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General Considerations

Preliminaries necessary for dealing with different aspects of physical chemistry are being considered here.

1.1 UNITS AND DIMENSIONS

Everything that can be numerically (quantitatively) expressed is termed a *quantity*. The quantities which are used to characterise matter or its observable change in nature are termed *physical* quantities.

Comparison of some quantity with a standard quantity is termed *measurement* and the standard quantity used is termed *unit of measurement* or simply *unit of the quantity*. The number of units considered in the measured quantity is termed the *numerical value of the quantity*. For example, when we say that a rod is 10 metres long, we mean that it is 10 times as long as a rod whose length has been defined to be 1 metre as unit.

Physical quantities are preferably defined in a way that reflects the operations that are to be carried out to measure the quantity. Such definitions are called *operational definitions*. For example, the speed of a body, defined as the distance travelled by it per unit time, can be obtained by measuring the distance travelled and the elapsed time, and dividing the first quantity by the second. It should be remembered that the physical quantities which cannot be operationally defined, e.g. entropy, wavefunction, etc. are also meaningful and have importance in the understanding of the operationally defined physical quantities.

The choice of a standard quantity rests on its high accessibility, permanency and reproducibility. It is for these factors that the unit originally defined for a quantity has been subsequently modified. Thus, the first international standard of length was provided by a bar of Pt-Ir alloy kept at the International Bureau of Weights and measured in Sèvres, near Paris. But due to lack of accessibility and inaccuracy in reproducibility of this bar, the standard of length has been changed (by international agreement in 1961) to an atomic constant, viz. the wavelength of the orange-red light emitted by the atoms of ^{86}Kr in the discharge tube. One metre has been redefined to be 1650763.73 times the wavelength of this light.

Sometimes modification of unit value for a physical quantity in a system of unit is done to make a simplier relation between the units of a physical quantity in different systems of measurement. Thus, common units of volume are cubic centimeter (cm^3), cubic meter (m^3) and liter (L). A liter was originally defined as the volume of 1000 g of water at 3.98 °C and 1 atm pressure, i.e. 1000.028 cm^3. However, in 1964, liter was redefined so that the following simple relations hold.

$$1\ L = 1000\ cm^3 = (10\ cm)^3 = 1\ dm^3$$

Nowadays, the numerical value of a physical quantity is usually expressed in an international system of unit, called Système International (SI), preferably in the form $y10^x$, where x is a convenient integer (+ve or –ve) and y is a decimal number that rarely requires more than three digits (considering the limits of accuracy in a measurement) with only one numeral (nonzero) before the decimal point. The number of digits in y gives the *number of significant figures* in the approximate numerical value of the concerned physical quantity. The factor 10^x can be avoided using specific prefix (depending on the value of x) to the basic unit as given in Table 1.1.

Table 1.1: Standard SI prefixes

Factor (10^x)	10^{-18}	10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{3}	10^{6}	10^{9}	10^{12}	10^{15}	10^{18}
Prefix	atto	femto	pico	nano	micro	milli	centi	kilo	mega	giga	tera	peta	exa
Abbreviations	a	f	p	n	μ	m	c	k	M	G	T	P	E

On the basis of operational definition, a complex physical quantity can be expressed as product of some simple directly measurable quantities (or their inverse) which are listed along with their symbols and SI units, in Table 1.2. Such an expression (in terms of symbols) represents the *dimensions* of the concerned physical quantity which reflects its complex nature. Thus l/t represents the dimensions of speed which is defined as the length (l) traversed divided by the time (t) elapsed. The seven basic physical quantities given in Table 1.2 are dimensionally independent, i.e. they cannot be derived from one another by algebraic combinations.

Table 1.2: Basic physical quantities

Physical quantity	*Symbol*	*SI unit*	*Abbreviation*
Mass	m	kilogram	kg
Length	l	meter	m
Time	t	second	s
Electric current	I	ampere	A
Luminous intensity	I_v	candela	cd
Thermodynamic temperature	T	kelvin	K
Amount	n	mole	mol

Definitions of Unit Basic Quantities

Mass: The SI unit of mass is kilogram, which is mass of a cylinder of Pt–Ir alloy kept at the International Bureau of Weights and Measures in Sèvres.

Length: The SI unit of length is kilometre.

Time: The SI unit of time is second which was originally defined as 1/86400 part of the mean solar day. Subsequently (in 1967), the astronomical standard has been given up with the adoption of a more precise atomic standard. The second has been redefined as the duration of 9192631770 cycles of radiation caused by the transition between the two hyperfine energy levels in the ground state of ^{133}Cs atom (differing only in the spin of the outermost electron).

Electric current: The SI unit of electric current is ampere. It is the current that causes a force of 2×10^{-7} newton per metre between two infinitely long parallel wires (carrying this current) of negligible cross-section and placed one meter apart in vacuum.

Luminous intensity: The SI unit of luminous intensity is the candela. It is the quantity of light emitted per unit solid angle by a surface of 1/600000 square meters of a black-body at the melting temperature of Pt at a pressure of 101325 newtons per metre. (The term *luminous intensity* is somewhat misleading as the flux per unit area decreasing with increasing distance).

Thermodynamic temperature: The SI unit of thermodynamic temperature is kelvin. One kelvin is 1/273.16 of the thermodynamic temperature of the tripple point of water (at which liquid water, water vapour and ice are in equilibrium). Since the normal freezing point (0°C) of water is 0.01 degree below its triple point, any temperature which is t in celsius scale and T in kelvin scale will be related by

$$T/K = t/°C + 273.15$$
$$\simeq t/°C + 273$$

Amount: The SI unit of amount is the mole which implies Avogadro number (i.e. 6.022×10^{23} which is the number of carbon atoms in 0.012 kg of ^{12}C) of elementary entities. Here specification must be made of elementary entity which may be an atom, a molecule, an ion, an electron, a photon, etc. or a specified group of such entities. The number of molecules (N_i) of the species i in a system is related to its amount (n_i) by $N_i = n_i N_A$, where N_A is the Avogadro constant having unit mol^{-1} (whereas Avogadro number is a pure number). It is correct to state that the amount of a species i in a system is n_i (and not n_i mol). Since n_i has a factor of 1 mol included in itself.

A mole is related to mass, provided the elementary entities possess mass. Thus:

i. one mole of electron weighs 5.486×10^{-7} kg
ii. one mole of H atom weighs 1.008×10^{-3} kg
iii. one mole of H_2 molecule weighs 2.016×10^{-3} kg
iv. one mole of $Fe_{0.95}O$ weighs 6.906×10^{-2} kg
v. one mole of air containing 80 mole % N_2 and 20 mole % O_2 weighs 2.882×10^{-2} kg
vi. one mole of a reaction mixture $H_2 + \frac{1}{2}O_2$ (which contains H_2 and O_2 in 2:1 mole ratio) weighs $\left(\frac{2}{3} \times 2.016 + \frac{1}{3} \times 32\right) \times 10^{-3}$ kg or 1.201×10^{-2} kg.

It is quite justifiable to define *one mole of a reaction*, e.g. $H_2 + \frac{1}{2}O_2 = H_2O$, as the reaction of one mole H_2 and half mole O_2. Chemists consider one mole of reaction as a unit reaction. This makes the unit J·mol^{-1} of ΔH for a chemical reaction obvious.

The amount of a substance has been introduced (by the general conference on Weights and Measures in 1971) into the set of basic physical quantities to deal with massless entities like photon (whose rest mass is zero) and also to serve the interest of the chemists. The quantity mass per amount of a substance (entity) is called its molar mass (M) whose SI unit is kg mol^{-1}. This renders the awkward term *molecular weight* obsolete.

Consistency of Dimension and Unit

Any equation relating to physical quantites must be dimensionally correct, i.e. same dimensions on both sides, as is found, for example, with the relation $\frac{1}{2}mc^2 = \frac{3}{2}PV$, where mc^2 has the dimensions $m(lt^{-1})^2$ and PV has the dimensions $(ml^{-1}t^{-2})$ (l^3) or ml^2t^{-2}. The dimensional consistency is useful in finding the dimensions of a complex quantity. This purpose will be readily served with the simplest relation involving the complex quantity concerned. Thus, the dimensions of molar gas constant R can be conveniently found from the ideal gas equation $PV = nRT$ or $R = PV/nT$ to be $(ml^{-1}t^{-2})$ $(l^3)/(n)$ (T) or ml^2t^{-2}/nT.

It should be remembered that from dimensional analysis, one cannot say whether a relation is physically meaningful or the constants involved are correct. Thus, molar entropy, molar heat capacity and molar gas constants all have same dimensions and SI unit ($JK^{-1}mol^{-1}$) but they are not of same kind, and hence addition and subtraction processes are not operative between them.

It is important to note that any physical quantity x in e^x, $\ln x$ and $\sin x$ must be dimensionless. This is in keeping with dimensional consistency. Thus, ln (x meter) carries no meaning, but ln (x/meter) or ln (x/cm) does have. To maintain the dimensional consistency, an expression is often written with reference to the unit choosen. For example, the variation of vapour pressure (p) in atmosphere of a liquid with temperature (T) in kelvin is more appropriately represented as

$$\ln (p/\text{atm}) = a - \frac{b}{T/K}$$

where a and b are dimensionless constants. Obviously, the values of a and b depends on the unit of p.

The dimensional consistency of an expression implies unit consistency. If all the quantities in a calculation are expressed in same system of units (say SI), the result will be in that system of units without involvement of any additional numerical factors. It is for this reason that the numerical calculations are preferably done using only one system of units.

A physical quantity may require to be converted from a given unit to some other unit. The conversion factor necessary for this can be found using the algebraic properties of units regarding multiplication, division and cancellation. For example, to convert time from min to sec, we have to use the relation 1 min = 60 sec or 1 = 60 sec min^{-1}. Then time in min can be converted into sec simply by multiplying with the conversion factor 60 sec min^{-1} (which amounts to multiplying by one). Hence, t min = t min (60 sec min^{-1}) = 60t sec, i.e. min, in effect, replaced by 60 sec. Common non-SI units and their SI equivalents are given in Table 1.3.

1.2 PRECISION AND APPROXIMATION

Numerical values of a physical quantity obtained from experimental observations are unlikely to be exact due to the deficiencies of the instrument and operator. The maximum instrumental error (called *precision*), unless mentioned on the instrument, is usually taken to be half of the smallest division on the instrument's scale, e.g. 0.5 mm in measuring length with a millimeter ruler. The personal error, which is random in nature, is less important but can be diminished using statistical means.

The precision of a numerical value can be expressed in relative form (often as percentage) or in absolute form. We can arrive at the significant figures of a numerical quantity from the specified error. Suppose in measuring length, one produces the result in form of absolute error as l = 14.31 cm $\pm$ 0.18 cm. Here there is no sense in writing out the hundredths, because the reported error is of the order of tenths of a centimeter. It is more correct to write l = 14.3 cm $\pm$ 0.2 cm. The last numeral in 14.3 is unreliable because it may be anything from 1 to 5. Since in this digit, the error is less than one half of a centimeter, we can disregard this and write l = 14 cm involving only two digits which are significant. Is there any difference between l = 14 cm and l = 14.0 cm? They differ in number of significant figures. 14.0 cm has three significant figures, where the zero after the decimal point implies that the tenths of a centimeter were measured but were not registered.

Table 1.3

Physical quantity	*Name and symbol for SI unit*	*Definition of SI*	*Non-SI units and their SI equivalents*
Volume	cubic meter (m^3)	m^3	1 liter = 10^{-3} m^3
Force	newton (N)	kg m s^{-2}	1 dyne = 10^{-5} N
Pressure	pascal (Pa)	Nm^{-2} = kg $m^{-1}s^{-2}$	1 atm (760 torr) = 1.01325 × 10^5 Pa
			1 bar = 10^5 Pa
Energy	joule (J)	Nm = kg m^2s^{-2}	1 erg = 10^{-7} J
			1 cal = 4.184 J
			1 electron volt (eV) = 1.602177 × 10^{-19} J
Power	watt (W)	Js^{-1} = kg m^2s^{-3}	1 horse power = 735.499 W
Electric charge	coulomb (C)	As	1 abcoulomb (emu) = 10 C
			1 statcoulomb (esu) = 3.336 × 10^{-10} C
Electric potential diff	volt (V)	JC^{-1} = kg $m^2s^{-3}A^{-1}$	1 abvolt = 10^{-8} V
			1 statvolt = 300 V
Electric resistance	ohm (Ω)	VA^{-1} = kg $m^2s^{-3}A^{-2}$	1 abohm = 10^{-9} Ω
Electric conductance	siemens (S)	Ω^{-1}	1 statohm = 9 × 10^{11} Ω
Dipole moment	Coulomb meter (C·m)	C·m	1 Debye = 3.335641 × 10^{-30} C·m
Magnetic flux	weber (Wb)	Vs = kg $m^2s^{-2}A^{-1}$	1 maxwell = 10^{-8} Wb
Magnetic flux density (magnetic induction)	tesla (T)	Wbm^{-2} = kg $s^{-2}A^{-1}$	1 gauss = 10^{-4}T
Luminous flux	lumen (lm)	cd·Sr*	
Illuminance	lux (lx)	lm·m^{-2}	
Luminance	nit (nt)	cd·m^{-2}	1 stibb (= 1 cd cm^{-2} = 10^{-4} nt)

* Sr is abbreviation of steradian which is SI unit of solid angle

Notes:

i. In writing units, words and symbols should not be mixed. Thus, it is improper to write N per sq metre; this should be written either as newton per sq metre or Nm^{-2}. Words in a unit should be in small letters. It is improper to write Newton per sq meter.

ii. It is safe to represent combination of units leaving a space in between. For instance, C·m stands for coulomb meter (unit of dipole moment) while cm for centimeter (unit of length).

iii. In writing units using slant line one should be cautious. Thus, the unit $JK^{-1}mol^{-1}$ of R might be written as J/K mol but never J/K/mol which implies J mol/K.

iv. The word degree and the symbol (°) should not be used with kelvin (K).

v. The definition of mole refers to 12 g, instead of 12 kg (as per SI), of ^{12}C to make *molecular weight* numerically (though not dimensionally) equal to mass per amount of substance in unit of g mol^{-1}.

vi. Exponents have effect also on prefixes. For example

$$1\text{ dm} = 10^{-1}\text{ m}$$
$$1\text{ dm}^3 = (10^{-1}\text{ m})^3 = 10^{-3}\text{ m}^3 \neq 10^{-1}\text{ m}^3$$

Algebraic operations with uncertain numerical quantities will obviously give uncertain results which can, however, be obtained in good approximation using the following simple rule. Generally, a numerical result will have same number of significant figures as that of the component number having least number of significant figures. Thus, although 7.46 m^2/3.2 m = 2.33125 m, it is enough to take the approximate value 2.3 m. But if the first significant figure of the result is 1, then the number of significant figures should be one more. For instance, 4.58 m^2/3.2 m = 143125 m can be better approximated to 1.43 m (and not 1.4 m).

In this book, it has been assumed that the numerical values are precise to three or at most four significant figures, and thus the answers are stated to at most four significant figures after rounding off the result at the last stage of calculation (usually done with a scientific calculator).

1.3 GUIDELINES FOR SOLVING NUMERICAL PROBLEMS

Solution of numerical problems involves calculation of some quantity (ies) from the given data using appropriate relation between them under the condition specified in the problem. Selection of working formula and substitution of given data in it will be facilitated, if the given data are presented in a compact form diagramatically (as in problem 4.22 or 4.27).

In calculating more than one quantity in a given problem, it is better to calculate each quantity independently (to avoid transmission error). If it is not possible, the one(s) which is calculable directly from the given data is computed first and the result is used to compute others using the relation between them.