.2.

Compounds

Formulas and names should correspond to the stoichiometric proportions, expressed in the simplest form that avoids the use of fractions [though semi ($\frac{1}{2}$) and sesqui ($1\frac{1}{2}$) may be used for solvates and other addition compounds]. The molecular formula, if different, is used only when dealing with discrete molecules whose degree of association is considered independent of temperature. When there is temperature-dependence, the simplest formula is again to be used unless the molecular complexity requires particular emphasis in the context. Thus we have KCl potassium chloride, PCl_3 phosphorus trichloride, S_2Cl_2 disulfur dichloride, and $H_4P_2O_6$ hypophosphoric acid (see Table 2.7); NO_2 nitrogen dioxide represents the equilibrium mixture of NO_2 and N_2O_4 for normal use, but N_2O_4 dinitrogen tetroxide is used where this doubling of the formula is significant.

In *formulas* the electropositive constituent is generally placed first, e.g., PCl_3 , HCl . But there are exceptions, some merely by usage, e.g., NH_3 and NCl_3 . When there is a central atom, that should normally be placed first with the remainder in alphabetical order, as in PBrCl_2 and PCl_2O ; but POCl_3 is also authorized because PO may be considered a radical (see p. 23).

Names of compounds are given in two (or more) words, the (most) electropositive constituent (cation) first and the (most) electronegative (anion) last. Exceptions are made for neutral coordination compounds, addenda such as solvent molecules (see p. 38), and some hydrides. However, no fundamental distinction is to be made between ionized and non-ionized molecules in general.

Proportions of the various parts are expressed by Greek numerical prefixes (see Table 3.1, p. 46; also p. 67); but there are extremely important qualifications that mono (for unity) is usually omitted and that other numerical prefixes may also be omitted if no ambiguity results. Multiplicative numerical prefixes (bis, tris, tetrakis, etc.) are used when followed directly by another numerical prefix and may be used whenever ambiguity might otherwise be caused; and prefixes may be delimited by parentheses to aid clarity further (examples are on pp. 28–29). The terminal 'a' of tetra, penta, etc., was formerly elided in English before another vowel in inorganic chemistry, but this is expressly forbidden in IUPAC inorganic nomenclature: e.g., diphosphorus pentoxide (not pentoxide).

Binary Compounds

Compounds between two elements are called binary compounds, independently of the number of atoms of each element in a molecule; e.g., they include N_2O , NO , NO_2 , and N_2O_4 .

In formulas and names of compounds between two nonmetals that constituent is placed first which occurs earlier in the sequence:

Rn , Xe , Kr , B , Si , C , Sb , As , P , N , H , Te , Se , S , At , I , Br , Cl , O , F

This order is arbitrary in places: it is not based solely on an order of electronegativity. The results are mostly familiar: NH_3 (not H_3N), CCl_4 , NO , etc. But Cl_2O (chlorine monoxide) contrasts with O_2F (dioxygen fluoride).

When neither atom of a binary compound occurs in the sequence $\text{Rn} \dots \text{F}$ above, the atoms are cited in the inverse order of the element sequence shown in Table 2.3 (p. 12). This applies to both formulas and names, e.g., Na_2Pb , disodium plumbide.