

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

APPLIED CHEMISTRY DIVISION
COMMISSION ON ATMOSPHERIC CHEMISTRY*

UNITS FOR USE IN ATMOSPHERIC CHEMISTRY

(IUPAC Recommendations 1995)

Prepared for publication by

STEPHEN E. SCHWARTZ¹ and PETER WARNECK²

¹Environmental Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA

²Abteilung Biogeochemie, Max-Planck-Institut für Chemie, Saarstr. 23, D-55020 Mainz, Germany

*Membership of the Commission during the period (1991–1995) in which the report was prepared was as follows:

Chairman: 1985–1993 J. Slanina (Netherlands); *Secretary:* 1987–1995 P. Warneck (Germany); *Titular Members:* H. Akimoto (Japan; 1987–1995); L. Barrie (Canada; 1991–1995); N. M. Bazhin (Russia; 1991–1995); R. H. Brown (UK; 1991–1995); X. Tang (China; 1987–1995); *Associate Members:* E. H. Adema (Netherlands; 1991–1995); J. G. Calvert (USA; 1991–1995); K. H. Eickel (Germany; 1989–1993); J. A. Kerr (UK; 1987–1995); L. Klasinc (Croatia; 1991–1995); O. Lindqvist (Sweden; 1989–1993); L. F. Philips (New Zealand; 1991–1995); H. I. Schiff (Canada; 1991–1995); S. E. Schwartz (USA; 1991–1995); Wm. E. Wilson (USA; 1989–1993); *National Representatives:* T. M. Tavares (Brazil; 1992–1993); H.-J. Grösse (Germany; 1986–1993); B. Bonsang (France; 1990–1993); S. Glavas (Greece; 1991–1993); L. Horváth (Hungary; 1990–1993); O. N. Singh (India; 1989–1993); I. Allegrini (Italy; 1991–1993); Ø. Hov (Norway; 1985–1993); Y. Y. Lee (Korea; 1991–1993); U. Özer (Turkey; 1987–1993).

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1995 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Units for use in atmospheric chemistry (IUPAC Recommendations 1995)

Synopsis

This document examines the utility and suitability of the International System of Units (Système International, SI) as a framework for units in atmospheric chemistry and presents recommendations regarding use of these units in reporting atmospheric chemistry data consistent with the special requirements of this subdiscipline. In general SI is well suited for application to atmospheric chemistry; specifically the wide range of magnitudes that are encountered can be dealt with by the prefixes denoting multiples and submultiples of units, and the application of SI units leads automatically to consistency in unit calculus. The use of special names and symbols for units that are not part of the SI, and are not products of powers of SI base units is discouraged; examples are atmosphere, Dobson unit, hectare. However, continued use of such units (especially the Dobson unit) alongside SI units is advisable for a time until the SI units become more familiar. Local abundances of substances in air may be expressed as mixing ratios or concentrations. Mixing ratio has the advantage of being independent of pressure or temperature, but concentration has advantages for reaction kinetics and material transport. Amount-based units for mixing ratios or concentrations of substances of known chemical composition are preferable to mass-based units. The dimensionless unit mol per mol of air is recommended for mixing ratio of a substance in air, e.g. nmol/mol, rather than the customary parts per billion (ppb). It is necessary to specify whether a mixing ratio refers to dry or moist air. Expressing mixing ratios as "reduced concentrations" relative to standard conditions of pressure and temperature leads to ambiguity and should be avoided where possible. Gas-phase concentrations may be expressed on the basis of either mole (mol m^{-3}) or molecule (molecule m^{-3} ; SI: m^{-3}). The universal use of a single set of units for gas-phase concentration does not seem forthcoming in the immediate future, although the use of mol m^{-3} affords advantages of consistency and convenience. An extensive table of recommended symbols and SI units for quantities in atmospheric chemistry is presented.

1. Introduction

Atmospheric chemistry has emerged as an important subdiscipline at the interface of laboratory chemistry and atmospheric science. The basis for this development has been a spectacular growth in recent decades of fundamental knowledge on the physico-chemical behavior of chemical substances in the atmosphere, often following recognition of complex environmental problems and the resultant need for better understanding of processes characterizing the unperturbed atmosphere. Much of the present interest is centered on global problems such as stratospheric ozone depletion, increasing concentrations of aerosols and infrared active gases that may cause climate changes, and interactions between the atmosphere and the biosphere. However, problems of local and regional air pollution continue to demand attention.

This study was performed in part under the auspices of the United States Department of Energy, under Contract No. DE-AC02-76CH00016

Contributors to atmospheric chemistry have come from many disciplines, primarily from analytical and physical chemistry and meteorology, but also from physics, biology, oceanography and engineering. Perhaps as a consequence of the diversity of backgrounds among researchers active in this field there is currently considerable diversity in the application of units and terminology. In view of the wide range of subjects that atmospheric chemistry must deal with, including atmospheric physics, meteorology, oceanography, and biology in addition to chemistry, standardization of terminology and units is particularly important to facilitate scientific communication. An important step in this direction is the recent publication of the *Glossary of Atmospheric Chemistry Terms*⁽¹⁾, which should greatly aid in the standardization of nomenclature and terminology.

Here, we examine the utility and suitability of the International System of Units (Système International, SI) as a framework for units in atmospheric chemistry. A major objective of the introduction of SI generally has been to foster cross-disciplinary communication in the sciences, and this objective has met with considerable success. Currently, SI is gaining ground in many scientific disciplines, and almost all countries now officially advocate its use. The publication of *Quantities, Units and Symbols in Physical Chemistry* (The "Green Book"), prepared by members of IUPAC Commission I,1 on Physicochemical Symbols, Terminology and Units,⁽²⁾ provides a comprehensive introduction and reference to SI, with emphasis on its application in chemical science.

With respect to application of SI to atmospheric chemistry, it is unfortunately not immediately clear whether SI units are sufficiently versatile to satisfy the needs of this subdiscipline in every respect, or whether certain supplements or departures are required. After all, one must take cognizance of special requirements and traditional usages. A set of recommendations too rigid and too much in conflict with previous practices would probably ultimately not be accepted. Still it is desirable to point out advantages or disadvantages of one or another set of units so that investigators can make informed choices. It is also important to ascertain that accuracy and precision of atmospheric data not be degraded merely to achieve consistent units of presentation.

In this paper we review the situation, recommend units and symbols that seem fully acceptable, and address issues that may cause problems. The aim is to foster a consensus among atmospheric chemists and atmospheric scientists generally on a system of units that ultimately can be adopted by all. It is hoped that the recommendations presented here will be adopted by authors, and insisted upon by referees and editors, to provide precision, consistency, and facility of intra-disciplinary and cross-disciplinary communication.

2. Prefixes to denote Multiples and Submultiples of SI Units

One motivation for the adoption of SI units is the flexibility offered when dealing with quantities that range over many orders of magnitude. This situation is common with quantities that describe the state of the atmosphere and its changes. For example, some processes such as gas-phase chemical reactions or the formation of cloud drops occur at molecular to microscopic levels, whereas other processes, such as long-range transport, extend over the entire atmospheric domain encircling the globe. Similarly wide ranges of

Table 1: Prefixes for decimal multiples and submultiples of SI units

Submultiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E
10^{-21} (note a)	zepto	z	10^{21} (note a)	zetta	Z
10^{-24} (note a)	yocto	y	10^{24} (note a)	yotta	Y

(a) recently adopted

magnitudes are encountered in concentrations or mixing ratios of atmospheric constituents and in rates of atmospheric processes. The requirement of treating such wide ranges of magnitudes is amply met by the provisions of SI for dealing with decimal fractions and multiples by means of prefixes to units, as given in Table 1. These prefixes have gained widespread use and acceptance generally. Their use in atmospheric chemistry is encouraged and should present no problem. Note that the table includes the recently adopted prefixes zepto (z), 10^{-21} ; yocto (y), 10^{-24} ; zetta (Z), 10^{21} ; and yotta (Y), 10^{24} , which considerably extend the range of magnitudes encompassed by such prefixes.⁽³⁾

With respect to the choice of prefix (k, M, G,... and m, μ , n,...), it is recommended that the appropriate prefix be selected so that the numerical value before the prefix be in the range 0.01 to 999. By such a choice it is generally possible to avoid a power-of-ten multiplier before a prefix, for example 253.7 nm or 0.2537 μ m, not 2.537×10^2 nm or 2.537×10^{-1} μ m. Note in addition that the use of compound prefixes such as hPa = 10^5 Pa is considered unacceptable and that a prefix is not to be used on its own.⁽²⁾ The use of powers of prefixed units and/or multiple prefixes in reporting quantities having derived units is permissible where appropriate to the circumstance or by custom, for example, cm^2 , V cm^{-1} , mmol dm^{-3} , $\text{mW m}^{-2} \text{nm}^{-1}$ (for spectral irradiance), $\mu\text{m}^3 \text{cm}^{-3} \mu\text{m}^{-1}$ (for volume-size distribution of an aerosol). In order to take advantage of the self-consistency of SI units in evaluating algebraic expressions, however, the quantities in such expressions should be given in SI units without prefixes.

3. SI Base Units

The International System of Units is built on seven base units: metre (m), kilogram (kg), second (s), ampere (A), kelvin (K), mole (mol), and candela (cd) for quantities having the dimensions length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity, respectively. It is a strength of SI that all derived units (e.g. newton, joule, watt, coulomb) can be expressed as products of powers of these seven base units and that the use of such units automatically leads to consistency in units, eliminating the need for conversions.

It is not intended to review all seven base units here, but some comments may be helpful with regard to their applicability to atmospheric chemistry. The Green Book⁽²⁾ should be consulted for precise definitions of these units. The candela is not employed in atmospheric chemistry; the intensity of radiation pertinent to photochemical considerations is expressed in terms of other base units, as discussed below in Section 4.5.

3.1 Length

The base SI unit for length is the metre (m); use of American spelling (meter) is also acceptable. Use of the metre as a measure of length is familiar in atmospheric science generally and in atmospheric chemistry specifically and raises no problems. The kilometre (km) is appropriate to describe altitudes or distances. Smaller scales are best described by prefixes, e.g., wavelength of solar radiation in nm, radius of aerosol particles or cloud drops in μm , size of rain drops in mm. The term micron (symbol μ) should not be used but replaced by micrometre (μm). The ångström ($1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$) likewise should no longer be used. The Mm (for 10^3 km) is used only occasionally, although it may have numerous applications in the atmospheric sciences consistent with comments in Section 2 dealing with avoidance of power of ten multipliers. An example is optical extinction, which has dimension length^{-1} . Because of the low magnitude typical of atmospheric extinction, the unit Mm^{-1} is convenient and appropriate.

Derived units are m^2 for area and m^3 for volume. Use of powers of prefixed length quantities, e. g., cm^2 , km^2 , cm^3 , μm^3 , km^3 is encouraged when appropriate in context and when large powers of ten can thereby be avoided. Use of hectare ($1 \text{ ha} = 10^4 \text{ m}^2$) should be discontinued, because neither the hectare nor the are (100 m^2) is an SI unit; the synonym hm^2 may be used where appropriate. The litre ($1 \text{ L} = 1 \times 10^{-3} \text{ m}^3 = 1 \text{ dm}^3$) is also not a SI unit. (The capital letter L is frequently used as a symbol for litre instead of the lower case l because the latter can be mistaken for the numeral one). While use of the litre is still tolerated in certain contexts, there is an increasing tendency to replace it by its synonym the cubic decimetre, dm^3 .

3.2 Mass

The base SI unit for mass is the kilogram (kg). This choice is unfortunate because for historical reasons the unit already contains a prefix (kilo, denoting 10^3). Certainly for consistency it would have made things easier if a new name had been created for the unit, but no change is currently in sight. Accordingly, as far as prefixes are concerned, the real (hidden) unit is the gram, and all fractions or multiples are derived from it, for example, mg (not μkg), μg (not nkg), etc. The use of "tonne" ($1 \text{ tonne} = 1 \times 10^3 \text{ kg}$) is discouraged. The Mg ($1 \text{ Mg} = 1 \times 10^3 \text{ kg}$) has not found favor but should be used where appropriate; it is an especially convenient replacement for tonne. If power-of-ten multipliers are used, it is preferable to use them with the base unit kg rather than with the hidden unit g. Thus 735 Tg or $7.35 \times 10^{11} \text{ kg}$ are equally acceptable, but $7.35 \times 10^{14} \text{ g}$ is to be avoided.

Many trace gases contained in the troposphere have a total mass in the range of 10^9 kg to 10^{15} kg . For this mass range the use of units Tg and Pg is recommended. For example, the total mass of carbonyl sulfide, OCS, in the troposphere is approximately 4.4 Tg, that of

hydrogen is approximately 160 Tg, and that of methane is approximately 3.7 Pg⁽⁴⁾. The mass of the entire atmosphere⁽⁵⁾ is about 5.13×10^{18} kg, or 5.13 Zg; here the newly adopted prefix Z (for zetta, denoting 10^{21}) is conveniently employed.

3.3 Time

The SI unit for time is the second (s), and the use of this quantity is encouraged wherever appropriate, for example in expressing chemical kinetic rates. Prefixes for submultiples of the second such as ms or μ s are commonly employed, but not for multiples such as ks or Ms.

Atmospheric chemistry is concerned with time periods ranging from less than a second (free radical lifetimes) to many years (geochemical time scales). Time thus is commonly expressed in non SI units that are predetermined by the clock and the calendar. For example, hour and day are used to display diurnal and seasonal variations of atmospheric chemical quantities. Accordingly, it is customary and acceptable to employ units of minute (min), hour (h), day (d), and year (a). Use of the symbol a (abbreviation for annum) for year follows the recommendation by the International Organization for Standardization (ISO).⁽⁶⁾

Table 2 shows suggested time periods and conversions to SI units. Minute, hour, and day are defined exactly in terms of the second (60 s, 3600 s, 86400 s, respectively). The length of the year is somewhat variable because of the occurrence of leap years; additionally, from time to time a "leap second" is added to a specified day to keep civil time in agreement with astronomical time, but this is of no practical consequence to atmospheric chemistry. In converting from seconds to years it is recommended that the conversion factor $3.155\ 695\ 2 \times 10^7\ \text{s a}^{-1}$ (exactly), corresponding to the mean Gregorian year (365.242 5 d), be employed for general purposes, or the actual number of days (365 or 366) multiplied by $86\ 400\ \text{s d}^{-1}$ for any specific year. Definitions of the year other than Gregorian are used in astronomy (for example sidereal). The differences in time periods⁽⁷⁾ for the different definitions of the year are small and are of no practical consequences to atmospheric chemistry.

Because of variability in the length of the calendar month it is recommended that use of month as a unit of time be avoided. Seasonal variations of atmospheric quantities such as trace gas abundances or emission fluxes can be reported and displayed on the basis of actual calendar days. Frequently it may be desirable to express averages of data on a monthly

Table 2: Time periods used in atmospheric chemistry

name of unit	symbol	Relation to SI
second	s	SI unit
minute	min	60 s
hour	h	3600 s
day	d	86 400 s
year (mean Gregorian)	a	31 556 952 s

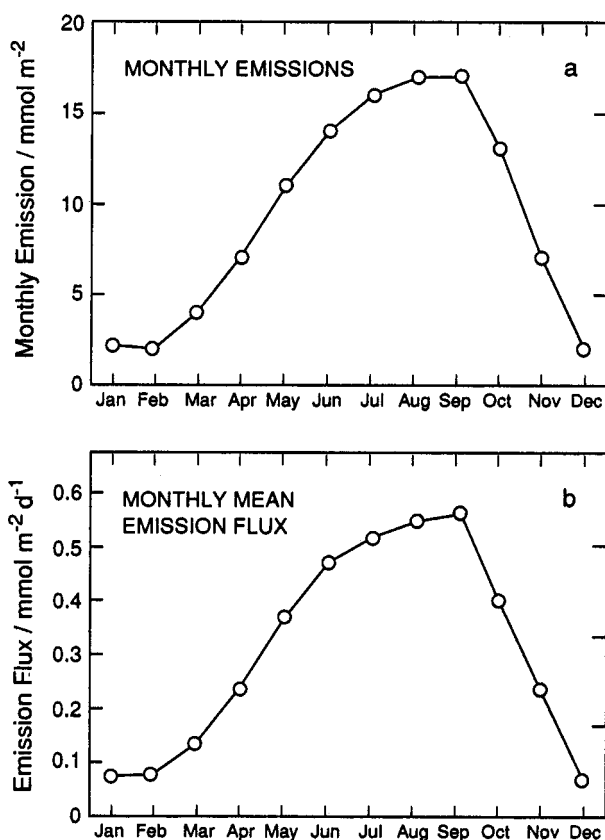


Figure 1. Example of plots of monthly data as a quantity that is extensive in time (a) and a quantity that is intensive in time (b), eliminating artificial variability due to variable length of month. Note for example differences between the two figures in relative values between January and February and between August and September. The quantity plotted is a pure, dimensionless number representing the ratio of emission (unit: mmol m^{-2}) or emission flux ($\text{mmol m}^{-2} \text{d}^{-1}$), respectively, to the unit.

basis, for example to display seasonal changes. In such cases it is permissible to use the actual calendar month as a basis for calculating averages. However, since the variable number of days in a month introduces artificial variability in the quantities that are extensive in time, such as amount of emission, it is preferable to express such data intensively, namely as emission rate, using a precise time unit. Figure 1 gives an example.

The convention employed in reporting time of day should be specified with care, specifically whether the reported time is local time (i.e. sun time for the particular longitude), local standard time, or Greenwich Mean Time (GMT; formally, Universal Time Coordinated, UTC).

Derived units for time are hertz ($\text{Hz} = \text{s}^{-1}$) for frequency and becquerel ($\text{Bq} = \text{s}^{-1}$) for radioactivity. Other units for radioactivity that have been employed include the curie ($1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$) and disintegrations per minute ($1 \text{ dpm} = 1/60 \text{ Bq}$). These non SI units should be supplanted by the SI unit, the becquerel.

3.4 Electric Current

The ampere (A) is rarely used in atmospheric chemistry. However, this quantity serves as base unit for all electric and magnetic units in SI. In particular it is part of the definition of the ohm, the SI unit of electric resistance, which is pertinent to atmospheric chemistry in specifying the electric conductivity of rain water, cloud water, etc. Electric conductivity of atmospheric liquid waters is discussed in Section 4.6.

3.5 Temperature

The base SI unit for temperature is the kelvin (K). The terminology "degrees Kelvin" and the symbol °K are obsolete. The use of kelvin is customary throughout the physical sciences and it creates no problems in atmospheric chemistry. In practical work it is acceptable to use the Celsius scale defined by $\theta/^{\circ}\text{C} = T/\text{K} - 273.15$.

3.6 Amount of Substance (Chemical Amount)

The SI unit for the amount of substance or chemical amount is the mole (mol). The amount n_{B} of an entity B in a system is defined by proportionality to the number N_{B} of entities B (e.g. molecules, atoms, ions, formula units) in the system according to the relation $N_{\text{B}} = N_{\text{A}}n_{\text{B}}$ where the proportionality constant N_{A} is the Avogadro constant⁽²⁾ ($6.022\,136\,7 \times 10^{23} \text{ mol}^{-1}$). Chemists are thoroughly familiar with the mole, but regrettably this unit has not been widely employed in the atmospheric chemistry literature. Instead, it has been more common to express the amount of a substance by its mass or, in treating chemical reaction kinetics, by the equivalent number of molecules or atoms. The use of units based on the mole is encouraged as it emphasizes chemical relationships (e.g., between concentrations of ozone, O₃, and nitrogen monoxide, NO, or between deposition fluxes of sulfur dioxide, SO₂, and ammonia, NH₃) and eliminates artificial variability associated with mass changes due to chemical reactions (e.g., as sulfur dioxide, SO₂, is oxidized to sulfuric acid, H₂SO₄). The Green Book⁽²⁾ also expressly allows the use of number of entities (molecules, atoms, ions, photons, etc.) and related units (e.g. number concentration, informally "number density"). This point is discussed in Section 4.4 dealing with concentrations. No matter whether mole or number of molecules is employed to describe the amount of substance, it is always necessary that the chemical formula of the entity considered be unambiguously specified.

3.7 Derived Units

It is a tenet of SI that all units that are not directly expressible as base units are to be expressed as products of powers of the base units discussed above. For example, the SI unit for the magnitude of velocity having dimension length time⁻¹ is m s⁻¹, but the use of cm s⁻¹ is permissible. Similarly the SI unit for density (dimension: mass length⁻³) is kg m⁻³, but use of g cm⁻³, kg dm⁻³ or the like is permissible. The molar mass has dimension mass per amount of substance; the SI unit for molar mass is kg mol⁻¹, although use of g mol⁻¹ is permissible.

The use of special names and symbols for derived units is encouraged, e.g. newton (force), $N = \text{kg m s}^{-2}$; joule (energy), $J = \text{N m} = \text{kg m}^2 \text{s}^{-2}$; watt (power), $W = \text{J s}^{-1} = \text{kg m}^2 \text{s}^{-3}$; pascal (pressure), $\text{Pa} = \text{N m}^{-2} = \text{kg m}^{-1} \text{s}^{-2}$; coulomb (electric charge), $C = \text{A s}$; volt (electric potential), $V = \text{J C}^{-1} = \text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$; ohm (electric resistance), $\Omega = \text{V A}^{-1} = \text{kg m}^2 \text{s}^{-3} \text{A}^{-2}$; hertz (frequency), $\text{Hz} = \text{s}^{-1}$; and becquerel (radioactivity), $\text{Bq} = \text{s}^{-1}$. As noted above the use of SI prefixes with such derived units is encouraged, e.g. hPa, kW, MW, kHz, etc. The use of special names or symbols for units that are not products of powers of SI base units is discouraged and should be discontinued, e.g. hectare (area), $\text{ha} = 10^4 \text{ m}^2$; erg (energy) = 10^{-7} joule, bar (pressure) = 10^5 pascal, and these units should be replaced by their SI synonyms, i.e. hm^2 , $0.1 \mu\text{J}$, 0.1 MPa , respectively. The use of litre is tolerated because of long precedent, but it is discouraged, especially in equations, as it necessitates conversion factors.

4. Specific Quantities Important in Atmospheric Chemistry

Atmospheric chemistry deals with chemical compounds in the atmosphere, their distribution, origin, chemical transformation into other compounds, and their removal from the atmosphere. Quantities needed to describe physico-chemical conditions and changes in various atmospheric regions include abundance (local or integrated over the atmosphere, the troposphere, etc.), optical extinction, rate of chemical reaction, and rate and flux of physical transport for any atmospheric constituent. Units and symbols for these quantities are discussed below.

For historical reasons certain units that are inconsistent with SI have commonly been employed in atmospheric chemistry as well as in other scientific disciplines. Examples are atmosphere and torr for pressure, Dobson unit for column abundance of ozone, and curie for radioactivity. The discussion in the following sections will show that these units can generally be supplanted without difficulty by the appropriate SI units. For reasons of consistency, facility of unit calculations, and, ultimately, ease of communication with scientists within and outside the discipline of atmospheric chemistry, SI units are clearly preferable. The continued use of such non-SI units therefore is discouraged. Nonetheless it is recognized that because of the familiarity with such units within the atmospheric science community there may be a tendency for their continued use, at least in the near term. We recommend that SI units be used alongside inconsistent units, for example by use of auxiliary labels for axes of graphs, until the SI units become more familiar.

4.1 Pressure

Pressure is an important parameter needed to define atmospheric conditions. It is regularly measured at meteorological stations as well as during aircraft flights or balloon ascents. The SI unit for pressure is pascal (Pa). Non SI units for pressure that have been used in the past include atmosphere (equal to 101.325 kPa), bar (1×10^5 Pa), torr (approximately 133.3 Pa) and micron (1×10^{-3} torr). These units, which are gradually falling out of favor, should no longer be used. In particular, the unit mbar = 1×10^{-3} bar, which has been widely used by meteorologists, is gradually being replaced by the equivalent hectopascal (hPa). Accordingly the pascal or an appropriate multiple is recommended for use in atmospheric chemistry.

4.1.1 Partial Pressure

The pressure or partial pressure of a gaseous substance is of fundamental importance in specifying thermodynamic properties, and by analogy, the partial pressure of a trace gas in the atmosphere would seem similarly important in atmospheric chemistry. Surprisingly this is not the case, and the role of partial pressure is largely supplanted by other measures of local abundance. One application of partial pressure which has recently received some attention is in connection with gas solubility in cloud water. According to Henry's law, the equilibrium aqueous-phase concentration (or mixing ratio) of a dissolved gas is proportional to its gas-phase partial pressure (if departures from ideal gas behavior are appreciable, fugacity should be used in place of partial pressure). In SI the unit for partial pressure (also fugacity) is the pascal. The partial pressure of a trace gas may be readily evaluated as the product of the mole fraction of the gas (see below) and the total pressure.

4.2 Mixing ratio of a constituent of the atmosphere

The local abundance of a substance is an intensive property of great importance in atmospheric chemistry. Mixing ratio and concentration are quantities commonly (and often indiscriminately) used to describe local abundance. It is hoped that more attention be paid to the distinction between these quantities and to their correct application.

Concentration is the amount (or mass) of substance of concern in a given volume divided by that volume. Mixing ratio in atmospheric chemistry is defined as the ratio of the amount (or mass) of substance of concern in a given volume to the amount (or mass) of all constituents of air in that volume,⁽¹⁾ here *air* denotes gaseous constituents, including water vapor, but not condensed phase water or particulate matter. This definition of mixing ratio is identical to the fraction that the amount (or mass) of the substance under consideration contributes to the total amount (or mass) of the whole mixture. Concentrations are generally preferred when dealing with optical extinction, material transport, or chemical reaction kinetics. The principal advantage of mixing ratio over concentration in atmospheric chemical applications is that mixing ratio is unchanged by differences in pressure or temperature associated with altitude or with meteorological variability, whereas concentration depends on pressure and temperature in accordance with the equation of state. Mixing ratios are thus better suited than concentrations to describe abundances of individual substances in air and for recording their spatial or temporal variation. Mixing ratios may be expressed as chemical amount fraction (amount of substance per amount of air), mass fraction (mass of substance per mass of air), or as hybrid quantities, such as the amount or mass of substance per volume of air "reduced" to a standard temperature and pressure by the ideal gas law. We deal with these quantities below.

Since mixing ratio refers to the total gas mixture, the presence of water vapor causes the mixing ratio to vary with humidity. This variation may amount to several percent, depending on temperature and relative humidity. For this reason it is advantageous and customary in many circumstances to refer to dry air when expressing mixing ratios of trace gases in the atmosphere. It is therefore important to specify whether the reported mixing ratio refers to dry air or to moist air, that is, air containing water vapor under the conditions

of the sampling or measurement. Unfortunately the quantity being reported is frequently not explicitly stated. Authors, referees, and editors should endeavor to see that this situation is rectified. It is recommended that mixing ratio referred to dry air be reported provided that there is no loss in accuracy or precision associated with the conversion from mixing ratio referred to moist air. Mixing ratio referred to moist air is acceptable, however, and preferred if there would otherwise be loss in accuracy or precision due to the conversion.

4.2.1 Mole Fraction

Strictly speaking the quantity commonly denoted *mole fraction* refers to the fraction that the amount of a substance contributes to the total amount of the sample, so that the correct name should be *amount of substance fraction* (a rather unwieldy term) or *chemical amount fraction*, as the name of a quantity should not involve the name of the unit. However, *mole fraction* is used by almost everyone without causing much confusion, and for this reason we retain this familiar name.

The use of mole fraction to express abundances of species in the atmosphere conveys chemically meaningful relationships and is therefore to be preferred over the use of mass fraction. The use of volume fraction to express the mixing ratio of a gaseous species, which is widespread in atmospheric chemistry, also enjoys that advantage. Because air at atmospheric pressure is essentially an ideal gas, the volume fraction is essentially equal to the mole fraction, and for all practical purposes the two quantities can be used interchangeably and without distinction. Mole fraction is preferable, however, because it does not require an implicit assumption of ideality of the gases and, more importantly, because it is applicable also to condensed-phase species. For example one can express abundances of gaseous SO₂, NH₃, and HNO₃ as well as aerosol sulfate, ammonium, and nitrate all as mole fraction, and thereby immediately infer chemical meaningful relationships among these quantities; it would be erroneous, of course, to achieve that objective by referring to the abundance of sulfate, ammonium, or nitrate as a volume fraction.

Table 3 presents a summary of notations that are currently in use by atmospheric scientists to indicate mixing ratios of atmospheric gases. Although the notation ppm, ppb, ... (for part per million, parts per billion, ..., respectively) is quite convenient, this notation raises

Table 3: Units and symbols for gas phase mixing ratio (mole fraction). It is recommended that the symbols currently in use be supplanted by the SI units.

unit	fraction	symbol currently in use	SI unit
percent	10 ⁻²	%	cmol/mol
per mille	10 ⁻³	‰	mmol/mol
parts per million	10 ⁻⁶	ppm	μmol/mol
parts per hundred million	10 ⁻⁸	pphm	see note (a)
parts per billion	10 ⁻⁹	ppb	nmol/mol
parts per trillion	10 ⁻¹²	ppt	pmol/mol

(a) since there is no prefix for 10⁻⁸, the use of parts per hundred million is discouraged

several problems. One difficulty with this notation is that it does not readily allow application of SI prefixes for decimal fractions. A second problem is the ambiguity inherent in the use of billion for 10^9 and trillion for 10^{12} , which derives from North American usage, whereas in some European countries a billion denotes 10^{12} and a trillion 10^{18} . Further, ppt (intended to stand for part per trillion) is sometimes used in analytical chemistry as an abbreviation for part per thousand. For these reasons the Green Book⁽²⁾ recommends that the symbols ppb and ppt not be used. Another complication arises from the fact that the units in Table 3 are used by some investigators to designate mole or volume fractions and by others to denote mass mixing ratios. These quantities are sometimes (but by no means always) distinguished by an added v (for volume) and m (for mass; rarely for mole) or w (for weight, inaccurately), for example: ppmv, ppmm, ppmw; however, such use is deprecated by the Green Book⁽²⁾, which notes that "qualifying labels may be added to symbols for physical quantities, but never to units." A different choice of units should make this practice unnecessary and resolve these ambiguities.

There can be no doubt that the current notation for mixing ratios requires revision and that a suitable replacement must be sought. Strictly speaking, the question of conformity with SI provides no guidance in this matter, because mole fraction like any other fraction is a dimensionless quantity (strictly, quantity of dimension one) and multiples of the unit one are not part of SI. This is a formality, however. If it is desired to distinguish between different types of fractions, it is necessary in any event to state what kind of fraction is involved (mole, mass, volume, etc.) and to use the appropriate units. Thus the SI unit associated with the mole fraction of an atmospheric constituent in air is mol/mol. (In most applications it will be clear from the context that the mixing ratio refers to a component of air, so that the reference to air can be omitted; however, it is still obligatory to specify whether the mole fraction is expressed with respect to dry or moist air.) Moreover, if mol/mol is employed as the unit for the gas phase mixing ratio, it will then be simple to add SI prefixes for decimal fractions to obtain a useful replacement for current notations, for example ppmv becomes $\mu\text{mol/mol}$. The corresponding cases are included in Table 3 for comparison. This system also is sufficiently flexible to allow extension into the range of mixing ratios smaller than 10^{-12} (e.g., $\text{fmol/mol} = 10^{-15}$).

On the basis of these considerations it is recommended that the current notation (ppm, ppb, etc.) for gas phase mixing ratios be abandoned and replaced by the unit mol/mol in combination with appropriate prefixes for submultiples. Although units such as nmol/mol are somewhat more cumbersome to use than the notation ppb, etc., this seems to be a small price to pay for added clarity and elimination of ambiguity. Certain exceptions probably will have to be tolerated. For example, the usage of percent (symbol %) is so widely practiced that it is unlikely that it will be replaced by cmol/mol; it is nonetheless imperative that the quantity being reported be explicitly denoted as mole fraction.

Use of mole fraction is also appropriate and convenient for complex mixtures of organic compounds that can be described only in terms of their carbon content. Thus, we advocate $\mu\text{mol/mol}$ as a replacement for ppmC, which has gained some currency to permit immediate

comparison of the relative abundance of carbon in different organic compounds and of mixing ratios of organic carbon and nitrogen oxides on a molar basis. However, as qualifying labels are not to be added to units, we advise against use of $\mu\text{mol}(\text{C})/\text{mol}$. The proper place for the qualifying label C is the symbol for mixing ratio (see Section 4.2.4).

4.2.2. Mass Fraction

For a gaseous constituent of air present at great dilution the mass mixing ratio w is approximately related to the mole fraction x by $w = (M/M_{\text{air}}) x$, where M and M_{air} are the molar masses of the constituent and air, respectively. Generally the mass fraction is specified with respect to dry air, but this should be explicitly stated. The molar mass of dry air is approximately 28.97 g mol^{-1} . The pertinent unit for mass fraction is kg/kg in combination with the appropriate SI prefix for submultiples, for example g kg^{-1} , mg kg^{-1} or $\mu\text{g kg}^{-1}$. The mass mixing ratio is rarely used to indicate the local abundance of a gaseous constituent of the atmosphere, and there seems little reason to recommend its use, although it does conform to SI requirements. However, the mass mixing ratio of water vapor is commonly used by meteorologists and atmospheric physicists to denote specific humidity. This usage is of long standing and is unlikely to change. Its advantage is that it affords an immediate comparison to the mass mixing ratio of condensed phase (liquid, solid) water in the atmosphere.

Use of mass-based units for the local abundance of trace atmospheric constituents is particularly appropriate when the chemical composition of the constituent is not known or not well defined. For example, the chemical composition of aerosol particles and in turn the associated molar mass are generally not known, so that the mole fraction for total suspended matter in air cannot be calculated. In this case it is appropriate and recommended to specify the local abundance of total particulate matter as a mass fraction.

4.2.3 Reduced Concentration

An alternative way of reporting the local abundance of either a trace gas or particulate matter in air, which has seen much utilization in the past, is to express it as a hypothetical concentration that the system would exhibit if the gaseous volume of air were normalized (or "reduced") to a specific standard density. This reduced concentration is a superficially attractive measure of local abundance, as it is similar to the familiar concentration and yet it obviates the concerns of sensitivity of that quantity to variation with pressure or temperature. Reduced concentration is usually taken to refer to dry air, but this should be explicitly stated. Thus, as for mole fraction and mass fraction it is necessary to specify whether prior to the normalization the volume was occupied by dry or moist air.

Specification of a standard density requires specification of a standard temperature and a standard pressure (STP), and the unit of the reduced concentration can then be taken as $\text{mol, kg, etc. per cubic metre}$ at those standard conditions. (This is sometimes, incorrectly, referred to as a "standard cubic metre"; it is not the cubic metre that is standard, but the conditions). The standard conditions of 0°C and pressure of 1 atmosphere have long been employed in laboratory work. A problem with respect to conformance with SI is that atmosphere is not an accepted SI unit; the standard pressure recommended by IUPAC⁽²⁾ is

1×10^5 Pa (= 1 bar). This suggests that the standard conditions of temperature and pressure might be taken as 273.15 K and 0.1 MPa, as recommended in the Glossary of Atmospheric Terms⁽¹⁾. However, a variety of other choices of standard conditions have been employed by chemists, meteorologists or by specific regulatory agencies. For example, the United States Code of Federal Regulations⁽⁸⁾ specifies that measurements of concentrations for the purpose of ascertaining compliance with air quality regulations are to be corrected to a "reference temperature of 25°C and a reference pressure of 760 millimeters of mercury (1,013.2 millibars)." In chemical thermodynamics the standard conditions adopted are 298.15 K and 0.1 MPa.⁽⁹⁾ Still another pair of standard pressure and temperature is that employed by the *U.S. Standard Atmosphere (1976)*⁽¹⁰⁾, 101 325 Pa and 288.15 K. The selection of a single, universally employed set of standard conditions of temperature and pressure does not appear forthcoming in the near future; therefore any use of reduced concentration for reporting local abundance must be accompanied by a specification of the standard conditions employed.

It should be emphasized that a concentration when reduced to a standard state of air, while giving the appearance of being a concentration, is not a true concentration but is actually a mixing ratio. For example the reduced molar concentration of a substance *s* in air, C_s^{red} , is related to its molar mixing ratio, x_s , by

$$C_s^{\text{red}} = (p^*/RT^*) x_s$$

where T^* and p^* are the specified standard temperature and pressure, respectively, and R is the gas constant, all constants. Because, as shown by this relation, the reduced concentration is related to the mixing ratio by a constant factor, there is no necessity for the use of reduced concentration in all cases where the local abundance can be expressed by the mole fraction.

In view of the lack of harmony currently existing in the specification of standard conditions of temperature and pressure and the observation that reduced concentration is redundant to other measures of the mixing ratio, it might seem reasonable to recommend that the use of reduced concentration be discontinued. However, as this unit is embodied in regulations, its use undoubtedly will continue for some time. Moreover, there are some applications, such as $\mu\text{g}/\text{m}^3$ at STP for the reduced concentration of aerosol mass and Bq/m^3 at STP for the reduced concentration of radioactivity, that do not readily translate into mole fraction terminology, although these mixing ratios might quite satisfactorily be expressed as mass or activity per mass of dry air, i.e. $\mu\text{g}/\text{kg}$, Bq/kg , respectively. For these reasons we are not entirely prepared to recommend that the use of reduced concentrations be discontinued. For the present we call attention to these issues and recommend that use of reduced concentrations be avoided where possible. Any use of reduced concentration requires explicit specification of the standard conditions including dry or moist state.

4.2.4 Symbols for Mixing Ratios

The symbol m has traditionally been used by atmospheric chemists to denote the volume fraction or the mole fraction of a trace gas. This symbol, however, is also used to denote

mass, and if the possibility for confusion exists, care must be exercised to distinguish both quantities. Clearly, a different symbol would be preferable. In equilibrium thermodynamics the mole fraction generally is denoted by x . This convention applies mainly to the condensed phase. The Green Book⁽²⁾ suggests use of x for condensed phases and y for the gas phase, but if this proposal were adopted, it would add yet another symbol to the list. In books on heterogeneous systems the usage x_L and x_g for condensed and gas phase mole fractions is common. Therefore, it is recommended to use generally x for the mole fraction of atmospheric trace constituents. For the mass fraction the Green Book⁽²⁾ lists the symbol w and this appears to be a good choice. In any of these cases it is necessary that the entity under discussion be specified. This may be done either in parentheses or by an appropriate subscript, for example for carbon monoxide $x(\text{CO})$ or x_{CO} . The notation traditionally used by meteorologists for specific humidity is q ; we see no need for changing this practice.

4.3 Column abundance

Some measurement techniques for atmospheric trace components, specifically long-path optical absorption techniques with the sun or the moon as background source or remote sensing from satellite platforms, yield data in the form of a column density, that is the total amount or mass of a substance within a vertical column of air above a specific location. Column abundances (or "column burdens") have units of amount per area, number of molecules per area, or mass per area; in SI units, mol m^{-2} , m^{-2} , or kg m^{-2} , respectively.

The most important trace gas in the atmosphere whose column abundance is routinely measured is ozone. The data are traditionally reported in Dobson units (DU). One DU is the thickness in units of 10^{-3} cm that the ozone column would occupy if compressed into a layer of uniform density at 273.15 K and 1 atmosphere⁽¹⁾. The Dobson unit clearly does not conform to SI. Moreover, as in the case of reduced concentration, one again runs into the problem of selecting an appropriate standard state. For these reasons the Dobson unit should eventually be replaced by an appropriate SI unit. For the purpose of conversion it may be noted that one DU is approximately equivalent to a column density of O_3 molecules of $2.69 \times 10^{20} \text{ m}^{-2}$, of O_3 chemical amount $446.2 \mu\text{mol m}^{-2}$ or of O_3 mass 21.4 mg m^{-2} . A typical column abundance of O_3 of 300 DU corresponds to roughly 134 mmol m^{-2} . The unit mmol m^{-2} seems most convenient and least cumbersome, and it is thus hoped that it will eventually supplant the Dobson unit.

4.4 Concentrations of substances in air

Concentrations of substances in air may be expressed in terms of amount of substance per volume, number of molecules per volume, mass per volume, or volume per volume. Thus one may report chemical amount concentration (SI unit: mol m^{-3}), number concentration (SI unit: m^{-3}), mass concentration (SI unit: kg m^{-3}) or, for condensed phase substances, volume concentration (SI unit: 1 or $\text{m}^3 \text{ m}^{-3}$). The choice among these units depends on the nature of the substance and to some extent on the situation. Amount concentration is appropriate and frequently preferred for a substance of known chemical formula. Number concentration is appropriate for aerosol particles and is also frequently used for specific

gaseous substances especially for species with very low concentrations, such as OH radicals. Mass concentration is required for a substance whose composition or chemical formula is unknown or indeterminate, e. g. particulate matter suspended in air. Volume concentration is appropriate for the volume of condensed-phase matter per volume of air (e.g., for cloud water $\text{cm}^3 \text{m}^{-3}$ is frequently employed; similarly, for aerosols, $\mu\text{m}^3 \text{m}^{-3}$). Other more specialized concentration units, which may have application in atmospheric chemistry, may be readily constructed, such as surface area concentration, activity concentration, or electric charge concentration.

As noted above, variation in pressure or temperature generally results in variation in concentration of a trace species in the open system of the atmosphere. Similarly variation in humidity will lead to variation in concentration of a trace species. It is thus mandatory that temperature, pressure, and humidity be specified when reporting concentrations of atmospheric substances.

4.4.1 Gas Phase Concentration

Use of concentration to express the local abundance of substances in the atmosphere is common in atmospheric chemistry, although as noted above, use of mixing ratio is frequently preferable. Units for mass concentration and number concentration have seen widespread use, whereas use of chemical amount concentrations is relatively rare. A standard reference for the total concentration of air as a function of altitude⁽¹⁰⁾ presents the data in units kg m^{-3} and m^{-3} .

Concentration units are commonly used in connection with chemical reaction rates and optical extinction. In laboratory studies of gas-phase reaction kinetics, chemical amount concentration was traditionally expressed in units mol L^{-1} or mol cm^{-3} . More recently, perhaps because of increased participation of chemical physicists, chemical amount concentration has gradually been replaced by number concentration, and molecule cm^{-3} has become a widely used unit. This unit violates the SI rule that a qualifying name should not be part of a unit. The SI unit for number concentration of molecules (or any other particles) is m^{-3} or cm^{-3} . However, inclusion of the qualifying term "molecule" is widespread in atmospheric chemistry. Here we use it for the purpose of illustration. Further comments regarding its application will be given below.

In expressing number concentration, centimetre-based units have been more widely employed than metre-based units, e.g. atom cm^{-3} , molecule cm^{-3} (or to be consistent with SI, simply cm^{-3}). Insofar as centimetre-based number concentration units are submultiples of SI units, there should be no objection to their use. For example optical depth can be given by the formula κcL , where κ denotes the molar (Napierian) extinction (or attenuation) coefficient ($\text{m}^2 \text{mol}^{-1}$), c denotes the concentration (mol m^{-3}), and L denotes the path length (m), or equivalently as σnL where σ denotes the extinction cross section ($\text{cm}^2 \text{molecule}^{-1}$), n denotes number concentration (molecule cm^{-3}), and L denotes path length (cm). Extinction describes attenuation of light intensity due to absorption and scattering combined. The corresponding coefficients and the equivalent cross sections are properties of the medium penetrated by the optical path.

The desire for consistency with other SI quantities makes it preferable to recommend the use of metre-based units, that is $\text{m}^2 \text{molecule}^{-1}$ for cross section and molecule m^{-3} for number concentration, especially since the cubic metre is so widely used as the unit of volume in the atmospheric sciences. For example, as indicated earlier, concentrations of trace gases and aerosol particles are commonly expressed in amount or mass per cubic metre. Further, since values for number densities commonly involve many powers of ten, powers of ten must be explicitly given irrespective of whether one employs molecule m^{-3} or molecule cm^{-3} as the concentration unit, because SI prefixes for multiples are not applicable in either case. Nonetheless, use of centimetre-based units has numerous adherents. Two standard references for rate coefficients of atmospheric gas-phase reactions employ molecule-cm^3 based units.^(11,12)

Since concentrations are conventionally employed in chemical kinetic expressions (collision rates and reaction rates depend on concentrations, not mixing ratios), it is useful to examine such rate expressions in the context of considering appropriate units for concentrations. For example, the rate of a chemical reaction involving substances A and B (bimolecular reaction) may be written

$$-dn_A/dt = k_{\text{bim}}n_A n_B$$

where n_A and n_B are the concentrations of A and B, respectively, and t is the time. The rate coefficient k_{bim} has dimension $\text{concentration}^{-1} \text{time}^{-1}$; possible units are $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$, $\text{m}^3 \text{molecule}^{-1} \text{s}^{-1}$, and $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$, corresponding to the concentration units molecule cm^{-3} , molecule m^{-3} , and mol m^{-3} , respectively. Table 4 compares ranges of concentrations and rate coefficients pertinent to atmospheric chemistry for the several systems of units. While nothing can be done about the wide range of the values, it appears that rate coefficients have the most convenient magnitudes when concentrations are expressed in units of mol m^{-3} . With this choice of unit, rate coefficients for second order reactions have values in the range 1 to 10^8 . In this case, too, SI prefixes for decimal fractions may be conveniently applied. For example, for gases whose mixing ratios are in the nmol/mol to $\mu\text{mol/mol}$ range the corresponding concentrations at 0.1 MPa pressure and 298.15 K temperature are in the range 40 nmol m^{-3} to $40 \mu\text{mol m}^{-3}$, approximately. The key atmospheric free radical, the OH radical, has an average number concentration in the troposphere of about $8 \times 10^5 \text{ molecule cm}^{-3}$ according to a recent estimate.⁽¹³⁾ The corresponding chemical amount concentration is approximately $1.3 \times 10^{-12} \text{ mol m}^{-3}$ or 1.3 pmol m^{-3} . The ease of expressing concentrations of these magnitudes in units based on the mole by means of the appropriate prefixes for submultiples suggests that it might be advantageous to use chemical amount concentrations expressed in units of mol m^{-3} rather than number concentration expressed in units of molecule cm^{-3} or molecule m^{-3} . However, number concentration is widely employed, and it appears that the use of multiple approaches for expressing concentrations will continue for some time.

Several inconsistencies are encountered in using number density to express concentration, and these require further comment. As noted above, the use in units of terms such as "particles", "molecules", "photons", etc. is inconsistent with SI, because pure numbers do

Table 4: Typical ranges of values in atmospheric chemistry for different choices of the system in which to express gas phase concentrations

System	molecule, cm ³	molecule, m ³	mole, m ³
Concentration	10 ⁴ - 10 ¹⁹	10 ¹⁰ - 10 ²⁵	10 ⁻¹⁴ - 10
Unit	molecule cm ⁻³	molecule m ⁻³	mol m ⁻³
Bimolecular rate coefficient	10 ⁻¹⁸ - 10 ⁻¹⁰	10 ⁻²⁴ - 10 ⁻¹⁶	1 - 10 ⁸
Unit	cm ³ molecule ⁻¹ s ⁻¹	m ³ molecule ⁻¹ s ⁻¹	m ³ mol ⁻¹ s ⁻¹
Termolecular rate coefficient	10 ⁻³⁶ - 10 ⁻²⁹	10 ⁻⁴⁸ - 10 ⁻⁴¹	1 - 10 ⁷
Unit	cm ⁶ molecule ⁻² s ⁻¹	m ⁶ molecule ⁻² s ⁻¹	m ⁶ mol ⁻² s ⁻¹
Optical absorption coefficient or cross section	10 ⁻²² - 10 ⁻¹⁶	10 ⁻²⁶ - 10 ⁻²⁰	10 ⁻² - 10 ⁴
Unit	cm ² molecule ⁻¹	m ² molecule ⁻¹	m ² mol ⁻¹
Solar flux	10 ⁹ - 10 ¹⁵	10 ¹³ - 10 ¹⁹	10 ⁻¹¹ - 10 ⁻⁵
Unit	photon cm ⁻² s ⁻¹	photon m ⁻² s ⁻¹	mol m ⁻² s ⁻¹

not carry a unit. Despite this, there is a definite advantage in making the entity involved part of the unit and writing, for example, molecule m⁻³ rather than m⁻³ in order to distinguish between several possibilities and thereby remove potential ambiguities. Accordingly, when number concentrations are employed in atmospheric chemistry, we advocate the use of identifying names together with units such as particle m⁻³, molecule cm⁻³, photon m⁻² s⁻¹, if it aids in clarification. On the other hand, there is no need to extend this practice to well established SI units for physico-chemical constants, for example the Avogadro constant (approximately 6.022 x 10²³ mol⁻¹) or the Boltzmann constant (approximately 1.381 x 10⁻²³ J K⁻¹).

A further problem encountered when including particles, molecules, photons, etc. in the unit arises from the common practice to refer to these entities in the plural, whereas units are always expressed in the singular. Yet another problem is that one cannot use a SI prefix before molecule and is thus obliged to use the power of ten multiplier, whereas use of a prefix is natural with concentration units based on the mole, e.g. nmol m⁻³, fmol m⁻³.

In view of the several considerations given to this subject above it is hoped that the atmospheric chemistry community will increasingly employ units based on the mole, the metre and the second for gas-phase concentrations, rates, and rate coefficients. At present, however, it does not appear that any single choice is likely to gain acceptance, and therefore no firm recommendation is made in this direction.

4.4.2 Aqueous-phase mixing ratios and concentrations

Concentrations and deposition fluxes of substances dissolved in precipitation have been of long standing interest in atmospheric chemistry. More recently increased attention has been paid to concentrations of species dissolved in cloudwater and in aqueous aerosols. Because of exchange of species between gaseous and aqueous phases, there is a need for expressing concentrations (or mixing ratios) of substances in aqueous solution, in air, and in the multiphase system as a whole, and similarly for expressing chemical reaction rates in solution as well as in the system as a whole. Unambiguous nomenclature and units are required for this purpose, and this section addresses the issues involved.

In chemical thermodynamics of solutions the preferred mode for expressing abundances of solutes is mixing ratio, frequently in the form of mole of solute per mole of solvent but commonly also in the form of mole of solute per kilogram of solvent, the latter quantity being denoted the molality (unit: mol kg^{-1}). In both cases, the value of the ratio remains unchanged as the density of solution changes with changing temperature, in contrast to concentration. As molality is expressed in SI base units of mole and kilogram, its use is encouraged. The choice of a 1 mol kg^{-1} solution as standard molality of aqueous solutions for chemical thermodynamics (see the Green Book,⁽²⁾ page 54) lends further impetus to use of this unit in atmospheric chemistry.

In much laboratory work as well as atmospheric chemistry work involving solutions the customary unit for concentration is mole per litre, mol L^{-1} rather than mol m^{-3} , as would be consistent with SI. Use of the molarity scale, in which a solution of concentration $c \text{ mol dm}^{-3}$ is referred to as "a c molar solution" (symbol: $c \text{ M}$), is so widespread in the chemical sciences that this terminology is explicitly tolerated by the IUPAC Commission on Physicochemical Symbols, Terminology and Units (Green Book, page 42), despite nonconformance with the SI principle that named units should be restricted to products of powers of base units. As emphasized above, use of nonconforming units is discouraged, especially in equations, because it necessitates conversion factors. Currently there exists a trend to replace the litre by its synonym, the cubic decimetre, dm^3 and thus to express concentrations in units mol dm^{-3} , for example nmol dm^{-3} , $\mu\text{mol dm}^{-3}$, mmol dm^{-3} , but even this usage require care in equations.

Dilute aqueous solutions in the atmosphere occur in cloud and rain drops, for which solute concentrations are typically in the range mmol dm^{-3} or less. This raises the question whether units such as nmol dm^{-3} , $\mu\text{mol dm}^{-3}$, and mmol dm^{-3} should be replaced by $\mu\text{mol m}^{-3}$, mmol m^{-3} , and mol m^{-3} , respectively. In order to take advantage of the self consistency of SI this would seem advisable; ultimately expressions of aqueous concentrations in submultiples of the unit mol m^{-3} may become more widely adopted in

other subdisciplines of chemistry than it has so far. Unless or until this happens, however, it does not seem necessary to mandate this practice in atmospheric chemistry.

A possible resolution of the situation arising from nonconformance of the molarity scale with SI would be use of the molality scale, which for dilute aqueous solutions is numerically approximately equal to mol L^{-1} and thus retains the familiarity of that widely employed unit. The molality of a solution is actually a mixing ratio. The conversion between concentration C and molality m is as follows:

$$m = \frac{C}{\rho - MC}$$

where ρ is the density of the solution and M is the molar mass of the solute. This equation serves also to illustrate the advantage inherent in a self consistent set of units as SI. For molar mass M expressed in units kg mol^{-1} , concentration C in mol m^{-3} , and density ρ in kg m^{-3} , the expression on the right hand side is entirely self consistent, having units mol kg^{-1} , without the necessity of employing units conversion factors, as would be required with non-self consistent units.

In studies of the composition of rainwater, aqueous solutions derived from dissolving particulate matter, and the like, it often is desirable to demonstrate charge balance between analyzed anions and cations. The customary procedure has been to multiply the concentration of each ionic species i by its valence z_i and to compare the totals. Here and elsewhere use of the term "equivalents" and of units such as "equ L^{-1} " or "normality" to represent valence concentrations of multiply charged ionic species should be avoided⁽¹⁴⁾. Rather, the concentration specified should be that of the equivalent entity, which is defined as the fraction $(1/z_i)$ of the molecular entity⁽¹⁵⁾ (see also the Green Book⁽²⁾, page 46). For example, the equivalent entity of the sulfate ion, SO_4^{2-} , is $\frac{1}{2}\text{SO}_4^{2-}$. For a solution having a 1 M concentration of sulfate ion, i.e. $[\text{SO}_4^{2-}] = 1 \text{ M}$, the concentration of the corresponding equivalent entity is $[\frac{1}{2}\text{SO}_4^{2-}] = 2 \text{ M}$; that is to say that 1 L of solution contains 2 mol of the entity $\frac{1}{2}\text{SO}_4^{2-}$. An example calculation of ion balance is given in Table 5.

Frequently, especially in reports of precipitation composition, mass-based concentration units are employed, e.g. milligram per litre (or kilogram) or, less formally, "ppm" denoting part per million by mass. For the several reasons noted above (elimination of ambiguity, explicit display of chemical equivalence relationships) use of such units should be avoided, the only exception being situations where the chemical identity of the substance is not known or not defined, the recurring example being suspended material. In the latter case, in order to be consistent with the above discussion, the use of m^3 or dm^3 based units is recommended, for example g m^{-3} or mg dm^{-3} .

In contrast to the situation with aqueous solutions, the cubic metre is unambiguously the appropriate reference volume to use when it is desired to describe the concentration of a substance relative to the multiphase system as a whole or to express the total concentration of a substance in the gaseous and aqueous phases combined. In these cases the appropriate units are nmol m^{-3} , $\mu\text{mol m}^{-3}$, etc.

Table 5. Example illustrating equivalent entites and use of equivalent entity concentrations to report composition and ion balance in aqueous solution. The solution corresponds nominally to a mixture of 25 $\mu\text{mol H}_2\text{SO}_4$, 45 $\mu\text{mol (NH}_4)_2\text{SO}_4$, 26 $\mu\text{mol NH}_4\text{NO}_3$, 30 $\mu\text{mol NaCl}$, 10 $\mu\text{mol KNO}_3$, 5 $\mu\text{mol CaSO}_4$, and 2 $\mu\text{mol Mg(NO}_3)_2$ in 1 litre of water. Note that the numerical entries are pure, dimensionless numbers, representing the ratio of concentration (unit: mmol m^{-3}) to the unit itself.

species	Symbol for species concentration	Species concentration	Equivalent entity	Symbol for equivalent entity concentration	Equivalent entity concentration
s	[s]	[s]/ mmol m^{-3}	$\frac{1}{2}s$	$[\frac{1}{2}s]$	$[\frac{1}{2}s]/\text{mmol m}^{-3}$
Cations:					
H ⁺	[H ⁺]	50	H ⁺	[H ⁺]	50
NH ₄ ⁺	[NH ₄ ⁺]	116	NH ₄ ⁺	[NH ₄ ⁺]	116
Na ⁺	[Na ⁺]	30	Na ⁺	[Na ⁺]	30
K ⁺	[K ⁺]	10	K ⁺	[K ⁺]	10
Ca ²⁺	[Ca ²⁺]	5	$\frac{1}{2}\text{Ca}^{2+}$	$[\frac{1}{2}\text{Ca}^{2+}]$	10
Mg ²⁺	[Mg ²⁺]	2	$\frac{1}{2}\text{Mg}^{2+}$	$[\frac{1}{2}\text{Mg}^{2+}]$	4
total cations					<u>220</u>
Anions:					
SO ₄ ²⁻	[SO ₄ ²⁻]	75	$\frac{1}{2}\text{SO}_4^{2-}$	$[\frac{1}{2}\text{SO}_4^{2-}]$	150
NO ₃ ⁻	[NO ₃ ⁻]	40	NO ₃ ⁻	[NO ₃ ⁻]	40
Cl ⁻	[Cl ⁻]	30	Cl ⁻	[Cl ⁻]	30
total anions					<u>220</u>

The concentration or mixing ratio of a dissolved substance relative to the multiphase system as a whole is readily evaluated as the product of the concentration or mixing ratio in aqueous solution times the concentration or mixing ratio of water in air. For example, given the molality (mol kg^{-1}) of substance s in cloudwater, m_s , and a cloudwater concentration L (kg m^{-3}), the concentration of solute relative to air is $C_s(\text{mol m}^{-3}) = L m_s$. Similar considerations obtain in relating the rate of reaction in solution to the rate referred to the multiphase system as a whole.

4.4.3 Aerosol Concentration-Size Distribution

In atmospheric chemistry it is frequently necessary to report the distribution of certain quantities with the size of aerosol particles or of cloud drops. The most commonly reported of these quantities are number distribution and mass distribution, that is the number or mass of particles per volume and per radius (or diameter) interval. The number distribution is generally expressed by the symbol dn/dr , which explicitly denotes the differential nature of this quantity. It is clear that dn/dr has the dimension length^{-4} , and the corresponding SI

units would be m^{-4} . However, because the volume and the radius interval are fundamentally different quantities they should not be combined. A more appropriate means of expressing the unit is therefore $\text{m}^{-3} \text{m}^{-1}$. Moreover, since radii of aerosol particles are conventionally expressed in units of μm , it is more convenient and clarifying to express the number distribution in units of $\text{m}^{-3} \mu\text{m}^{-1}$. Similarly, an area distribution dA/dr is conventionally expressed in units of $\mu\text{m}^2 \text{m}^{-3} \mu\text{m}^{-1}$, a volume distribution dV/dr in units of $\mu\text{m}^3 \text{m}^{-3} \mu\text{m}^{-1}$, and a mass concentration distribution dC/dr in units of $\mu\text{g} \text{m}^{-3} \mu\text{m}^{-1}$. Expressing an amount concentration distribution (of a chemical constituent of aerosol particles) in units of $\text{nmol} \text{m}^{-3} \mu\text{m}^{-1}$ should also present no problem.

4.4.4 Symbols for Concentration

The usual symbol for concentration in the general case is c or C . It is advantageous, however, to distinguish concentrations in the gas phase and in aqueous solution. For aqueous solutions it has been common practice to denote the concentration of a solute s by square brackets, $[s]$, where s is the chemical formula for the substance, for example, $[\text{SO}_4^{2-}]$. This practice is extremely convenient and its continuation is highly recommended provided the units are specified ($\text{mol} \text{m}^{-3}$ or $\text{mol} \text{dm}^{-3}$).

For molality the International Organization for Standardization⁽⁶⁾ has adopted b_{B} or m_{B} with B denoting the dissolved entity. The symbol b has not found a widespread acceptance, however, and the symbol m may be confused with mass (see also the Green Book⁽²⁾ on this issue, p. 42). Despite this, the use of m for molality is recommended. As in other cases it is necessary to specify the entity involved, and this requirement can be met either by a subscript or in parentheses (m_{B} or $m(\text{B})$).

With regard to gas phase concentration, the symbol n is generally used by atmospheric chemists and reaction kineticists for number concentration. Unfortunately, n is also used to indicate the amount of substance. For example, the equation of state may be written in either of two forms: $p = nk_{\text{B}}T$, where n is the number density and k_{B} the Boltzmann constant, or $p = nRT/V$, where n is the amount of substance present in a given volume V , $R = k_{\text{B}}N_{\text{A}}$ is the gas constant and N_{A} is the Avogadro constant. Care should be exercised to avoid confusion between both applications. The symbol N has often been employed by atmospheric scientists instead of n to denote number density, in particular the number density of aerosol particles. According to international standard⁽⁶⁾ the symbol N is now reserved strictly for the number of entities so that it should no longer be used in the above context. Specifically, N serves to define number concentration ($n = N/V$). The Green Book⁽²⁾ suggests use of either n or C as symbols for number concentration. Here again, the symbol C has multiple uses, for example to denote heat capacity. However, use of the symbol n is now so common as to justify its continued use in atmospheric chemistry.

If chemical amount concentration (unit: $\text{mol} \text{m}^{-3}$) should find a wider acceptance also for the gas phase, a special symbol for it may eventually be required. For the time being the symbol c is recommended. However, we also recognize the need for some flexibility. One possibility is to work with qualifying labels. Thus, where necessary for clarification the symbol c may be labeled with a subscript to distinguish different types of concentrations. In

this regard there does not appear to exist any universally accepted convention. For the purpose of illustration we suggest the following subscripts: n for number of entities, a for amount of substance, m for mass. Accordingly, c_n denotes the concentration of number of entities; c_a the concentration of amount of substance; c_m the mass concentration. Similar labels may also be used with symbols for other quantities, and examples are given in Table 6. In the absence of an accepted convention and to avoid ambiguity, however, it will be necessary in the general case that the quantity identified by a subscript be explicitly defined.

Table 6: Symbols, SI units and common units for quantities in atmospheric chemistry

Quantity	Symbol	Si Unit	Common Unit
altitude	z	m	m, km
radius of aerosol particles and cloud drops	r, a	m	μm , mm
wavelength (of light)	λ	m	nm, μm
area	A	m^2	m^2 , km^2 , μm^2 ...
volume	V	m^3	m^3 , dm^3 , μm^3 ...
deposition velocity	v_d	m s^{-1}	cm s^{-1}
pressure	p	Pa	hPa, kPa, MPa
mass content of a substance s in an atmospheric region	G_s	kg	Tg, Pg
tropospheric mass	G_T	kg	kg, Zg
mass column density (of substance s)	W_s	kg m^{-2}	kg m^{-2}
mass density of air	ρ_{air}	kg m^{-3}	kg m^{-3}
mass density of water	ρ_w	kg m^{-3}	kg m^{-3} , g cm^{-3}
chemical amount concentration of a substance s in air	$c_s, c_a(s)$	mol m^{-3}	mol m^{-3}
number concentration of a substance s in air	$n_s, C_s, c_n(s)$	m^{-3}	molecule m^{-3} molecule cm^{-3}
mass concentration of a substance s in air	$c_s, c_m(s)$	kg m^{-3}	kg m^{-3} , g m^{-3} , ...
chemical amount concentration of a substance s in aqueous solution	[s]	mol m^{-3}	mol m^{-3} , mol dm^{-3}
molality of a substance s in aqueous solution	$m_s, m(s)$	mol kg^{-1}	mmol kg^{-1} , $\mu\text{mol kg}^{-1}$, ...
mole fraction of a substance s in air	$x_s, x(s)$	1	mol mol^{-1} , $\mu\text{mol mol}^{-1}$, ...
mass mixing ratio of a substance s in air	w_s	1	kg kg^{-1} , g kg^{-1} , ...
liquid water mass concentration in air	L	kg m^{-3}	kg m^{-3} , g m^{-3} , ...
chemical reaction rate	r	$\text{mol m}^{-3} \text{s}^{-1}$	$\text{mol m}^{-3} \text{s}^{-1}$, molecule $\text{m}^{-3} \text{s}^{-1}$ molecule $\text{cm}^{-3} \text{s}^{-1}$
unimolecular reaction rate coefficient	k_{uni}	s^{-1}	s^{-1}

Table 6: continued

quantity	symbol	SI Unit	Common Unit
bimolecular reaction rate coefficient	k_{bim}	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$ $\text{m}^3 \text{molecule}^{-1} \text{s}^{-1}$ $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$
termolecular reaction rate coefficient	k_{ter}	$\text{m}^6 \text{mol}^{-2} \text{s}^{-1}$	$\text{m}^6 \text{mol}^{-2} \text{s}^{-1}$ $\text{m}^6 \text{molecule}^{-2} \text{s}^{-1}$ $\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$
chemical amount flux for substance s	$F_{\text{a}}(\text{s})$	$\text{mol m}^{-2} \text{s}^{-1}$	$\text{mol m}^{-2} \text{s}^{-1}$
number flux for substance s	$F_{\text{n}}(\text{s})$	$\text{m}^{-2} \text{s}^{-1}$	$\text{molecule m}^{-2} \text{s}^{-1}$
mass flux for substance s	$F_{\text{m}}(\text{s})$	$\text{kg m}^{-2} \text{s}^{-1}$	$\text{kg m}^{-2} \text{s}^{-1}$
radiant energy flux	J	W m^{-2}	W m^{-2}
photon number flux	I_{n}	$\text{m}^{-2} \text{s}^{-1}$	$\text{photon m}^{-2} \text{s}^{-1}$
photon amount flux	I_{a}	$\text{mol m}^{-2} \text{s}^{-1}$	$\text{mol m}^{-2} \text{s}^{-1}$
molecular absorption cross section	σ	m^2	$\text{m}^2 \text{molecule}^{-1}$ $\text{cm}^2 \text{molecule}^{-1}$
molar Napierian absorption coefficient	κ	$\text{m}^2 \text{mol}^{-1}$	$\text{m}^2 \text{mol}^{-1}$
photodissociation coefficient	j	s^{-1}	s^{-1}
quantum yield	ϕ	1	$\text{molecule photon}^{-1}$
molecular diffusion coefficient	D	$\text{m}^2 \text{s}^{-1}$	$\text{m}^2 \text{s}^{-1}$
eddy diffusion coefficient	K	$\text{m}^2 \text{s}^{-1}$	$\text{m}^2 \text{s}^{-1}$
local production rate for substance s	$q_{\text{a}}(\text{s})$	$\text{mol m}^{-3} \text{s}^{-1}$	$\text{mol m}^{-3} \text{s}^{-1}$
	$q_{\text{n}}(\text{s})$	$\text{m}^{-3} \text{s}^{-1}$	$\text{molecule m}^{-3} \text{s}^{-1}$
	$q_{\text{m}}(\text{s})$	$\text{kg m}^{-3} \text{s}^{-1}$	$\text{kg m}^{-3} \text{s}^{-1}$
local sink rate for substance s	$s_{\text{a}}(\text{s})$	$\text{mol m}^{-3} \text{s}^{-1}$	$\text{mol m}^{-3} \text{s}^{-1}$
	$s_{\text{n}}(\text{s})$	$\text{m}^{-3} \text{s}^{-1}$	$\text{molecule m}^{-3} \text{s}^{-1}$
	$s_{\text{m}}(\text{s})$	$\text{kg m}^{-3} \text{s}^{-1}$	$\text{kg m}^{-3} \text{s}^{-1}$
integrated source strength for substance s	$Q_{\text{a}}(\text{s})$	mol s^{-1}	mol a^{-1}
	$Q_{\text{n}}(\text{s})$	s^{-1}	molecule a^{-1}
	$Q_{\text{m}}(\text{s})$	kg s^{-1}	kg a^{-1}
integrated sink strength for substance s	$S_{\text{a}}(\text{s})$	mol s^{-1}	mol a^{-1}
	$S_{\text{n}}(\text{s})$	s^{-1}	molecule a^{-1}
	$S_{\text{m}}(\text{s})$	kg s^{-1}	kg a^{-1}

4.5 Transfer Rates and Fluxes

Many considerations in atmospheric chemistry are related to transport of material, energy, or other quantities in the atmosphere. Material fluxes in the atmosphere result from local and large-scale winds and from turbulent and molecular mixing. The principal energy flux of concern in atmospheric chemistry is the photochemically relevant part of solar irradiation.

In treating transport processes it is necessary to distinguish between transfer (or flow) rates associated with the exchange of material, energy, etc. between compartments or volume

elements, and fluxes of materials, energy, etc. that describe the rate of transport of these quantities per area. In the first case the appropriate unit for material transfer is mol s^{-1} , and the unit for energy transfer is J s^{-1} (W). The corresponding units for the fluxes are $\text{mol m}^{-2} \text{s}^{-1}$ and W m^{-2} , respectively. The term flux is sometimes used (incorrectly) to denote a transfer rate; this usage is discouraged. Similarly the usage flux density for flux should be avoided.

4.5.1 Global Transfer Rates

Global transfer rates quantify the globally integrated transfer of materials into or out of the atmosphere or exchange between major compartments. Examples are the outflow of gases at the surface of the earth, the exchange of materials between principal atmospheric domains such as between stratosphere and troposphere or between the northern and southern tropospheres, etc. Appropriate SI units for these rates might be mol s^{-1} , molecule s^{-1} , or kg s^{-1} . For a variety of reasons many rates exhibit appreciable temporal fluctuations. To eliminate diurnal and seasonal effects it is usual to take an average over at least one year. Transfer rates thus are frequently expressed in units of mol a^{-1} or kg a^{-1} . These units when combined with the appropriate SI prefixes for multiples are particularly suitable for describing global cycles of trace gases.

4.5.2 Material Fluxes within the Atmosphere

Apart from bulk motion, material fluxes are associated with concentration gradients. In molecular diffusion, which takes place on a microscopic scale, the flux is proportional to the concentration gradient

$$F_{\text{dif}} = -D \nabla c$$

where D , the diffusion coefficient, has the unit $\text{m}^2 \text{s}^{-1}$. Large scale transport along a concentration gradient is effected by turbulent mixing. This is usually parametrized by analogy to molecular diffusion but with the nabla (gradient) operator applied to the mixing ratio x_s of the trace constituent considered:

$$F_{\text{eddy}} = -K c_{\text{air}} \nabla x_s$$

where K is the so-called eddy diffusion coefficient, and c_{air} is the concentration of air; K also has the unit $\text{m}^2 \text{s}^{-1}$. If c_{air} is given in mol m^{-3} , the above equation indicates the molar flux (unit: $\text{mol m}^{-2} \text{s}^{-1}$). Appropriate prefixes for decimal fractions should be applied; fluxes of trace gases typically have magnitudes of $\text{nmol m}^{-2} \text{s}^{-1}$ or $\mu\text{g m}^{-2} \text{s}^{-1}$.

4.5.3 Emission and Deposition Rates and Fluxes

The input of chemical substances into the atmosphere from anthropogenic and natural sources and the removal of chemical substances from the atmosphere are essential processes of atmospheric chemistry. Emission rates for point sources such as stacks of electric power stations can be calculated from flow rates and concentrations of effluent gases in the stack. Frequently, the rates are given in units such as kg h^{-1} or Mg a^{-1} . This practice is acceptable provided the substance is chemically stable and its molar mass is well defined, because the mass flow rate can unambiguously be converted to the equivalent chemical

amount flow rate. Difficulties arise in some cases, notably the mixture of NO and NO₂ called NO_x, for which the components are not generally analytically separated. The practice of specifying emission rates for nitrogen oxides in kg h⁻¹ "as NO₂" (meaning to be calculated as NO₂) is at best cumbersome and may lead to confusion and should therefore be discontinued. In this case it is necessary to specify the entity for which the emission rate is reported either in words or in symbols. Consistency with arguments put forth in Section 4.2.1 requires that the entity not be included in the unit, for example mol(NO_x) s⁻¹. Instead, the entity should be included as a qualifying label of the symbol used to represent the quantity, for example the emission rate of nitrogen oxides $q(\text{NO}_x) = 5 \text{ mol s}^{-1}$.

Similar issues may arise in describing fluxes of trace gases from soils or aquatic systems. Here again, difficulties are encountered when the flux refers to a mixture of compounds. A case in point is the emission of reduced sulfur compounds. At least four such compounds are usually involved (H₂S, OCS, CS₂, H₃CSCH₃), but the number may be much larger, and a full differentiation is not always possible. Accordingly it is necessary to specify the flux in terms of a specific entity and express it in appropriate units. In the present case, the sulfur atom (S) is an appropriate entity, so that, for example, the emission flux of reduced sulfur compounds may be reported as $F(\text{S}) = 0.1 \text{ nmol m}^{-2} \text{ s}^{-1}$.

Expression of emission or deposition amount per hectare has been common, perhaps because of the widespread use of hectare as a unit in agriculture. However, as noted previously, the hectare is not consistent with SI and its use should be discontinued. In order to take into account diurnal and seasonal variations of the fluxes, averages over longer time periods are often reported in units such as mole or gram per hectare and day or year (g ha⁻¹ d⁻¹; mol ha⁻¹ d⁻¹; mol ha⁻¹ a⁻¹; etc.). Appropriate units are ng m⁻² s⁻¹, nmol m⁻² d⁻¹ or μmol m⁻² a⁻¹, etc. However, use of hm² as a synonym for hectare is permissible, for example μmol hm⁻² d⁻¹, and this might be convenient for comparison with previous data.

The rate of deposition of a reactive atmospheric trace material to the surface is generally proportional to the atmospheric concentration of the material, where the proportionality constant depends on transport conditions in the atmospheric boundary layer and the resistance of the surface to the uptake of the material. The deposition flux can therefore be expressed as

$$F_d = v_d c_s$$

where v_d has dimension of velocity (length time⁻¹) and is therefore commonly referred to as the "deposition velocity" of substance *s* (which is directed vertically downward), and where c_s is the concentration of the trace substance *s* at a reference height, generally 1 to 10 m above the ground or the plant canopy. Deposition velocities of reactive gases typically range between 10⁻⁴ and 10⁻¹ m s⁻¹. Units of m s⁻¹ or cm s⁻¹ are appropriate.

The inverse of a deposition velocity (unit: s m⁻¹) is the resistance to deposition. Use of this quantity rather than the deposition velocity is convenient, since it consists of additive terms representing aerodynamic and surface components of the overall resistance.

4.5.4 Energy Flux

The most important energy flux pertinent to atmospheric chemistry is that of ultraviolet and visible solar radiation, because absorption of light within these wavelength regions is responsible for photochemical activity in the atmosphere. A photochemically active volume of the lower atmosphere receives radiation from all directions, and the actinic radiation flux is that incident on the total surface of a reference volume. Irradiance, in turn, is the radiant energy transported from all directions across a plane surface. The appropriate SI unit for actinic flux or irradiance is W m^{-2} . The appropriate SI unit for spectral irradiance, $dJ/d\lambda$, is W m^{-3} , but since area and wavelength interval are fundamentally different quantities they should not be combined. It is thus preferable to write $\text{W m}^{-2} \text{m}^{-1}$, or better $\text{W m}^{-2} \mu\text{m}^{-1}$ or $\text{W m}^{-2} \text{nm}^{-1}$. For the visible and near infrared wavelength region the spectral irradiance of the sun has been presented in units of $\text{W m}^{-2} \mu\text{m}^{-1}$.⁽¹⁶⁾ In the photochemically more important ultraviolet spectral region the spectral irradiance of the sun outside the earth's atmosphere usually is presented in units of $\text{photon m}^{-2} \text{s}^{-1}$ for specified wavelength intervals.⁽¹⁷⁾ Strictly speaking, such a unit violates the convention that entity names not be included in units. However, as noted in Section 4.4.1, the advantage of clarity gained by specifying the entity in this way may mitigate the formal violation.

In photochemical considerations, it is frequently desirable to express the radiation flux as a flux of photons, because in the act of optical absorption a single photon is taken up by the absorbing molecule. The process thus resembles that of a chemical reaction between molecules and photons. If J denotes the energy flux in units of W m^{-2} , the photon flux I_n for monochromatic radiation of wavelength λ is given by

$$I_n = J/h\nu = J\lambda/hc \quad (\text{photon m}^{-2} \text{s}^{-1}), \text{ (SI unit: m}^{-2} \text{s}^{-1})$$

where h is the Planck constant, ν is the frequency of the radiation and c is the speed of light. It is also possible to express the photon flux as a chemical amount flux:

$$I_a = J/N_A h\nu = J\lambda/N_A hc \quad (\text{mol m}^{-2} \text{s}^{-1})$$

where N_A is the Avogadro constant. Although photochemists sometimes refer to one mole of photons as one Einstein, this unit has not found a widespread acceptance, and its use is discouraged⁽¹⁸⁾. The spectral actinic flux (as well as spectral irradiance) can similarly be expressed as a spectral photon flux:

$$dI_n/d\lambda = (\lambda/hc) dJ/d\lambda$$

The rate of a photochemical reaction of species s having concentration $c_n(s)$ (molecule m^{-3}) can be evaluated as

$$-dc_n(s)/dt = c_n(s) \int \phi(\lambda)\sigma(\lambda)(dI_n/d\lambda)d\lambda$$

where $\sigma(\lambda)$ is the absorption cross section ($\text{m}^2 \text{molecule}^{-1}$) and $\phi(\lambda)$ is the quantum yield of reaction per absorbed photon ($\text{molecule photon}^{-1}$). The photodissociation coefficient of species s is given by

$$j \equiv -(c_n(s))^{-1} dc_n(s)/dt = \int \phi(\lambda)\sigma(\lambda)(dI_n/d\lambda)d\lambda$$

A comparison of values commonly encountered for absorption cross sections and solar fluxes in different units is included in Table 4.

The above consideration of quantities such as the photodissociation coefficient makes apparent why atmospheric chemists tend to use molecule and photon as part of the unit. The advantage is a distinction between both types of particles. Specifically the unit for the quantum yield (molecule photon⁻¹) immediately conveys the intimate relation between both types of particles. In SI the quantum yield is a pure number.

4.5.5 Symbols for Fluxes

The symbol recommended by the Green Book⁽²⁾ for any type of flux is J . This symbol has been reserved here to denote the energy flux (SI unit: W m^{-2}), whereas material fluxes are designated by F . Note, however, that F is also used to denote mechanical forces, and care must be exercised to avoid confusion if both quantities appear in the same text.

The usual symbol for irradiance, that is radiant flux received, is I (for intensity). We recommend the continued use of this symbol for the light flux, with the notation I_n when the flux is given in photon $\text{m}^{-2} \text{s}^{-1}$ and I_a when the photon flux is given in $\text{mol m}^{-2} \text{s}^{-1}$. This is consistent with comments of the Green Book and the subscripts introduced above.

4.6 Electric Conductivity

The ohm, the unit of electric resistance, which is the ratio of electromotive force to electric current ($\Omega = \text{V/A} = \text{kg m}^2 \text{s}^{-3} \text{A}^{-2}$), and its inverse, the siemens (S, the unit of conductance), are derived SI units. Accordingly, they are appropriate units to use in reporting electric conductivity of rain- or cloudwater. Since these units are conventionally employed by atmospheric chemists and chemists generally, no particular effort is necessary to achieve consistency with SI. The specific conductance of a solution denotes the current per area and field strength, that is in SI units $\text{A m}^{-2} (\text{V/m})^{-1}$ or S m^{-1} . Similarly it is acceptable to express molar ionic conductivity in units of $\text{S cm}^{-1} (\text{mol/dm}^3)^{-1}$ rather than SI units $\text{m}^2 \text{S mol}^{-1}$. The use of "mho" for ohm^{-1} is obsolete and to be avoided; the ohm^{-1} (Ω^{-1}) or siemens (S) should be used instead.

5. Summary and Recommendations

The principal recommendations presented in this document are summarized as follows.

SI base and derived units generally are well suited for reporting quantities pertinent to atmospheric chemistry. Because of the increasing use of SI by the broader chemistry and atmospheric science research communities and the resultant increasing familiarity with this system of units, and also because of the self-consistency inherent in SI, the use of SI units in atmospheric chemistry is encouraged. Table 6 lists recommended symbols and units for the most commonly encountered quantities. The table presents SI units for these quantities as well as common units convenient for routine use, which are derived from SI units by use of prefixes for decimal multiples and submultiples.

The use of units that are not products of powers of SI base units (e.g. atmosphere, Dobson unit, hectare) is discouraged. However, in view of longstanding use of certain non-standard units it is advisable for a period of time that such non-standard units be used alongside the less familiar SI units. This can most readily be accomplished by using double labels on axes of graphs, e.g. Dobson units in addition to mol m^{-2} .

The use of SI prefixes for multiples and submultiples of base or derived units is recommended. The appropriate prefix should be selected so that the coefficient before the prefix be in the range 0.01 to 999.

A special need for non SI units exists in atmospheric chemistry with regard to time periods that are predetermined by the clock and the calendar. Minute, hour, day and year are acceptable units. The use of month should be avoided. Care should be given to specifying the convention employed in reporting time of day.

The use of amount-based units is preferable to mass-based units for substances whose chemical formula is known. The chemical formula of the entity should be unambiguously specified.

Mixing ratios of substances in air should be reported as referred to dry air or moist air. Reference to dry air is recommended provided there is no loss in accuracy or precision associated with the conversion from mixing ratio referred to moist air. Otherwise, mixing ratio referred to moist air is preferred.

The unit mol per mol is recommended for mixing ratio of a substance in air, i.e. nmol/mol, rather than the customary parts per billion (ppb), etc. The use of reduced concentration should be restricted to those cases that cannot be reported in terms of mol per mol.

6. Acknowledgments

We are grateful for comments from members of the IUPAC Atmospheric Chemistry Commission and the following individuals: T. Bitter, P. Brimblecombe, H.L. Crutcher, T. Cvitaš, H.A. Das, A.J. Dobbs, H.A. Favre, S. Fuzzi, J. Garland, P. Glavič, S.E. Harnung, J. Heintzenberg, P.V. Hobbs, J.P. Lodge, R. Metselaar, I.M. Mills, B.W. Petley, M. Quack, H. Rodhe, W.G.N. Slinn, A.W. Stelson, A.J. Thor, W.E. van der Linden. SES was supported by the United States Department of Energy under Contract No. DE-ACO2-78CH00016.

7. References

- (1) J.G. Calvert (1990) Glossary of atmospheric chemistry terms, *Pure Appl. Chem.* **62**, 2167-2219.
- (2) I. Mills, T. Cvitas, K. Homann, N. Kallay, K. Kuchitsu (1993) *Quantities, Units and Symbols in Physical Chemistry*, 2nd edition, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, Oxford.
- (3) Bureau International des Poids et Mesure (1991) *Le Système International d'Unités (SI)*, 6th French and English edition, BIPM, Sèvres.

- (4) P. Warneck (1988) *Chemistry of the Natural Atmosphere*, Academic Press, San Diego, California.
- (5) K. E. Trenberth (1981) Seasonal variations in global sea level pressure and the total mass of the atmosphere, *J. Geophys. Res.* **86**, 5238-5246.
- (6) ISO Standards Handbook 2 (1993) *Quantities and Units*, International Organization for Standardization Central Secretariat, Geneva, Switzerland.
- (7) United States Naval Observatory, Nautical Almanac Office; Science and Engineering Research Council (Great Britain), Nautical Almanac Office; Science Research Council (Great Britain) *The astronomical almanac for the year 1991*, Washington, U.S.G.P.O.; London, H.M.S.O.
- (8) United States Code of Federal Regulations Title 40, Part 50 (1991) Office of the Federal Register, Archives and Records Service, Washington, U.S.G.P.O.
- (9) D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney, R. L. Nuttall, (1982) The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C₁ and C₂ organic substances in SI units, *J. Phys. Chem. Ref. Data* **11**, Suppl. 2, 1-392.
- (10) U.S. Standard Atmosphere (1976) National Oceanic and Atmospheric Administration, Washington, D.C.
- (11) R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, Jr., J.A. Kerr and J. Troe (1989) IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry: Evaluated Kinetic and Photochemical data for Atmospheric Chemistry: Supplement III, *J. Phys. Chem. Ref. Data* **18**, 881-1097.
- (12) W.B. DeMore, S.P. Sander, C.J. Howard, A.R. Ravishankara, D.M. Golden, C.E. Kolb, R.F. Hampson, M.J. Kurylo, M.J. Molina (1992) *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. Evaluation Number 10, JPL Publication 92-20, Jet Propulsion Laboratory, Pasadena, California.
- (13) R. Prinn, D. Cunnold, P. Simmonds, F. Alyea, R. Boldi, A. Crawford, P. Fraser, D. Gutzler, D. Hartley, R. Rosen and R. Rasmussen (1992) Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (methyl chloroform) data for 1978-1990, *J. Geophys. Res.* **97**, 2445-2461.
- (14) M. L. McGlashan (1973) Internationally recommended names and symbols for physicochemical quantities and units, *Ann. Rev. Phys. Chem.* **24**, 51-76.
- (15) T. Cvitas and I. Mills (1994) Replacing gram-equivalents and normalities, *Chem. Intern.* **16**, 123-124.
- (16) C.F. Campen, Jr., A.E. Cole, T.P. Condron, W.S. Ripley, N. Sissenwine, I. Solomon, editors (1957) *Handbook of Geophysics for Air Force Designers*, Geophysics Research Directorate, United States Air Force Cambridge Research Center, Bedford, Massachusetts.
- (17) World Meteorological Organization (1986) Global ozone research and monitoring project - Report No. 16: *Atmospheric Ozone 1985*, Vol. I, Geneva, Switzerland.
- (18) A. A. Lamola and M. S. Wrighton (1984) Recommended standards for reporting photochemical data, *Pure Appl. Chem.* **56**, 939-944.