

Units in Physical Chemistry - 59-240 Physical Chemistry - University of Windsor

Introduction

This handout (compiled from web pages at Oxford University) provides an introduction to the notation and systems of units common in Physical Chemistry. **SI units and prefixes** and their use are described, together with conversions to some **common non-SI units**. To keep track of physical quantities and their units in calculations, the technique of **quantity calculus** is recommended. The definitions of some accepted standard conditions are also described, as well as a brief introduction to reporting and interpreting errors and uncertainties in measurements.

It is recommended that you look at the examples and attempt the questions at the end of this section. A table of fundamental constants is provided.

Finally, if there is one important message from these pages it is to think about units:
Never blindly use a number in a calculation without thinking about its associated units, and never leave off the units in an answer unless it is a genuinely dimensionless quantity.

SI Units

The International System of Units, the SI system, is the modern metric system of measurement, established in 1960 by international treaty at the 11th General Conference on Weights and Measures (SI is the abbreviation for Le Système International d'Unités). There are seven SI base units for the following quantities, which are assumed to be mutually independent:

Base Quantity	SI Base Unit	
	Name	Symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric Current	ampere	A
Thermodynamic Temperature	kelvin	K
Amount of Substance	mole	mol
Luminous Intensity	candela	cd

The standards which determine the physical magnitude of these base quantities are also decided international agreement through the General Conference on Weights and Measures (CGPM, *Conférence Générale des Poids et Mesures*). For example:

- 1 kilogram is *defined* to be the mass of the 'international prototype', a lump of platinum-iridium alloy kept at the International Bureau of Weights and Measures just outside Paris.

- 1 m is the length of the path travelled by light in a vacuum in $1/299\,792\,458$ of a second (note that this means that the speed of light, c , is *fixed by definition* at $299\,792\,458\text{ m s}^{-1}$).
- 1 s is the duration of $9\,192\,631\,770$ periods of the radiation corresponding to the transition between the two hyperfine energy levels of the ground state of the Caesium 133 atom at 0 K.
- 1 K is the fraction $1/273.16$ of the thermodynamic temperature of the triple point of water.
- 1 mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kg of carbon 12. This number is about 6.022×10^{23} . The elementary entities must be specified (for example, the amount of water molecules in a litre of water is about 55.6 mol , but the amount of hydrogen atoms is 111.1 mol).

Other quantities are derived from these seven base quantities, and many are given their own names and symbols as listed below for some chemically important examples.

Derived Quantity	SI Derived Unit	
	Name	Symbol Base Units
Force	newton	N kg m s^{-2}
Pressure	pascal	Pa $\text{N m}^{-2} = \text{kg m s}^{-2} \text{m}^{-2}$
Energy	joule	J $\text{N m} = \text{kg m}^2 \text{s}^{-2}$
Power	watt	W $\text{J s}^{-1} = \text{kg m}^2 \text{s}^{-3}$
Frequency	hertz	Hz s^{-1}
Electric Charge	coulomb	C A s
Electric Potential Difference	volt	V $\text{W A}^{-1} = \text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$

SI Prefixes

The series of prefixes and symbols of prefixes to form the names and symbols of decimal multiples and sub-multiples (i.e. powers) of SI units is given below.

- The length of the Cl-Cl bond in Cl_2 is $2 \times 10^{-10}\text{ m}$, which can be written as 200 pm ('200 picometres') or 0.2 nm ('0.2 nanometres').
- A typical chemical bond vibrates with a period of about $2 \times 10^{-14}\text{ s} = 20\text{ fs}$ ('20 femtoseconds'), a frequency of 50 THz ('50 terahertz').
- Prefixes are never mixed within the SI system. For example, the mass of the moon is about $7.35 \times 10^{22}\text{ kg} = 73.5\text{ Yg}$ ('73.5 yottagrams'), not 73.5 Zkg .
- These prefixes are often used in front of non-SI units as well. For example, the human genome consists of 3164.7 million nucleotide bases ('A', 'C', 'G', 'T'), which is about 3 'gigabases'.

- A common source of error in calculations arises from a failure to account for units raised to powers properly. For example, $1 \text{ cm}^3 = (10^{-2} \text{ m})^3 = 10^{-6} \text{ m}^3$.

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

Non-SI Units

There are several other unit systems in common use, and conversions between them are given below. Closely related to the SI system is another metric system, the *cgs system* with base units including centimetre, gram, second (the SI system is also known as the MKS system for metre, kilogram, second). For example, the derived unit of force in cgs is the *dynes*: $1 \text{ dyn} = 1 \text{ g cm}^{-2} = 10^{-5} \text{ N}$.

Americans are inexplicably fond of the *Imperial system*, which used to contain all sorts of silly definitions (an inch was once defined as the width of a man's thumb), but now has a fixed relationship to the SI system (e.g. $1 \text{ inch} = 0.0254 \text{ m}$). The shortcomings of the Imperial system are too numerous to go into here, but suffice it to mention that pints are different sizes in the UK (578 ml) and US (473 ml), a pound of gold doesn't weigh the same as a pound of coal, and there are at least three different definitions of the calorie. All scientific calculations should be carried out in SI (or at least metric) units; when attempts are made to mix unit systems, inconvenient

Length

Distances on the scale of atoms and molecules are often reported in *angstroms*:

$$1 \text{ \AA} = 10^{-10} \text{ m} = 0.1 \text{ nm.}$$

Volume

Although not strictly an SI unit name, the litre (symbol: L, ℓ) is defined as:

$$1 \text{ L} = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3.$$

Mass

Although the SI system suggests that 1000 kg should be equal to 1 'megagram', the word 'tonne' (sometimes called a 'metric ton') is in common use:

$$1 \text{ t} = 10^3 \text{ kg} = 10^6 \text{ g.}$$

Angle

The SI (derived) unit of plane angle is the radian (symbol: rad). It is still common to see degrees (°), minutes (′), and seconds (″) in use, however:

$$1^\circ = (\pi / 180) \text{ rad}$$

$$1' = (1 / 60)^\circ = (\pi / 10\,800) \text{ rad}$$

$$1'' = (1 / 60)' = (\pi / 648\,000) \text{ rad.}$$

Time

Timescales significantly longer than a second are generally not reported in metric units, but in the familiar minutes, hours and days:

$$1 \text{ min} = 60 \text{ s}$$

$$1 \text{ hr} = 60 \text{ min} = 3600 \text{ s}$$

$$1 \text{ day} = 24 \text{ hr} = 86400 \text{ s.}$$

Temperature

For historical reasons, thermodynamic temperatures are often still reported in degrees Celsius (°C).

The exact conversion is given by the formula:

$$T / ^\circ\text{C} = T / \text{K} - 273.15.$$

To convert a temperature in degrees Fahrenheit to degrees Celsius, use:

$$T / ^\circ\text{C} = (5 / 9) \times (T / ^\circ\text{F} - 32).$$

Pressure

The common non-SI units of pressure are the bar (cgs), atmosphere, torr, and millimetres of mercury:

$$1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ N m}^{-2} \text{ (exactly)}$$

$$1 \text{ atm} = 101325 \text{ Pa} = 760 \text{ Torr (exactly)}$$

$$1 \text{ mmHg} = 133.3224 \text{ Pa.}$$

Energy

The Imperial unit of energy is the thermodynamic calorie, defined by:

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ Cal} = 4184 \text{ J}$$

It is exactly this sort of lunacy that the modern SI system was designed to avoid. For the small energies involved in individual atoms, the electron volt is a popular unit; in thermodynamic calculations, energies are often reported in kilojoules per mole:

$$1 \text{ eV} = 1.60219 \times 10^{-19} \text{ J}$$

$$1 \text{ kJ mol}^{-1} = 1.6605 \times 10^{-21} \text{ J}$$

Quantity Calculus

Quantity calculus is a powerful way of handling calculations involving physical quantities and their units. A *physical quantity* is considered to be the product of a *numerical value* (i.e., pure number) and a *unit*:

$$\text{physical quantity} = \text{numerical value} \times \text{unit}$$

In this way, the units in which a physical quantity is measured are included in its specification, and they can be kept track of in calculations by applying the usual rules of algebra. For example, the wavelength of blue light, λ (the physical quantity) is about 450 nm, which may be written:

$$\lambda = 450 \text{ nm, or, equivalently: } \lambda / \text{nm} = 450.$$

Now, since the units m and nm are related by $\text{nm} = 10^{-9} \text{ m}$,

$$\lambda = 4.5 \times 10^{-7} \text{ m, or equivalently: } \lambda / \text{m} = 4.5 \times 10^{-7}$$

In equations, only pure numbers can be manipulated (if you doubt this, consider what could possibly be meant by raising a number to the power of a distance, or taking the natural logarithm of a temperature). Therefore, it is common in writing equations to specify both the physical quantity and its units. For example, to convert a temperature in kelvin, T , to a temperature in degrees celsius, $\theta / ^\circ\text{C}$:

$$\theta / ^\circ\text{C} = T / \text{K} - 273.15.$$

T is a physical quantity, say 298 K; T / K is a pure number, 298. So to apply the equation, subtracting the numbers $298 - 273.15$ gives the number $\theta / ^\circ\text{C} = 24.85$, and the physical quantity $\theta = 24.85 ^\circ\text{C}$.

Quantity calculus is useful in tabulating the numerical values of physical quantities and in labelling the axes of graphs. For example:

T / K	$10^3 \text{ K} / T$	p / MPa	$\ln(p / \text{MPa})$
150	6.667	0.85	-0.1625

200	5.000	2.64	0.9708
298	3.336	6.97	1.9416

The usual rules of algebra are followed to interpret tables like this. So, for example, the second entry in the second column, $10^3 \text{ K} / T = 5.000$ implies that $1/T = 5 \times 10^{-3} \text{ K}^{-1}$. An equivalent way of writing this column heading would be $(1/T) / 10^{-3} \text{ K}^{-1}$.

Standard Conditions

There are two important sets of conditions which are referred to as 'standard':

- Standard Temperature and Pressure (STP) is taken to mean a temperature of $0 \text{ }^\circ\text{C}$ (273.15 K) and 1 atm ($1.01325 \times 10^5 \text{ Pa}$) pressure.
- Standard Ambient Temperature and Pressure (SATP) refers to $25 \text{ }^\circ\text{C}$ (298.15 K) and 1 bar (10^5 Pa) pressure.
- The standard pressure of 1 bar is frequently used in thermodynamics, and is given its own symbol: $p^\circ = 1 \text{ bar}$.
- The *standard state* of a substance is its pure form at $p^\circ = 1 \text{ bar}$ and a *specified temperature*.

Avogadro's principle states that equal volumes of gases at the same temperature and pressure contain the same number of molecules, regardless of the identity of the gases. It applies to *ideal* (or *perfect*) gases, and is a good approximation for real gases in many instances. Stated another way, Avogadro's principle implies that a given amount of any gas at a specified temperature and pressure occupies a particular volume. Specifically, for one mole of any gas, its *molar volume*, V_m is equal to:

- $V_m = 22.414 \text{ L mol}^{-1}$ at STP (273.15 K, 1 atm)
- $V_m = 24.790 \text{ L mol}^{-1}$ at SATP (298.15 K, 1 bar)

In the case of liquid solutions, the standard state of a solute may be defined as unit *activity* in a specified solvent at a given temperature, $a = 1$. For very dilute aqueous solutions, activities are almost equal to *molarities*, m , in the sense $a \approx m / m^\circ$, where $m^\circ = 1 \text{ mol kg}^{-1}$, and to *molarities* (amount concentrations), $a \approx c / c^\circ$, where $c^\circ = 1 \text{ M} = 1 \text{ mol dm}^{-3}$.

Errors and Uncertainties

All of science is based on empirical observations, that is, measurements, made with physical instruments. These are inevitably imperfect in the sense that they provide an *estimate* of an assumed true value of a physical quantity. For example, the potential difference across a given electrochemical cell has some value which we may attempt to measure with a voltmeter. A number will be displayed on this instrument and we need to be able to state how well we think this represents the true voltage. At this point, it is important to distinguish between *accuracy* and *precision*. Suppose the display reads 2.134 V, and that a series of repeated measurements gives the same reading. The *precision* of the measurement may then be stated as ± 0.001 V, but there is a further question to ask: how close is this value to the true value - in other words, how *accurate* is the voltmeter? In general this can be quite a difficult question to answer, but an indication is usually given by the manufacturer's specification of the instrument. For example, it may have been calibrated against a more accurate instrument and found to have an accuracy of "0.2 %". In this case, the accuracy of our measurement is about 0.004 V, and the displayed digits (precision) have given a false impression of the uncertainty in our measurement. The true uncertainty (or *error*) may be indicated along with the measurement by writing "2.134 \pm 0.004 V".

Now, assume we have made a series of measurements in an experiment, and determined the error associated with each one. Typically, we will need to perform some kind of algebraic manipulation of the data (adding it together, multiplying by constants, taking square roots, etc...) in order to determine some physical quantity of interest. The error associated with this final result is determined by a procedure known as *propagation of errors*. For example, if we have two measurements A and B , with associated errors δdA and δdB , and add them to form a quantity X , the uncertainty in X , δdX is given by: $(\delta dX)^2 = (\delta dA)^2 + (\delta dB)^2$. Some more relations are given below.

Algebraic relationship †

$$X = A \pm B$$

$$X = cA$$

$$X = c(A \times B) \text{ or } X = c(A/B)$$

$$X = e^{cA}$$

$$X = \ln(cA)$$

$$X = cA^n$$

Error in the result, δdX

$$(\delta dX)^2 = (\delta dA)^2 + (\delta dB)^2$$

$$(\delta dX) = c(\delta dA)$$

$$(\delta dX/X)^2 = (\delta dA/A)^2 + (\delta dB/B)^2$$

$$(\delta dX/X) = c\delta dA$$

$$(\delta dX) = (\delta dA/A)$$

$$(\delta dX/X) = |n|(\delta dA/A)$$

† c is a precisely known constant

A full analysis of a calculation including propagation of errors requires estimates of uncertainties in the input quantities, which are often not given in simple physical chemistry problems. Nevertheless, answers to these problems should be expressed in a way which gives some indication of their likely accuracy. A good rule of thumb is to take any physical constants you need to one or two more significant figures than the data given, and then to round down the final answer to the same number of significant figures as this data.

Basic Examples

1. The force due to gravity exerted (on Earth) by a 60 kg man (i.e. his weight, W) is given by $W = mg$, where the standard acceleration of free fall, $g \approx 10 \text{ m s}^{-2}$.
So $W = 60 \times 10 = \mathbf{600 \text{ N}}$.
2. Standing in ordinary shoes (surface area 150 cm^2 each), what pressure, p , does he exert on the ground? Total area, $A = 2 \times 150 \times 10^{-4} = 0.03 \text{ m}^2$
So $p = W / A = 20000 \text{ Pa} = \mathbf{20 \text{ kPa}}$.
3. The change in potential energy of an object of mass m raised through a height h is $V = mgh$. The energy required to lift a 1 kg book vertically through 2 m is about
 $V = 1 \times 2 \times 10 = \mathbf{20 \text{ J}}$.
4. To heat a kettle of water from $25 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$ requires an energy of about $E = 300 \text{ kJ}$. If the heating takes $t = 2 \text{ min}$, the average power of the kettle is:
 $P = E / t = (3 \times 10^5) / (2 \times 60) = 2.5 \times 10^3 \text{ W} = \mathbf{2.5 \text{ kW}}$.
5. There are about 150 billion galaxies in the universe, each containing an average of 400 billion stars, so the total number of stars in the universe is about $(150 \times 10^9) \times (400 \times 10^9) = 6 \times 10^{22}$. Comparing this value with Avogadro's constant, $6.022 \times 10^{23} \text{ mol}^{-1}$, suggests that there are about about $\mathbf{0.1 \text{ mol of stars}}$ in the universe.
6. How many seconds were there in the 20th century?
There were $100 \times 365 + 100 / 4 = 36\,504$ days (including leap-days).
Which is $36\,504 \times 24 \times 60 \times 60 = 3.15 \times 10^9 \text{ s} = \mathbf{3.15 \text{ Gs}}$
7. Which temperature has the same numerical value in degrees Celsius and degrees Fahrenheit?
 $T / ^\circ\text{C} = (5/9) \times (T / ^\circ\text{F} - 32)$ implies $9 T / ^\circ\text{C} = 5 T / ^\circ\text{F} - 160$
and if $T / ^\circ\text{C} = T / ^\circ\text{F}$, then $4 T / ^\circ\text{C} = -160$, so $T / ^\circ\text{C} = -40$.
So $\mathbf{-40 \text{ }^\circ\text{C} = -40 \text{ }^\circ\text{F}}$
8. The air pressure at an altitude z is given approximately by the formula $p(z) = p(0)\exp[-z / H]$, where $p(0) = 1 \text{ atm}$ is the air pressure at sea level, and $H = 7 \text{ km} \pm 1.5 \text{ km}$ is the *scale height*. What is the air pressure at the summit of Mt. Everest (8848 m)?
Using quantity calculus, the equation for $p(z)$ may be written:
 $p(z) / \text{atm} = (1 \text{ atm}) \times \exp[-(z / \text{km}) / (7 \text{ km})]$ and so $p(8.848 \text{ km}) = 0.28 \text{ atm}$.
To assess the uncertainty in this result, note that the greatest source of error is in the estimate of H . The error in the quantity $X = z / H$ is given by $(\delta dX/X)^2 = (\delta dz/z)^2 + (\delta dH/H)^2$, and so since $(\delta dz/z)^2$ is negligible, $\delta dX = (1.5 / 7) \times (8.848 / 7) = 0.271$. This error propagates in the calculation of $Y = \exp(-X)$, such that $(\delta dY/Y) = \delta dX$ and thus $\delta dY = 0.271 \times (0.28 \text{ atm}) = 0.076 \text{ atm}$.
The final result may therefore be quoted $\mathbf{p = 0.28 \pm 0.08 \text{ atm}}$.

Physical Constants

Quantity	Symbol	Value
	π	3.141 592 653
	e	2.718 281 828
Speed of light	c	$2.998 \times 10^8 \text{ m s}^{-1}$
Avogadro constant	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Atomic mass unit	u or au	$1.661 \times 10^{-27} \text{ kg}$
Boltzmann constant	k	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Vacuum permeability †	μ_0	$4\pi \times 10^{-7} \text{ T}^2 \text{ J}^{-1} \text{ m}^3$
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	$8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
	$4\pi p \epsilon_0$	$1.113 \times 10^{-10} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}$
Elementary charge	e	$1.602 \times 10^{-19} \text{ C}$
Faraday constant	$F = eN_A$	$96 485 \text{ C mol}^{-1}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
Electron rest mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
Proton rest mass	m_p	$1.673 \times 10^{-27} \text{ kg}$
Neutron rest mass	m_n	$1.675 \times 10^{-27} \text{ kg}$
Bohr magneton	μ_B	$9.274 \times 10^{-24} \text{ J T}^{-1}$
Nuclear magneton	μ_N	$5.051 \times 10^{-27} \text{ J T}^{-1}$
Electron magnetic moment	μ_e	$9.285 \times 10^{-24} \text{ J T}^{-1}$
Free electron Landé g -factor	g_e	2.002
Rydberg constant	R_∞	109737 cm^{-1}
Bohr radius	a_0	$5.292 \times 10^{-11} \text{ m}$
Stefan-Boltzmann constant	σ	$5.671 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$

† indicates exact (defined) values