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EXPLANATORY GLOSSARY OF TERMS USED IN EXPRESSION OF RELATIVE ISOTOPE RATIOS AND GAS RATIOS

(IUPAC Recommendations 2008)

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Explanatory Glossary of Terms Used in Expression of Relative Isotope Ratios and Gas Ratios

(IUPAC Recommendations 2008)

Abstract: To minimize confusion in the expression of measurements of isotope and gas ratios, a glossary based on recommendation by the Commission on Isotopic Abundances and Atomic Weights of the IUPAC is presented. Entries in the glossary are consistent with the SI system of units or with recommendations of the Commission. The recommendations presented herein are designed to clarify expression of quantities related to measurement of isotope and gas ratios by ensuring that quantity equations and not numerical-value equations are used to define quantities. Examples of column headings consistent with SI recommendations and examples of various deprecated usages connected with the terms recommended are presented herein.

Keywords: IUPAC Inorganic Chemistry Division; delta value; isotope-ratio mass spectrometry; number fraction; number ratio; per mill; isotope ratio; ICP-MS.

INTRODUCTION

During the meeting of the Commission on Isotopic Abundances and Atomic Weights at the General Assembly of IUPAC in 2003 in Ottawa, it was recognized that there is confusion about delta value, which is used to express the difference in the relative ratios of the numbers (or the amounts) of two isotopes in a specimen and an international measurement standard. Such isotopic measurements increasingly are being used in oceanography, atmospheric sciences, biology, paleoclimatology, geology, environmental sciences, food and drug authentication, and forensic applications. It was recommended that a report be prepared to clarify the terminology and concepts behind the terms involved in expressing relative isotope ratios. This report is the result and provides information on reporting relative differences in ratios of volumes, numbers of molecules, and, a similar topic, amounts of gases.

Many chemical elements have more than one isotope. Molecules and ions having different isotopes of the same chemical element possess slightly different physical and chemical properties. Consequently, isotopes of elements can vary in their abundances in naturally occurring and non-terrestrial substances, and the physical and chemical properties of materials with different isotopic abundances vary. The purpose of this report is to improve the global exchange of scientific information in different disciplines making use of variations in isotope abundances. This document should aid the reader in what may be called 'good practice of scientific language' in fields utilizing isotope-abundance variations. In those cases where certain common uses are deprecated, there are strong reasons for this and the reader should follow the corresponding recommendations to be consistent with the SI (Système International d'Unités or the International System of Units), ISO (International Organization for Standardization), BIPM (Bureau International des Poids et Mesures), and *Quantities, Units and Symbols in Physical Chemistry* [1], IUPAC's "Green Book," which is updated regularly by IUPAC's Physical and

Biophysical Chemistry Division. Some recommendations herein are at variance with those of the "Green Book" and justification is provided for these recommendations.

The mass number of a nuclide of chemical element E may be specified by attaching the mass number as a left superscript to the symbol for the element, as in ^{15}N, or adding it after the name of the element, as in nitrogen-15. The atomic number may be attached as a left subscript, for example, $^{15}_{7}N$. The ionic charge is shown as a right superscript, by sign alone when the charge number is equal to plus one or minus one. For example, Na^+, $^2H^+$, and $^{34}S^{2-}$. The widely used notation S^{-2} and the old notation $S^=$ are both obsolete [2]. In writing the formula for a complex ion, spacing for the charge number can be added, as well as parentheses; for example, $^{34}SO_4{}^{2-}$, $(^{34}SO_4)^{2-}$. The staggered arrangement is now recommended [2]. It is recommended by the Commission on Isotopic Abundances and Atomic Weights that the heavy isotopes of hydrogen be written as ^2H and ^3H rather than D and T, or written out as deuterium and tritium, which is in agreement with *Nomenclature of Inorganic Chemistry* [2]. Molecules that differ only in isotopic composition (number of isotopic substitutions), e.g. $^{28}SiF_4$ and $^{30}SiF_4$, are isotopologues [2]. Isomers having the same number of each isotopic atom, but differing in their positions, e.g. $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$, are isotopomers. The term is a contraction of "isotopic isomer" [2].

GLOSSARY OF TERMS

This glossary is based on recommendations by the Commission on Isotopic Abundances and Atomic Weights of the IUPAC. Entries in the glossary conform to specific requirements that are consistent with the SI system of units.

For readers unfamiliar with the basic ideas of quantity calculus and coherent quantities and equations in the International System of Units, Appendix 1 describes these in sufficient detail for explanation of why various symbols used in the literature are not acceptable as SI units or equations. Appendix 2 gives examples of column headings consistent with SI recommendations, and Appendix 3 gives various deprecated usages connected with the terms recommended here.

In the glossary itself, each term is defined with notes as appropriate. Following many of the definitions are to be found Explanatory comments, which expand on the reasons for the definitions.

1. amount-of-substance ratio
See *amount ratio*.

2. amount ratio, *r*
amount-of-substance ratio
mole ratio
Amount of a defined constituent (usually molecules, atoms, or ions) divided by the amount of another constituent of the same kind within the mixture.

Note: When the defined constituents are isotopes of an element, the amount ratio is equal to the *isotope ratio*, $R(^iE, {}^jE)$. Thus, $r(^iE, {}^jE) = n_B(^iE) / n_B(^jE)$, where $n_B(^iE)$ and $n_B(^jE)$ are amounts of the two isotopes, *i* and *j*, of chemical element E in substance B. The quantity $r(^iE, {}^jE)$ has dimension 1.

Explanatory comments

The "number of entities", N, is a fundamental base quantity in any system of units, such as the SI, because it can be regarded as a base quantity in any and all systems of quantities, where an entity is an atom, molecule, ion, or formula unit. Measurement of the numbers of *isotopologues*, e.g. $^{28}SiF_4$ and $^{30}SiF_4$, or of the ratio of the number of isotopologues is the basis of *isotope-ratio mass spectrometry*, carried out with a variety of *isotope-ratio mass spectrometers*, including the increasingly common *continuous flow isotope-ratio mass spectromete*r, the *thermal ionization mass spectrometer* (TIMS), the *inductively coupled plasma mass spectrometer* (ICP-MS), and the *multi-collector inductively coupled plasma mass spectrometer* (MC-ICP-MS).

The *number ratio*, R, is the number obtained by counting of a defined entity in a mixture (usually molecules, atoms, or ions) divided by the number of another defined entity of the same kind within the mixture [3]. For isotopes the ratio of the number of atoms of one isotope to another isotope of a chemical element in a specimen is the isotope-number ratio, commonly shortened to *isotope ratio*, and is defined by the relation

$$R_B\left(^i E, {}^j E\right) = \frac{N_B\left(^i E\right)}{N_B\left(^j E\right)} \tag{1}$$

where $N_B(^i E)$ and $N_B(^j E)$ are the numbers of the two isotopes, i and j, of chemical element E in substance B. The units of $N_B(^i E)$, $N_B(^j E)$, and $R(^i E, {}^j E)$ are 1; they are properly called quantities of dimension 1 [1]. The number ratio, $R(^i E, {}^j E)$, is equal to the corresponding *amount ratio*[1], $r_B(^i E, {}^j E)$, which is defined by the relation

$$r_B\left(^i E, {}^j E\right) = R_B\left(^i E, {}^j E\right) = \frac{n_B\left(^i E\right)}{n_B\left(^j E\right)} \tag{2}$$

Although the unit of $r_B(^i E, {}^j E)$ is 1, mol is the unit of $n_B(^i E)$ and $n_B(^j E)$.[2] Equations (1) and (2) express relations among quantities and are quantity equations.

Commonly, the superscripts i and j denote a heavier (higher atomic mass) and a lighter (lower atomic mass) isotope, respectively. Although equations herein use "$(^i E, {}^j E)$" as a descriptor to a quantity, it is fully satisfactory to substitute "$(^{i,j} E)$" for "$(^i E, {}^j E)$." The ratio of the number of isotopes, R_B, and the isotope-amount ratio, r_B, are variables; thus, r and R are always printed in italic font [4]. When there can be no confusion about $^i E$ and $^j E$, such as in the case for di-isotopic elements, the quantities R and r commonly are used with the convention that the

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[1] Amount ratio is the abbreviated form of amount-of-substance ratio and both are alternatives to mole ratio [1].

[2] The term $n_A(^i E) / n_A(^j E)$ had been denoted in the literature by the term "mole ratio," which is accepted in the "Green Book" [1]. Some believe it should be avoided because it mixes units with physical quantities, such as referring to "mass ratio" as "kilogram ratio." It is important to eliminate confusion between quantities and units by writing, for example, "amount of specimen A = y mol" rather than "number of moles of specimen A = y." This is analogous to preference being given to "the mass of specimen B = 4 g" rather than "the number of grams of specimen B is 4." The latter is usage to be avoided.

isotope referred to is the heavier stable isotope. Thus, $R_B(^{13}C)$ stands for $N_B(^{13}C) / N_B(^{12}C)$ and $r_B(^{13}C)$ stands for $n_B(^{13}C) / n_B(^{12}C)$. $R_B(^iE)$ and $r_B(^iE)$ are sometimes shortened to $R_B{}^iE$ and $r_B{}^iE$, but $R_B(^iE)$ and $r_B(^iE)$ are preferred. The unabbreviated formats, $R_B(^iE, {}^jE)$ and $r_B(^iE, {}^jE)$, are preferred for polyisotopic elements.

3. atom fraction, x

stable isotope-amount fraction
stable isotope-mole fraction
isotopic abundance
Amount of a defined atom (isotope) of a chemical element divided by the total amount of atoms of the element within the mixture.
See *isotopic abundance*.

Note: Previously, this term was called "atom %" or AP, but neither should be used because they are not a valid SI quantity names.

The quantity is numerically equal to the *number fraction*, the *isotope-number fraction*, and the *stable isotope-number fraction*.

Explanatory comments
The stable isotope-amount fraction or atom fraction, $x_B(^iE)$, or $y_B(^iE)$ for gases, is a valid SI quantity and is of use in stable isotope studies, including some stable carbon and nitrogen isotopic investigations. It is defined for atom ^iE in specimen B by the relation

$$x_B\left(^iE\right) = \frac{n_B\left(^iE\right)}{\sum n_B(E)} = \frac{N_B\left(^iE\right)}{\sum N_B(E)} \qquad (3)$$

where the summation includes all isotopes of element E. For elements with two isotopes, equation (3) reduces to

$$x_B\left(^iE\right) = \frac{n_B\left(^iE\right)}{n_B\left(^iE\right) + n_B\left(^jE\right)} = \frac{N_B\left(^iE\right)}{N_B\left(^iE\right) + N_B\left(^jE\right)} \qquad (4)$$

The relation between $x_B(^iE)$, the stable isotope-amount ratio $r_B(^iE, {}^jE)$, and the ratio of the numbers of isotopes $R_B(^iE, {}^jE)$ of specimen B for two isotopes is

$$x_B\left(^iE\right) = \frac{r_B\left(^iE, {}^jE\right)}{1 + r_B\left(^iE, {}^jE\right)} = \frac{R_B\left(^iE, {}^jE\right)}{1 + R_B\left(^iE, {}^jE\right)} \qquad (5)$$

The relation between $x_B(^iE)$ and $\delta_B{}^iE$ for specimen B for two isotopes is

$$x_B\left({}^iE\right) = \cfrac{1}{1+\cfrac{1}{\left(\delta_B({}^iE)+1\right) r_{std}\left({}^iE,{}^jE\right)}} = \cfrac{1}{1+\cfrac{1}{\left(\delta_B({}^iE)+1\right) R_{std}\left({}^iE,{}^jE\right)}} \qquad (6)$$

As an example, the $\delta_B({}^{13}C)$ of specimen B measured relative to the VPDB scale, for which $R_{VPDB}({}^{13}C,{}^{12}C)$ is 0.011 18 [5], is given by the relation

$$x_B\left({}^{13}C\right) = \cfrac{1}{1+\cfrac{1}{\left(\delta_B({}^{13}C)+1\right) 0.01118}} \qquad (7)$$

In the literature [6], one can find equations such as

$$AP\ {}^{13}C = \cfrac{100}{1+\cfrac{1}{\left(\cfrac{\delta}{1000}+1\right) R_{PDB}}} \qquad (8)$$

where "*AP*" stands for "*atom %.*" "*AP*" and "*atom %*" are not valid SI quantity names because names of quantities in the SI must consist of at most one character, followed by a subscript and superscript as needed.[3] The names "*AP*" and "*atom %*" should not be used. In addition, equation (8) contains extraneous factors of 100 and 1000, both of which should be deleted from the equation to be a consistent coherent quantity equation.

For stable nitrogen isotope-amount fractions, $x({}^{15}N)$, determined from $\delta({}^{15}N)$ measurements, the relation $n({}^{14}N)/n({}^{15}N) \equiv 272$ should be incorporated into the calculation for $r({}^{15}N)^{-1}$ of N_2 in air [7]. The relation to be used is

$$x_A\left({}^{15}N\right) = \frac{\delta_B\left({}^{15}N\right)+1}{\delta_B\left({}^{15}N\right)+273} \qquad (9)$$

where $\delta({}^{15}N)$ values are measured relative to the international measurement standard N_2 in air.

4. continuous flow isotope-ratio mass spectrometer
Mass spectrometer in which a gaseous analyte is delivered to an *isotope-ratio mass spectrometer* to be ionized and separated (analyzed) according to the quotient mass/charge, and in which the number of ions or the amounts of the ions are measured electrically.

5. delta, δ
For isotopes, relative difference in isotope ratios; the ratio of $(R_B - R_D)/R_D$, where R is the isotope ratio expressed as the *number ratio* of two isotopes in substances B and D. For gases, relative differences in ratios of numbers, amounts, or volumes of two gases.

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[3] An exception is made for pH and for certain characteristic numbers or "dimensionless quantities" used in the study of transport processes for which the internationally agreed symbols consist of two letters. These include *Re*, *Eu*, and others listed in section 2.15.1 of ref [1].

Note: Most commonly, delta values are measured relative to an *international measurement standard*, std, which replaces substance D. Because differences in relative ratios are small, δ values commonly are expressed with the unit ‰, which is 0.001. The quantity δ has dimension 1. Units of mg/g, μg/g, or any such units should never be substituted for per mill or ppm of delta values.

Explanatory comments

(a) Isotopes

The delta value, $\delta(^iE)$, and is defined by:

$$\delta^iE = \delta\left(^iE\right) = \delta\left(^iE,{}^jE\right) = \frac{R_B\left(^iE,{}^jE\right) - R_{std}\left(^iE,{}^jE\right)}{R_{std}\left(^iE,{}^jE\right)} = \frac{N_B\left(^iE\right)/N_B\left(^jE\right) - N_{std}\left(^iE\right)/N_{std}\left(^jE\right)}{N_{std}\left(^iE\right)/N_{std}\left(^jE\right)} \qquad (10)$$

or the mathematically equivalent version

$$\delta^iE = \delta\left(^iE\right) = \delta\left(^iE,{}^jE\right) = \frac{R_B\left(^iE,{}^jE\right)}{R_{std}\left(^iE,{}^jE\right)} - 1 = \frac{N_B\left(^iE\right)/N_B\left(^jE\right)}{N_{std}\left(^iE\right)/N_{std}\left(^jE\right)} - 1 \qquad (11)$$

where $N_B(^iE)$ and $N_B(^jE)$ are the amounts of the two isotopes, i and j, of chemical element E in specimen B, $R_B(^iE,{}^jE)$ is $N_B(^iE)/N_B(^jE)$ in specimen B, and equivalent parameters follow for an international measurement standard, "std" [8]. Commonly, the superscripts i and j denote a heavier (higher atomic mass) and a lighter (lower atomic mass) isotope, respectively. Although equations herein use "$(^iE,{}^jE)$" as a descriptor to a quantity, it is fully satisfactory to substitute "$(^{i,j}E)$" for "$(^iE,{}^jE)$." Although delta values are usually measured and expressed relative to an international measurement standard, a delta value can be defined between two substances, B and D, in which case "std" would be replaced by "D" in eqns (10) and (11). Commonly, $\delta(^iE)$ is shortened to δ^iE, which is more prevalent in the scientific literature; nevertheless, there is a preference by many for the format $\delta(^iE)$. The pronunciation of the symbol δ as del is incorrect because del is the symbol ∇, which is the del operator (section 4.2 of ref [1]). Because $\delta(^iE)$ is a variable, δ is always printed in italic font [4].

One can express delta values using relative differences of isotope-amount ratios and the equation equivalent to equation (10) is

$$\delta^iE = \delta\left(^iE\right) = \delta\left(^iE,{}^jE\right) = \delta^iE = \frac{r_B\left(^iE,{}^jE\right) - r_{std}\left(^iE,{}^jE\right)}{r_{std}\left(^iE,{}^jE\right)} = \frac{n_B\left(^iE\right)/n_B\left(^jE\right) - n_{std}\left(^iE\right)/n_{std}\left(^jE\right)}{n_{std}\left(^iE\right)/n_{std}\left(^jE\right)} \qquad (12)$$

or the mathematically equivalent version

$$\delta^iE = \delta\left(^iE\right) = \delta\left(^iE,{}^jE\right) = \frac{r_B\left(^iE,{}^jE\right)}{r_{std}\left(^iE,{}^jE\right)} - 1 = \frac{n_B\left(^iE\right)/n_B\left(^jE\right)}{n_{std}\left(^iE\right)/n_{std}\left(^jE\right)} - 1 \qquad (13)$$

where $r_B(^iE, ^jE)$ and $r_{std}(^iE, ^jE)$ are the ratios of the numbers of the two isotopes, i and j, of chemical element E in specimen B and the international measurement standard ("std"), and $n_B(^iE)/n_B(^jE)$ and $n_{std}(^iE)/n_{std}(^jE)$ are the ratios of the numbers of isotopes in specimen B and in the international measurement standard ("std"), respectively. Isotope pairs found in the literature to define $N(^iE)/N(^jE)$ and $n(^iE)/n(^jE)$ commonly include: ^2H, ^1H; ^7Li, ^6Li; ^{11}B, ^{10}B; ^{13}C, ^{12}C; ^{15}N, ^{14}N; ^{17}O, ^{16}O; ^{18}O, ^{16}O; ^{26}Mg, ^{24}Mg; ^{30}Si, ^{28}Si; ^{34}S, ^{32}S; ^{37}Cl, ^{35}Cl; ^{53}Cr, ^{52}Cr; ^{56}Fe, ^{54}Fe; ^{65}Cu, ^{63}Cu; ^{66}Zn, ^{64}Zn; ^{82}Se, ^{76}Se; ^{98}Mo, ^{95}Mo; ^{110}Pd, ^{104}Pd; ^{130}Te, ^{122}Te; and ^{205}Tl, ^{203}Tl.

A positive $\delta(^iE)$ value indicates that the number fraction (or amount fraction) of the heavier isotope is greater in substance B than in the international measurement standard. A negative $\delta(^iE)$ value indicates that the number fraction (or amount fraction) of the heavier isotope is lower in substance B than in the international measurement standard. Because variations in isotopic abundances typically are small, the range in $\delta(^iE)$ values for many commonly studied chemical elements is less than 0.2 [9], and in the literature $\delta(^iE)$ values have been reported in parts per hundred (% or per cent), parts per thousand (‰ or per mill[4]), parts per ten thousand, and parts per million (ppm). The ISO spelling, "per mill," is used in this report [10]. The symbols %, ‰, and ppm represent the units 0.01, 0.001, and 0.000 001, respectively, and they are correctly printed with a non-breaking space between the numerical value and the symbol [1,11]. The use of the unit, "per meg," which is defined as 0.000 001, is strongly deprecated by IUPAC; instead the unit "ppm" can be used. Adding descriptors to units and inventing new units to provide a new descriptive unit is "a practice strongly deprecated" according to Cvitaš [3]. Text such as "The samples is enriched" or "the enriched specimen" to indicate a sample enriched in a heavy isotope should be avoided. Instead, using oxygen isotopes as an example, authors should write "The sample is enriched in ^{18}O" or "the sample enriched in ^{18}O is".

For elements having three or more isotopes and for situations in which it is helpful to designate the international measurement standard, authors may use the fully expanded version of equation (10), which is

$$\delta_{B,std}\left(^iE, ^jE\right) = \frac{R_B\left(^iE, ^jE\right) - R_{std}\left(^iE, ^jE\right)}{R_{std}\left(^iE, ^jE\right)} = \frac{N_B\left(^iE\right)/N_B\left(^jE\right) - N_{std}\left(^iE\right)/N_{std}\left(^jE\right)}{N_{std}\left(^iE\right)/N_{std}\left(^jE\right)} \quad (14)$$

or the mathematically equivalent version

$$\delta_{B,std}\left(^iE, ^jE\right) = \frac{R_B\left(^iE, ^jE\right)}{R_{std}\left(^iE, ^jE\right)} - 1 = \frac{N_B\left(^iE\right)/N_B\left(^jE\right)}{N_{std}\left(^iE\right)/N_{std}\left(^jE\right)} - 1 \quad (15)$$

Authors may also use the two equivalent equations written with amounts of isotopes, $n(^iE)$ and $n(^jE)$, or with ratios of amounts of isotopes, $r(^iE)$. With fully expanded equations, it is easy to differentiate between $\delta(^{44}Ca, ^{42}Ca)$ and $\delta(^{44}Ca, ^{40}Ca)$, or the acceptable equivalents $\delta(^{44,42}Ca)$ and $\delta(^{44,40}Ca)$, both of which would be indicated as $\delta^{44}Ca$ with eqns (10), (11), (12), and (13). The quantity $\delta_{seawater,NBS915a}(^{44}Ca, ^{42}Ca)$ clearly specifies the delta value of the isotope pair ^{44}Ca and ^{42}Ca of a seawater specimen expressed relative to the international measurement standard

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4 Per mill is also written in the literature as permil, per mil, and per mille.

NBS 915a calcium carbonate. To eliminate confusion, authors are encouraged to use eqns (14) and (15) or their equivalents having isotope-amount ratios. Although eqns (14) and (15) are mathematically equivalent, many authors prefer the format of equation (14) because it more clearly indicates that delta values are differences in relative isotope ratios between a sample and an international measurement standard. Eqns (10) through (15) are quantity equations and hold irrespective of the units.

The subscripts "B" and "std" directly follow the "δ" symbol as for other quantities [1]. For example, the standard chemical potential of substance B is $\mu_B^{\ominus}(T)$, not $\mu^{\ominus}(T)_B$ (see section 2.11.1 of reference [1]). The significance is that subscript "B" and subscript "std" are specifications of the meaning of the quantity delta, whereas $(^iE,^jE)$ specifies the particular isotopes to which delta subscripts "B" and "std" refer. What is implied is the value of delta subscripts "B" and "std" for the particular isotope pair in parentheses. Thus, $(^iE,^jE)$ is a second label. If one places the subscript B after the parentheses, the meaning changes, or at least is confusing, because it is not clear which label takes precedence. As an example, one can write $\delta_{NBS19,VPDB}{}^{13}C = +1.95$ ‰ or $\delta_{NBS19}{}^{13}C = +1.95$ ‰, but the formats $\delta^{13}C_{NBS19,VPDB} = +1.95$ ‰ and $\delta^{13}C_{NBS19} = +1.95$ ‰ should be avoided.

Values of $\delta(^iE)$ can be reported in several ways. For example, suppose in equation (10) that $N_B(^{18}O)/N_B(^{16}O)$ is 0.002 034 and $N_{std}(^{18}O)/N_{std}(^{16}O)$ is 0.002 005. One calculates: $\delta^{18}O = (0.002\ 034/0.002\ 005 - 1) = +0.0146$. Because delta values are difference measurements, values more positive that zero commonly are given a leading + symbol. Recognizing that ‰ represents 0.001, this delta value can be expressed in the following ways

$$\delta(^{18}O) = +0.0146$$
$$\delta(^{18}O) = +14.6 \times 10^{-3}$$
$$10^3\ \delta(^{18}O) = +14.6$$
$$\delta^{18}O = +14.6\ ‰$$

The preferred SI solutions are any of the first three forms because multiples of the unit 1 (%, ‰, and ppm) are not part of the SI, and ISO recommends that these symbols never be used. However, the Commission on Isotopic Abundances and Atomic Weights recommends that the symbols %, ‰, and ppm be used when their meaning is clearly understood and their use clarifies and simplifies comprehension of text. For example, many readers find "with a $\delta^{18}O$ of −45.45 ‰" easier to read and comprehend than "with a $\delta^{18}O$ of −0.045 45." The reader should note that the third method of expression, $10^3\delta(^{18}O)$, is analogous to the method for expressing $\ln\alpha$ values, namely as $10^3\ln\alpha$ or $1000\ln\alpha$ values. Expressing $\delta(^iE)$ values as either $10^3\delta(^iE)$ or $1000\delta(^iE)$ values has the advantage that authors can eliminate the use of the ‰ symbol. A preference may be given to $10^3\delta(^iE)$ over $1000\delta(^iE)$ because the former is shorter.

The Third Edition of *Quantities, Units and Symbols in Physical Chemistry* [1] indicates that the symbol ‰ might be replaced by either mmol/mol or mg/g; this document indicates that −9 mg/g or −9 mmol/mol is preferable to −9 ‰. Consider the dimension of equation (10). The unit of the quantity number of entities (properly called a quantity of dimension 1) is 1, and the ratio of the number of entities is 1. Likewise, the ratio of these ratios from equation (10) is 1. Nowhere in equation (10) do units of "mol" or "g" appear. Adding extraneous symbols of mol/mol or g/g to quantities whose dimension never included amount of substance or mass is

confusing and should never be done[5]. To avoid confusion, the Commission on Isotopic Abundances and Atomic Weights recommends that mmol/mol and mg/g never be used in such cases to replace the symbol ‰ in expressing isotopic delta values.

   A shortened version of equation (10) or (12) often appears in the literature. For the oxygen-isotope pair, ^{18}O and ^{16}O, equation (10) or (12) commonly is shortened to

$$\delta^{18}O \ = \ \frac{\left(^{18}O/^{16}O\right)_B}{\left(^{18}O/^{16}O\right)_{std}} - 1 \tag{16}$$

When using the format of equation (16), authors should define $(^{18}O/^{16}O)_B$ in their text and this parameter will be either $N_B(^{18}O)/N_B(^{16}O)$, $n_B(^{18}O)/n_B(^{16}O)$, $R_B(^{18}O,{}^{16}O)$, or $r_B(^{18}O,{}^{16}O)$. The parameter, $(^{18}O/^{16}O)_{std}$, should be defined in a similar manner.

   In the literature, equation (16) commonly is shown as

$$\delta^{18}O \ = \ \left[\frac{\left(^{18}O/^{16}O\right)_B}{\left(^{18}O/^{16}O\right)_{std}} - 1\right]\cdot 1000 \tag{17}$$

The problem with equation (17) is that it can be confusing. With equation (17), one calculates with the data given above: $\delta^{18}O = (0.002\ 034/0.002\ 034 - 1) \cdot 1000 = +14.6$, not +14.6 ‰. But, convention requires users to place the ‰ symbol following the numeric value. Thus, one would report +14.6 ‰. Confusion arises because in comparing eqns (16) and (17), the left sides appear identical, but the right sides differ by 10^3. In actuality, the left sides are different quantities for which the same designator, $\delta^{18}O$, has been used.

   Equation (17) is not a coherent quantity equation. Rather, it is a numeric-value equation that "expresses a relation among numerical values of quantities and therefore *does* depend upon the units used to express the values of the quantities" [12]. It is the strong recommendation of BIPM, ISO, and IUPAC that authors employ only coherent quantity equations because of their universality; they hold for any units [1,8,12]. Because the SI is coherent, algebraic equations used with SI units should never contain extraneous numerical factors or units. The factor 1000 in equation (17) is an extraneous numerical factor and it should be deleted. Another version of this equation is

$$\delta^{18}O \ (in\ ‰) \ = \ \left[\frac{\left(^{18}O/^{16}O\right)_B}{\left(^{18}O/^{16}O\right)_{std}} - 1\right]\cdot 1000 \tag{18}$$

and this version should be avoided for two reasons: (1) it contains the extraneous quantity 1000 and (2) it contains the extraneous text "(in ‰)". Because the symbol ‰ equals 10^{-3}, an algebraically correct formulation of equation (18) is

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[5] The recommendation to use mmol/mol, pg/g, and other similar symbols is a response to the SI requirement that "A prefix shall never be used on its own, and prefixes are not to be combined into compound prefixes" [1]. Applying this recommendation, however, could result in bizarre symbols for ratios of numbers of isotopes and ratios of their ratios. For example, mcd/cd, mA/A, ms/s, and mK/K are all numerically valid replacements for the ‰ symbol, but their use is not recommended.

$$\frac{\delta^{18}O}{‰} = \left[\frac{\left(^{18}O/^{16}O \right)_B}{\left(^{18}O/^{16}O \right)_{std}} - 1 \right] \cdot 1000 \tag{19}$$

Although equation (19) is mathematically correct, it should be avoided because it contains extraneous numerical factors and because ‰ × 1000 equals 1.

^{17}O is enriched by mass-independent processes in atmospheric ozone, nitrate, sulfate, *etc*. The magnitude of this mass-independent ^{17}O production, expressed by $\Delta(^{17}O)$, can be defined by the relation

$$\Delta\left(^{17}O \right) = \Delta^{17}O = \frac{1 + \delta(^{17}O)}{\left(1 + \delta(^{18}O) \right)^{\lambda}} - 1 \tag{20}$$

or by the relation

$$\Delta\left(^{17}O \right) \cong \ln\left(\delta(^{17}O) + 1 \right) - \lambda \ln\left(\delta(^{17}O) + 1 \right) \tag{21}$$

where the coefficient λ is approximately one-half. Equivalent equations can be found in the literature containing the factor 1000. This is incorrect and the factor of 1000 should be deleted. Because Δ is a variable, Δ should always be printed in italic font [4].

Numerous isotopic relationships have been published as numeric value equations and should be updated to be in compliance with IUPAC recommendations and the SI. For example, from over 200 globally-distributed precipitation sites Rozanski et al. [13] report a relation between δ^2H and $\delta^{18}O$ of

$$\delta^2H = 8.20\,\delta^{18}O + 11.27 \tag{22}$$

This numeric value equation should be replaced by the quantity equation

$$\delta^2H = 8.20\,\delta^{18}O + 11.27 \times 10^{-3} \tag{23}$$

Other numeric value definitions are found in the literature and should be avoided. One can find definitions for relative isotope-amount ratios of isotopes, such as

$$\varepsilon^{65}Cu = \left[\frac{r_B}{r_{std}} - 1 \right] \cdot 10\,000 \tag{24}$$

where r_B and r_{std} are $n_B(^{65}Cu)/n_B(^{63}Cu)$ and $n_{std}(^{65}Cu)/n_{std}(^{63}Cu)$, respectively, and where "B" and "std" are specimen B and an international measurement standard. Typical usage in a text might be "the $\varepsilon^{65}Cu$ of these specimens range between −5.2 and +1.8." This equation is nothing more than a numeric value isotope delta-definition equation and its use is to be avoided for three reasons. First, no new quantity is defined by ε. This equation is a δ-definition equation and ε should be replaced by δ. Secondly, the factor 10 000 is extraneous and should not appear in a δ-definition equation. Thirdly, historically ε has been defined as the isotopic enrichment factor, which is discussed below. Equation (24) could be correctly written

$$\delta^{65}\text{Cu} = \delta\left(^{65}\text{Cu}\right) = \frac{r_\text{B}}{r_\text{std}} - 1 \tag{25}$$

A typical $\delta(^{65}\text{Cu})$ value might be written as any of the following:

$\delta(^{65}\text{Cu}) = -0.000\ 18$

$\delta(^{65}\text{Cu}) = -1.8 \times 10^{-4}$

$10^4 \delta(^{65}\text{Cu}) = -1.8$

$\delta^{65}\text{Cu} = -0.18\ ‰$

$\delta(^{65}\text{Cu}) = -1.8$ parts per ten thousand

$\delta^{65}\text{Cu} = -1.8$ pptt

If pptt is used as a symbol for parts per ten thousand, it should be explained by a footnote. The preferred SI solutions are any of the first three. The Commission on Isotopic Abundances and Atomic Weights accepts any of these formats. Expressing delta values as $10^4 \delta(^{65}\text{Cu})$ values has the advantage of eliminating the use of "parts per ten thousand", "pptt," or the "‰" symbol.

The quantity defined in equation (12) has been called the "isotopic abundance", "isotopic composition," and "isotope ratio" in the scientific literature. According to H. R. Krouse [University of Calgary, Calgary, Alberta, Canada, personal communication, 2005], "isotope ratio" does not specify the quantity used as a measure of the ratio. "Isotope ratio" might refer to a ratio of the numbers of two isotopes in a sample, a ratio of the masses of two isotopes in a sample, *etc*. The term "isotopic composition" suffers from the same problem; it does not specify the quantity used as a measure of composition, such as, number of atoms, volume, or mass. The "isotopic abundance" was defined in IUPAC's 1987 *Compendium of Analytical Nomenclature* [14] as "The relative number of atoms of a particular isotope in a mixture of the isotopes of an element, expressed as a fraction of all the atoms of the element." The sum of the isotopic abundances of all isotopes of an element must be 1. The term "isotopic composition" has been used by the Commission on Isotopic Abundances and Atomic Weights (CIAAW), which publishes a Table of Isotopic Compositions of the Elements [15]. The CIAAW isotopic composition of an element is the set of isotope-amount fractions of that element, and they sum to 1. If "isotopic composition" is a set of isotope-amount fractions, this term does not explicitly apply to the quantity δ, which is not an isotope-amount fraction. In the general scientific literature, "isotopic composition" and "isotopic abundance" are used in a variety of ways with overlapping meanings.

The name to which δ refers can be determined as follows. $N_\text{B}(^i\text{E})/N_\text{B}(^j\text{E})$ is the isotope ratio. The numerator of equation (10), $N_\text{B}(^i\text{E})/N_\text{B}(^j\text{E}) - N_\text{std}(^i\text{E})/N_\text{std}(^j\text{E})$, is a difference in isotope ratios. Dividing the numerator of equation (10) by its denominator, $N_\text{std}(^i\text{E})/N_\text{std}(^j\text{E})$, is indicated by adding the word relative. Thus, $\delta(^i\text{E})$ is a "relative difference in isotope ratios."

In summary, the terms isotopic composition, isotope ratio, and isotopic abundance are being used with overlapping definitions. Authors can use "relative difference in isotope ratios" with clarity as the name of the quantity $\delta(^i\text{E})$.

(b) Gases

Precise measurement of gas ratios is important in various earth science investigations. Keeling and Shertz [16] demonstrate that relative differences of O_2/N_2 ratios in the atmosphere can provide information on the global carbon cycle. They report:

"Changes in O_2/N_2 are reported as relative deviations from a reference

$$\delta\left(O_2 / N_2\right) \;=\; \left[\frac{\left(O_2 / N_2\right)_{sample}}{\left(O_2 / N_2\right)_{ref}} - 1\right]$$

We propose the convention of multiplying $\delta(O_2/N_2)$ by 10^6 and expressing the result in units of 'per meg.' In these units $1/0.2095 = 4.8$ per meg is equivalent to 1 p.p.m. by volume (p.p.m.v) because O_2 comprises 20.95% of air by volume."

The unit for parts per 10^6 is parts per million and it is given the symbol "ppm" [1,11]. There is no need to invent another unit when a satisfactory unit already exists. Inventing a unit to provide a descriptor of the quantity in the unit is to be avoided in the SI [3]. Therefore, it is recommended that "per meg" be considered as a strongly deprecated unit. It is not clear what the authors mean by "p.p.m.v." in the text above because ratios of gas volumes in the SI have the unit 1 and because p.p.m.v. is not an SI unit or even a unit to be used with the SI [3]. This is an example of confusion between a quantity and its units; definition of the quantity includes specification that volumes are being measured, so "v" in the unit is redundant at best.

To clarify what theses authors meant, one might write

$$\delta_V\left(O_2, N_2\right) \;=\; \frac{V_{sample}\left(O_2\right) / V_{sample}\left(N_2\right)}{V_{ref}\left(O_2\right) / V_{ref}\left(N_2\right)} - 1 = \frac{\varphi_{sample}\left(O_2, N_2\right)}{\varphi_{ref}\left(O_2, N_2\right)} - 1 \qquad (26)$$

where φ is the symbol for volume ratio and the subscript V of δ_V indicates a delta value determined from volume measurements. This equation makes it clear that volume ratios are expressed.

In the literature, one can also find the gas ratio defined as

$$\delta\left(O_2 / N_2\right) \;=\; \left[\frac{R_A}{R_{ref}} - 1\right] \cdot 1\,000\,000 \qquad (27)$$

where R is $N(O_2) / N(N_2)$. The factor $1\,000\,000$ is an extraneous numerical factor and it should be deleted. Equation (27) is a numeric value equation and should be avoided.

Using numbers of O_2 and N_2 molecules or amounts of these gases, one can define a delta value as

$$\delta\left(O_2, N_2\right) \;=\; \frac{N_{sample}\left(O_2\right) / N_{sample}\left(N_2\right)}{N_{ref}\left(O_2\right) / N_{ref}\left(N_2\right)} - 1 \;=\; \frac{n_{sample}\left(O_2\right) / n_{sample}\left(N_2\right)}{n_{ref}\left(O_2\right) / n_{ref}\left(N_2\right)} - 1 \qquad (28)$$

Because gases commonly are not ideal, $\delta(O_2, N_2)$ will not be identical to $\delta_V(O_2, N_2)$ defined in eqn (26). Compression factors or the fugacity coefficients can be used to convert between $\delta(O_2, N_2)$ and $\delta_V(O_2, N_2)$.

In reporting relative differences in amount ratios of gases or volume ratios of gases, one of the equations given above can be used. The following examples of data reporting are all acceptable:

$$\delta(O_2, N_2) = -1.1 \times 10^{-6}$$

$$10^6 \, \delta(O_2, N_2) = -1.1$$

$$\delta(O_2, N_2) = -1.1 \text{ ppm}$$

Although the Commission on Isotopic Abundances and Atomic Weights accepts the use of the unit ppm, the preferred SI reporting solutions are the first two. Expressing delta values as $10^6 \delta(O_2, N_2)$ values has the advantage of eliminating the use of "parts per million" or "ppm," which are not recognized in the SI or by ISO.

6. excess atom fraction, x_B^E

excess stable isotope-amount fraction

Difference between the amount fraction of an isotope in substance B and that of a reference. The superscript E signifies an excess quantity. The quantity x_B^E has dimension 1.

See also *atom fraction*.

Note: Previously, this term was called "atom % excess" or APE, but neither should be used because they are not a valid SI quantity names.

Explanatory comments

In the literature [6], one can find a quantity named "*atom % excess*" (*APE*) that indicates the "excess" isotope tracer in substance B relative to that in a reference ("ref"). It is defined as

$$APE = (atom \%)_B - (atom \%)_{ref} \tag{29}$$

"*APE*" is not a valid name of a quantity in the SI because names of SI quantities should be single characters with superscripts and subscripts as needed [1]. Use of equation (29) should be avoided. The appropriate quantity, excess stable isotope-amount fraction or excess atom fraction, is $x_B^E \, (^iE)$. It is determined from the *stable isotope-amount fractions* of substance B and reference, "ref," by the relation

$$x_B^E \, (^iE) = x_B(^iE) - x_{ref}(^iE) \tag{30}$$

where superscript E is the usual way in thermodynamics to indicate an excess quantity.

7. excess stable isotope-amount fraction
See *excess atom fraction*.

8. inductively coupled plasma
ICP
Plasma source in which the energy is supplied by electrical currents that are produced by electromagnetic induction, that is, by time-varying magnetic fields.

9. inductively coupled plasma mass spectrometer
ICP-MS
Mass spectrometer in which an analyte is delivered to a mass spectrometer to be ionized with an *inductively coupled plasma* and ions separated (analyzed) according to the quotient mass/charge, and in which the number of ions or the amounts of the ions are measured electrically, or the ions are counted.

Note: An ICP-MS with more than one collector is a *multi-collector inductively coupled plasma mass spectrometer* (MC-ICP-MS) and can be used for measurement of isotope ratios.

10. international measurement standard
Measurement standard recognized by signatories to an international agreement and intended to serve worldwide needs.
See also *isotopic reference material*.

Note: VSMOW reference water, distributed by the International Atomic Energy Agency, is such a standard.

11. isotope-amount fraction, *x*, (*y* for gaseous mixtures)
isotopic abundance
atom fraction
stable isotope-amount fraction
stable isotope-mole fraction
Amount of a defined atom (isotope) of a chemical element divided by the total amount of atoms of the element within the mixture.

Note: This quantity has dimension 1 and it is numerically equal to the *number fraction*, the *isotope-number fraction*, and the *stable isotope-number fraction*.
See also *number fraction*.

12. isotope-number fraction
See *number fraction*.

13. isotope ratio, *R*
See *number ratio*.

14. isotope-ratio mass spectrometer

Mass spectrometer in which isotopomers are separated (analyzed) according to the quotient mass/charge, and in which the number of ions or the amounts of ions are measured electrically, commonly simultaneously on two or more ion collectors, or the ions are counted.

15. isotope-ratio mass spectrometry
Branch of science dealing with all aspects of *isotope-ratio mass spectrometers* and the results obtained with these instruments.

16. isotopic abundance
See *isotope-amount fraction*.

17. isotopic composition
The set of amount fractions of the isotopes of a specified chemical element, and they sum to 1. See *isotope-amount fraction*.

18. isotopic enrichment factor, ε
$\alpha - 1$, where α is the *isotopic fractionation factor*.

Note: Because values of ε commonly are small, they regularly are expressed with the unit ‰, which is 0.001. The quantity ε has dimension 1. Units of mg/g, μg/g, or any such units should never be substituted for per mill or ppm of isotopic enrichment factor values.
See also *isotopic fractionation factor*.

Explanatory comments
The isotopic enrichment factor, $\varepsilon_{B,D}$, is useful in discussing chemical reactions and is defined for substances B and D by

$$\varepsilon_{B,D} = \varepsilon_{B,D}(^iE) = \varepsilon_{B,D}(^iE,{}^jE) = \alpha_{B,D} - 1 = \alpha_{B,D}(^iE,{}^jE) - 1 \qquad (31)$$

When the isotope ^iE is clear from the context, $\varepsilon_{B,D}(^iE)$ can be shortened to $\varepsilon_{B,D}$. Because $\varepsilon_{B,D}$ is a variable, ε is always printed in italic font [4]. As an example, the value of $\varepsilon_{calcite, water}$ at 33.7 °C [17] is $\alpha_{calcite, water} - 1$, which equals $1.028\,49 - 1$, which is $0.028\,49$. Because it is more convenient to work with numbers that are large, values of ε commonly are expressed in parts per thousand or per mill using the symbol ‰. Thus, $\varepsilon_{calcite, water}$ at 33.7 °C is 28.49 ‰. Although the Commission on Isotopic Abundances and Atomic Weights accepts the use of the ‰ symbol, the preferred BIPM-ISO solution is to use one of the following methods of expression:

$10^3\,\varepsilon_{calcite, water}(^{18}O,{}^{16}O) = 28.49$ at 33.7 °C

$10^3\,\varepsilon_{calcite, water}(^{18,16}O) = 28.49$ at 33.7 °C

$10^3\,\varepsilon_{calcite, water} = 28.49$ at 33.7 °C

$\varepsilon_{calcite, water} = 28.49 \times 10^{-3}$ at 33.7 °C

Although the Third Edition of *Quantities, Units and Symbols in Physical Chemistry* [1] indicates that the symbol ‰ might be replaced by either mmol/mol or mg/g, as discussed above, the Commission on Isotopic Abundances and Atomic Weights recommends that mmol/mol and mg/g never be used to replace the symbol ‰ in expressing ε values.

Equation (31) has appeared in the literature as

$$\varepsilon_{B,D} = 1000 \, (\alpha_{B,D} - 1)$$

(32)

The 1000 is an extraneous numerical factor and should be deleted to be consistent with the SI, ISO, and IUPAC.

19. isotopic fractionation factor, α

Ratio of R_B / R_D, where R is the *isotope ratio* expressed as the number ratio of two isotopes in substances B and D.

$$\alpha_{B,D} = \alpha_{B,D}{}^i E = \alpha_{B,D}\left(^i E\right) = \alpha_{B,D}\left(^i E, ^j E\right) = \frac{R_B\left(^i E, ^j E\right)}{R_D\left(^i E, ^j E\right)} = \frac{N_B\left(^i E\right)/N_B\left(^j E\right)}{N_D\left(^i E\right)/N_D\left(^j E\right)}$$

Note: This quantity has dimension 1. If B and D are in isotopic equilibrium, this is an equilibrium isotopic fractionation factor. Otherwise, it is a non-equilibrium or kinetic isotopic fractionation factor.

See also *isotopic enrichment factor*.

Explanatory comments

There are two types of fractionation factors: equilibrium or thermodynamic and kinetic. The former is related to equilibrium constants and the latter to rate coefficients of reactions. For a system with two substances or phases, B and D, in chemical and isotopic equilibrium

$$B \rightleftharpoons D$$

(33)

and for the exchange of one atom, the equilibrium isotopic fractionation factor, $\alpha_{B,D}^{eq}\left(^i E, ^j E\right)$, can be defined by the relation

$$\alpha_{B,D}^{eq}\left(^i E, ^j E\right) = \frac{R_B\left(^i E, ^j E\right)}{R_D\left(^i E, ^j E\right)} = \frac{N_B\left(^i E\right)/N_B\left(^j E\right)}{N_D\left(^i E\right)/N_D\left(^j E\right)} = \frac{X_B\left(^i E\right)/X_B\left(^j E\right)}{X_D\left(^i E\right)/X_D\left(^j E\right)}$$

(34)

where $R_B(^i E, ^j E)$ and $R_D(^i E, ^j E)$ are the ratios of the number of the two isotopes, i and j, of chemical element E in substances B and D, respectively. $N_B(^i E)$ and $N_B(^j E)$ are the numbers of the two isotopes, i and j, of chemical element E in specimen B, and equivalent parameters follow for substance D. Commonly $\alpha_{B,D}^{eq}\left(^i E, ^j E\right)$ is shortened to $\alpha_{B,D}(^i E, ^j E)$. When it is clear from the text, such as with di-isotopic elements, the symbol $\alpha(^i E)$ can be used with the convention that the isotope referred to is the heavier isotope. Although both formats $\alpha_{B,D}(^i E)$ and $\alpha_{B,D}{}^i E$ are acceptable, $\alpha_{B,D}(^i E)$ is preferred by many authors. When both $^i E$ and $^j E$ are clear from the context, presumably because they have been defined in an author's text, both can be deleted. Thus,

$$\alpha_{B,D} = \alpha_{B,D}{}^{i}E = \alpha_{B,D}\left({}^{i}E\right) = \alpha_{B,D}\left({}^{i}E,{}^{j}E\right) = \frac{R_B\left({}^{i}E,{}^{j}E\right)}{R_D\left({}^{i}E,{}^{j}E\right)} \tag{35}$$

The isotopic fractionation factor $\alpha_{B,D}$ is a variable; thus, α is always printed in italic font [4]. The isotopic fractionation factor, $\alpha_{B,D}$, is equal to the quotient of the corresponding isotope-amount ratios. Thus,

$$\alpha_{B,D} = \alpha_{B,D}{}^{i}E = \alpha_{B,D}\left({}^{i}E\right) = \alpha_{B,D}\left({}^{i}E,{}^{j}E\right) = \frac{r_B\left({}^{i}E,{}^{j}E\right)}{r_D\left({}^{i}E,{}^{j}E\right)} = \frac{n_B\left({}^{i}E\right)/n_B\left({}^{j}E\right)}{n_D\left({}^{i}E\right)/n_D\left({}^{j}E\right)} = \frac{x_B\left({}^{i}E\right)/x_B\left({}^{j}E\right)}{x_D\left({}^{i}E\right)/x_D\left({}^{j}E\right)} \tag{36}$$

where $n_B({}^{i}E)$, $n_B({}^{j}E)$, $n_D({}^{i}E)$, and $n_D({}^{j}E)$ are the amounts of the two isotopes, i and j, of chemical element E in substances B and D. The quantities $n_B({}^{i}E)$ and $n_B({}^{j}E)$ are the amounts of the two isotopes, i and j, of chemical element E in specimen B, and equivalent parameters follow for substance D. Isotope pairs found in the literature to define $n({}^{i}E)/n({}^{j}E)$ and $N({}^{i}E)/N({}^{j}E)$ commonly include: ${}^{2}H$, ${}^{1}H$; ${}^{7}Li$, ${}^{6}Li$; ${}^{11}B$, ${}^{10}B$; ${}^{13}C$, ${}^{12}C$; ${}^{15}N$, ${}^{14}N$; ${}^{17}O$, ${}^{16}O$; ${}^{18}O$, ${}^{16}O$; ${}^{26}Mg$, ${}^{24}Mg$; ${}^{30}Si$, ${}^{28}Si$; ${}^{34}S$, ${}^{32}S$; ${}^{37}Cl$, ${}^{35}Cl$; ${}^{53}Cr$, ${}^{52}Cr$; ${}^{56}Fe$, ${}^{54}Fe$; ${}^{65}Cu$, ${}^{63}Cu$; ${}^{66}Zn$, ${}^{64}Zn$; ${}^{82}Se$, ${}^{76}Se$; ${}^{98}Mo$, ${}^{95}Mo$; ${}^{110}Pd$, ${}^{104}Pd$; ${}^{130}Te$, ${}^{122}Te$; and ${}^{205}Tl$, ${}^{203}Tl$.

Based on theoretical studies, $\ln\alpha_{B,D}$ commonly is inversely correlated with either reciprocal temperature, $1/T$, or its square $1/T^2$. The values of $\alpha_{B,D}$ typically are near 1 and values of $\ln\alpha_{B,D}$ are near zero. As an example, at 33.7 °C the oxygen isotopic fractionation factor between calcite and water ($\alpha_{calcite,water}$) has been determined as 1.028 49(13) [17], with the uncertainty in parentheses, following the last significant figure to which it is attributed. The value of $\ln\alpha_{calcite,water}$ is 0.028 09(13). These values generally are expressed as $10^3 \ln\alpha$ values, and $10^3 \ln\alpha_{calcite,water}$ equals 28.09(13).

The kinetic isotopic fractionation factor, $\alpha_D^{kin}\left({}^{i}E,{}^{j}E\right)$, is given by the ratio of the rate coefficients for the heavier and lighter isotopes in the slowest reaction step leading to the product. Thus,

$$\alpha_D^{kin}\left({}^{i}E,{}^{j}E\right) = \alpha_D^{kin} = \frac{k\left({}^{i}E\right)}{k\left({}^{j}E\right)} \tag{37}$$

where ${}^{i}E$ and ${}^{j}E$ are the heavier and lighter isotope, respectively. Commonly, kinetic isotopic fractionation is expressed in the same manner as the equilibrium isotopic fractionation. Consider the reaction of a carbonate with an acid. Two-thirds of the oxygen of the carbonate is converted to CO_2. This CO_2 is enriched in ${}^{18}O$ relative to that of the carbonate. As an example, the oxygen isotopic fractionation by treatment of $PbCO_3$ at 25 °C with H_3PO_4 has a reported value of 1.010 13 [18]. This can be expressed by any of the following:

$$\alpha_{CO_2,PbCO_3}^{kin}\left({}^{18}O,{}^{16}O\right) = 1.010\,13 \text{ at } 25\,°C$$

$$\alpha_{CO2,PbCO3}\left({}^{18}O,{}^{16}O\right) = 1.010\,13 \text{ at } 25\,°C$$

$$\alpha_{CO2,PbCO3}\left({}^{18,16}O\right) = 1.010\,13 \text{ at } 25\,°C$$

$$\alpha_{CO2,PbCO3} = 1.010\,13 \text{ at } 25\,°C$$

$\alpha(CO_2, PbCO_3) = 1.010\ 13$ at 25 °C

20. isotopic reference material
Substance sufficiently stable and homogeneous in isotopic composition to serve in measurement
of isotope ratios.
See also *international measurement standard*.

Note: An isotopic reference material can be locally prepared in an individual laboratory or can be
an internationally distributed isotopic reference material, *e.g.*, USGS40 L-glutamic acid, which is
used measurement of $\delta^{13}C$ and $\delta^{15}N$ values (see *delta*).

21. isotopologue
A molecular entity that differs only in isotopic composition (number of isotopic substitutions),
e.g. CH_4, $CH_3{}^2H$, $CH_2{}^2H_2$.
[19].

22. isotopomers
Isomers having the same number of each isotopic atom but differing in their positions. The term
is a contraction of 'isotopic isomer'. Isotopomers can be either constitutional isomers (*e.g.*
$CH_2{}^2HCH=O$ and $CH_3C^2H=O$) or isotopic stereoisomers [*e.g.* (R)- and (S)-CH_3CH^2HOH or (Z)-
and (E)-$CH_3CH=CH^2H$].
[19].

23. mass spectrometer
An instrument in which beams of ions are separated (analysed) according to the quotient
mass/charge, and in which the number of ions or amounts of ions are measured electrically. This
term should also be used when a scintillation detector is employed.
See also

24. mole ratio
See *amount ratio*.

25. multi-collector inductively coupled plasma mass spectrometer
See *inductively coupled plasma mass spectrometer*.

26. number fraction, X (Y for gaseous mixtures)
Number of defined entities of a mixture divided by the total number of entities in the mixture.
Number fraction is equal to the amount fraction: the amount of a constituent divided by the total
amount of all constituents in the mixture. This quantity has dimension 1.

Note: When the defined entity is an isotope of an element, the number fraction is the *isotope-
number fraction* or the *stable isotope-number fraction*, and it is numerically equal to the *atom
fraction* and to the *isotopic abundance*.

Explanatory comments
The number fraction, X (Y for gaseous mixtures), is defined for atom ${}^iE$ in specimen B by:

$$X_B\left({}^{i}E\right) = \frac{N_B\left({}^{i}E\right)}{\sum N_B(E)} \tag{38}$$

where the summation includes all isotopes of element E. The number fraction, $X({}^{i}E, {}^{j}E)$, is equal to the corresponding amount fraction[6], $x_B({}^{i}E, {}^{j}E)$, which is defined by the relation

$$x_B\left({}^{i}E\right) = \frac{n_B\left({}^{i}E\right)}{\sum n_B(E)} = \frac{N_B\left({}^{i}E\right)}{\sum N_B(E)} \tag{39}$$

as the isotopic abundance [1,2]. It should be pointed out that no symbol is given in the latest edition of the "Green Book" [1] for number fraction.

27. number ratio, R
isotope ratio
Number obtained by counting a defined entity in a mixture (usually molecules, atoms, or ions) divided by the number of another defined entity of the same kind within the mixture.

Note: When the defined entities are isotopes of an element, the number ratio is the *isotope ratio*. Thus, $R({}^{i}E, {}^{j}E) = N_B({}^{i}E) / N_B({}^{j}E)$, where $N_B({}^{i}E)$ and $N_B({}^{j}E)$ are numbers of the two isotopes, i and j, of chemical element E in substance B. R has dimension 1.

28. per cent, %
Part per hundred, which is 0.01; has been used as unit of isotopic delta values.

Note: Per cent is also written in the literature as percent. The Commission on Isotopic Abundances and Atomic Weights accepts the use of the symbol ‰ in expressing delta values. See also *delta*.

29. per mill, ‰
Part per thousand, which is 0.001; commonly used as unit of isotopic delta values and isotopic enrichment factors.

Note: Per mill is also written in the literature as permil, per mil, and per mille. The Commission on Isotopic Abundances and Atomic Weights recommends the use of the symbol ‰ in expressing delta values and isotopic enrichment factors.
See also *delta* and *isotopic enrichment factor*.

30. ppm
Part per million, which is 0.000 001; commonly used as unit of delta values of gases and less commonly of isotopes.

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[6] Amount fraction is the abbreviated form of amount-of-substance fraction and both are alternatives to mole fraction [1].

Note: The Commission on Isotopic Abundances and Atomic Weights recommends the use of the symbol ppm in expressing delta values of isotopes and gases.
See also *delta*.

31. stable isotope-amount fraction
See *isotope-amount fraction*.

32. stable isotope-mole fraction
See *isotope-amount fraction*.

33. stable isotope-number fraction
See *number fraction*.

34. thermal ionization mass spectrometer
TIMS
Mass spectrometer in which analyte on a filament is heated to be ionized and separated (analyzed) according to the quotient mass/charge, and in which the number of the ions or the amounts of the ions are measured electrically, or numbers of ions are counted.

ACKNOWLEDGMENTS

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APPENDIX 1. QUANTITY CALCULUS AND COHERENT UNITS

Equations that express a relation among quantitie*s* are termed quantity equations. Quantity equations are discussed by T. Cvitaš in his review of principles of quantity calculus [12]. He points out that

> "each symbol of a physical quantity (single letter italic) in an equation stands for the value of the quantity which is

$$(\text{quantity}) = (\text{numerical value}) \times (\text{unit}) \tag{40}$$

> In this way the equations hold for any units as we believe the laws of nature should. Units are a matter of human choice and no law in nature should depend on it. Thus

> force = mass × acceleration

> or with symbols

$$F = m\,a \tag{41}$$

> irrespective of what units we choose.

> **Equations should therefore be written in a form not implying certain units."**

Neither the name of the physical quantity, nor the symbol used to denote it, should imply a particular choice of unit.

If equations between numerical values have the same form as equations between physical quantities, then the system of units defined in terms of base units avoids numerical factors between units, and is said to be a coherent system [1]. The International System (SI) is a coherent system of units.

The advantage of a coherent system of units is that if the value of each quantity is substituted for the quantity symbol in any quantity equation, then the units may be canceled, leaving an equation between numerical values which is exactly similar (including all numerical factors) to the original equation between the quantities.

The use of a coherent system of units is not essential. In particular, the use of multiple or submultiple prefixes destroys the coherence of the SI, but is nonetheless often convenient.

APPENDIX 2. COLUMN HEADING OF TABLES AND AXIS LABELS OF GRAPHS

IUPAC's recommendation [1] for table-column headings and for axis-labels of graphs, based upon quantity calculus and recommended by numerous journals,[7] is to use the quotient of the physical quantity and a unit so that the values are pure numbers. Consider an example of elevation, which as dimension L, is expressed in meters. An axis label could be expressed as "Elevation / m" or as "Elevation m^{-1}." Suppose the mass concentration of dissolved sodium in a water sample (having dimension $M\,L^{-3}$) is reported with units of mg/l. The SI quantity of mass concentration is γ. Therefore, an axis label could be expressed as "$\gamma_{Na}/(mg/l)$", "$\gamma_{Na}\,(mg/l)^{-1}$", "$\gamma(Na)/(mg/l)$", or "$\gamma(Na)\,(mg/l)^{-1}$." Examples of column headings and axis labels for isotopic and gas-ratio data are given in Tables 1 and 2. To indicate that $\delta^{13}C$ values in a column are expressed relative to the international measurement standard VPDB, one can write "$\delta^{13}C_{VPDB}$" instead of "$\delta^{13}C_{B,VPDB}$." The use of the %, ‰, or ppm symbols in the denominator, such as "$\delta^{18}O/‰$," although numerically correct, should be avoided [1]. Isotope and gas-ratio data examples of column headings of tables, axis labels of graphs, and text to be avoided are shown in Table 3.

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[7] Column headings and axis labels based upon quantity calculus are requested by numerous journals including *Accounts of Chemical Research*, *ACS Chemical Biology*, *ACS Nano*, *Analytical Chemistry*, *Biochemistry*, *Bioconjugate Chemistry*, *Biomacromolecules*, *Biotechnology Progress*, *Chemical Research in Toxicology*, *Chemistry of Materials*, *Crystal Growth & Design*, *Energy & Fuels*, *Environmental Science & Technology*, *Industrial & Engineering Chemistry Research*, *Inorganic Chemistry*, *Journal of Agricultural and Food Chemistry*, *Journal of Chemical & Engineering Data*, *Journal of Chemical Information and Modeling*, *Journal of Chemical Theory and Computation*, *Journal of Combinatorial Chemistry*, *Journal of the American Chemical Society*, *Journal of Medicinal Chemistry*, *Journal of Natural Products*, *Journal of Proteome Research*, *Langmuir*, *Macromolecules*, *Molecular Pharmaceutics*, *Nano Letters*, *Organic Letters*, *Organic Process Research & Development*, *Organometallics*, *The Journal of Organic Chemistry*, *The Journal of Physical Chemistry A*, *The Journal of Physical Chemistry B*, and *The Journal of Physical Chemistry C* [20], and Journal of Chemical Thermodynamics, Journal of Physics and Chemistry Reference Data, and Pure and Applied Chemistry.

Table 1 Examples of axis labels of graphs, column headings of tables, and data in tables for isotopic and gas-ratio measurements to be consistent with the SI.

$\delta_{A,VPDB}(^{18}O)$	$10^3\delta(^{44,42}Ca)$ relative to SRM 915a	$10^3\,\varepsilon_{cal,water}$	$\varepsilon_{calcite,water}$	$\delta(^{65}Cu)$	$10^4\delta^{65}Cu$	$100x(^{15}N)$	$x^E(^{15}N)$	$10^6\delta(O_2,N_2)$	$\delta(O_2, N_2)$
+0.0091	+9.1	+28.49	-8.4×10^{-3}	$-0.000\,18$	-1.8	2.51	0.0451	-1.1	-1.1×10^{-6}
$+9.1\times10^{-3}$			$-0.008\,4$	-1.8×10^{-4}			4.51×10^{-2}		

Table 2 Examples of axis labels of graphs, column headings of tables, and data in tables for isotopic and gas-ratio measurements consistent with recommendation of the Commission on Isotopic Abundances and Atomic Weights.

$\delta_{A,VSMOW}{}^2H$	$\varepsilon_{calcite,\,water}$	$\delta^{65}Cu$	$x(^{15}N)$	$x^E(^{15}N)$	$\delta(O_2, N_2)$
+9.1 ‰	-8.49 ‰	-0.18 ‰	2.51 %	0.0451	-1.1×10^{-6}
+0.0091		-1.8 pptt[a]	0.0251	4.51×10^{-2}	-1.1 ppm
		$-0.000\,18$		4.51 %	
		-1.8×10^{-4}			

[a] If pptt (parts per ten thousand) is used, the symbol should be defined in a footnote.

APPENDIX 3. EXAMPLES OF DEPRECATED USAGE

Table 3 Examples of isotopic and gas-ratio data of column headings of tables, axis labels of graphs, and text to be avoided to be consistent with IUPAC and the SI.

Deprecated Usage	Problems
$\delta^{18}O$ (in ‰)	Label should not contain the symbol ‰ or the text "in ‰."
$\delta^{15}N$ (in per mill)	Label should not contain the text "in per mill."
$\delta^{13}C_{NBS19}$	The substance upon which δ is measured, NBS 19, should directly follow the quantity δ as a subscript; thus, one should write $\delta_{NBS19}{}^{13}C$ or $\delta_{NBS19}(^{13}C)$.
$\delta(O_2/N_2) = 1.1$ per meg	The symbol "ppm" should be used instead of "per meg." Alternatively, express values as $10^6\,\delta(O_2, N_2)$ values.
$\varepsilon^{65}Cu = -0.14$	The symbol ε is already defined as $\alpha - 1$. Replace ε with δ.
Deuterium (‰)	The label or column heading is missing the δ symbol. No column heading or axis label should contain the "‰" symbol.
AP	"*AP*" is not a valid SI quantity and should not be used. Use "stable isotope-amount fraction" or "atom fraction" instead, symbol $x_B(^iE)$, or $y_B(^iE)$ for gases.
Atom %	"*Atom %*" is not a valid SI quantity and should not be used. Use "stable isotope-amount fraction" or "atom fraction" instead, symbol $x_B(^iE)$, or $y_B(^iE)$ for gases.
APE	"*Atom % excess*" is not a valid SI quantity and should not be used. Use "excess stable isotope-amount fraction" or "excess atom fraction" instead, symbol $x_B{}^E(^iE)$, or $y_B{}^E(^iE)$ for gases.
$\delta(O_2/N_2)$ (in ppm)	Labels should not contain "in %", "in ‰", or "in ppm."
$\delta(O_2/N_2)$ / ppm	Although numerical correct, the "Green Book" [1] recommends against having "%", "‰", or "ppm" in the denominator.

Table 4 Examples of delta-definition equations to be avoided to be consistent with the SI and IUPAC.
 [std, international measurement standard]

Deprecated Usage	Problems
$\delta^{18}O = \left[\dfrac{\left(^{18}O/^{16}O\right)_B}{\left(^{18}O/^{16}O\right)_{std}} - 1 \right] \cdot 1000$	Equation should not contain the extraneous factor 1000. If not previously defined, $(^{18}O/^{16}O)_B$ needs to be defined as $n_B(^{18}O)/n_B(^{16}O)$, $N_B(^{18}O)/N_B(^{16}O)$, $r_B(^{18}O)$, or $R_B(^{18}O)$, and the equivalent definitions for the std.
$\delta^{13}C_B = \dfrac{R_B{}^{13}C - R_{VPDB}{}^{13}C}{R_{VPDB}{}^{13}C}$	The substance referred to by the quantity should immediately follow the quantity name as its subscript [1]; therefore, replace $\delta^{13}C_B$ by $\delta_B{}^{13}C$. The nomenclature $\delta_B(^{13}C)$ is preferred to $\delta_B{}^{13}C$, although both are acceptable.
$\delta^{18}O \text{ (in ‰)} = \left[\dfrac{\left(^{18}O/^{16}O\right)_B}{\left(^{18}O/^{16}O\right)_{std}} - 1 \right] \cdot 1000$	Equation should not contain the extraneous factor 1000 or the text "in ‰." If not previously defined, $(^{18}O/^{16}O)_B$ needs to be defined as $n_B(^{18}O)/n_B(^{16}O)$, $N_B(^{18}O)/N_B(^{16}O)$, $r_B(^{18}O)$, or $R_B(^{18}O)$. Equivalent definitions should be provided for the international measurement standard, "std."
$\varepsilon^{65}Cu = \left[\dfrac{\left(^{65}Cu/^{63}Cu\right)_B}{\left(^{65}Cu/^{63}Cu\right)_{std}} - 1 \right] \cdot 10\,000$	The symbol ε is already defined as $\alpha - 1$. Replace ε with δ. Equation should not contain the extraneous factor 10 000. If not previously defined, $(^{65}Cu/^{63}Cu)_B$ needs to be defined as $n_B(^{65}Cu)/n_B(^{63}Cu)$, $N_B(^{65}Cu)/N_B(^{63}Cu)$, $r_B(^{65}Cu)$, or $R_B(^{65}Cu)$ for substance B and the equivalent definitions should be provided for the international measurement standard, "std."
$\delta(O_2/N_2) = \left[\dfrac{R_B}{R_{std}} - 1 \right] \cdot 1\,000\,000$	Equation should not contain the extraneous factor 1 000 000. If not previously defined, R need to be defined as $N(O_2)/N(N_2)$ or as $n(O_2)/n(N_2)$.