Basic Physical Chemistry Calculations

H. E. Avery   D. J. Shaw

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Preface

The purpose of this book is to illustrate methods of approach towards solving numerical problems encountered in Physical Chemistry and to facilitate a general understanding of this subject. The book should prove to be suitable for students studying at the levels of 1st and 2nd year B.Sc., Higher National Certificate, Higher National Diploma and Part 1 G.R.I.C. A companion volume entitled *Advanced Physical Chemistry Calculations* covers material appropriate to the levels of Honours B.Sc. and Part 2 G.R.I.C.

The first chapter consists of a discussion of Système International (SI) units and of physico-chemical methods of expression. The next six chapters are devoted to various branches of Physical Chemistry and consist of a series of worked examples followed by additional examples to be solved by the reader. In the worked examples, theoretical discussion is kept to a reasonable minimum. Answers to the additional examples are provided and, in the few cases where there is no corresponding worked example, a brief directive towards the method of solution is given with the answer. Values of commonly encountered physical constants and conversion factors are given in Appendices I and II rather than with each individual question. The final chapter consists of a number of multiple choice and true-false questions, designed to test the reader's awareness of some of the basic concepts in Physical Chemistry. Some of these questions have been prompted by examiners' criticisms of past performances in Royal Institute of Chemistry examinations.

Some of the calculations are taken from past examination papers, and in this respect we wish to thank the Royal Institute of Chemistry, the Universities of Birmingham, Bristol, Durham, Leeds, Liverpool, Manchester, Nottingham, Salford and Sheffield, and Liverpool Polytechnic for permission to publish. Where necessary, we have amended the original questions so as to conform with SI units and the physico-chemical notation outlined in Chapter 1.

Finally, we wish to thank Dr. A. R. Denaro, Dr. L. F. Moore

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CHAPTER 1

Units and Methods of Expression in Physical Chemistry

A good case can be made in favour of a single international language to replace the many national and regional languages in present use; however, for various reasons, the prospect of such a change taking place in the forseeable future is extremely remote. A much stronger case can be made in favour of an international scientific and technological language in which the adopted methods of expression avoid any possible ambiguity as to their meaning and in which physical quantities are expressed, as far as possible, in relation to a single coherent set of units. Such a language (albeit not, as yet, entirely perfected) now exists in physical science, and is outlined in this chapter in so far as it is relevant to the contents of this book. (For a more detailed account than that given in this chapter, see M. L. McGlashan, *Physico-Chemical Quantities and Units*, Royal Institute of Chemistry, Monographs for Teachers No 15, 1968.)

SI Units

Since our system of pure numbers is decimal, the manipulation and recording of physical quantities is facilitated if the alternative units in which a particular physical quantity might be expressed differ by factors of ten. Moreover, matters are simplified further

if a single system of such units is adopted. An international system of units has now been formulated. It is referred to as SI (abbreviation for Système International d'Unités).

SI is based on the following seven independent physical quantities (see *Table 1.1*).

Table 1.1

Physical quantity	Symbol(s)	Basic SI unit	Unit symbol
length	l, b, d, h, r, s, etc.	metre	m
mass	m	kilogramme	kg
time	t	second	s
electric current	I	ampere	A
thermodynamic temperature	T	kelvin	K
amount of substance*	n	mole	mol
luminous intensity	I_v	candela	cd

*See section on molar quantities, page 15.

[*Note*. A reason for selecting metre, kilogramme and second (m.k.s.) as the basic units of mass, length and time, rather than, for example, centimetre, gramme and second (c.g.s.) is so that the unit of work (mass×acceleration×distance) is the joule (kg m² s⁻²), the magnitude of which is more convenient than that of the erg (g cm² s⁻² = 10⁻⁷ joule). The unit of electric current, the ampere, is so defined that the unit of electric energy (potential difference ×current×time) is also the joule.]

(Electric charge or electric potential difference could, alternatively, have been chosen as a basic quantity instead of electric current; this is apparent from the definitions of their units.)

SI also includes two fundamental quantities with *dimensionless units* (see *Table 1.2*).

Table 1.2

Physical quantity	Symbols	SI unit	Unit symbol
plane angle	$\alpha, \beta, \gamma, \theta, \phi$	radian	rad
solid angle	ω, Ω	steradian	sr

Other physical quantities can be expressed in SI units which are derived from the above basic units by appropriate multiplication, division, integration and/or differentiation without the introduction of any numerical factors (including powers of ten). In this sense, SI is described as a coherent system of units. A selection of derived SI units, some of which have been given special names, is given in *Tables 1.3* and *1.4*.

Table 1.3

DERIVED SI UNITS WITH SPECIAL NAMES

Physical quantity	Symbol(s)	Name of SI unit	Unit symbol	Definition
frequency	v, f	hertz	Hz	s^{-1}
force	F	newton	N	$kg\ m\ s^{-2} = J\ m^{-1}$
energy (all forms)*	E, U, V, etc.	joule	J	$N\ m = kg\ m^2\ s^{-2} = C\ V = V\ A\ s$
power	P	watt	W	$J\ s^{-1} = kg\ m^2 s^{-3} = V\ A$
electric charge	Q	coulomb	C	$A\ s$
electric potential difference	$E, \psi, \zeta, \phi, \eta$, etc.	volt	V	$J\ A^{-1}\ s^{-1} = kg\ m^2\ s^{-3}\ A^{-1}$
electric resistance	R	ohm	Ω	$V\ A^{-1} = kg\ m^2\ s^{-3}\ A^{-2}$
electric capacitance	C	farad	F	$C\ V^{-1} = A^2\ s^4\ kg^{-1}\ m^{-2}$
inductance	L, M	henry	H	$V\ A^{-1}\ s = kg\ m^2\ s^{-2}\ A^{-2}$
magnetic flux	Φ	weber	Wb	$V\ s = kg\ m^2\ s^{-2}\ A^{-1}$
magnetic induction	B	tesla	T	$Wb\ m^{-2} = kg\ s^{-2}\ A^{-1}$
luminous flux	Φ	lumen	lm	$cd\ sr$
illumination	E	lux	lx	$lm\ m^{-2} = cd\ sr\ m^{-2}$

* See *Note* on page 2.

Note. (1) Quantity symbols are always printed in italic (sloping) type (bold-faced italic for vector quantities). Unit symbols are printed in roman (upright) type.

(2) Full stops are not used between units to represent multiplication, but units are spaced to avoid possible confusion, such as between 1 m s $^{-1}$ (1 metre per second) and 1 ms $^{-1}$ (which could be misinterpreted as 1 reciprocal millisecond). 10^3 s $^{-1}$ is an unambiguous representation of the latter quantity.

(3) Plural forms to unit symbols are not used, e.g. 10 kg and not 10 kgs.

Table 1.4

SOME OTHER SI UNITS AND RECOMMENDED QUANTITY SYMBOLS

(A number of points which are particularly relevant to the quantities marked with an asterisk are discussed later in this chapter.)

Physical quantity	Symbol(s)	SI unit (if any)
area: $A = \int l \, db$	A	m^2
volume: $V = \int A \, dh$	V	m^3
velocity: $u = ds/dt$	u, v, c	$m \, s^{-1}$
angular velocity: $\omega = d\theta/dt$	ω	$rad \, s^{-1}$
momentum: $P = mu$	p	$kg \, m \, s^{-1} = N \, s$
angular momentum: $L = rp$	L	$kg \, m^2 \, s^{-1} = J \, s$
acceleration: $a = du/dt$	a, g (free fall)	$m \, s^{-2}$
moment of inertia: $I_z = \int (x^2 + y^2) \, dm$	I	$kg \, m^2$
weight	$G, (W)$	N
density: $\varrho = m/V$	ϱ	$kg \, m^{-3}$
*specific volume: $v = V/m$	v	$m^3 \, kg^{-1}$
pressure†	p	$N \, m^{-2} = J \, m^{-3}$ $= kg \, m^{-1} \, s^{-2}$
shear stress	τ	$N \, m^{-2}$
dynamic viscosity: $\eta = \tau_{zx}/(du_x/dz)$	η	$kg \, m^{-1} \, s^{-1}$
kinematic viscosity: $v = \eta/\varrho$	v	$m^2 \, s^{-1}$
diffusion coefficient	D	$m^2 \, s^{-1}$
surface tension	γ, σ	$N \, m^{-1} = J \, m^{-2}$ $= kg \, s^{-2}$
molecular mass	m	kg
*molar mass: $M = m/n$	M	$kg \, mol^{-1}$
*molar volume: $V_m = V/n$	V_m	$m^3 \, mol^{-1}$
*relative atomic mass	A_r	dimensionless
*relative molecular mass	M_r	dimensionless
work: $w = Fs$	w	J
quantity of heat	q	J
thermodynamic (internal) energy	U	J
enthalpy: $H = U + pV$	H	J
Helmholtz free energy function: $A = U - TS$	A	J
Gibbs free energy function: $G = H - TS = U + pV - TS$	G	J

† Although not, as yet, officially adopted as a specially named SI unit, the name pascal (symbol, Pa) is sometimes used to denote the SI unit of pressure, $N \, m^{-2}$.

Table 1.4 *(cont.)*

Physical quantity	Symbol (s)	SI unit (if any)
entropy	S	$J\ K^{-1}$
heat capacity: $C_V = (\partial U/\partial T)_V$		
$C_p = (\partial H/\partial T)_p$	$C_V,\ C_p$	$J\ K^{-1}$
molar gas constant: $R = N_A k$	R	$J\ K^{-1}\ mol^{-1}$
Boltzmann constant: $k = R/N_A$	k	$J\ K^{-1}$
*Avogadro constant	$N_A,\ L$	mol^{-1}
*concentration of substance B:		
$c_B = n_B/V$	$c_B,\ [B]$	$mol\ m^{-3}$
*molality of solute B:		
$m_B = n_B/n_A\ M_A$	m_B	$mol\ kg^{-1}$
mole fraction of substance B:		
$x_B = n_B/\sum n_B$	x_B	dimensionless
stoichiometric coefficient		
of substance B		
(+ ve for products, − ve for	ν_B	dimensionless
reactants)		
degree of dissociation	α	dimensionless
*molar thermodynamic energy:		
$U_m = U/n$	U_m	$J\ mol^{-1}$
*molar enthalpy: $H_m = H/n$	H_m	$J\ mol^{-1}$
*molar free energy: $A_m = A/n$,		
$G_m = G/n$	$A_m,\ G_m$	$J\ mol^{-1}$
*molar entropy: $S_m = S/n$	S_m	$J\ K^{-1}\ mol^{-1}$
*molar heat capacity: $C_{V,\ m} = C_V/n$,		
$C_{p,\ m} = C_p/n$	$C_{V,\ m},\ C_{p,\ m}$	$J\ K^{-1}\ mol^{-1}$
partial molar volume of substance B:		
$V_B = (\partial V/\partial n_B)_{T,\ p,\ n_c\ \ldots}$	V_B	$m^3\ mol^{-1}$
chemical potential of substance B		
$\mu_B = (\partial G/\partial n_B)_{T,\ p,\ n_c\ \ldots}$	μ_B	$J\ mol^{-1}$
fugacity	p^*	$N\ m^{-2}$
*absolute activity of substance B:		
$\lambda_B = \exp(\mu_B/RT)$	λ_B	dimensionless
*relative activity of solvent A:		
$a_A = \lambda_A/\lambda_A^{\bullet\dagger}$	a_A	dimensionless
*relative activity of solute B:		
$a_B = m_B \gamma_B/m^{\ominus\dagger}$	a_B	dimensionless
*activity coefficient of solute B:		
$\gamma_B = (\lambda_B/m_B)/(\lambda_B/m_B)^{\infty\dagger}$	γ_B	dimensionless
$y_B = (\lambda_B/c_B)/(\lambda_B/c_B)^{\infty\dagger}$	y_B	dimensionless
osmotic pressure of a solution	Π	$N\ m^{-2}$
osmotic coefficient of solvent A	$g,\ \phi$	dimensionless

† $\bullet$ indicates a pure substance; $\ominus$ indicates a standard value of a property (e.g. 1 atm, 1 mol kg^{-1}); ∞ indicates a limiting value at infinite dilution.

Table 1.4 *(cont.)*

Physical quantity	Symbol(s)	SI unit (if any)
*equilibrium constant: $K_p = \Pi(p_B)^{\nu_B}$	K_p	$(N\ m^{-2})^{\Sigma_i \nu_B}$
*equilibrium constant: $K_c = \Pi(c_B)^{\nu_B}$	K_c	$(mol\ m^{-3})^{\Sigma_i \nu_B}$
*equilibrium constant: $K_m = \Pi(m_B)^{\nu_B}$	K_m	$(mol\ kg^{-1})^{\Sigma_i \nu_B}$
*equilibrium constants $$K_p*/_{p\ominus} = \Pi\left(\frac{p_B^*}{p\ominus}\right)^{\nu_B},$$	$K_p*/_{p\ominus},$	
$$K_m\gamma/_{m\ominus} = \Pi\left(\frac{m_B\gamma_B}{m\ominus}\right)^{\nu_B}, \text{ etc.}$$	$K_m\gamma/_{m\ominus}$, etc.	dimensionless
partition functions	Q, q	dimensionless
electric field strength	E	$V\ m^{-1}$
magnetic field strength	H	$A\ m^{-1}$
charge density: $\varrho = Q/V$	ϱ	$C\ m^{-3}$
surface charge density: $\sigma = Q/A$	σ	$C\ m^{-2}$
electric current density	j	$A\ m^{-2}$
*permittivity	ε	$F\ m^{-1} = kg^{-1}$ $m^{-3}\ s^4\ A^2$
*relative permittivity‡: $\varepsilon_r = \varepsilon/\varepsilon_0$ (ε_0 = permittivity of vacuum)	ε_r	dimensionless
*permeability	μ	$H\ m^{-1} = kg\ m$ $s^{-2}\ A^{-2}$
*relative permeability: $\mu_r = \mu/\mu_0$ (μ_0 = permeability of vacuum)	μ_r	dimensionless
polarizability of a molecule	α	$C\ m^2\ V^{-1}$
dipole moment of a molecule	μ, p	$C\ m$
elementary charge (proton or electron)	e	C
charge number of ion i (+ve or −ve)	z_i	dimensionless
Faraday constant: $F = N_A e$	F	$C\ mol^{-1}$
ionic strength: $I = \frac{1}{2}\sum m_i z_i^2$	I	$mol\ kg^{-1}$
*mean ionic activity coefficient of an electrolyte: $\gamma_\pm = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$	$\gamma_\pm$	dimensionless
*electric conductance: $G = 1/R$	G	Ω^{-1}
*electric conductivity: $\varkappa = j/E$	$\varkappa$	$\Omega^{-1}\ m^{-1}$
*molar conductivity: $\Lambda = \varkappa/c$	Λ	$\Omega^{-1}\ m^2\ mol^{-1}$
transport number of ion i	t_i	dimensionless
mobility of a charged particle $u = v/E$	u	$m^2\ s^{-1}\ V^{-1}$
rate of increase of concentration of substance B	$v_B, \dfrac{dc_B}{dt}, \dfrac{d[B]}{dt}$	$mol\ m^{-3}\ s^{-1}$
rate constant of a $(n+1)$th order reaction	k, k_r	$m^{3n}\ mol^{-n}\ s^{-1}$

‡ Also called dielectric constant (symbol, D) when it is independent of E.

Table 1.4 *(cont.)*

Physical quantity	Symbol (s)	SI unit (if any)
activation energy of a reaction	$\Delta E, \Delta E^{\ddagger}$	J mol^{-1}
collision number	Z	m^{-3} s^{-1}
quantum yield	Φ	dimensionless
quantum numbers	J, v, etc.	dimensionless
refractive index	n	dimensionless
Planck's constant	h	J s
wavelength	λ	m
*wave number: $\bar{\nu} = 1/\lambda$	$\bar{\nu}, \sigma$	m^{-1}
transmittance: $T = I/I_0$	T	dimensionless
decadic absorbance (decadic extinction)§:		
$A = -\log_{10} T$	A	dimensionless
molar Napierian extinction coefficient	$\varkappa$	m^2 mol^{-1}
molar decadic extinction coefficient:		
$\varepsilon = A/lc$	ε	m^2 mol^{-1}

§ Formerly called optical density.

(4) The use of a single solidus (/) for expressing derived units (e.g. m s^{-1}/V m^{-1} for mobility rather than m^2 s^{-1} V^{-1}) is permissible, but better avoided. More than one solidus in the same expression (e.g. m/s/V/m for mobility) should never be used owing to the ambiguity which is created.

PREFIXES FOR SI UNITS

SI permits the use of the following prefixes *(Tables 1.5* and *1.6)* to denote decimal fractions and multiples of basic SI units and derived SI units with special names. To avoid a multiplicity of prefixes, the factors are 10^{3n} except around unity where additional prefixes are available to denote 10^{-2}, 10^{-1}, 10 and 10^2. Compound prefixes should not be used.

These prefixes are, of course, not absolutely necessary, but are convenient in so far as they avoid the use of inconveniently large and small numerical values and sometimes facilitate appreciation of the magnitudes of physical quantities, as illustrated by the following examples.

Table 1.5		
Factor	Prefix	Symbol
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

Table 1.6		
Factor	Prefix	Symbol
10	deka	da
10^2	hecto	h
10^3	kilo	k
10^6	mega	M
10^9	giga	G
10^{12}	tera	T

(1) The collision diameter of a nitrogen molecule is $3 \cdot 75 \times 10^{-10}$ m or $0 \cdot 375$ nm (nanometre).

(2) The concentration of an aqueous solution of potassium chloride is 100 mol m^{-3} or $0 \cdot 1$ mol dm^{-3}. $0 \cdot 1$ mol dm^{-3} is the more convenient of these alternatives because, (a) 1 m^3 of solution is in considerable excess of the scale of a typical laboratory experiment, (b) it is numerically the same as the now obsolete term, molar concentration (mol l^{-1}), and (c) it is numerically similar to the molality expressed in mol kg^{-1}.

Since SI is a coherent system of units, it follows that, when performing numerical calculations, no thought about conversion factors is necessary if physical quantities are expressed in unprefixed SI units, as illustrated by the following examples.

(1) Use the relationship, $E = N_A hc\bar{\nu}$, to calculate the molar energy which corresponds to a wave number, $\bar{\nu}$, of 1 cm^{-1}. Substituting $N_A = 6 \cdot 022\,5 \times 10^{23}$ mol^{-1}, $h = 6 \cdot 625\,6 \times 10^{-34}$ J s, $c = 2 \cdot 997\,9 \times 10^8$ m s^{-1} and $\bar{\nu} = 10^2$ m^{-1}, automatically gives the value of E in J mol^{-1}, i.e.

$$E = 6 \cdot 022\,5 \times 10^{23} \times 6 \cdot 625\,6 \times 10^{-34} \times 2 \cdot 997\,9 \times 10^8 \times 10^2$$
$$(\text{mol}^{-1})\ (\text{J s})\ (\text{m s}^{-1})(\text{m}^{-1}) = 11 \cdot 962\ \text{J mol}^{-1}$$

(2) Calculate the potential, ψ, such that the relationship, $ze\psi = kT$, is valid at 25°C. Substituting $e = 1 \cdot 60 \times 10^{-19}$ C, $k = 1 \cdot 38 \times 10^{-23}$ J K^{-1}, $T = 298$ K and the appropriate value for z (dimensionless), automatically gives the value of ψ in volts, i.e.

$$\psi = \frac{1 \cdot 38 \times 10^{-23} \times 298}{z \times 1 \cdot 60 \times 10^{-19}}\ \frac{\text{J K}^{-1}\ \text{K}}{\text{C}} = \frac{0 \cdot 025\,7}{z}\ \text{V}$$

When using prefixed SI units in a numerical calculation, a conversion factor of an appropriate power of ten may be necessary to

obtain the final answer in the desired unit. If the data for a numerical calculation is presented in prefixed SI units or non-SI units, the risk of miscalculation will often be minimized if conversion to non-prefixed SI units is made before substitution into the appropriate equation(s).

NON—SI UNITS

The following two tables *(1.7* and *1.8)* list a selection of units which are exactly defined in terms of SI but which are not coherent with SI. The units in the first table are decimal fractions or multiples of the corresponding SI unit and those in the second table are non-decimal with respect to the corresponding SI unit.

With the exception of the atmosphere (which must be retained in Physical Chemistry in view of its role as a standard state), these non-SI units are unnecessary and most of them must be regarded as obsolete (see first footnote to *Table 1.7*).

Some non-SI units, such as the minute, hour, degree Celsius and, possibly, the litre, will, of course be retained for everyday usage. The degree Celsius will doubtless continue to be used in some branches of physical science as a colloquialism for the thermodynamic temperature in excess of 273·15 K.

Table 1.7

Physical quantity	Name of unit	Unit symbol	Definition
length	ångström*	Å	10^{-10} m $= 10^{-1}$ nm
length	micron	$\mu^\dagger$	10^{-6} m $= \mu$m
length	millimicron	m$\mu^\dagger$	10^{-9} m $=$ nm
volume	litre	l	10^{-3} m^3 $=$ dm^3
force	dyne	dyn	10^{-5} N
energy	erg	erg	10^{-7} J
pressure	bar	bar	10^5 N m^{-2}
dynamic viscosity	poise	P	10^{-1} kg m^{-1} s^{-1}
concentration	'molar'‡	M	mol dm^{-3}
magnetic flux	maxwell	Mx	10^{-8} Wb
magnetic flux density (magnetic induction)	gauss	G	10^{-4} T

* In view of its convenience with respect to molecular dimensions, a number of scientists urge retention of the ångström as a recognized unit of length.

† μ means 10^{-6} and not 10^{-6} m; mμ, at best, means n or 10^{-9} and not 10^{-9}m.

‡ See page 16.

Table 1.8

Physical quantity	Name of unit	Unit symbol	Definition
energy	thermochemical calorie§	cal	$4 \cdot 184$ J
pressure	atmosphere	atm	$1 \cdot 013\ 25 \times 10^5$ N m^{-2}
pressure	conventional millimetre of mercury	mmHg	$13 \cdot 595\ 1 \times 9 \cdot 806\ 65$ N m^{-2} $= 133 \cdot 322\ 39$ N m^{-2}
pressure	torr	Torr	$\dfrac{1 \cdot 013\ 25 \times 10^5}{760}$ N m^{-2} $= 133 \cdot 322\ 37$ N m^{-2}
temperature	degree Celsius**	°C	$T/\ \text{C} = T/\text{K} - 273 \cdot 15$††

§ Unlike the joule, the calorie is an ambiguous unit without further specification, e.g. 1 international calorie $= 1 \cdot 000\ 67$ thermochemical calories.

** Celsius not Centrigrade.

†† See page 12 for explanation of this type of notation.

It may be convenient to express experimental data in non-SI units in view of the method of measurement. Non-SI units should, however, in general, be avoided when recording physical quantities which have been calculated from experimental data. For example, if a mercury manometer is used for the purpose of investigating the pressure variation which accompanies a second-order gas phase reaction at constant temperature and volume taking place over a period of several minutes, it is convenient, and quite permissible, to tabulate pressures in mmHg or torr with the corresponding reaction times in min; however, the calculated rate constant should be expressed in units such as N^{-1} m^2 s^{-1} or mol^{-1} dm^3 s^{-1}, but not in torr^{-1} min^{-1}, etc.

ELECTRICAL AND MAGNETIC QUANTITIES AND UNITS— RATIONALIZATION

In SI electrical and magnetic units are based on the fundamental units of metre, kilogramme, second and ampere, and equations are rationalized.

The force, F, between charges, Q_1 and Q_2, separated by a distance, r, in a medium of permittivity, ε, is given by the rationalized expression,

$$F = \frac{Q_1 Q_2}{4\pi\varepsilon r^2}$$

Since Q has the dimension [current] [time], ε has the dimension [length]$^{-3}$ [mass]$^{-1}$ [time]^4 [current]^2. The permittivity of a vacuum, ε_0, in accordance with the above equation is equal to $8 \cdot 854\ 2 \times 10^{-12}$ kg^{-1} m^{-3} s^4 A^2.

The *relative permittivity* of a medium, $\varepsilon/\varepsilon_0$, can be referred to as the *dielectric constant*, D, of the medium if it is independent of electric field strength.

The above equation differs from the traditional Coulomb inverse square law equation by the inclusion of the factor, 4π, and is said to be rationalized. The reason for including 4π is so that its occurrence or otherwise in derived expressions might be in accordance with geometric expectation and not vice versa. For example, the equation for a parallel plate condenser, where the occurrence of 4π would not be expected from geometric considerations, is $\sigma = \dfrac{\varepsilon U}{4\pi d}$ in non-rationalized form and $\sigma = \dfrac{\varepsilon U}{d}$ in rationalized form; whereas the equation for an isolated spherical condenser, where the occurrence of 4π is expected from geometric considerations, is $Q = \varepsilon a U$ in non-rationalized form and $Q = 4\pi\varepsilon a U$ in rationalized form.

The force, F, between electric currents, I_1 and I_2, in parallel conductors of length, l, separated by a distance, d, in a medium of permeability, μ, is given by the rationalized expression,

$$F = \frac{2\mu I_1 I_2 l}{4\pi d}$$

Permeability, therefore, has the dimension, [length] [mass] [time]$^{-2}$ [current]$^{-2}$, and the permeability of a vacuum, μ_0, in accordance with the above equation is equal to $4\pi \times 10^{-7}$ kg m s^{-2} A^{-2}.

ε_0 and μ_0 are related by the expression, $\varepsilon_0 \mu_0 = c_0^{-2}$, where c_0 is the velocity of light in a vacuum.

Methods of Expression

SUPERSCRIPTS AND SUBSCRIPTS

Some commonly used superscripts and subscripts are listed below.

Superscripts

- ●   pure substance
- ϴ   standard value of a property (e.g. 1 atm, 1 mol kg^{-1})
- ∞   limiting value at infinite dilution
- ‡   transition state (activated complex)

Subscripts

A	solvent
B. etc.	solute(s)
B, C, etc.	components of a mixture
i	typical ionic species
+, —	+ve or —ve ion
m	molar quantity
p, T, V, etc.	constant pressure, temperature, volume, etc.
f, e, s, t, d	fusion or formation, evaporation, sublimation, transition, and dissolution, respectively
c	critical state, critical value

TABLES AND GRAPHS

The value of a physical quantity is expressed as the product of a pure number and a unit,

e.g. $$p = 1 \cdot 013 \times 10^5 \text{ N m}^{-2}$$

which rearranges to $p/\text{N m}^{-2} = 1 \cdot 013 \times 10^5$

or $$p/10^5 \text{ N m}^{-2} = 1 \cdot 013$$

To avoid repetition of the unit symbol, it is common practice to tabulate data in the form of pure numbers. It follows that column headings should be dimensionless, e.g. $p/\text{N m}^{-2}$ and not $p(\text{N m}^{-2})$. A column heading such as $p(\text{N m}^{-2})$ implies pressure multiplied by N m^{-2}, when one really means pressure divided by N m^{-2}. As an example of this notation, the following tabulated data *(Table 1.9)* refer to the vapour pressure of acetone at various temperatures:

Table 1.9

$t/°C$	T/K	$p/10^5 \text{ N m}^{-2}$	$10^3 \text{ K}/T$	$\log_{10}(p/\text{N m}^{-2})$
40	313	0·561	3·195	4·749
50	323	0·817	3·096	4·912
60	333	1·155	3·003	5·063
70	343	1·600	2·915	5·204

The same considerations apply to the labelling of graphs.