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Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results[†, ‡]

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To minimize confusion in the expression of measurement results of stable isotope and gas-ratio measurements, recommendations based on publications of the Commission on Isotopic Abundances and Atomic Weights of the International Union of Pure and Applied Chemistry (IUPAC) are presented. Whenever feasible, entries are consistent with the Système International d'Unités, the SI (known in English as the International System of Units), and the third edition of the International Vocabulary of Basic and General Terms in Metrology (VIM, 3rd edition). The recommendations presented herein are approved by the Commission on Isotopic Abundances and Atomic Weights and are designed to clarify expression of quantities related to measurement of isotope and gas ratios to ensure that quantity equations instead of numerical value equations are used for quantity definitions. Examples of column headings consistent with quantity calculus (also called the algebra of quantities) and examples of various deprecated usages connected with the terms recommended are presented. Published in 2011 by John Wiley & Sons, Ltd.

During the 2003 meeting in Ottawa, Canada, of the Commission on Isotopic Abundances and Atomic Weights of the International Union of Pure and Applied Chemistry, members recognized that there is confusion about the notation of delta values in isotope studies. The delta value (δ) is used to express the relative difference of a ratio of the numbers (or the amounts) of two isotopes in a specimen compared with that of a reference, commonly an international measurement standard. Results of such isotopic measurements are used in anthropology, atmospheric sciences, biology, chemistry, environmental sciences, food and drug authentication, forensic applications, geochemistry, geology, oceanography, and paleoclimatology. The Commission on Isotopic Abundances and Atomic Weights (the Commission hereafter) recommended that an article be prepared to clarify the terminology and concepts behind the terms involved in expressing relative differences in stable isotope ratios. These guidelines also apply to radioactive isotopes with half-lives sufficiently great to be treated as stable isotopes, such as ^{238}U and ^{235}U.[1] This article is a result of this initiative and provides information on the reporting of relative differences in ratios of volumes, numbers of molecules, and amounts of gases. Many of the recommendations in this article also apply to reporting and expressing radioactive isotope ratios although this is not the topic of this document.

Most chemical elements have more than one stable isotope. Molecules, atoms, and ions having different stable isotopes of the same chemical element possess slightly different physical and chemical properties, and they commonly will be fractionated during physical, chemical, and biological processes giving rise to variations in isotopic abundances and in atomic weights.[2,3] The purpose of this article is to improve the global exchange of scientific information in different disciplines that measure or make use of variations in isotopic abundances. This document should aid the reader in what may be called 'good scientific language' in fields utilizing isotopic abundance variations. In those cases where certain common usages are deprecated, there are strong reasons for this and the reader should follow these recommendations for consistency with the Système International d'Unités, the SI (known in English as the International System of Units),[4] and the *International Vocabulary of Metrology – Basic and General Concepts and Associated Terms* (VIM, 3rd edn.),[5] both published by BIPM (Bureau International des Poids et Mesures). In general, published results of measurements should be provided with their measurement uncertainties, which can be calculated following the *Guide to the Expression of Uncertainty in Measurement*.[6] For purposes of brevity, uncertainty values are omitted in most of the examples in this article.

CONCEPTS AND ASSOCIATED TERMS

The entries in this article are organized in the form of a glossary and listed in alphabetical order. They conform to specific requirements that are consistent with the International System of Quantities (ISQ),[5] upon which the SI is based. A number of recommendations apply to several glossary items and are listed here. For definitions of terms in recommendations, see corresponding entry below.

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‡ Dedicated to Prof. Etienne Roth, the consummate gentleman and expert on isotopic terminology – a long-time friend of and contributor to the Commission on Isotopic Abundances and Atomic Weights of the International Union of Pure and Applied Chemistry.

- The mass number of a nuclide of a chemical element may be specified by attaching the mass number as a left superscript to the symbol for the element, as in ^{15}N, or by adding it after the name of the element, as in nitrogen-15.
- An isotope of a chemical element in a substance may be specified by adding the substance as a right subscript following the right parenthesis, e.g., $n(^{15}N)_{(NH_4)_2^{32}SO_4}$.
- Sub-subscripts and super-subscripts may improve readability and are acceptable in the specification of the substance.
- The ionic charge is shown as a right superscript and 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.[7] In writing the formula for a complex ion, spacing for the charge number (ionic charge) and parentheses can be added; for example, $^{34}SO_4^{2-}$ or $(^{34}SO_4)^{2-}$. This staggered arrangement is now recommended[7] as opposed to the format $^{34}SO_4^{2-}$ in which '2–' is directly written above '4'.
- Molecular masses should not be written as superscripts to molecular formulae. For example, writing ^{30}CO for $^{12}C^{18}O$ to indicate that the mass of the molecule is 30 is incorrect and should be avoided.
- It is recommended that the heavy isotopes of hydrogen be written as ^2H and ^3H rather than as D and T, and that they be written out as deuterium and tritium, which is in agreement with *Nomenclature of Inorganic Chemistry*.[7]
- In specifically and selectively isotopically labeled compounds, the nuclide symbol is placed in square brackets before the name of the part of the compound that is isotopically modified,[7] i.e., $[^{15}N]H_2[^2H]$ and $[^2H_1,^{15}N]$ammonia. In isotopically substituted compounds, the appropriate nuclide symbol(s) is placed in parentheses before the name of the part of the compound that is isotopically substituted,[7] i.e., compare H^2HO and $(^2H_1)$water.
- A space should be printed between the numerical value and symbol of the unit,[4] for example:

$$m = 6.4\ \text{kg} \qquad \delta^2H_{\text{VSMOW-SLAP}} = +16.4\ ‰$$
$$t = 14\ °C \qquad x(^{13}C) = 1.11\ \%$$

Even when the value of a quantity is used as an adjective, a space is left between the numerical value and the unit symbol.[4] Only when the name of the unit is spelled out would the ordinary rules of grammar apply, so that in English a hyphen would be used to separate the number from the unit.[4] Compare 2-mg sample and two milligram sample.

- In compliance with established use in the literature, parentheses following an isotope-quantity symbol regularly are omitted, e.g. compare $\varepsilon^{13}C$ versus $\varepsilon(^{13}C)$ and $\delta^{18}O$ versus $\delta(^{18}O)$, which is usually pronounced delta oxygen eighteen or delta oh eighteen, rather than delta eighteen oxygen.
- The solidus (oblique stroke or forward slash,/) regularly is used as a record separator for isotopes in a quantity, e.g. $R(^{44}Ca/^{42}Ca)$ or $R(^{44/42}Ca)$, and for separation of the unknown and standard, e.g. $\delta^{34}S_{P/VCDT}$.
- The notation $^{13}C/^{12}C$, as in '$^{13}C/^{12}C$ determinations', is acceptable. However, on first use it should be defined, e.g. 'determinations of $N(^{13}C)/N(^{12}C)$, abbreviated herein as $(^{13}C/^{12}C)$, are' or 'determinations of $n(^{13}C)/n(^{12}C)$, abbreviated herein as $(^{13}C/^{12}C)$, are'.
- All quantity symbols are printed in italic font and their superscripts and subscripts are printed in Roman upright font,[4,5] e.g. $\Delta_{P/Q}$, α, x_P, $\varepsilon^{13}C$, and $\delta^{44/42}Ca_{\text{standard}}$, unless superscripts or subscripts are symbols of quantities, in which case they are printed in italic font, e.g. ^iE.
- If the absolute value of the number is less than one, a zero should precede the decimal sign. Thus, '.113‰' should be written '0.113 ‰'.[4]
- For camera-ready copy, an en dash symbol (–), rather than a hyphen (-), should be used to indicate negative values.
- The symbols ‰, %, ppm, and per meg are used in the expression of values of dimensionless quantities because δ^iE values are small. Examples of reporting that include the symbols %, ‰, and ppm are provided throughout these recommendations. When any of the terms %, ppm, etc., are used, it is important to state the dimensionless quantity whose value is being specified; see section 5.3.7 of the 8th SI brochure.[4] Use of the symbols ‰ and ppm is encouraged when their meaning is clearly understood and their use clarifies and simplifies comprehension of text. For example, many readers find 'with the value $\delta^{13}C = -5.45$ ‰' easier to read and comprehend than 'with the value $\delta^{13}C = -0.00545$'.
- The isotope should be specified when using words such as 'depleted' and 'enriched' because depleted or enriched could refer to either an isotope with lower mass number or with higher mass number. The text 'The sample is enriched by crystallization and ...' or 'the enriched specimen...' written to specify a sample enriched in a heavy isotope should be avoided. Instead, using carbon isotopes as an example, authors should write 'The sample is enriched in ^{13}C by...' or 'the specimen enriched in ^{13}C is...'.

Each term is presented with notes as appropriate. To assist the reader, cross-references to other terms are denoted in italic typeface, and a figure (Fig. 1) is provided that relates selected quantities.

absolute isotopic abundance, x

Isotopic abundance value that is free from all known sources of bias within stated uncertainty.

Note 1: These values can be determined by calibrating a mass spectrometer by means of gravimetrically prepared synthetic mixtures of materials in which an isotope is enriched (or depleted) by a known or measurable factor.

Note 2: This name is a misnomer in that 'absolute' indicates absence of uncertainty, but each abundance value of an isotope has an uncertainty associated with its determination.

Example: The absolute isotopic abundance of ^{13}C in the *international measurement standard* NBS 19 calcite is $x(^{13}C)_{NBS19} = 0.011\ 078 \pm 0.000\ 028$.[8,9]

See *isotope-amount fraction*.

absolute isotope ratio, R

Isotope ratio that has been determined by *isotope-ratio calibration* using an *international measurement standard*, certified isotopic reference materials, or gravimetric mixtures of highly enriched (or depleted) isotopes.

Note 1: These values can be determined by calibrating a mass spectrometer by means of gravimetrically prepared synthetic mixtures of materials in

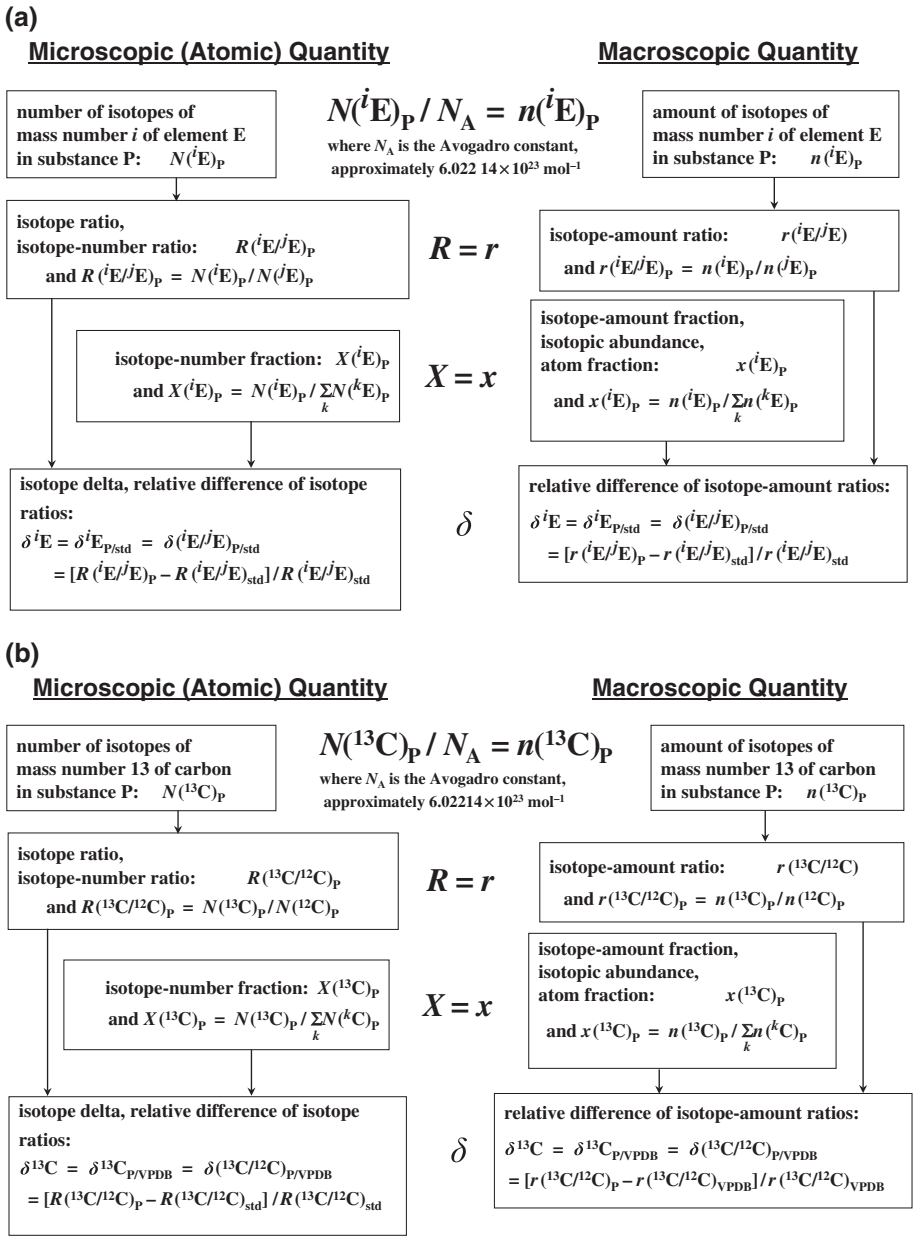

Figure 1. (a) Relations among selected quantities. The heavier (higher atomic mass) and lighter (lower atomic mass) isotopes of element E are, respectively, ^{i}E and ^{j}E; k is the mass number of any isotope for a summation over all isotopes of element E. The isotope ^{i}E in substance P is specified by $^{i}E_{P}$. For a given non-Greek symbol, lowercase font signifies the macroscopic quantity and uppercase font denotes the microscopic (atomic) quantity, e.g., r and R. Alternative names are listed for the quantities isotope ratio, isotope delta, and isotope-amount fraction. (b) Example of selected quantities using stable carbon isotopes, ^{12}C and ^{13}C.

which an isotope is enriched (or depleted) by a known or measurable factor.

Note 2: To determine absolute isotope ratios by *isotope-ratio calibration*, the *true isotope ratio* that the calibration material carries has to lie within the uncertainty interval stated for the material used at a given statistical probability.

Note 3: This name is a misnomer in that 'absolute' indicates absence of uncertainty, but a *measured isotope ratio* has an uncertainty associated with its determination.

Note 4: The forms using a comma as a record separator, $R(^{i,\,j}E)_P$ or $R(^{i}E,\,^{j}E)_P$, instead of a forward slash, have also been used in the literature. They are equivalent to, but not preferred over, the definitions given above.

Example: The stable carbon absolute isotope ratio of NBS 19 calcite as reported by Chang and Li[9] is $R(^{13}C)_{NBS19} = R(^{13}C/^{12}C)_{NBS19} = R(^{13/12}C)_{NBS19} = 0.011\,202 \pm 0.000\,028$.

See also *measured isotope ratio*, *true isotope ratio*, and *isotope-number ratio*.

amount of substance, *n*
amount
chemical amount
Base quantity in the system of quantities upon which the SI is based.[4] The name of the SI base unit is mole with symbol mol. One mole is the amount of substance of a system that contains as many defined elementary entities as there are atoms in 0.012 kg of ^{12}C in their nuclear and electronic ground states (approximately $6.022\ 14 \times 10^{23}$ entities).

Note 1: Amount of substance reflects the particulate nature of matter and reflects the fact that these particles have a property of matter known as 'numerosity' and requires that the substance always be specified; e.g., when counting, the counted particles must be identical and specified.[10]
Note 2: This quantity had no name prior to 1969 and was simply referred to as the number of moles.[11]
See *Avogadro constant* and Fig. 1.

APE
Abbreviation for the deprecated term *atom percent excess*. The recommended name for this quantity is *excess atom fraction*, x^E.

atom fraction, *x*
Amount of a specified atom (isotope) of a chemical element divided by the total amount of atoms of the element within the mixture.

Note 1: Previously, this term was called 'atom %', 'atom percent', or AP; however, these are deprecated because they are not valid symbols of quantity names. Neither the name of a quantity, nor the symbol used to denote it, should imply any particular choice of unit; see section 5.3.1 of the 8th SI brochure.[4] Symbols of ISQ quantity names should be, in general, a single character.
Note 2: Atom fraction is a *dimensionless quantity*, and the units of mmol/mol and μmol/mol (and similar units) are permissible.
Note 3: The atom fraction (*isotope-amount fraction*), $x(^iE)_P$, is a valid ISQ *quantity* of use in tracer studies and *isotope balance* (or amount-of-substance balance) studies,[12] commonly with isotopes of H, C, N, and O. Use of atom fraction is preferred over use of *delta* values for tracer and mixing calculations because $x(^iE)_P$ is linearly correlated to mixing fraction, whereas δ is not.[12] Delta values generally are measured and then converted into atom fractions.
Note 4: In the literature, the symbols *f* and *F* have been used for atom fraction in isotope-balance equations, and their use should be avoided.
Note 5: For an element with two isotopes ^iE and ^jE, the atom fraction, $x(^iE)_P$, in specimen P is given by the relation:

$$x(^iE)_P = \frac{n(^iE)_P}{n(^iE)_P + n(^jE)_P}$$

where $n(^iE)_P$ is the amount of isotope ^iE of element E in substance P.

Note 6: The relation between $x(^iE)_P$, the *isotope-amount ratio* $r(^iE/^jE)_P$, and the ratio of the numbers of isotopes, $R(^iE/^jE)_P$, of specimen P for two isotopes is:

$$x(^iE)_P = \frac{r(^iE/^jE)_P}{1 + r(^iE/^jE)_P} = \frac{R(^iE/^jE)_P}{1 + R(^iE/^jE)_P}$$

The relation between $x(^iE)_P$ and the quantity $\delta^iE_{P/std}$ of specimen P for two isotopes is:

$$x(^iE)_P = \frac{1}{1 + \frac{1}{(\delta^iE_{P/std}+1)\cdot r(^iE/^jE)_{std}}} = \frac{1}{1 + \frac{1}{(\delta^iE_{P/std}+1)\cdot R(^iE/^jE)_{std}}}$$

As an example, the $x(^{13}C)_P$ of specimen P expressed relative to the VPDB (Vienna Peedee Belemnite) scale, for which $R(^{13/12}C)_{VPDB}$= 0.011 179 60 (ignoring its uncertainty for this example),[9] is given by the relation:

$$x(^{13}C)_P = \frac{1}{1 + \frac{1}{(\delta^{13}C_{P/VPDB}+1)\cdot 0.011\ 179\ 60}}$$

Note 7: In the literature, one can find equations such as:

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

where '*AP*' stands for '*atom %*'. As recommended by Milton and Wielgosz,[13] their use should be avoided. This relation contains the extraneous factors 100 and 1000, both of which should be deleted from the equation so that it is a coherent quantity equation.[4,13]
See also *isotopic abundance* and Fig. 1.

atom percent
atom %
AP
Deprecated term that includes both a quantity and a unit or a symbol for a quantity that is not a valid symbol in the SI because symbols of ISQ quantities names must be a single character, except in a few cases. Neither the name of a quantity, nor the symbol used to denote it, should imply any particular choice of unit; see section 5.3.1 of the 8th SI brochure.[4] Replace with *atom fraction* expressed as percent.

Examples:	Deprecated:	The abundance of ^{13}C in sample P is 1.5 atom %.
	Recommended:	The ^{13}C fraction, $x(^{13}C)$, of sample P is $x(^{13}C)_P$=1.5 %.

atom percent excess
APE
Deprecated term that includes both a quantity and a unit, or a symbol for a quantity that is not a valid symbol in the SI, because symbols of ISQ quantities names must be a single character, except in a few cases. In addition, neither the name of a quantity, nor the symbol used to denote it, should imply any particular choice of unit; see section 5.3.1 of the 8th SI brochure.[4]

APE is defined by two different relations (*excess atom fraction* and *relative exceedance*) that are not equivalent, but may yield similar numerical values for isotopic compositions near natural terrestrial values, depending upon the chemical element.[12] For example, the two versions of APE equations yield substantially different values for Cl, B, and Li isotopic measurements.
See *excess atom fraction* and *relative exceedance*.

Avogadro constant, N_A
A universal constant that relates the number of entities to the amount of substance for any sample. Its value is the number of ^{12}C atoms in their nuclear and electronic ground states in 0.012 kg of ^{12}C (designated as 1 mole) and is about $6.022\ 14 \times 10^{23}$; thus, the Avogadro constant has the coherent SI unit reciprocal mole; see section 2.1.1.6 of the 8th SI brochure.[4]

Note: The Avogadro constant has long been known as the scaling factor between the macroscopic and the microscopic or atomic worlds, as shown in Fig. 1.[14]
See also *number of entities*.

certified isotopic reference material
Reference material accompanied by documentation issued by an authoritative body, such as a national measurement institute, and providing one or more *isotope-number* or *isotope-amount ratios* or *fractions* with associated uncertainties and traceabilities using valid procedures.

consensus delta value
See *reference delta value*.

delta, δ
See *relative difference of isotope ratios* and *relative difference of gas ratios*.

delta over baseline, Δ
DOB
Difference between the *isotope delta* (*relative difference of isotope ratios*) of a sample (usually called a tracer sample) and that of a stated baseline. The delta over baseline, symbol $\Delta(^iE/^jE)_{P/reference}$, is a measurement of the enrichment of a specimen in a heavier isotope relative to a specified baseline (reference) according to the relation:

$$\Delta(^iE/^jE)_{P/reference} = \delta(^iE/^jE)_P - \delta(^iE/^jE)_{reference}$$

where $\delta(^iE/^jE)_P$ is the delta value of isotopes ^iE and ^jE of element E of specimen P and likewise for a stated reference (both of which could be measured relative to a laboratory working standard that is not indicated).

Note 1: The quantity $\Delta(^iE/^jE)_{P/reference}$ should be defined by authors to avoid confusion because this symbol can also be used to express *mass-independent isotopic variation*.
Note 2: When it is clear from the context, $\Delta(^iE/^jE)_{P/reference}$ may be shortened to $\Delta(^iE)_{P/reference}$ or $\Delta^iE_{reference}$, as appropriate. When the element has more than two stable isotopes, $\Delta(^iE/^jE)_{P/reference}$ is preferred.
Note 3: Delta over baseline regularly is used in tracer studies and studies of *isotope balance*. For tracer studies and isotope-mass balances at isotope tracer levels greater than those of natural abundance, the use of the isotope-amount fraction, $x(^iE)_{P/std}$, yields accurate results and is preferred to delta over baseline, which yields increasingly incorrect mass-balance results with increasing values of δ^iE_P.[12,13]
Example: The stable carbon delta over baseline value of a specimen relative to the baseline RefQ, $\Delta(^{13}C)_{RefQ} = \Delta^{13}C_{RefQ} = +9.55 \times 10^{-3} = +9.55‰$. Delta values are difference measurements and authors may give a leading+symbol to values greater than zero.
See also *isotopic difference* and *relative difference of isotope ratios*.

dimensionless quantity
quantity of dimension one

(a) Ratio of two quantities of the same kind. The coherent SI unit for all such ratios is the number one (symbol 1) because the unit must be the ratio of two identical SI units.[5] The values of such quantities are simply expressed as numbers, and the unit one is not explicitly shown. Because SI prefix symbols can neither be attached to the symbol 1 nor to the name 'one', the symbol and terms %, ‰, ppm, and such, are used to express values of dimensionless quantities. The powers of 10 are used to express the values of particularly large or small dimensionless quantities.[5]
(b) Numbers that represent a count; e.g., number of molecules.

Note 1: Either definition implies a quantity for which the sum of all of the exponents of the factors corresponding to the base quantities in its quantity dimension is zero.
Note 2: While the measurement units and values of dimensionless quantities are numbers, such quantities convey more information than a number; they are characteristic of particular types of quantities of the same kind.
Examples: *mole fraction*, *isotope ratio*, and *isotope-number fraction*.

excess atom fraction, $x^E(^iE)_{P/reference}$
excess (stable) isotope-amount fraction
Difference between the *mole fraction* of an isotope ^iE of element E in substance P and that of a reference. The superscript E signifies an excess quantity.

Note 1: Previously, this term was called 'atom percent excess', 'atom % excess', or 'APE'. However, none of these should be used because this quantity does not have a unique definition and because 'APE' is not a valid symbol for an ISQ quantity name as symbols of ISQ quantities names must be a single character, except in a few cases. In addition,

neither the name of a quantity, nor the symbol used to denote it, should imply any particular choice of unit; see section 5.3.1 of the 8th SI brochure.[4]

Note 2: One definition in the literature is that this quantity is the 'excess' isotope tracer in substance P relative to that in a reference; [12,15] thus, 'APE' can be replaced by $x^{\mathrm{E}}(^{i}\mathrm{E})_{\mathrm{P/reference}}$, which is the excess stable isotope-amount fraction or excess atom fraction defined by the relation:

$$x^{\mathrm{E}}\left(^{i}\mathrm{E}\right)_{\mathrm{P/reference}} = x\left(^{i}\mathrm{E}\right)_{\mathrm{P}} - x\left(^{i}\mathrm{E}\right)_{\mathrm{reference}}$$

where superscript E is the usual way in thermodynamics to indicate an excess quantity. When it is clear from the context, $x^{\mathrm{E}}(^{i}\mathrm{E})_{\mathrm{P/reference}}$ may be shortened to $x^{\mathrm{E}}(^{i}\mathrm{E})_{\mathrm{P}}$, $x^{\mathrm{E}}(^{i}\mathrm{E})_{\mathrm{reference}}$, or $x^{\mathrm{E}}_{\mathrm{reference}}$, as appropriate.

Note 3: The macroscopic quantity excess stable isotope-amount fraction is equal to the microscopic (atomic) quantity excess stable isotope-number fraction, $X^{\mathrm{E}}_{\mathrm{P}}$, which is defined similarly to *isotope ratios* (isotope-number ratios).

Note 4: For a second definition of this quantity,[16] see *relative exceedance*.

The following are examples of data reporting of $x^{\mathrm{E}}_{\mathrm{P}}$ and $X^{\mathrm{E}}_{\mathrm{P}}$:

$x^{\mathrm{E}}\left(^{34}\mathrm{S}\right)_{\mathrm{VCDT}} = 0.93\ \%$	$X^{\mathrm{E}}\left(^{34}\mathrm{S}\right)_{\mathrm{VCDT}} = 0.93\ \%$
$x^{\mathrm{E}}\left(^{2}\mathrm{H}\right)_{\mathrm{P/reference}} = 0.008$	$X^{\mathrm{E}}\left(^{2}\mathrm{H}\right)_{\mathrm{P}} = 0.008$
$x^{\mathrm{E}}\left(^{13}\mathrm{C}\right)_{\mathrm{P/reference}} = 9.3 \times 10^{-3}$	$X^{\mathrm{E}}\left(^{13}\mathrm{C}\right)_{\mathrm{P/reference}} = 9.3 \times 10^{-3}$
$10^{6} x^{\mathrm{E}}\left(^{17}\mathrm{O}\right)_{\mathrm{reference}} = 8.42$	$10^{6} X^{\mathrm{E}}\left(^{17}\mathrm{O}\right)_{\mathrm{reference}} = 8.42$
$x^{\mathrm{E}}\left(^{17}\mathrm{O}\right)_{\mathrm{reference}} = 8.42\ \mathrm{ppm}$	$X^{\mathrm{E}}\left(^{17}\mathrm{O}\right)_{\mathrm{P}} = 8.42\ \mathrm{ppm}$

See also *atom fraction* and *relative exceedance*.

gas delta, δ

See *relative difference of gas ratios*.

international measurement standard

Measurement standard recognized by signatories to an international agreement and intended to serve worldwide.[5]

Note 1: VSMOW2 reference water, SLAP2 water, IAEA-S-1 silver sulfide, and L-SVEC lithium carbonate, which are distributed by the International Atomic Energy Agency (Vienna, Austria), are such standards for measurement of *relative difference of isotope ratios*. These materials are assigned *reference delta values* by agreement.

Note 2: The assigned uncertainties of delta values of some international measurement standards (e.g., NBS 19 calcite, SLAP water, and IAEA-S-1 silver sulfide) are zero even though their *isotope ratios* may not be well known.

Note 3: Information on values of internationally distributed isotopic reference materials and their sources is provided by IUPAC's Commission on Isotopic Abundances and Atomic Weights.[17]

See also *isotopic reference material*, *reference delta value*, and *reference isotope-ratio value*.

isotope balance

Determination of the *amount* or *isotope-amount ratio* of a substance in a mixture by making use of the fact that the sum of the amounts of the isotopes of each constituent of the mixture must equal the total in the system. Balance of amount of material is performed with *isotope-number fractions* or *isotope-amount fractions* to yield a relation such as:

$$n_{\mathrm{P}} \cdot x\left(^{i}\mathrm{E}\right)_{\mathrm{P}} + n_{\mathrm{Q}} \cdot x\left(^{i}\mathrm{E}\right)_{\mathrm{Q}} = \left(n_{\mathrm{P}} + n_{\mathrm{Q}}\right) \cdot x\left(^{i}\mathrm{E}\right)_{\mathrm{F}}$$

where P and Q are two samples that are combined to form mixture F with *isotope-amount fractions* $x(^{i}\mathrm{E})_{\mathrm{P}}$, $x(^{i}\mathrm{E})_{\mathrm{Q}}$, and $x(^{i}\mathrm{E})_{\mathrm{F}}$, respectively, of isotope $^{i}\mathrm{E}$ of element E.

Note 1: Isotope-delta values commonly are used for mass balance or amount-of-substance balance calculations in tracer and natural isotopic variation studies. An example is the relation:

$$n_{\mathrm{P}}\ \delta^{13}\mathrm{C}_{\mathrm{P}} + n_{\mathrm{Q}}\ \delta^{13}\mathrm{C}_{\mathrm{Q}} \approx \left(n_{\mathrm{P}} + n_{\mathrm{Q}}\right)\ \ \delta^{13}\mathrm{C}_{\mathrm{F}}$$

The quantity δ is not proportional to *atom fraction*; for example, the relation above will give increasingly incorrect results with larger differences between $\delta^{13}\mathrm{C}_{\mathrm{P}}$ and $\delta^{13}\mathrm{C}_{\mathrm{Q}}$. For accurate isotope-balance calculations, deltas can be replaced by atom fractions; Brenna *et al.*[12] show the disparity between balances calculated with δ values and *atom fractions*.

Note 2: For tracer studies, Corso and Brenna[18] have proposed the use of the quantity relative difference in *isotope-amount fraction* between a specimen P and a standard, which they write as $\varphi^{i}\mathrm{E}$. Writing $\varphi(^{i}\mathrm{E})$ is preferred and is defined by the relation:

$$\varphi\left(^{i}\mathrm{E}\right)_{\mathrm{standard}} = \frac{x\left(^{i}\mathrm{E}\right)_{\mathrm{P}} - x\left(^{i}\mathrm{E}\right)_{\mathrm{standard}}}{x\left(^{i}\mathrm{E}\right)_{\mathrm{standard}}}$$

where $x(^{i}\mathrm{E})_{\mathrm{P}}$ is the *isotope-amount fraction* of isotope $^{i}\mathrm{E}$ in specimen P and likewise for a measurement standard or an *international measurement standard*. An analytical correct amount-of-carbon-balance equation for $^{13}\mathrm{C}$ is written:

$$\varphi\left(^{13}\mathrm{C}\right)_{\mathrm{P}} n(\mathrm{C})_{\mathrm{P}} + \varphi\left(^{13}\mathrm{C}\right)_{\mathrm{Q}} n(\mathrm{C})_{\mathrm{Q}} = \varphi\left(^{13}\mathrm{C}\right)_{\mathrm{F}}\left(n(\mathrm{C})_{\mathrm{P}} + n(\mathrm{C})_{\mathrm{Q}}\right)$$

where $n(\mathrm{C})_{\mathrm{P}}$ and $n(\mathrm{C})_{\mathrm{Q}}$ are the amounts of carbon in substances P and Q of mixture F. For tracer studies and isotope balances at isotope tracer levels greater than those of natural abundance, either of the quantities *atom fraction*, *isotope-number fraction*, or $\varphi^{i}\mathrm{E}$ give accurate results as opposed to the quantities $R(^{i}\mathrm{E})$ or $\delta^{i}\mathrm{E}$, which yield increasingly incorrect mass or amount-of-substance balance with increasing values of $x(^{i}\mathrm{E})$.[12,13,18] The symbol φ also is used for the quantity volume fraction.[20] If there is any possibility of confusion, the format $\varphi(^{i}\mathrm{E})_{\mathrm{P/standard}}$ should be used.

isotope delta, δ
See *relative difference of isotope ratios*.

isotope effect
Alteration of either the equilibrium constant or the rate constant of a reaction if an atom in a reactant molecule is replaced by one of its isotopes.[11]

(a) *Kinetic isotope effect*.
The effect of isotopic substitution on a rate constant is referred to as a kinetic isotope effect.[19] For example, in the reaction:

$$Q + B \rightarrow P$$

where B is a reactant in which isotopic substitution does not appear and P is a product, the effect of isotopic substitution in reactant Q is expressed as the ratio of rate constants ${}^{j}k/{}^{i}k$, where the superscripts j and i represent reactions in which the molecules contain the light and heavy isotopes, respectively. A kinetic isotope effect is referred to as 'normal' if the reactant with the lighter isotope reacts more rapidly, so that ${}^{j}k/{}^{i}k$ is greater than 1. It is termed 'inverse' if the reactant with the heavier isotope reacts more quickly and ${}^{j}k/{}^{i}k$ is less than 1.

(b) *Equilibrium isotope effect*.
The effect of isotopic substitution on an equilibrium constant is referred to as a thermodynamic (or equilibrium) isotope effect. The equilibrium constant for isotopic exchange reactions can be written in either of two ways, depending upon the scientific discipline, and the reader must pay attention to which form is being used. For example, the effect of isotopic substitution in reactant Q and product P that participates in the equilibrium:

$$Q + B \rightleftharpoons P$$

is the ratio ${}^{j}K/{}^{i}K$ of the equilibrium constant for the reaction in which Q contains the light isotope compared with the reaction in which Q contains the heavy isotope, where B is a reactant in which isotopic substitution does not appear.[19] The ratio can be expressed equivalently as the equilibrium constant for the isotopici exchange reaction:

$${}^{j}Q + {}^{i}P \rightleftharpoons {}^{i}Q + {}^{j}P$$

in which reactants that are not isotopically substituted, such as B, do not appear. The inversely formulated reaction:

$${}^{j}P + {}^{i}Q \rightleftharpoons {}^{i}P + {}^{j}Q$$

is widely used and is essentially identical from a chemical point of view; however, the value of the equilibrium constant also is the inverse of that of the previous equation.

(c) *Primary isotope effect*
Kinetic isotope effect attributable to isotopic substitution of an atom to which a bond is made or broken in a specified reaction.[19] The corresponding isotope effect on the equilibrium constant of a reaction in which one or more bonds to the isotopic atoms are broken is called a 'primary equilibrium isotope effect'.

(d) *Secondary isotope effect*
Kinetic isotope effect that is attributable to isotopic substitution of an atom to which bonds are neither made nor broken in a specified reaction. One speaks of α, β (etc.) secondary isotope effects, where α, β (etc.) denote the position of isotopic substitution relative to the reaction center. The corresponding isotope effect on the equilibrium constant of such a reaction is called a 'secondary equilibrium isotope effect'.

Note 1: An isotope effect is related to, and may be predicted from, molecular structures of reactants, transition states, and products of an elementary chemical reaction. It is position- and reaction-specific (i.e., for the same reaction, each molecular position has a different isotope effect, and the same position shows different isotope effects in different reactions).

Note 2: If isotope effect is used to describe a weighted average over all molecular positions of a compound, this should be specified explicitly. To avoid misunderstandings, such use is discouraged, and it is recommended that the quantity *isotopic fractionation factor* be used instead.[21]

Note 3: If kinetic isotope effect is used to describe a cascade of reaction steps instead of an elementary chemical reaction (e.g., in enzyme reactions or environmental processes), the value will be affected by all processes leading up to and including the first irreversible step.[22] In such cases, it is recommended that the term 'apparent kinetic isotope effect' be used.[21,22]

See also *isotopic fractionation factor* and *isotopic fractionation*.

isotope ratio, R
isotope-number ratio
stable isotope ratio
Ratio of the number of atoms of one isotope to the number of atoms of another isotope of the same chemical element in the same system. The *number ratio*, R, is the number obtained by counting a specified entity (usually molecules, atoms, or ions) divided by the number of another specified entity of the same kind in the same system.[23] 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*. Because of historical use, *isotope-number ratio* is shortened to isotope ratio, and it is defined by the relation:

$$R({}^{i}E/{}^{j}E)_P = \frac{N({}^{i}E)_P}{N({}^{j}E)_P}$$

where $N({}^{i}E)_P$ and $N({}^{j}E)_P$ are the number of each isotope, ${}^{i}E$ and ${}^{j}E$, of chemical element E in substance P.

Note 1: 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 ${}^{15}N$, and should not be confused with 'isotope-number' as in *isotope-number fraction X* or *isotope-number ratio R*.

Note 2: Superscripts *i* and *j* should denote mass numbers of a heavier (higher atomic mass) and a lighter (lower atomic mass) isotope, respectively. In this manner, a 'heavier' sample will have a higher atomic weight.

Note 3: Isotope pairs found in the literature to define $N(^iE)/N(^jE)$ or $n(^iE)/n(^jE)$ include, but are not limited to:

$^2H/^1H$	$^{18}O/^{16}O$	$^{36}S/^{32}S$	$^{56}Fe/^{54}Fe$	$^{97}Mo/^{95}Mo$
$^7Li/^6Li$	$^{26}Mg/^{24}Mg$	$^{37}Cl/^{35}Cl$	$^{57}Fe/^{54}Fe$	$^{98}Mo/^{95}Mo$
$^{11}B/^{10}B$	$^{29}Si/^{28}Si$	$^{42}Ca/^{40}Ca$	$^{65}Cu/^{63}Cu$	$^{110}Pd/^{104}Pd$
$^{13}C/^{12}C$	$^{30}Si/^{28}Si$	$^{44}Ca/^{40}Ca$	$^{66}Zn/^{64}Zn$	$^{130}Te/^{122}Te$
$^{15}N/^{14}N$	$^{33}S/^{32}S$	$^{53}Cr/^{52}Cr$	$^{82}Se/^{76}Se$	$^{205}Tl/^{203}Tl$
$^{17}O/^{16}O$	$^{34}S/^{32}S$	$^{54}Cr/^{52}Cr$	$^{88}Sr/^{86}Sr$	

^{238}U and ^{235}U compose a pair when U isotopes are treated as stable isotopes.[1]

Note 4: In the mass spectrometric analysis of a gas, the quantity *R* commonly is used for the ratio of the number of ions collected by Faraday-cup collectors. For example, for analysis of CO_2, the ratio of the number of ions on the *m*/*z*-45 collector to the number on the *m*/*z*-44 collector is:

$$^{45}R_P = {}^{45/44}R_P = \frac{N\left(^{13}C^{16}O^{16}O\right)_P + N\left(^{12}C^{16}O^{17}O\right)_P}{N\left(^{12}C^{16}O^{16}O\right)_P}$$

where $N(^{13}C^{16}O^{16}O)$, $N(^{12}C^{16}C^{17}O)$, and $N(^{12}C^{16}O^{16}O)$ are, respectively, the number of $^{13}C^{16}O^{16}O^+$, $^{12}C^{16}C^{17}O^+$, and $^{12}C^{16}O^{16}O^+$ ions collected.

Note 5: The atomic quantity isotope ratio, $R(^iE/\,^jE)_P$, is equal to the corresponding macroscopic quantity *isotope-amount ratio*, $r(^iE/^jE)_P$, as shown by the relation:

$$R\left(^iE/^jE\right)_P = \frac{N\left(^iE\right)_P}{N\left(^jE\right)_P} = \frac{\dfrac{N\left(^iE\right)_P}{N_A}}{\dfrac{N\left(^jE\right)_P}{N_A}} = \frac{n\left(^iE\right)_P}{n\left(^jE\right)_P} = r\left(^iE/^jE\right)_P$$

where N_A is the *Avogadro constant* and where $n(^iE)_P$ and $n(^jE)_P$ are the amounts of the two isotopes ^iE and ^jE of chemical element E in substance P.

Note 6: When there can be no confusion about ^iE and ^jE, such as in the case for elements with two isotopes, the quantity *R* commonly is used with the convention that the isotope referred to is the heavier stable isotope. In a manner similar to that of $r(^{13}C)_P$, $R(^{13}C)_P$ stands for $N(^{13}C)_P/N(^{12}C)_P$. $R(^iE)_P$ is sometimes shortened to ^iR.

Note 7: The unabbreviated format, $R(^iE/\,^jE)_P$, is preferred for elements with more than two stable isotopes to prevent confusion, as with $R(^{57}Fe)_P$, which could be either $R(^{57}Fe/^{56}Fe)_P$ or $R(^{57}Fe/^{54}Fe)_P$.

Note 8: Although isotope ratio is a *dimensionless quantity*, the units µmol/mol and mmol/mol should not be used for *R*.

Note 9: The forms using a comma as a record separator, $R(^{i,j}E)_P$ or $R(^iE,^jE)_P$, instead of a forward slash, also have been used in the literature. They are equivalent to, but not preferred over, the notation given above. The form $R_{i,j}$ also has been used in the literature.

Examples: (a) $R(^{33}S/^{32}S)_P = 0.008\,03$; $R(^{33}S/^{32}S)_P = 0.803$ %; $R(^{46}Ca/^{40}Ca)_P = 43.2$ ppm.
(b) $R(^{13}C)_{Li_2CO_3} = 9.5 \times 10^{-3}$.

isotope scale

An ordered set of *isotope-delta* values or *isotopic abundance* values used in ranking, according to magnitude.[5]

Note 1: A scale of isotope-delta values must be normalized (anchored) by a substance that can be measured by other laboratories, and an *international measurement standard* is preferred.

Note 2: It is preferable that isotope scales be normalized with two *international measurement standards*, e.g., consider the VSMOW–SLAP scale and the VPDB–LSVEC scale.

Example: The hydrogen isotopic composition of the brine expressed as a delta value on the VSMOW–SLAP scale is $\delta^2H_{VSMOW-SLAP} = -5$ ‰.

isotope-amount fraction, *x*

atom fraction

isotopic abundance

stable isotope-amount fraction

Amount of a specified isotope in a mixture divided by the amount of all atoms of all isotopes of an element in the mixture. The isotope-amount fraction, $x(^iE)_P$, is specified for isotope ^iE of element E in specimen P by the relation:

$$x\left(^iE\right)_P = \frac{n\left(^iE\right)_P}{\sum n(E)_P} = \frac{\dfrac{N\left(^iE\right)_P}{N_A}}{\dfrac{\sum N(E)_P}{N_A}}$$

where the summation includes all isotopes of element E, N_P is the number of entities, and N_A is the *Avogadro constant*.

Note 1: The sum of the isotope-amount fractions of all isotopes of an element is 1.

Note 2: The isotope-amount fraction is a macroscopic quantity, and it is equal to the atomic quantity *isotope-number fraction*, X_P.

Note 3: There is no preference between isotope-amount fraction, isotopic abundance, and atom fraction. The choice commonly is based upon historical use and depends upon the scientific discipline.

Examples: (a) The ^{13}C amount fraction in specimen P is $x(^{13}C)_P = 0.0095 = 9.5 \times 10^{-3} = 0.95$ %.
(b) $x(^{13}C)_{aragonite} = 0.95$ % = 9.5 mmol/mol

See *atom fraction*, Note 2 of *mole fraction*, and Fig. 1.
See also *absolute isotopic abundance*.

isotope-amount ratio, *r*

stable isotope-amount ratio

Amount of an isotope divided by the amount of another isotope of the element in the same system. The isotope-amount ratio, $r(^iE/\,^jE)_P$, is defined by the relation:

$$r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}} = \frac{n({}^{i}\mathrm{E})_{\mathrm{P}}}{n({}^{j}\mathrm{E})_{\mathrm{P}}}$$

where $n({}^{i}\mathrm{E})_{\mathrm{P}}$ and $n({}^{j}\mathrm{E})_{\mathrm{P}}$ are the *amounts* of the two isotopes, ${}^{i}\mathrm{E}$ and ${}^{j}\mathrm{E}$, of chemical element E in substance P. Superscripts *i* and *j* should denote mass numbers of a heavier (higher atomic mass) and a lighter (lower atomic mass) isotope, respectively. The primary exceptions are reporting of He isotope ratios and isotope ratios of extra-terrestrial materials in cosmochemistry.

Note 1: When there can be no confusion about ${}^{i}\mathrm{E}$ and ${}^{j}\mathrm{E}$, such as in the case for elements with two isotopes, the quantity *r* commonly is used with the convention that the isotope referred to is the heavier stable isotope. Thus, $r({}^{13}\mathrm{C})_{\mathrm{P}}$ stands for $n({}^{13}\mathrm{C})_{\mathrm{P}}/n({}^{12}\mathrm{C})_{\mathrm{P}}$. The quantity $r({}^{i}\mathrm{E})_{\mathrm{P}}$ is sometimes shortened to ${}^{i}r$.

Note 2: The unabbreviated format, $r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}}$, is preferred for elements with more than two stable isotopes when there can be confusion about ${}^{i}\mathrm{E}$ and ${}^{j}\mathrm{E}$.

Note 3: The macroscopic quantity isotope-amount ratio, $r({}^{i}\mathrm{E}/\ {}^{j}\mathrm{E})_{\mathrm{P}}$, is equal to the corresponding atomic quantity *isotope ratio*, $R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}}$, as shown by the relation:

$$r({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}} = \frac{n({}^{i}\mathrm{E})_{\mathrm{P}}}{n({}^{j}\mathrm{E})_{\mathrm{P}}} = \frac{\frac{N({}^{i}\mathrm{E})_{\mathrm{P}}}{N_{\mathrm{A}}}}{\frac{N({}^{j}\mathrm{E})_{\mathrm{P}}}{N_{\mathrm{A}}}} = \frac{N({}^{i}\mathrm{E})_{\mathrm{P}}}{N({}^{j}\mathrm{E})_{\mathrm{P}}} = R({}^{i}\mathrm{E}/{}^{j}\mathrm{E})_{\mathrm{P}}$$

where N_{A} is the *Avogadro constant* and where $N({}^{i}\mathrm{E})_{\mathrm{P}}$ and $N({}^{j}\mathrm{E})_{\mathrm{P}}$ are the numbers of the two isotopes, ${}^{i}\mathrm{E}$ and ${}^{j}\mathrm{E}$, of chemical element E in substance P.

Note 4: Isotope-amount ratio is a *dimensionless quantity*, and the units of mmol/mol and μmol/mol (and similar units) are permissible.

Note 5: The forms using a comma as a record separator, $r({}^{i,}\ {}^{j}\mathrm{E})_{\mathrm{P}}$ or $r({}^{i}\mathrm{E},{}^{j}\mathrm{E})_{\mathrm{P}}$, instead of a forward slash, have also been used in the literature. They are equivalent to, but not preferred over, the notation given above.

Examples: $r({}^{33}\mathrm{S}/{}^{32}\mathrm{S})_{\mathrm{P}}=0.00803$, $r({}^{2}\mathrm{H})_{\mathrm{methane}}=6.04\times10^{-3}$, $r({}^{46}\mathrm{Ca}/{}^{40}\mathrm{Ca})_{\mathrm{P}}=43.2\times10^{-6}$, and $r({}^{46/40}\mathrm{Ca})_{\mathrm{calcite}}=r({}^{46}\mathrm{Ca}/{}^{40}\mathrm{Ca})_{\mathrm{calcite}}=43.2$ μmol/mol. The form 4.32×10^{-5} is preferred to 43.2×10^{-6}.

See also Fig. 1.

isotope-number fraction, *X*

stable isotope-number fraction

Number of atoms of a specified isotope in a mixture divided by the total number of atoms of all isotopes of an element in the mixture. The isotope-number fraction, *X*, is defined for isotope ${}^{i}\mathrm{E}$ in specimen P as

$$X({}^{i}\mathrm{E})_{\mathrm{P}} = \frac{N({}^{i}\mathrm{E})_{\mathrm{P}}}{\sum N(\mathrm{E})_{\mathrm{P}}}$$

where the summation includes all isotopes of element E. The choice of uppercase *X* for the *number fraction* is in agreement with the German standard.[23,24]

Note 1: 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 ${}^{15}\mathrm{N}$, and should not be confused with 'isotope-number' as in *isotope-number fraction*, *X*, or *isotope-number ratio*, *R*, which is also known as the *isotope ratio*.

Note 2: The sum of the isotope-number fractions of all isotopes of an element is 1.

Note 3: The units mol/mol, mmol/mol, g/g, or similar units should not be used for *isotope-number fraction* although isotope-number fraction is a *dimensionless quantity* because neither dimensions of amount of substance nor mass appear in *N*. Adding extraneous units of mol/mol or g/g to quantities whose dimension never included amount of substance or mass is confusing and therefore should not be done.

Note 4: The atomic quantity isotope-number fraction, $X({}^{i}\mathrm{E})_{\mathrm{P}}$, is equal to the corresponding macroscopic quantity *isotope-amount fraction*, $x({}^{i}\mathrm{E})_{\mathrm{P}}$.

Examples: (a) $X({}^{13}\mathrm{C})_{\mathrm{methane}}=0.993$ %, $X({}^{15}\mathrm{N})_{\mathrm{P}}=0.00485$, and $X({}^{17}\mathrm{O})_{\mathrm{P}}=8.42$ ppm.
(b) $X({}^{2}\mathrm{H})_{\mathrm{methane}}=2.5\times10^{-3}$.

See also Note 3 of *isotope-amount fraction*, *number fraction*, and Fig. 1.

isotope-number ratio, *R*

See *isotope ratio*. See also Fig. 1.

isotope-ratio calibration

A two-step operation in which the first step is to establish a relation between an isotope-ratio value of an *international measurement standard* (or a *certified isotopic reference material* or gravimetric mixtures of isotopes) and values of ion currents or counts of ions provided from an isotope-ratio mass spectrometer (or other measuring device or system).[5] The second step is to use this information to establish the isotope ratio of an unknown sample, using ion-current measurements or counts of ions provided by the mass spectrometer. Measurement results should be provided with uncertainties throughout this two-step process.

Note 1: A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty.

Note 2: Calibration should not be confused with adjustment of a measuring system, often mistakenly called 'self-calibration', nor with verification of calibration. The first step alone in the above definition often is mistakenly perceived as being calibration.

Note 3: Factors that enter into an assessment of calibrated isotope-ratio measurements by IUPAC's Commission on Isotopic Abundances and Atomic Weights are discussed by Wieser and Berglund.[25]

isotopic abundance, x
See *isotope-amount fraction* and *atom fraction*. See also *absolute isotopic abundance*.

isotopic composition
Term indicating that qualitative or generalized, non-numerical isotopic information has been gathered.

Note 1: Although this is not an SI quantity, this term often is followed by SI-quantity values.
Note 2: Use such as 'Sample Q is not homogeneous; its copper-65 isotopic composition varies by 0.5 %' should be avoided because the reader does not know if this is a variation of isotope-amount fraction or of isotope-amount ratio, each of which would have a different value.
Note 3: The term 'absolute' isotopic composition' should be avoided; instead use '*absolute' isotopic abundance*. IUPAC's Commission on Isotopic Abundances and Atomic Weights regularly publishes a 'Table of Isotopic Compositions of the Elements' that provides evaluated isotopic abundance data.[8]
Example: The isotopic composition of total dissolved sulfur in Lake Audubon is highly variable, $\delta^{34}S_{VCDT}$= −12.2 to +6.55 ‰.

isotopic difference, Δ
The difference between the *isotope deltas* of two substances. The isotopic difference between the two substances P and Q is given by the relation:

$$\Delta^{i}E_{P/Q} = \Delta^{i}E_{P,Q,reference} = \Delta^{i/j}E_{P,Q,reference} = \delta^{i/j}E_{P/reference} - \delta^{i/j}E_{Q/reference}$$

where $\delta^{i/j}E_{P/reference}$ is the *delta* value of substance P relative to a reference for heavier isotope ^{i}E and lighter isotope ^{j}E of element E. The quantity $\delta^{i/j}E_{Q/reference}$ is defined similarly for substance Q. The reference should be clearly specified; using the form $\Delta^{i}E_{P,Q,reference}$ clearly identifies the reference.

Note 1: The quantity $\Delta^{i}E_{P/Q}$ should be defined by authors to avoid confusion because this symbol can also be used to express *mass-independent isotopic variation* and this quantity has been defined in different ways in the literature.[26]
Note 2: The value of $\Delta^{i}E_{P/Q}$ is dependent upon the reference and can vary greatly depending upon the isotopic composition of the reference (e.g., for hydrogen isotopes).
Note 3: This quantity is not proportional to *isotope-amount fraction*.
Note 4: Closely related to $\Delta^{i}E_{P/Q}$ are the *isotopic fractionation* $\varepsilon^{i}E_{P/Q}$ and the *isotopic fractionation factor* $\alpha^{i}E_{P/Q}$, which are related by the expressions:

$$\Delta^{i}E_{P,Q,reference} \approx \varepsilon^{i}E_{P/Q} = \alpha^{i}E_{P/Q} - 1 = \frac{\delta^{i}E_{P/reference}+1}{\delta^{i}E_{Q/reference}+1} - 1$$

and

$$\Delta^{i}E_{P/Q} = \Delta^{i}E_{P,Q,reference} = \delta^{i}E_{P} - \delta^{i}E_{Q} \approx \ln \alpha^{i}E_{P/Q}$$

The quantities $\alpha^{i}E_{P/Q}$ and $\varepsilon^{i}E_{P/Q}$ are preferred to $\Delta^{i}E_{P,Q,reference}$ because the former two quantities are independent of the reference. Note the approximation symbols in these two equations. In some cases, the approximation can be poor.
Note 5: The forms using a comma as a record separator of isotopes, $\Delta(^{i,j}E)_{P,Q,reference}$ and $\Delta(^{i}E,^{j}E)_{P,Q,reference}$, have been used in the literature. They are equivalent to, but not preferred over, the notation given above.
Example: The stable carbon isotopic difference between the two specimens P and Q is $\Delta^{13}C_{P/Q}$=+8.55 × 10^{-3}=+8.55 ‰.
See also *delta over baseline* and *relative difference of isotope ratios*.

isotopic fractionation, ε
The quantity $\varepsilon=\alpha-1$, where α is the *isotopic fractionation factor*. The isotopic fractionation, $\varepsilon_{P/Q}$, is useful in discussing distributions of isotopes between substances, and it is defined for substances P and Q by the relations:

$$\varepsilon(^{i}E/^{j}E)_{P/Q} = \varepsilon(^{i}E,^{j}E)_{P,Q} = \alpha_{P/Q} - 1 = \alpha(^{i}E/^{j}E)_{P/Q} - 1$$

$$\varepsilon^{i}E_{P/Q} = \varepsilon^{i/j}E_{P/Q} = \varepsilon(^{i}E/^{j}E)_{P/Q} = \alpha^{i}E_{P/Q} - 1 = \alpha^{i/j}E_{P/Q} - 1$$

where α is the *isotopic fractionation factor* of heavier isotope ^{i}E and lighter isotope ^{j}E of element E between substances P and Q.

Note 1: In the literature, the quantity ε (or an equivalent quantity defined as $\alpha - 1$) has been called the 'isotopic enrichment factor', 'discrimination', 'isotopic discrimination', and 'isotopic fractionation constant'. The IUPAC Gold Book[11] has another definition for 'isotopic enrichment factor'. Of these names, 'isotopic fractionation' is preferred. The name 'isotopic fractionation' should not be shortened to 'fractionation' because it is important to distinguish between chemical fractionation and isotopic fractionation.
Note 2: When it is clear from the context, $\varepsilon(^{i}E/^{j}E)_{P/Q}$ may be shortened to $\varepsilon^{i}E_{P/Q}$ or $\varepsilon_{P/Q}$, as appropriate. When the element has more than two stable isotopes, $\varepsilon(^{i}E/^{j}E)_{P/Q}$ or $\varepsilon^{i/j}E_{P/Q}$ is preferred.
Note 3: The isotopic fractionation is a *dimensionless quantity* (SI unit 1) and because values of ε commonly are small, they regularly are expressed with the symbol ‰, which is 10^{-3}.
Note 4: The quantity $\varepsilon_{P/Q}$ has been defined in the literature as:

$$\varepsilon_{P/Q} = 1000(\alpha_{P/Q} - 1)$$

This equation is incorrect. The factor 1000 is an extraneous numerical factor and should be deleted to give a coherent equation.[4]
Note 5: The quantities isotopic fractionation (ε), *isotopic fractionation factor* (α), and *isotope delta* (δ), of sample P and a reference, and a sample Q and the reference are related by:

$$\varepsilon^{i}\mathrm{E}_{\mathrm{P/Q}} = \alpha^{i}\mathrm{E}_{\mathrm{P/Q}} - 1 = \frac{\delta^{i}\mathrm{E}_{\mathrm{P/reference}} + 1}{\delta^{i}\mathrm{E}_{\mathrm{Q/reference}} + 1} - 1$$

If the reference is an *international measurement standard*, 'reference' can be updated as appropriate.

Note 6: The quantity ε, like the quantity α from which it is derived, can refer to (1) an 'apparent' or 'net' distribution of isotopes between phases in complex biogeochemical systems having unknown reactions or pathways (thus, unknown whether it is a kinetic or an equilibrium process), (2) a thermodynamic (equilibrium) process, or (3) a kinetic process. If $\alpha^{i}\mathrm{E}_{\mathrm{P/Q}}$ is the *isotopic fractionation factor* of an equilibrium process, $\varepsilon^{i}\mathrm{E}_{\mathrm{P/Q}}$ is the equilibrium isotopic fractionation, most commonly with the isotopic exchange reaction written as:

$$^{j}\mathrm{P} + {}^{i}\mathrm{Q} \rightleftharpoons {}^{i}\mathrm{P} + {}^{j}\mathrm{Q}$$

However, the reader should be alert because the exchange reaction written as:

$$^{j}\mathrm{Q} + {}^{i}\mathrm{P} \rightleftharpoons {}^{i}\mathrm{Q} + {}^{j}\mathrm{P}$$

also is found in the literature. Readers need to pay attention to the format used to write the isotopic exchange reaction.

Note 7: If the *isotopic fractionation factor* is that of a kinetic process, the kinetic isotopic fractionation can thus be designated by adding subscript 'kin', as $\varepsilon_{\mathrm{kin}}(^{i}\mathrm{E})_{\mathrm{P/Q}}$. If $\alpha_{\mathrm{kin}}(^{i}\mathrm{E})_{\mathrm{P/Q}}$ is the kinetic isotopic fractionation factor of an irreversible reaction, $\varepsilon_{\mathrm{kin}}(^{i}\mathrm{E})_{\mathrm{P/Q}}$ reflects the difference in isotopic composition of the substrate and the weighted average of all instantaneously formed products. A negative value of $\varepsilon_{\mathrm{kin}}(^{i}\mathrm{E})_{\mathrm{P/Q}}$ indicates that product P is enriched in light isotope $^{j}\mathrm{E}$ and the underlying *isotope effect* is normal. A positive value of $\varepsilon_{\mathrm{kin}}(^{i}\mathrm{E})_{\mathrm{P/Q}}$ indicates that the product P is enriched in the heavy isotope $^{i}\mathrm{E}$ and the *isotope effect* is inverse. Readers should be aware that ε sometimes was defined with the heavy isotope in the denominator, such that a positive ε value corresponds to a normal *isotope effect*.

Examples:

(a) The equilibrium oxygen isotopic fractionation factor between calcite and water, written for the exchange of one atom of oxygen as:

$$^{1}/_{3}\mathrm{CaC}^{16}\mathrm{O}_3 + \mathrm{H}_2{}^{18}\mathrm{O} \rightleftharpoons {}^{1}/_{3}\,\mathrm{CaC}^{18}\mathrm{O}_3 + \mathrm{H}_2{}^{16}\mathrm{O}$$

is $\alpha_{\mathrm{calcite/water}}$. Its value with combined standard uncertainty at 33.7 °C is 1.028 49 ± 0.000 13,[27] which can be written 1.028 49(13). The value of $\varepsilon_{\mathrm{calcite/water}}$, which equals 1.028 49(13) – 1, is 0.028 49(13). Thus, the value of $\varepsilon_{\mathrm{calcite/water}}$ at 33.7 °C is 28.49(13) ‰. The following are three examples of data reporting:

$$\begin{aligned}\varepsilon^{18}\mathrm{O}_{\mathrm{CaCO_3/H_2O}} &= \varepsilon\left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{\mathrm{calcite/water}}\\ &= \varepsilon_{\mathrm{calcite/water}}\\ &= 28.49(13)\ ‰ \text{ at } 33.7\ ^{\circ}\mathrm{C}\\ \varepsilon_{\mathrm{calcite/water}} &= 28.49(13)\times 10^{-3} \text{ at } 33.7\ ^{\circ}\mathrm{C}\end{aligned}$$

$$\begin{aligned}10^{3}\varepsilon\left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{\mathrm{calcite/H_2O}} &= 10^{3}\varepsilon\left(^{18/16}\mathrm{O}\right)_{\mathrm{calcite/H_2O}}\\ &= 28.49(13) \text{ at } 33.7\ ^{\circ}\mathrm{C}\end{aligned}$$

The first form with the symbol ‰ (or % or ppm) is suggested because ε is a quantity of dimension 1. The value $28.49(13)\times 10^{-3}$ usually is written $2.849(13)\times 10^{-2}$.

(b) The kinetic isotopic fractionation for treatment of aragonite at 25 °C with 100 % $\mathrm{H_3PO_4}$ is $\alpha_{\mathrm{kin}}(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{CO_2/aragonite}} = 1.010\ 63$,[28] and it can be expressed by $\varepsilon_{\mathrm{kin}}(^{18}\mathrm{O}/^{16}\mathrm{O}$, 25 °C, $\mathrm{H_3PO_4})_{\mathrm{CO_2/aragonite}} = 10.63$ ‰.

(c) In a biological controlled diet experiment, the net carbon isotopic fractionation between consumer food and consumer blood plasma is expressed by $\varepsilon_{\mathrm{net}}(^{13}\mathrm{C})_{\mathrm{food/plasma}} = 9.1$ ‰.

See also *isotopic difference*, *isotopic fractionation factor*, and *isotope effect*.

isotopic fractionation factor, α

Ratio of $R(^{i}\mathrm{E}/\,^{j}\mathrm{E})_{\mathrm{P}}$ and $R(^{i}\mathrm{E}/\,^{j}\mathrm{E})_{\mathrm{Q}}$, where R is the *isotope ratio* of heavier isotope $^{i}\mathrm{E}$ and lighter isotope $^{j}\mathrm{E}$ of element E in substances P and Q. In many biogeochemical systems, the changes in isotopic composition between reactant and product can be a complex function of multiple reaction pathways, branching pathways, fractional yields of various products, and quite frequently of unknown reactions or pathways. It frequently is unknown whether an isotopic fractionation between two substances is an equilibrium or a kinetic isotopic fractionation. One cannot know which it is without a full understanding of the reaction network that connects the two, and often this is impossible. Advances in the understanding of such systems are made by measuring the isotopic compositions of two or more substances and reporting a 'net' or 'apparent' distribution (or fractionation) of isotopes between them.[29] The distribution of isotopes between substances P and Q is given by the isotopic fractionation factor, $\alpha^{i}\mathrm{E}_{\mathrm{P/Q}}$, which is defined by the relation:

$$\begin{aligned}\alpha^{i}\mathrm{E}_{\mathrm{P/Q}} = \alpha^{i/j}\mathrm{E}_{\mathrm{P/Q}} = \alpha\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{P,Q}} &= \frac{N\left(^{i}\mathrm{E}\right)_{\mathrm{P}}\ /N\left(^{j}\mathrm{E}\right)_{\mathrm{P}}}{N\left(^{i}\mathrm{E}\right)_{\mathrm{Q}}\ /N\left(^{j}\mathrm{E}\right)_{\mathrm{Q}}}\\ &= \frac{R\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{P}}}{R\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{Q}}}\end{aligned}$$

where N is the number of isotopes and R is the *isotope ratio* of heavier isotope $^{i}\mathrm{E}$ and lighter isotope $^{j}\mathrm{E}$ of element E.

Note 1: The name 'isotopic fractionation factor' should not be shortened to 'fractionation factor' because it is important to distinguish between chemical fractionation factor and isotopic fractionation factor.

Note 2: One also can define $\alpha^{i}E_{P/Q}$ using isotope-amount ratios or isotope amounts.

Note 3: When it is clear from the context, $\alpha^{i/j}E_{P/Q}$ may be shortened to $\alpha^{i}E_{P/Q}$ or $\alpha_{P/Q}$, as appropriate.

Note 4: The isotopic fractionation factor is a *dimensionless quantity* (SI unit 1).

Note 5: The isotopic fractionation factor is related to the quantity δ by the relation:

$$\alpha^{i}E_{P/Q} = \frac{\delta^{i}E_{P/\mathrm{reference}} + 1}{\delta^{i}E_{Q/\mathrm{reference}} + 1}$$

where $\delta^{i}E_{P/\mathrm{reference}}$ is the *relative difference of isotope ratios* of sample P and a reference and the same for Q. If the reference is an *international measurement standard*, 'reference' can be updated accordingly.

Note 6: In well-constrained reactions, isotopic fractionation factors may be linked to the causative *isotope effects* and can be classified as 'equilibrium' or 'kinetic'. For a system with two substances or phases, P and Q, in chemical and isotopic equilibrium and for the exchange of one atom between Q and P with heavier isotope ^{i}E and lighter isotope ^{j}E of chemical element E according to:

$$Q(^{i}E) + P(^{j}E) \rightleftharpoons Q(^{j}E) + P(^{i}E)$$

the distribution of isotopes between Q and P is given by the isotopic fractionation factor, $\alpha^{i/j}E_{P/Q}$. The equilibrium isotopic fractionation factor is exactly the inverse of the equilibrium *isotope effect* when the reaction is written in the same direction.

Note 7: The kinetic isotopic fractionation factor of the reaction of product P formed irreversibly from reactant Q is $\alpha_{\mathrm{kin}}(^{i}E/^{j}E)_{P/Q}$, where the subscript 'kin' indicates a kinetic process; it is expressed by the relation:

$$\alpha_{\mathrm{kin}}(^{i}E/^{j}E)_{P/Q} = \frac{R_{\mathrm{instantaneous}}(^{i}E/^{j}E)_{P}}{R(^{i}E/^{j}E)_{Q}} = \frac{R_{\mathrm{reacting}}(^{i}E/^{j}E)_{Q}}{R(^{i}E/^{j}E)_{Q}}$$

where $R_{\mathrm{instantaneous}}(^{i}E/\,^{j}E)_{P}$ is the corresponding *isotope ratio* of the weighted average of all reaction products that are being formed in an infinitesimally short time. $R_{\mathrm{reacting}}(^{i}E/\,^{j}E)_{Q}$ is the *isotope ratio* of reactant molecules that are consumed through reaction in this short time, and $R(^{i}E/\,^{i}E)_{Q}$ is the *isotope ratio* of the remaining reactant. This kinetic isotopic fractionation factor differs from a kinetic *isotope effect* in that kinetic isotope effects are position-specific, whereas isotopic fractionation factors are derived from isotope ratios of reacting molecules and express average effects. Taking into account non-reacting positions and intramolecular competition, it is possible to estimate kinetic *isotope effects* from kinetic isotopic fractionation factors.[21] When it is clear from the context, $\alpha_{\mathrm{kin}}(^{i}E/^{j}E)_{P/Q}$ may be shortened to $\alpha_{\mathrm{kin}}(^{i}E)_{P/Q}$ or $\alpha_{\mathrm{kin}}(^{i}E)$, as appropriate.

Note 8: The isotopic fractionation factor (and the related *isotopic fractionation*, ε) is therefore a term that can be used to describe several different concepts: two or more phases in chemical and isotopic equilibrium, reactants and products of non-reversible reactions, or the measured distributions of isotopes in poorly understood complex systems. Despite the same name, these quantities have fundamentally different meanings – in particular, the first two quantities are assumed to be invariant while the third is not. Thus, a clear definition by authors is required as to whether α is descriptive of a thermodynamic (equilibrium) isotopic fractionation factor, a kinetic isotopic fractionation factor, or a measured distribution.

Note 9: Position specificity may be indicated by letting P and Q be specific isotopic molecular species. For example, suppose one is investigating the isotopic fractionation between carbonate isotopic species, $(CO_3)^{2-}$, having specified isotopes in a carbonate mineral. For the reaction:

$$Q(^{i}E) + P(^{j}E) \rightleftharpoons Q(^{j}E) + P(^{i}E)$$

if P is $(^{12}C^{16}O_2)O^{2-}$ and Q is $(^{12}C^{16}O^{18}O)O^{2-}$, the reaction for the exchange of one ^{16}O atom and one ^{17}O atom in the carbonate mineral (slightly modified from Eqn. (2) of Schauble *et al.*[30]) is:

$$(^{12}C^{16}O_2{}^{17}O)^{2-} + (^{12}C^{16}O_2{}^{18}O)^{2-} \rightleftharpoons (^{12}C^{16}O_3)^{2-} + (^{12}C^{16}O^{18}O^{17}O)^{2-}$$

for which the extended form of alpha at 25 °C is:

$$\alpha(^{17/16}O,\ 25\ ^{\circ}C)_{(^{12}C^{16}O^{18}O)O^{2-}/(^{12}C^{16}O_2)O^{2-}}$$

or alternatively as

$$\alpha\left[^{17/16}O, (^{12}C^{16}O^{18}O)O^{2-}, (^{12}C^{16}O_2)O^{2-}, 25^{\circ}C\right].$$

Examples: (a) The oxygen isotopic fractionation factor between calcite and water written for the exchange reaction

$$^{1}/_{3}CaC^{16}O_3 + H_2{}^{18}O \rightleftharpoons {}^{1}/_{3}CaC^{18}O_3 + H_2{}^{16}O$$

has been determined as $\alpha^{18}O_{\mathrm{calcite/water}} = \alpha^{18/16}O_{\mathrm{calcite/water}} = 1.028\ 49(13)$,[27] with the uncertainty in parentheses, following the last

significant figure to which it is attributed. The value $\ln \alpha^{18}O_{calcite/water} = 0.028\,09(13)$. These values generally are expressed as $10^3 \ln \alpha$ values, and $10^3 \ln \alpha^{18}O_{calcite/water} = 28.09(13)$.

(b) The kinetic isotopic fractionation for treatment of aragonite at 25 °C with 100 % H_3PO_4, which has a reported $\alpha_{kin}(^{18}O/^{16}O)_{CO_2/aragonite}$ value of 1.010 63,[28] can be expressed by any of the following:

$$\alpha_{kin}\left(^{18}O/^{16}O\right)_{CO_2/aragonite} = 1.010\ 63 \text{ at } 25\ ^\circ C$$

$$\alpha_{kin}\left(^{18/16}O, 25\ ^\circ C,\ H_3PO_4\right)_{CO_2/aragonite} = 1.010\ 63$$

$$\alpha_{kin}\left(^{18/16}O\right)_{CO_2/aragonite} = 1.010\ 63 \text{ at } 25\ ^\circ C$$

See also *isotopic difference*, *isotope effect*, and *isotopic fractionation*.

isotopic reference material

Substance that is sufficiently stable and homogeneous in isotopic composition to serve as a measurement standard in the measurement of *isotope ratios*.[5]

Note 1: 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 for the measurement of $\delta^{13}C$ and $\delta^{15}N$ values (see *relative difference of isotope ratios*).

Note 2: Reference materials with or without assigned *isotope ratios* or delta values can be used for measurement precision control, whereas only reference materials with assigned isotope ratios or delta values can be used for calibration or measurement trueness control.

Note 3: A reference material's delta value can be assigned a *reference delta value* that will have no uncertainty; however, its *isotope ratios* will have uncertainty values.

See also *certified isotopic reference material* and *international measurement standard*.

isotopocules

Molecular species that only differ in either the number or positions of isotopic substitutions. The term is a contraction of 'isotopically substituted molecules'.[31]

Note: The molecular species can be an *isotopologue*, an *isotopomer*, or neither. For example, the three molecular species $^{15}N_2^{16}O$, $^{14}N^{15}N^{16}O$, and $^{15}N^{14}N^{16}O$ are isotopocules, but they are neither *isotopologues* (because the latter two do not differ in isotopic composition) nor *isotopomers* (only the latter two are isotopomers).

isotopologue

isotopolog

Molecular species that differ only in isotopic composition (number of isotopic substitutions) and relative molecular mass, e.g., $C^{35}Cl_4$, $C^{35}Cl_3{}^{37}Cl$, $C^{35}Cl_2{}^{37}Cl_2$.[11] The term isotopologue is a contraction of 'isotopic analogue'.

isotopomers

Molecular species having the same number of each isotopic atom (thus, the same relative molecular mass) but differing in their positions.[11] The term is a contraction of 'isotopic isomer'.

Note: Isotopomers can be either constitutional *isomers* (e.g., $CH_2{}^2HCH{=}O$ and $CH_3C^2H{=}O$ or $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$) or isotopic stereoisomers [e.g., (*R*)- and (*S*)-CH_3CH^2HOH or (*Z*)- and (*E*)-$CH_3CH{=}CH^2H$].[11]

K-factor, *K*

A correction factor for mass discrimination effects in a mass spectrometer that relates an *isotope ratio* and a *measured isotope ratio*.

Note 1: In an isotope-ratio mass spectrometer, the correction factor for mass discrimination, *K*, is equal to the *true isotope ratio*, *R*, divided by the observed *isotope ratio*. The *true isotope ratio* can, in practice, be an isotope ratio of a *certified isotopic reference material* or an IUPAC-recommended value. The factor *K* can then be used to convert the *measured isotope ratio* of a sample P into a true isotope ratio with the relation $R_P = K \times r_{Pm}$, where R_P is the true isotope ratio and r_{Pm} is the measured isotope-amount ratio.

Note 2: In evaluating isotope ratios, IUPAC's Commission on Isotopic Abundances and Atomic Weights includes system linearity, baseline correction, isobaric interferences, instrumental fractionation, and sample preparation in its determination of *K*-factors, where *r* is the published *isotope-amount ratio*.[25]

kind of quantity

Aspect common to mutually comparable quantities.[5]

Note: Examples of kind of quantity include length, energy, electrical charge, and *amount of substance*. Quantities of the same kind within a given system of quantities have the same quantity dimension. However, quantities of the same dimension are not necessarily of the same kind. For example, the *isotope ratio*, *R*, and the *isotope-amount ratio*, *r*, are both quantities of dimension 1, but they are not the same kind of quantity.

mass-independent isotopic variation, Δ

mass-independent (isotopic) fractionation

non-mass-dependent (isotopic) fractionation

Measure of the deviation of the isotopic composition of a sample from a specified mass-dependent isotopic fractionation relation for an element with three or more stable isotopes.

Note 1: The majority of the isotopic variations observed in stable isotope amounts of elements with more than two stable isotopes in terrestrial materials are approximately linearly correlated with differences in isotope masses. For example, classical *isotope effects* generally will produce $\delta^{17/16}$O values that are about one half those of $\delta^{18/16}$O values, $\delta^{34/32}$S values that are about twice those of $\delta^{33/32}$S values, and $\delta^{36/32}$S values that are approximately four times those of $\delta^{33/32}$S values. Such isotopic variations are termed mass-dependent isotopic fractionation because the physical and chemical processes that produce these isotope effects have a strong and direct dependence on isotope mass. Some isotope effects are produced by physical and chemical processes that have strong dependences on parameters other than isotope mass and are termed mass-independent isotope effects. Mass-independent isotopic fractionation has been observed for the elements oxygen,[32,33] sulfur, and mercury. All elements of even atomic number greater than that of oxygen have three or more stable isotopes and have the potential to exhibit non-mass-dependent isotopic fractionation. Mass-independent isotopic fractionation (MIF) has also been referred to as non-mass-dependent fractionation and anomalous fractionation of isotopes of an element. Mass-independent isotope effects can yield large values of Δ. For this reason, Δ has been used to describe situations where mass-independent isotopic fractionation has occurred. How mass-independent effects are defined and expressed for elements is a matter of active discussion and investigation.[33]

Note 2: To avoid confusion, Δ should be defined by authors. The symbol Δ also is used for the quantity *delta over baseline*.

Note 3: The factors of 1000, 10000, and 1000000 are extraneous numerical factors and none of them should appear in any equation used to define Δ^{i}E to ensure that the equation is coherent.[4]

measured isotope ratio

measured *isotope-number ratio*

The *isotope ratio* of an element in a sample obtained as a measurement result by mass spectrometric or chemical measurement procedures or from standard reference data.[5]

Note: A measurement procedure is sometimes called a standard operating procedure, abbreviated SOP.

See also *true isotope ratio*.

mole fraction, *x*

amount-of-substance fraction

amount fraction

Amount of a constituent divided by the total amount of all constituents in a mixture.[4,11,20]

Note 1: When the defined constituents are isotopes of an element, the mole fraction is the amount of a defined atom (isotope) in a mixture divided by the amount of all isotopes of the same element in the mixture. This macroscopic quantity is equal to the atomic quantity *isotope fraction*, *X*.

Note 2: Mole fraction is a *dimensionless quantity*, and the units of mmol/mol and μmol/mol (and similar units) are permissible.

See also *atom fraction*, *isotope-amount fraction*, and Fig. 1.

mole ratio, *r*

amount-of-substance ratio

amount ratio

Amount of a specified constituent (usually molecules, atoms, or ions) divided by the amount of another constituent in the same system.[4,23,34]

Note 1: When the defined constituents are isotopes of an element, the mole ratio is the amount of the specified atom (isotope) in a mixture divided by the amount of another specified isotope of the same element in the mixture. This macroscopic quantity is equal to the atomic quantity *isotope ratio*, *R*.

Note 2: Mole ratio is a *dimensionless quantity*, and the units of mmol/mol and μmol/mol (and similar units) are permissible.

See *isotope-amount ratio*.

non-mass-dependent (isotopic) fractionation

See *mass-independent isotopic variation*.

number fraction, *X*

Number of specified entities of a mixture divided by the total *number of entities* in the mixture. The number fraction is numerically equal to the *mole fraction*: the amount of a constituent divided by the total amount of all constituents in the mixture.

Note 1: When the specified entity is an isotope of an element, the number fraction is the *isotope-number fraction* or the *stable isotope-number fraction*, and this microscopic (atomic) quantity is equal to the macroscopic quantities *atom fraction* and *isotopic abundance*.

Note 2: The sum of the *isotope-number fractions* of all isotopes of an element is 1.

Note 3: Although number fraction is a *dimensionless quantity*, the units μmol/mol or mmol/mol (or any such units) should not be used for *X*.

Note 4: The symbol *X* for number fraction is in accord with the German standard.[24]

See also *isotope-number fraction*.

number of entities, *N*

Integer number obtained by counting of entities, which are usually molecules, atoms, ions, or formula units.[4,5]

Note 1: 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 all systems of quantities.[4,5]

Note 2: The microscopic (atomic) quantity N is related to the macroscopic quantity *amount of substance*, n, through the scaling factor N_A, the *Avogadro constant*,[14] as shown in Fig. 1 and discussed in the section on *isotope-amount fraction*.

Note 3: Number of entities is a *dimensionless quantity* and the *kind of quantity* is not the same as mass fraction or *isotope-amount fraction* even though they have the same dimension.[5]

Note 4: Measurement of the numbers of isotopes, e.g. of ^{6}Li and ^{7}Li, or of *isotopologues*, e.g. $^{28}SiF_4$ and $^{30}SiF_4$, or of the ratio of the numbers of isotopes or isotopologues, is the basis of isotope-ratio mass spectrometry.

See also Fig. 1 and *amount of substance*.

number ratio, R

Number obtained by counting a specified entity (usually molecules, atoms, or ions) divided by the number of another specified entity of the same kind in the same system.[23]

Note 1: When the specified entities are isotopes of an element, the microscopic (atomic) quantity number ratio is the *isotope-number ratio*, also termed the *stable isotope ratio* and *isotope ratio*, and it is numerically equal to the macroscopic quantity *isotope-amount ratio*.

Note 2: Although number ratio is a *dimensionless quantity*, the units µmol/mol or mmol/mol (or any such units) should not be used for R.

Example: The atomic ratio of carbon to nitrogen in a molecule of acetanilide is $R(\mathrm{C/N})_{\mathrm{acetanilide}} = N(\mathrm{C})_{\mathrm{acetanilide}}/N(\mathrm{N})_{\mathrm{acetanilide}} = 8$, where N is the *number of entities*.

See also *isotope ratio*.

part per million, ppm

One part in one million parts, with value 10^{-6}.

Note 1: The unit part per million is not an SI unit, but it commonly is used.[4]

Note 2: This unit is dimensionless. It does not imply any *quantity*, and the value associated with the symbol may be negative or positive.

Note 3: Units and their symbols should not be modified to provide further information about the quantity, as for instance ppmv, where v indicates volume; see section 5.3.2 of the 8th SI brochure[4] and Cvitaš.[35] All ppm are equal in the same sense as all meters are equal irrespective of whether we express heights, depths, lengths, widths, diameters, etc. A 'p.p.m.v. ' or 'ppmv' is not an SI symbol or even a symbol to be used with the SI.

Note 4: The symbol ppm may be replaced by µmol/mol for expressing the ratio of two quantities of the same kind, the *kind of quantity* being *amount of substance*; for example, it may be used with *mole fraction*, *isotope-amount fraction*, *isotope-amount ratio*, and *isotopic abundance*. The units µmol/mol or similar should not be used with the quantities *isotopic fractionation factor*, *isotope ratio*, *isotopic fractionation*, nor with *relative difference of isotope ratios*.

Note 5: The symbol ppm may be replaced by µg/g for expressing the ratio of two quantities of the same kind, where the *kind of quantity* is mass.

Examples:
(a) The *relative difference of gas ratios* of sample P relative to standard AIR04 is $\delta(O_2/N_2)_{P/AIR04} = -50$ ppm $= -50$ µmol/mol.
(b) The mass-independent ^{17}O enrichment of specimen P expressed by its Δ^{17}O value $= 88 \times 10^{-6} = 88$ ppm.
(c) For a specimen of chromium(III) nitrate, $\delta^{54/52}\mathrm{Cr}_{\mathrm{Cr(NO_3)_3/SRM979}} = -9.8 \times 10^{-6} = -9.8$ ppm.
(d) The molybdenum *isotopic fractionation* between substances P and Q is $\varepsilon^{98/95}\mathrm{Mo}_{\mathrm{P/Q}} = -75 \times 10^{-6} = -75$ ppm.

See also Note 4 of *per mil*.

part per ten thousand, pptt

One part in ten thousand parts, with value 10^{-4}.

Note 1: The unit pptt is not an SI unit, but is used in some specialized scientific fields. When used, pptt should be explained in the text or a footnote.

Note 2: This unit is dimensionless. It does not imply any *quantity*, and the value associated with the symbol may be negative or positive.

Example: For a zinc-bearing specimen and a reference ZnREF, $\delta^{66/64}\mathrm{Zn}_{\mathrm{ZnREF}} = -5 \times 10^{-4} = -5$ pptt.

See also Note 4 of *per mil*.

percent, %

per cent

One part in one hundred parts, with value 10^{-2}.

Note 1: Units and their symbols should not be modified to provide further information about the quantity, as for instance %%, %v, etc; see section 5.3.2 of the 8th SI brochure[4] and Cvitaš.[35] All percents are equal in the same sense as all meters are equal, irrespective of whether we express heights, depths, lengths, widths, diameters, etc.

Note 2: The symbol % may be replaced by cg/g, e.g., for expressing the ratio of two quantities of the same kind, where the *kind of quantity* is mass.

Note 3: The symbol % may be replaced by cmol/mol, e.g., for expressing the ratio of two quantities of the same kind, the *kind of quantity* being amount of substance; for example, it may be used for *mole fraction*, *isotope-amount fraction*, *isotope-amount ratio*, and *isotopic abundance*. The units cmol/mol or similar units should not be used with the quantities *isotopic fractionation factor*, *isotope ratio*, *isotopic fractionation*, nor with *relative difference of isotope ratios*.

Example: The ^{13}C fraction of sample P is $x(^{13}\mathrm{C}) = 1.5 \times 10^{-2} = 1.5$ %.

See also Notes 2 and 4 of *per mil*.

per meg

One part in one million parts, with value 10^{-6}.

Note 1: The unit per meg is not an SI unit, but it is used in some specialized scientific fields. When used, per meg should be explained in the text or a footnote.

Note 2: This unit is dimensionless. It does not imply any *quantity*, and the value associated with the symbol may be negative or positive.

Note 3: The value of per meg and ppm are both 10^{-6}; therefore, ppm can be substituted for per meg.

Note 4: The symbol per meg may be replaced by μmol/mol for expressing the ratio of two quantities of the same kind, the *kind of quantity* being amount of substance; for example, it may be used for *mole fraction*, *isotope-amount fraction*, *isotope-amount ratio*, and *isotopic abundance*. The units μmol/mol or similar units should not be used with the quantities *relative difference of isotope ratios*, *relative difference of gas ratios*, *isotopic fractionation factor*, *isotope ratio*, nor with *isotopic fractionation*.

Examples:
(a) The *relative difference of gas ratios* of a sample relative to standard AIR04 is $\delta(O_2/N_2)_{AIR04} = -50$ per meg $= -50$ ppm.
(b) The approximate preindustrial mole fraction of CO_2 in the Earth's atmosphere is $x(CO_2)_{AIR} = 275$ per meg $= 275$ ppm $= 275\ \mu mol/mol = 275 \times 10^{-6} = 0.275$ ‰ $= 0.0275$ %.
(c) The mass-independent ^{17}O enrichment of specimen P expressed by the value of $\Delta^{17}O = +88$ per meg $= +88 \times 10^{-6} = 88$ ppm.
(d) For a specimen of chromium(III) boride, $\delta^{54/52}Cr_{CrB/SRM979} = -9.8$ per meg $= -9.8 \times 10^{-6} = -9.8$ ppm.
(e) The molybdenum *isotopic fractionation* between substances P and Q is $\varepsilon^{98/95}Mo_{P/Q} = -75$ per meg $= -75 \times 10^{-6} = -75$ ppm $= -0.075$ ‰.

per mil, ‰
per mill
per mille
permil
permille

One part in one thousand parts, with value 10^{-3}.

Note 1: The unit per mil is not an SI unit, but it commonly is used.

Note 2: The unit is dimensionless. It does not imply any *quantity*, and the value associated with the symbol may be negative or positive.

Note 3: Units and their symbols should not be modified, as for instance to provide further information about the quantity ‰‰, ‰v, etc; see section 5.3.2 of the 8th SI brochure[4] and Cvitaš.[35] All per mils are equal in the same sense as all meters are equal irrespective of whether we express heights, depths, lengths, widths, diameters, etc.

Note 4: The symbol may be used in expressing the ratio of two quantities where the *kind of quantity* is *number of entities*; for example, it may be used for *number fraction*, *number ratio*, *isotope-number fraction*, *isotope ratio*, and *relative difference of isotope ratios*.

Note 5: The symbol ‰ may be replaced by mg/g, for example, for expressing the ratio of two quantities of the same kind, where the *kind of quantity* is mass.

Note 6: The symbol ‰ may be replaced by mmol/mol, for example, for expressing the ratio of two quantities of the same kind, the *kind of quantity* being amount of substance; for example, it may be used with *mole fraction*, *isotope-amount fraction*, *isotope-amount ratio*, and *isotopic abundance*. The units mmol/mol or similar should not be used with the quantities *isotopic fractionation factor*, *isotope ratio*, *isotopic fractionation*, nor with *isotope delta*.

Examples:
(a) The hydrogen isotopic composition of the brine expressed as a delta value on the VSMOW–SLAP scale is $\delta^2H_{VSMOW-SLAP} = -5$ ‰.
(b) For a zinc sample and a reference ZnREF2, $\delta^{66/64}Zn_{ZnREF2} = -1.18 \times 10^{-3} = -1.18$ ‰.
(c) The value of the oxygen *isotopic fractionation* between calcite and water is $\varepsilon^{18/16}O_{calcite/water} = 2.849 \times 10^{-2} = 28.49$ ‰.

quantity

Property of a phenomenon, body, or substance, where the property has a magnitude that can be expressed as a number and a reference.[4,5] The reference can be a measurement unit, a measurement procedure, a reference material, or a combination of such.

Note 1: Quantities are variables and their symbols are written in italic font, even if their symbols are Greek characters.

Note 2: A given symbol can indicate different quantities.

Example:
(a) The deuterium mole fraction of the methane is $x(^2H)_{CH_4} = 15$ %; the atom fraction of deuterium in the methane is $x(^2H)_{CH_4} = 15$ %; the isotopic abundance of ^2H in the methane is $x(^2H)_{CH_4} = 15$ %.
(b) For a sample, $\delta^{18}O_{VSMOW-SLAP} = -9.1$ ‰.

quantity of dimension one

See *dimensionless quantity*.

reference delta value, δ
consensus delta value

Value of the *relative difference of isotope ratios* (δ) carried by an *isotopic reference material* that is used as a basis for comparison of a specified $\delta(^iE/^jE)$ value between a sample and a reference material, where ^iE and ^jE are heavier and lighter isotopes, respectively, of element E.

Note: The uncertainty value may be zero, such as in the case of international agreement of a quantity value of an *international measurement standard*. For example, the $\delta^{18/16}O$ of NBS 19 calcite relative to VPDB is $\delta^{18/16}O_{NBS19/VPDB} = -2.2$ ‰.

Example: The hydrogen isotopic composition of SLAP2 reference water on the VSMOW–SLAP scale is $\delta^2H_{SLAP2/VSMOW-SLAP} = -427.5 \pm 0.3$ ‰.[36]

reference isotope-ratio value
Value of an *isotope ratio* carried by an *isotopic reference material* that is used as a basis for comparison of a specified isotope ratio between a sample and a reference material.

Note: The value can be either an *isotope (number) ratio* or an *isotope-amount ratio*.

Example: The reference isotope-ratio value of SRM 975a sodium chloride is $R(^{35}Cl/^{37}Cl) = 3.1279 \pm 0.0047$.[37]

relative difference of gas ratios, δ
gas delta
relative gas-ratio difference
Relative differences in ratios of numbers, amounts, or volumes occupied by two gaseous components in two systems. The components usually are gases, such as O_2, N_2, and Ar. The synonym *gas delta* may be preferred to relative difference of gas ratios because the former is shorter.

The relative difference in the amounts of components B_1 and B_2 in a sample P and a standard (std), $\delta(B_1/B_2)_{P/std}$, is expressed by the relation:

$$\delta(B_1/B_2)_{P/std} = \frac{\frac{n(B_1)_P}{n(B_2)_P} - \frac{n(B_1)_{std}}{n(B_2)_{std}}}{\frac{n(B_1)_{std}}{n(B_2)_{std}}} = \frac{\frac{n(B_1)_P}{n(B_2)_P}}{\frac{n(B_1)_{std}}{n(B_2)_{std}}} - 1$$

Alternatively, $\delta(B_1/B_2)_{P/std}$ can equally well be defined with number of entities, N, of B_1 and B_2.

For measurement of the relative difference in the amounts of O_2 and N_2 in a sample P and a standard (std), one can write:

$$\delta(O_2/N_2)_{P/std} = \frac{\frac{n(O_2)_P}{n(N_2)_P} - \frac{n(O_2)_{std}}{n(N_2)_{std}}}{\frac{n(O_2)_{std}}{n(N_2)_{std}}} = \frac{\frac{n(O_2)_P}{n(N_2)_P}}{\frac{n(O_2)_{std}}{n(N_2)_{std}}} - 1$$

Note 1: When it is clear from the context, either or both of the subscripts P and std may be deleted, e.g., $\delta(O_2/N_2) = -6.1 \times 10^{-6}$.

Note 2: It is important for authors to state the quantity on which $\delta(B_1/B_2)$ is based, e.g., *mole ratio*, volume ratio, *number ratio*, or mass ratio because the numerical value will be different when the quantity is defined with mass ratios, mole ratios, or volume ratios.

Note 3: The gas delta is a *dimensionless quantity* (SI unit 1). Because variations in this quantity typically are small, values commonly are reported in *part per million* (ppm) or per meg (one part in one million parts).

Note 4: The relative difference of gas ratios of O_2 and N_2 between a sample P and a standard can be defined with volumes of gas by the relation:

$$\delta_V(O_2/N_2)_{P/std} = \frac{\frac{V(O_2)_P}{V(N_2)_P}}{\frac{V(O_2)_{std}}{V(N_2)_{std}}} - 1$$

where the subscript V of δ_V indicates a *delta* value determined from volume measurements. This symbol and equation make it clear that volume ratios are measured. Because gases usually are not ideal, $\delta(O_2/N_2)$ and $\delta_V(O_2/N_2)$ are not numerically identical. Compression factors or fugacity coefficients can be used to convert from $\delta(O_2/N_2)$ into $\delta_V(O_2/N_2)$, and vice versa.

Note 5: In the literature, one finds equations such as:

$$\delta(O_2/N_2) = \left[\frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{ref}} - 1\right] \times 1000\,000$$

The factor 1000 000 is an extraneous numerical factor that should be deleted to make the relation coherent.[4]

Examples: (a) For an air sample, $\delta(O_2/N_2)_{std} = -7.1$ ppm $= -7.1$ per meg $= -7.1 \times 10^{-6}$.
(b) For a sample P, $10^6\ \delta(O_2/N_2)_{P/std} = 10^6\ \delta(O_2/N_2)_{std} = -7.1$.

See also *per meg* and *part per million*.

relative difference of isotope ratios, δ
isotope delta
relative isotope-ratio difference
Ratio $(R(^iE/^jE)_P - R(^iE/^jE)_Q)\ /\ R(^iE/^jE)_Q$ equals $\delta^{i/j}E_{P,Q}$, where R is the *isotope ratio* of heavier (higher atomic mass) isotope ^iE and lighter (lower atomic mass) isotope ^jE of element E in substances P and Q. The same relative differences can be used to calculate delta values from frequencies,[38] ion currents, and numbers or amounts of *isotopomers* or *isotopologues*. When delta values are expressed relative to an *international measurement standard*, the symbol of the standard replaces Q. Equal weights of different isotopes correspond to different amounts of isotopes. The synonym *isotope delta* may be preferred to relative difference of isotopic ratios because the former is shorter.

Although the delta value, $\delta^{i/j}E$, can be determined between any two substances P and Q, most published delta values are measured using an international measurement standard (std), and the delta value is defined by:

$$\delta^iE_{std} = \delta^{i/j}E_{std} = \frac{R(^iE/^jE)_P - R(^iE/^jE)_{std}}{R(^iE/^jE)_{std}} = \frac{\frac{N(^iE)_P}{N(^jE)_P} - \frac{N(^iE)_{std}}{N(^jE)_{std}}}{\frac{N(^iE)_{std}}{N(^jE)_{std}}}$$

or the mathematically equivalent version:

$$\delta^iE_{std} = \frac{R(^iE/^jE)_P}{R(^iE/^jE)_{std}} - 1 = \frac{N(^iE)_P/N(^jE)_P}{N(^iE)_{std}/N(^jE)_{std}} - 1$$

where $N(^iE)_P$ and $N(^jE)_P$ are the numbers of the two isotopes ^iE and ^jE of chemical element E in specimen P, $R(^iE/^jE)_P$ is $N(^iE)_P\ /\ N(^jE)_P$ in specimen P, and equivalent parameters follow for the *international measurement standard*, 'std'. Superscripts i and j should denote mass numbers of a heavier and a lighter isotope, respectively, so that the quantity of the

heavier isotope is in the numerator and that of the lighter isotope is in the denominator. In this manner, when one says colloquially that sample P is heavier than the standard, the delta value of P is more positive than that of the standard, and the atomic weight of the element in question is higher in P than in the standard. The latter would not be the case if the isotope with the lower atomic mass were in the numerator.

A positive $\delta^{i/j}E$ value indicates that the *number fraction* (and *mole fraction*) of the heavier isotope is greater in substance P than in the international measurement standard. A negative $\delta^{i/j}E$ value indicates that the number fraction (and mole fraction) of the heavier isotope is lower in substance P than in the standard. Numerically identical delta values can be determined by substituting equivalent *isotope-amount ratios*, $r({}^{i}E/{}^{j}E)_P$ and $r({}^{i}E/{}^{j}E)_{std}$, or isotope amounts, $n({}^{i}E)_P$ and $n({}^{j}E)_P$, for *isotope ratios* or number of isotopes in equations above.

Note 1: Commonly, $\delta^{i/j}E$ is shortened to $\delta^{i}E$, but for elements having three or more isotopes, $\delta^{i/j}E$ is preferred. With the fully expanded format, it is easy to differentiate between $\delta^{44/42}Ca$ and $\delta^{44/40}Ca$, which could otherwise be indicated as $\delta^{44}Ca$.

Note 2: The forms using a comma instead of a forward slash as a record separator and parentheses, e.g. $\delta({}^{i,\,j}E)_P$ or $\delta({}^{i}E,\,{}^{j}E)_P$, have also been used in the literature. They are equivalent to, but not preferred over, the definitions given above.

Note 3: The name of the quantity derives from the definition equation. $N({}^{i}E)_P/N({}^{j}E)_P$ is the *isotope ratio*. The numerator of the delta definition equation, $N({}^{i}E)_P/N({}^{j}E)_P - N({}^{i}E)_{std}/N({}^{j}E)_{std}$, is a difference of isotope ratios. Dividing the numerator by its denominator, $N({}^{i}E)_{std}/N({}^{j}E)_{std}$, is indicated by adding the word relative, and $\delta^{i/j}E$ is a 'relative difference of isotope ratios'. However, this term is too long for convenient use and it is suggested that $\delta^{i}E$ or $\delta^{i/j}E$ be used in text. When the isotope is clear from the context, authors may also write text such as 'The delta value of specimen P relative to VCDT is −44 ‰'. In the literature, the quantity $\delta^{i}E_{std}$ has been called the 'isotopic abundance', 'isotopic composition', and 'isotope ratio'. Isotope delta or its synonym, relative difference of isotopic ratios, is preferred.

Note 4: The symbol δ is pronounced 'delta'; 'del' is incorrect because it is the name for the del operator, symbol ∇.[20]

Note 5: The standard should be a substance that can be distributed or a scale defined in terms of such a substance. Constructs, such as 'average composition of the Earth' or 'Bulk Earth', are unacceptable.

Note 6: Delta values are difference measurements and authors are encouraged to give a leading+ symbol to values greater than zero.

Note 7: The isotope delta is a *dimensionless quantity* (SI unit 1). Because variations in isotopic abundances typically are small, the range in $\delta^{i}E$ values for many commonly studied chemical elements[3] is less than 0.2 and values are reported in part per hundred (% or *percent*), part per thousand (‰ or *per mil*), *part per million* (ppm), and *per meg*. For expressing an isotope δ value, the units mg/g, µg/g, mmol/mol, or any such units, should not be substituted for the symbols ‰, pptt, per meg, or ppm.

Note 8: To express delta values in *part per ten thousand*, authors can use the abbreviation pptt, which should be explained in the text or in a footnote.

Note 9: Equations used to define the quantity $\delta^{i/j}E_{std}$ should be coherent quantity equations. Because of their universality, they hold for any units as they do not contain extraneous numerical factors or units.[4,5] Equations, such as:

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

are found in the literature. A shortened version of this equation is:

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

where the author should define $({}^{18}O/{}^{16}O)_P$ in their text, and this parameter typically will be either $N({}^{18}O)_P/N({}^{16}O)_P$ or $R({}^{18}O)_P$ and the parameter $({}^{18}O/{}^{16}O)_{std}$ is defined in a similar manner. The problem with the former equation is that it can be confusing. For example, suppose that $N({}^{18}O)_P/N({}^{16}O)_P = 0.001\,986$ and $N({}^{18}O)_{std}/N({}^{16}O)_{std} = 0.002\,005$. One calculates: $\delta({}^{18}O) = (0.001986/0.002\,005) - 1 = -0.0095$. With use of the first equation in this note, one calculates with these same data: $\delta^{18}O = (0.001986/0.002\,005 - 1)\times 1000 = -9.5$, not −9.5 ‰. But, convention requires users to place the ‰ symbol following the numerical value. Thus, one would report −9.5 ‰. Confusion arises because in comparing the two equations, the left sides appear identical (both are $\delta^{18}O$), but the right sides differ by 10^3. In fact, the left sides are different quantities for which the same designator, $\delta^{18}O$, has been used. The factor 1000 is an extraneous numerical factor and should be deleted from the former equation above.

To minimize confusion, it is important to pay attention to which equation has been used to determine delta values. Using equations such as those above, a $\delta^{18}O$ value could yield either −0.05 ‰ or −50 ‰. Either value could be possible, but the wrong choice would be very problematic.

Note 10: The left-hand side of a coherent quantity delta-definition equation should not contain the text 'in %', 'in per mil', '(in ‰)', or any similar extraneous text.

Note 11: The symbol for the quantity relative difference of isotope ratios is δ. The symbol ε should not be substituted for the quantity δ. In the literature, one finds definitions for relative differences in isotope ratios of isotopes, such as:

$$\varepsilon^{i/j}X_{A,B} = \left(\frac{\text{isotope ratio of sample}}{\text{isotope ratio of standard}} - 1\right)\cdot 10,000$$

where X is the element in phase A and standard B, and for Nd isotopes, one finds:

$$\varepsilon_0^{\text{CHUR}} = \left[\frac{^{143}\text{Nd}/^{144}\text{Nd}}{\text{I}_{\text{CHUR}}(0)} - 1\right]\cdot 10\ 000$$

For Cu isotopes one finds:

$$\varepsilon^{65}\text{Cu} = \left[\frac{r_{\text{P}}}{r_{\text{std}}} - 1\right]\cdot 10\ 000$$

where r_{P} and r_{std} are $n(^{65}\text{Cu})_{\text{P}}$ / $n(^{63}\text{Cu})_{\text{P}}$ and $n(^{65}\text{Cu})_{\text{std}}$ / $n(^{63}\text{Cu})_{\text{std}}$, respectively, for specimen P and a standard, std. A typical example of incorrect usage is 'the ε^{65}Cu of these specimens range between −5.2 and +1.8'. These three equations are numerical value isotope delta-definition equations and their use is deprecated for four reasons. First, no new quantity is defined by ε. These equations are δ-definition equations, and ε should be replaced by δ. Second, the factor 10 000 is extraneous and should not appear in a coherent quantity δ-definition equation. Third, historically ε has been defined as the quantity *isotopic fractionation*, $1 - \alpha$. Fourth, neither the name of the quantity nor the symbol used to denote it should imply a particular choice of unit (see sections 5.3.1 and 5.3.2 of the 8th SI brochure).[4] The equation for Cu isotopes could be written correctly as:

$$\delta^{65}\text{Cu}_{\text{std}} = \delta^{65/63}\text{Cu}_{\text{P/std}} = \frac{r_{\text{P}}}{r_{\text{std}}} - 1 = \frac{r_{\text{P}} - r_{\text{std}}}{r_{\text{std}}}$$

To express values in *part per ten thousand* authors can use the abbreviation pptt, which should be explained in the text or in a footnote. Examples of delta-definition equations to be avoided for consistency with quantity calculus are shown in Table 1.

Note 12: Equations expressing relations among delta values should be quantity equations in coherent form.[4] Numerical value equations should be updated to quantity equations by authors. For example, from over 200 globally distributed precipitation sites, Rozanski *et al.*[39] report a relation between δ^2H and δ^{18}O of:

$$\delta^2\text{H} = 8.20\ \delta^{18}\text{O} + 11.27$$

This numerical value equation can be replaced by a quantity equation, such as:

$$\delta^2\text{H}_{\text{VSMOW-SLAP}} = 8.20\ \delta^{18}\text{O}_{\text{VSMOW-SLAP}} + 0.011\ 27$$

where the subscript VSMOW–SLAP indicates that delta values are expressed relative to VSMOW on scales normalized such that the δ^2H and δ^{18}O values of SLAP reference water are −428 and −55.5 ‰ relative to VSMOW, respectively.[40] To keep the value '11.27' prominent, some users may prefer:

$$\delta^2\text{H}_{\text{VSMOW-SLAP}} = 8.20\ \delta^{18}\text{O}_{\text{VSMOW-SLAP}} + 11.\ 27 \times 10^{-3}$$

Note 13: The form $\delta^{i/j}$E sometimes is shortened to $^{i}\delta$, such as $^{18}\delta$ for δ^{18}O, $^{44/42}\delta$ for $\delta^{44/42}$Ca, or $^{45}\delta$ for analysis of CO_2 from the ratio of the number of ions on the m/z-45 and m/z-44 collectors (see *isotope ratio*). Such notation, in which the element symbol is missing, should not be used in axis labels of figures or column headings of tables unless the notation is redefined in each figure caption or table in which it is used. This is needed because figures and tables regularly are separated from reports, and they need to stand on their own. This will eliminate confusion, such as $^{124}\delta$ or $^{124/120}\delta$, where the reader cannot determine if the element is Sn or Te.

Note 14: The form $\delta^{i/j}\text{E}_{\text{P/std}}$ is useful for expressing delta values of *isotopologues* substituted with several isotopes, for example, for the isotopic fractionation between carbonate isotopic species (CO_3^{2-}) having specified isotopes in a carbonate mineral. For the exchange of one ^{16}O atom and one ^{17}O atom in a carbonate mineral according to the reaction (slightly modified from Eqn. (2) of Schauble *et al.*[30])

$$\left(^{12}\text{C}^{16}\text{O}_2{}^{17}\text{O}\right)^{2-} + \left(^{12}\text{C}^{16}\text{O}_2{}^{18}\text{O}\right)^{2-} \rightleftharpoons \left(^{12}\text{C}^{16}\text{O}_3\right)^{2-} + \left(^{12}\text{C}^{16}\text{O}^{18}\text{O}^{17}\text{O}\right)^{2-}$$

the δ value of the carbonate species $(^{12}\text{C}^{16}\text{O}^{18}\text{O})\text{O}^{2-}$ in a specimen P relative to the carbonate species $(^{12}\text{C}^{16}\text{O}_2)\text{O}^{2-}$ in the same solid specimen can be written as $\delta^{17/16}\text{O}_{\text{P}((^{12}\text{C}^{16}\text{O}^{18}\text{O})\text{O}^{2-})/\text{P}((^{12}\text{C}^{16}\text{O}_2)\text{O}^{2-})}$.

Examples:
(a) The nitrogen isotope delta value of a specimen Q relative to nitrogen in atmospheric air is $\delta^{15}\text{N}_{\text{Q/Air}} = \delta^{15}\text{N}_{\text{Air}} = \delta^{15/14}\text{N}_{\text{Q/Air}} = -0.0095 = -9.5 \times 10^{-3} = -9.5$ ‰.
(b) Alternatively, $10^3\,\delta^{15}\text{N}_{\text{Air}} = -9.5$, $1000\,\delta^{15}\text{N}_{\text{Air}} = -9.5$.

Note that the form $10^3\,\delta^{15}$N is analogous to the method for expressing ln α values, namely as 10^3ln α or 1000 ln α values in that they both comply with quantity calculus recommendations. A preference may be given to $10^3\,\delta^{i}$E over $1000\,\delta^{i}$E because the former is shorter.

Table 1. Examples of delta-definition equations to be avoided for consistency with quantity calculus and recommendations in the 8th SI brochure[4]

Usage to be avoided	Problems
$\delta^{18}\mathrm{O} = \left[\frac{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{P}}}{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{std}}} - 1\right]\cdot 1000$	Equation should not contain the extraneous factor 1000. If not previously defined, $(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{P}}$ should be defined, commonly as $N(^{18}\mathrm{O})_{\mathrm{P}}/N(^{16}\mathrm{O})_{\mathrm{P}}$ or $R(^{18}\mathrm{O})_{\mathrm{P}}$ for substance P. Equivalent definitions should be provided for the measurement standard or international measurement standard, 'std'.
$\delta^{18}\mathrm{O}(\text{in ‰}) = \left[\frac{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{P}}}{(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{std}}} - 1\right]\cdot 1000$	Equation should not contain the factor 1000 or the text 'in ‰'. If not previously defined, $(^{18}\mathrm{O}/^{16}\mathrm{O})_{\mathrm{P}}$ needs to be defined, commonly as $N(^{18}\mathrm{O})_{\mathrm{P}}/N(^{16}\mathrm{O})_{\mathrm{P}}$ or $R(^{18}\mathrm{O})_{\mathrm{P}}$ for substance P. Equivalent definitions should be provided for the 'std'.
$\varepsilon^{65}\mathrm{Cu} = \left[\frac{(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})_{\mathrm{P}}}{(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})_{\mathrm{std}}} - 1\right]\cdot 10\ 000$	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, $(^{65}\mathrm{Cu}/^{63}\mathrm{Cu})_{\mathrm{P}}$ needs to be defined, commonly as $n(^{65}\mathrm{Cu})_{\mathrm{P}}/n(^{63}\mathrm{Cu})_{\mathrm{P}}$, $N(^{65}\mathrm{Cu})_{\mathrm{P}}/N(^{63}\mathrm{Cu})_{\mathrm{P}}$, $r(^{65}\mathrm{Cu})_{\mathrm{P}}$, or $R(^{65}\mathrm{Cu})_{\mathrm{P}}$ for substance P. Equivalent definitions should be provided for the 'std'.
$\delta(\mathrm{O_2}/\mathrm{N_2}) = \left[\frac{R_{\mathrm{P}}}{R_{\mathrm{std}}} - 1\right]\cdot 1000\ 000$	Equation should not contain the extraneous factor 1000 000. If not previously defined, R needs to be defined, commonly as $N(\mathrm{O_2})/N(\mathrm{N_2})$ or $n(\mathrm{O_2})/n(\mathrm{N_2})$.

(c) For a specimen, $10^4\ \delta(^{66/64}\mathrm{Zn})_{\mathrm{ZnREF}} = -1.8$. Expressing delta values as $10^4\,\delta^{66/64}\mathrm{Zn}_{\mathrm{ZnREF}}$ values has the advantage of eliminating the use of 'part per ten thousand', 'pptt', or the '‰' symbol.

(d) $\delta^{18/16}\mathrm{O}_{\mathrm{VSMOW\text{–}SLAP}} = -9.1$ ‰; $\delta^{18}\mathrm{O}_{\mathrm{VSMOW\text{–}SLAP}} = -9.1$ ‰ $= -9.1\times 10^{-3} = -0.0091$; $10^3\,\delta^{18}\mathrm{O}_{\mathrm{VSMOW\text{–}SLAP}} = -9.1$.

(e) For a sample of seawater, $\delta^{44/42}\mathrm{Ca}_{\mathrm{NBS915a}} = +1.2$ ‰ (relative to NBS 915a calcium carbonate).

See also *mass-independent isotope variation* and Fig. 1.

relative exceedance, ψ

Relative difference between the *mole fraction* of an isotope in substance P and that of a reference according to the relation:

$$\psi\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{P/reference}} = \frac{R\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{P}} - R\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{reference}}}{1 + R\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{P}} - R\left(^{i}\mathrm{E}/^{j}\mathrm{E}\right)_{\mathrm{reference}}}$$

where R_{P} is the *isotope ratio* of a sample P of heavier isotope $^{i}\mathrm{E}$ and lighter isotope $^{j}\mathrm{E}$ of element E, and similarly for the reference. The symbol ψ also is used for the quantity volume ratio.[23]

Note 1: When it is clear from the context, $\psi(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{P/reference}}$ may be shortened to $\psi_{\mathrm{reference}}$, $\psi(^{i}\mathrm{E})_{\mathrm{P}}$, or $\psi(^{i}\mathrm{E})_{\mathrm{reference}}$, as appropriate. If there is any possibility of confusion, the extended format $\psi(^{i}\mathrm{E}/^{j}\mathrm{E})_{\mathrm{P/reference}}$ should be used.

Note 2: This is a second definition for '*APE*'.[16] Previously, this term was called 'atom percent excess', 'atom % excess', or 'APE', but none of these should be used because this quantity does not have a unique definition and because 'APE' is not a valid symbol for an ISQ quantity name.

Note 3: The name of the quantity for the other definition of 'APE' is *excess atom fraction*.

Examples: The stable carbon relative exceedance of sample P can be expressed by $\psi(^{13}\mathrm{C})_{\mathrm{P/reference}} = 0.0093 = 9.3\times 10^{-3} = 0.93$ %; $10^6\psi(^{13}\mathrm{C})_{\mathrm{P/reference}} = 8.42$; $\psi(^{13}\mathrm{C})_{\mathrm{P/reference}} = 8.42$ ppm.

See also *excess atom fraction*.

true isotope ratio, R

Isotope-ratio value that is consistent with the definition of an *isotope ratio*.

Note 1: In the Error Approach (sometimes called Traditional Approach or True Value Approach) to describing measurement,[5] a true isotope-ratio value is considered unique and unknowable, in practice.

Note 2: This value carries no uncertainty.

Note 3: The true isotope ratio of a sample cannot be determined experimentally as there is no isotope-ratio measurement that is free of measurement uncertainty apart from direct counting of individual entities at the atomic scale.

See also *measured isotope ratio* and *absolute isotope ratio*.

REPORTING ISOTOPE-DELTA VALUES

To maximize the worth of measurement results in articles and reports, authors should abide by some guidelines. Current published guidelines for some common δ measurements include: for $\delta^{2}\mathrm{H}$ measurements,[41] $\delta^{13}\mathrm{C}$ measurements,[42] $\delta^{15}\mathrm{N}$ measurements,[43] $\delta^{18}\mathrm{O}$ measurements,[41] and $\delta^{34}\mathrm{S}$ measurements.[44]

Table 2. Examples of axis labels of graphs, column headings of tables, and data in tables for isotopic and gas-ratio measurement results for consistency with quantity calculus.[4] [First row is column heading or axis label of graph. Second through fifth rows are example data values]

$\delta^{34}S_{VCDT}$	$\delta^{34}S_{VCDT}$/‰	$\varepsilon_{N_2/NO}$	$\delta^{65}Cu_{SRM976}$	$x(^{15}N)$	$\delta(O_2/N_2)$	$10^6\delta(O_2/N_2)$
+9.1 ‰	+9.1	−7.1‰	−0.000 18	0.045	-1.1×10^{-6}	−1.1
$+9.1\times10^{-3}$		-7.1×10^{-3}	−0.18 ‰	4.5 %	−1.1 per meg	
+0.0091		−0.0071	−1.8 pptt[a]	45 ‰	−1.1 ppm	
			-1.8×10^{-4}	4.5×10^{-2}		

[a]If pptt (*part per ten thousand*) is used, the symbol should be defined in the text or by a footnote.

Table 3. Examples of isotopic and gas-ratio data of column headings of tables, axis labels of graphs, and text for consistency with quantity calculus and (or) IUPAC

Usage to be avoided	Description of problem	Preferred usage
$\delta^{18}O$ (in ‰)	Labels of column headings and axes should not contain the text 'in ‰'.	$\delta^{18}O$/‰ or $10^3\ \delta^{18}O$
$\delta^{15}N$, in per mil	Labels of column headings and axes should not contain the text 'in per mil'.	$\delta^{15}N$/‰ or $10^3\ \delta^{15}N$
$\delta^{57}Fe_{AverageEarth}$	For elements with more than two isotopes, use the fully expanded version showing both isotopes when there is any possiblilty of confusion. Including the international measurement standard is encouraged, and use of a non-quantifiable quantity, such as 'Average Earth' or 'Bulk Earth' is deprecated.	$10^4\ \delta^{57/54}Fe_{IRMM\text{-}014}$ $\delta^{57/54}Fe_{IRMM\text{-}014}$ (in text)
$^{18}\delta$	This format in which the element symbol is missing is acceptable in tables and figures if the format is defined in each figure and table in which this format is used.	$\delta^{18}O$/‰ or $10^3\ \delta^{18}O$
$\varepsilon^{65}Cu=-9.1$	The symbol ε is already defined as $\alpha-1$. Replace $\varepsilon^{65}Cu$ with $\delta^{65}Cu_{std}$ or with $\delta^{65/63}Cu_{std}$.	$\delta^{65}Cu=-9.1$ pptt (or) $\delta^{65}Cu=-0.91$ ‰
Deuterium (‰)	The label or column heading is missing the δ symbol; the word 'Deuterium' is unacceptable. No column heading or axis label should contain the text 'in ‰' or ', ‰'.	δ^2H / ‰ or $10^3\ \delta^2H$
AP	'*AP*' is not a valid ISQ quantity and should not be used. Use '*stable isotope-amount fraction*' or '*atom fraction*' instead, symbol $x(^iE)_P$.	$x(^iE)$
Atom %	'*Atom %*' is not a valid symbol for an ISQ quantity and should not be used. Instead, use '*stable isotope-amount fraction*' or '*atom fraction*'; symbol $x(^iE)_P$.	$x(^iE)$
APE	'*Atom % excess*' is not a valid symbol for an ISQ quantity and should not be used. Instead, use '*excess stable isotope-amount fraction*' or '*excess atom fraction*', symbol $x^E(^iE)_P$.	$x^E(^iE)$
$\delta(O_2/N_2)$ (in ppm)	Labels should not contain the text 'in %', 'in ‰', or 'in ppm'.	$10^6\ \delta(O_2/N_2)$

- Authors should express δ values relative to current *international measurement standards*, avoiding out-of-date references such as SMOW, PDB, and CDT.[45]
- If a second *international measurement standard* defines the size of a delta scale, such as L-SVEC lithium carbonate for $\delta^{13}C$ measurements[42] or SLAP water for δ^2H and $\delta^{18}O$ measurements,[41] δ values should be normalized using both standards. And authors should state this clearly in their articles and reports.
- Authors are strongly encouraged to report δ values of international distributed (secondary) *isotopic reference materials* as though they had been interspersed among and used for normalization of unknowns, as appropriate for the measurement method. In this manner, measurement results can be adjusted in the future as analytical methods improve and consensus values of internationally distributed *isotopic reference materials* change.
- The analytical procedure should be provided in sufficient detail that a reader clearly understands how the measurements were performed.

COLUMN HEADINGS OF TABLES AND AXIS LABELS OF GRAPHS

The SI suggestion for table-column headings and for axis labels of graphs,[4] based upon quantity calculus (also called the algebra of quantities) and recommended by numerous journals, is to use the quotient of the physical, chemical, or biological 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 ML^{-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 even $\gamma(Na)(mg/L)^{-1}$. However, $\gamma_{Na}/(mg\,dm^{-3})$ is preferred.

Examples of column headings and axis labels for isotopic and gas-ratio data are given in Table 2. 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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