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Units and Dimensions[1]

In the physical chemistry laboratory we deal with measurable quantities or properties. Some of these, such as length, time, mass, and volume, are quite simple. Others, such as entropy, surface tension, and voltage, are more complex. These quantities or properties are expressed in terms of certain arbitrarily selected units. For example, we can select the meter, the foot, or the mile as the unit of length. Since we have complete choice in selecting our units, we could select a separate and independent unit for each quantity. But we would have as many units as we have measurable quantities, and the result would be both confusing and cumbersome. To simplify the situation, we select a minimum number of units and define all other units in terms of these fundamental units.

For many years chemists were inclined to work in a system of units called the centimeter-gram-second (cgs) system. This system is still found in numerous chemistry texts and is still used by most practicing chemists who received their formal education prior to 1965. The International System of Units (SI) was adopted by the General Conference of Weights and Measures (CGPM) in 1960 as the recommended units for use in science and technology. The SI is constructed from seven base units for independent quantities (Table 1), plus two supplementary units for plane and solid angle.

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[1] Quoted or adapted from *J. Chem. Ed.*, **48**, 569–572 (1971), with permission.

TABLE 1

Physical quantity	Name of unit	Symbol
length	metre*	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
luminous intensity	candela	cd
amount of substance	mole	mol

*The spelling meter is also acceptable.

The second (s) is defined as the duration of 9 192 631 770 cycles of the radiation associated with a specified transition of the cesium-133 atom. It is realized by tuning an oscillator to the resonance frequency of the cesium atoms as they pass through a system of magnets and a resonant cavity into a detector. The SI unit for frequency is the hertz (Hz), which equals one cycle per second.

The meter (m) is defined as 1 650 763.73 wavelengths in vacuum of the orange-red line of the spectrum of krypton-86. The SI unit of area is the square meter (m^2). The SI unit of volume is the cubic meter (m^3). Fluid volume is often measured by the liter (0.001 m^3).

The standard for the unit of mass, the kilogram (kg), is a cylinder of platinum-iridium alloy kept by the International Bureau of Weights and Measures at Paris. A duplicate in the custody of the National Bureau of Standards (NBS) serves as the mass standard for the U.S. The SI unit of force is the newton (N), which is that force which when applied for 1 second will give to a 1 kg mass a speed of 1 m/s. The SI unit for work and energy of any kind is the joule (J), 1 J = 1 N · 1 m. The SI unit for power of any kind is the watt (W), 1 W = 1 J/1 s.

The thermodynamic or Kelvin scale of temperature used in the SI has its origin or zero point at absolute zero and has a fixed point at the triple point of water defined as 273.16 kelvins (K). The Celsius scale is derived from the Kelvin scale. The triple point is defined as 0.01°C on the Celsius scale.

The mole is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. (When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.)

The ampere (A) is defined as the magnitude of the current that, when flowing through each of two long parallel wires separated by 1 m in free space, results in a force between the two wires (due to their magnetic fields) of 2×10^{-7} newton for each meter length. The SI unit of voltage is the volt (V), which is defined 1 V = 1 W/1 A. The SI unit of electrical resistance is the ohm (Ω), which is defined 1Ω = 1 V/1 A.

Units expressed as combinations of the foregoing are called derived units.

There are certain non-SI units which are still acceptable and two of these classes merit attention in this manual. The first group may be called natural units. These are units that are tied directly to the properties of microscopic constituents of matter or to fundamental Lorentz-invariant constants of nature.. Typical examples of natural units are:

TABLE 2

Unit	Symbol
electrical charge	e
electron mass	m_e
proton mass	m_p
Bohr radius	a_o
electron radius	r_e
Compton wavelength of electron	λ_c
Bohr magneton	μ_B
nuclear magneton	μ_N
velocity of light	c
Planck's constant	h or $\hbar$

The second group may be called units defined in terms of the best available experimental values of certain physical constants. This group of units does not belong to the SI scheme, but has achieved universal acceptance because of convenience and conceptual advantage associated with their use. Some of this group of units follows:

TABLE 3

Physical quantity	Name of unit	Symbol for unit	Conversion factor
energy	electron volt	eV	$\approx 1.6021 \times 10^{-19}$ J
mass	unified atomic mass unit	u	$\approx 1.660\ 41 \times 10^{-27}$ kg
electric dipole moment	debye	D	$\approx 3.335\ 64 \times 10^{-30}$ A·m·s
charge per mole	Faraday	$\mathcal{F}$	$\approx 9.648 \times 10^{4}$ C/mol

Certain special considerations should be pointed out.

1. In combinations such as meter-kelvin, use of the product (m·K) avoids confusion with "millikelvin." It is good practice to indicate all unit products with multiplication dots, since some unit symbols consist of more than one letter, e.g., Wb for weber, versus W·b for "watt-barn."

2. When a compound unit is formed by division of one unit by another, its symbol consists of the symbols for the separate units either separated by a solidus or multiplied by using negative powers (for example, m/s or m·s^{-1} for meter per second). In simple cases use of the solidus is preferred, but in no case should more than one solidus be included in a combination unless parentheses are inserted to avoid ambiguity. In complicated cases, negative powers should be used.

3. Words and symbols should not be mixed; if mathematical operations are indicated, only symbols should be used. For example, one may write "joules per mole," "J/mol," "J·mol^{-1}," but not "joules/mole," "joules mol^{-1}," etc.

A revised list of general physical constants is given in Appendix I. In this tabulation the values are given both in SI units and in cgs units to assist in conversion from one system to another when necessary.

Finally, we conclude this section with Table 4, which lists the dimensions and SI units (repeated from other tables in some cases) for a number of quantities which are frequently encountered in physical chemistry.

TABLE 4

Quantity	Dimensions	SI Unit and Symbol
Length	ℓ	meter (m)
Area	ℓ^2	square meter (m^2)
Volume	ℓ^3	cubic meter (m^3)
Time	t	second (s)
Speed	$\ell \cdot t^{-1}$	meter per second ($m \cdot s^{-1}$)
Acceleration	$\ell \cdot t^{-2}$	meter per second squared ($m \cdot s^{-2}$)
Mass	m	kilogram (kg)
Force	$\ell \cdot t^{-2} \cdot m$	newton (N), $kg \cdot m \cdot s^{-2}$
Pressure	$\ell^{-1} \cdot t^{-2} \cdot m$	pascal (Pa), $N \cdot m^{-2}$
Density	$\ell^{-3} \cdot m$	$kg \cdot m^{-3}$
Surface tension	$t^{-2} \cdot m$	$J \cdot m^{-2}$
Energy	$\ell^2 \cdot t^{-2} \cdot m$	joule (J), $kg \cdot m^2 \cdot s^{-2}$
Temperature	T	kelvin (K)
Heat capacity	$\ell^2 \cdot t^{-2} \cdot m \cdot T^{-1}$	$kg \cdot m^2 \cdot s^{-2} \cdot K^{-1}$
Specific heat	$\ell^2 \cdot t^{-2} \cdot T^{-1}$	$m^2 \cdot s^{-2} \cdot K^{-1}$
Entropy	$\ell^2 \cdot t^{-2} m \cdot T^{-1}$	$kg \cdot m^2 \cdot s^{-2} \cdot K^{-1}$
Charge	e	coulomb (C), $A \cdot s$
Current	$I(e \cdot t^{-1})$	ampere (A)
Potential	$\ell^2 \cdot t^{-2} \cdot m \cdot e^{-1}$	volt (V), $J \cdot A^{-1} \cdot s^{-1}$
Resistance	$\ell^2 \cdot t^{-1} \cdot m \cdot e^{-2}$	ohm (Ω), $V \cdot A^{-1}$

The student should become thoroughly conversant with Table 4 before proceeding to the next chapter on Dimensional Analysis.

Dimensional Analysis

Dimensional analysis is a potent tool in learning the proper use of various mathematical relationships in physical chemistry. If your equation is correct and if you have properly interpreted the various quantities, the substitution of the dimensions should reduce the expression to an identity.

Let us consider two simple cases to see exactly how a dimensional analysis is carried out. The expression for surface tension as a function of capillary rise is given by the equation:

$$\gamma = \tfrac{1}{2}hdgr$$

The terms in this expression, with their dimensions, are

Quantity	Symbol	Dimensions
Surface tension	γ	$t^{-2} \cdot m$
Height of column	h	ℓ
Density of liquid	d	$m \cdot \ell^{-3}$
Acceleration of gravity	g	$\ell \cdot t^{-2}$
Radius of tube	r	ℓ

Substituting in the equation:

$$t^{-2} \cdot m = \ell \cdot m \cdot \ell^{-3} \cdot \ell \cdot t^{-2} \cdot \ell$$

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Thus the equation reduces dimensionally to an identity.

The speed of a gas molecule is given by the expression

$$s = \sqrt{\frac{3RT}{M}}$$

This speed has the dimensions of $\ell \cdot t^{-1}$. The molecular weight of the gas, M, has the units of kilograms per mole and the dimensions of mass. R is the gas constant, whice in this case must be expressed in joules per mole per degree. It has the dimensions of $m \cdot \ell^2 \cdot t^{-2} \cdot T^{-1}$. Substituting these dimensions gives an expression which reduces to an identity.

$$\ell \cdot t^{-1} = \sqrt{\frac{m \cdot \ell^2 \cdot t^{-2} \cdot T^{-1} \cdot T}{m}} = \ell \cdot t^{-1}$$

This last example differs from the first in that a physical constant, R, is introduced. Where such constants are used, their dimensions must be known before dimensional analysis can be applied.

One type of expression often encountered may appear a little startling from the standpoint of dimensional analysis. This is an expression containing a logarithmic term. We shall state at once that the logarithm of any quantity is dimensionless. Let us consider the various equations relating vapor pressure to temperature. The differential equation for the change of vapor pressure with temperature is

$$\frac{d \ln p}{dT} = \frac{\Delta H_v}{RT^2}$$

in wnich R has the dimensions of $m \cdot \ell^2 \cdot t^{-2} \cdot T^{-1}$. The heat of vaporization, ΔH_v, has the dimensions of energy, $m \cdot \ell^2 \cdot t^{-2}$. Thus d ln p reduces to a dimensionless quantity.

$$d \ln p = \frac{m \cdot \ell^2 \cdot t^{-2} \cdot T}{m \cdot \ell^2 \cdot t^{-2} \cdot T^{-1} \cdot T^2}$$

Remembering that one of our standard forms of differentiation is d ln x = dx/x, or in this case dp/p, and noting that dp and p have the same dimensions, we see why the expression, d ln p, is dimensionless.

The integral equation for vapor pressure as a function of temperature is

$$\ln p = -\frac{\Delta H_v}{RT} + I$$

$\Delta H_v/RT$ is a dimensionless magnitude, therefore $(\ln p - I)$ must be dimensionless. The explanation of this must be sought in a consideration of the process of integration. Mathematically I stands for an expression, $\ln P_o$, wherein P_o has the dimensions of pressure. The combination of the two logarithmic terms results therefore in the elimination of the dimensions associated with pressure.

Measurements, Precision, and the Treatment of Data.

INTRODUCTION

The general procedure in the usual experiment in elementary physical chemistry includes the following basic steps.

(1) *Measurements are made with certain instruments.* Some of the instruments used are quite simple in nature, like a burette or a thermometer, for example; others are more complicated, like a potentiometer or a refractometer.

(b) The data from the measurements *may be substituted* in certain formulas or relationships in order *to calculate* certain other desired magnitudes.

(c) In the utilization and study of the various data, *plotting procedures* may be employed. In some cases a *statistical study* of the data is made.

If the various steps are to be followed in a proper scientific manner, attention must be given to the precision of the measurements and to the precision of the computed quantities. We must decide whether to make a single measurement of a given magnitude or a set of measurements in order to obtain the desired precision. This section of the manual deals, for the most part, with various definitions, equations, and concepts concerned with precision.

If a large number of measurements of a particular magnitude are made, *statistical procedures* are necessary to utilize the data properly. The manual includes, therefore, a discussion of the concepts, definitions, and equations used in statistical procedures.

Because of the extreme importance of plotting procedures, a discussion of this topic is given. This discussion, as well as the discussions of precision and statistical procedures, is on an elementary level. Those

who wish to study these topics in greater detail may consult the biblio-
graphy for suitable references. The student should develop as soon as
possible a precision-minded approach to the various experiments. The
lack of proper attention to precision is one of the glaring weaknesses in
most laboratory training.

CERTAIN AND UNCERTAIN FIGURES. SIGNIFICANT FIGURES

We shall start our discussion of precision by defining the terms:
certain figures, *uncertain figures*, and *significant figures*. These per-
tain to the process of making a measurement and recording the value obtain-
ed.

The instruments used in physical chemistry have what we shall refer
to as *least count*. This is the smallest division of the instrument scale
that can be read directly. The thermometer in Figure 1 has a least count
of 1°, whereas a Beckmann thermometer, which is graduated in hundredths
of degrees, has a least count of 0.01°. With most instruments, however,
you can estimate a reading to one digit beyond that which expresses the
least count. In Figure 1, for instance, you can read a temperature of
25.2° and feel confident that you are within 0.2°
of the proper value.

In this value of 25.2° we term the digits to
the left of the decimal point *certain figures* and
the digit to the right of the decimal point an
uncertain figure. Although we have considerable
confidence in the uncertain figure, we should
express the extent of our certainty by writing the
temperature as 25.2 ± 0.2°. If we record a volume
measurement as 35.35 ± 0.05 ml, we are confident
that the actual value lies between 35.40 ml and
35.30 ml.

Of more importance than the terms certain and
uncertain figures is the term *significant figures*.
The significant figures in a measurement include
both the certain and the uncertain figures. All
of the figures in the readings 25.2° and 35.35 ml
referred to above are significant figures.

The peculiarities of our number system require
that zero be given special attention in considering
significant figures. If the zero or zeros are
immediately to the right of the decimal point, they
serve merely to locate the decimal point. In 0.00013
g, the three zeros following the decimal point are
not significant figures. However, in 0.130 g, the
zero following the three is a significant figure. In 250 g, the zero may
or may not be significant; it may serve merely to locate the decimal point.
Any doubt, however, concerning this number would vanish if it were written:

Figure 1.

Section of
thermometer.

$$2.50 \times 10^2 \text{ g}$$

Exercise 1.   Indicate the significant figures in each of the following:

0.0018 volt   1650 ml   12.5260 g
0.1800 volt 1.650×10^3 ml   1.65 dynes per cm
1.800 volt 1.65×10^{-3} ml   16.2 miles

PRECISION AND ACCURACY

The terms *precision* and *accuracy* are often used interchangeably, although they are actually quite different in meaning. *Accuracy* concerns the correctness of a measurement, whereas *precision* concerns the reproducibility of the measurement and the number of significant figures in its value.

To illustrate, let us measure the temperature of a constant-temperature bath with two thermometers, one with a least count, or ultimate subdivision, of 1° and one with a least count of 0.1°. With the first thermometer we read a temperature of 25.2 ± 0.2° and with the second a temperature of 25.18 ± 0.02°. The second reading, with its four significant figures, is the more *precise* reading. In this sense we are using the word *precise* in connection with the number of significant figures which we can with confidence write down for the measured magnitude. The thermometer with the least count of 0.1° is the more precise instrument.

Now we may make a series of readings with a single thermometer. The readings may show little divergence among themselves, or they may differ rather widely. If the differences are small we may say that the method of measurement is one of high precision and that the procedure is a precise one.

In summary, *precision concerns both the reproducibility of the magnitude and the number of figures we may with confidence express in the answer.*

After we have made a number of readings of a given magnitude and are sure that our values are precise in both senses of the word, we still do not know whether unknown or constant errors have entered into the determination. In measuring temperature, for example, there may be an error in the marking of the thermometer. Therefore, the recorded temperature, although very precise, may be entirely wrong. Accuracy deals with the difference between the measured value and the true value. Good precision does not insure high accuracy, but high accuracy is improbable without good precision. It is possible, on the other hand, to have high accuracy, provided sufficient readings of fair precision are made and provided a proper statistical procedure is used.

It should be noted that, properly used, the term accuracy requires a modifying adjective. To say that a result is accurate means that it is exactly right. But only in a few cases do we know the exact value of the quantity being measured. Hence we should speak of a high order of accuracy or a low order of accuracy rather than stating merely that a result is accurate.

Let us now examine how we may express precision in a quantitative manner. One way to do this is to consider the extent of the uncertainty of the uncertain figure. If a temperature is recorded as 25.24 ± 0.02°, the value of 0.02° is a measure of the precision. We can speak of such a value as the least-count precision or, sometimes, the decimal precision. We note that it is expressed in the same units as the measured quantity. We may also express the preciseness of a measurement in terms of relative precision, which may be defined as the relative uncertainty of the measured magnitude. This is obtained by dividing the value of the magnitude into the least-count precision. The result may be expressed in parts per hundred (per cent) or in parts per thousand.

The determination of relative precision is illustrated in Example 1.

Example 1.   What are the least-count precisions and the relative precision in per cent of the two magnitudes: 25.26 ± 0.01 g and 125.26 ± 0.01 g? In both cases the least-count precision is 0.01 g.

The relative precisions are:

$$\frac{0.01 \text{ g}}{25.26 \text{ g}} = 100 = 0.04\% \qquad \frac{0.01 \text{ g}}{125.26 \text{ g}} \times 100 = 0.008\%$$

Thus, we see that the least-count precision depends on the measuring instrument and the relative precision on the value of the magnitude being measured. You should note that the relative precision is dimensionless.

ERRORS

In all laboratory procedures and in subsequent calculations there are certain factors that lower the accuracy of the results. Included in these factors are *mistakes* made by the experimenter in reading an instrument, in recording the data, or in performing the calculations. Other factors lowering the accuracy are grouped under the terms *errors*. We shall now consider the various types of errors and how they affect the results.

Errors encountered in conducting experiments may be divided into two groups: (1) determinate errors and (2) indeterminate errors.