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Valency

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Preface

This book was written after one of us published two editions of a smaller book (*Atomic Structure and Valency* by R. D. Brown, 1961 and 1966) and from the experiences of all three of us teaching a first-year university course in valency at Monash University. Our object has been to give enough of an historical introduction to quantum mechanics to enable a student to grasp the fundamental ideas without being subjected to much mathematical formalism. We have also tried to avoid making erroneous statements in the interest of simplicity (e.g., the widespread tendency to ignore the difference between $2p_1$, $2p_0$, $2p_{-1}$ and $2p_x$, $2p_y$, $2p_z$) because these lead to irritation and confusion of the better students, when they proceed to further studies of chemical quantum mechanics. The topics we have chosen to expand upon—i.e., energy levels of electrons in atoms, energetic considerations of bonding in diatomic molecules, and packing of ions in the simplest solid state structures—we believe form a good basis for students to progress to more complicated systems in a qualitative way. Both space and the intended level of the book have necessitated that the experimental section on spectroscopic and diffraction methods be very introductory. Again we believe that it is essential for a student to have some acquaintance with this, if the whole subject is to have a firm basis.

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1 Introduction

Before we embark on this introductory study of various theories and concepts about atoms and molecules, it is necessary to lay some groundwork concerning units of measurement of physical quantities. In particular, we are very interested here in the units of mass and energy. The units of mass are simple; chemists and, in fact, most scientists use the metric *gram*—or more correctly, as we see in a moment—the *kilogram*. With energy the common units are more varied among scientists and thus the student must take special care to avoid confusion. One of the best ways to avoid confusion in any unit is to define a consistent and standardized set of units. This was devised and internationally accepted in 1960; the set is known as *Système International d'Unités*, or simply SI units.

SI Units These are *rational* or *coherent* units in that there are no constants built into the units. Known also as MKSA units, there are seven basic quantities from which all other units are derived. These seven units are given in Table 1.1.

Derived SI Units All the other units of physical quantities derive directly from these seven basic SI units. Some of these have familiar names and symbols often named after famous scientists; those most frequently encountered are shown in Table 1.2.

Others do not have special names. Table 1.3 lists some examples of SI units in this category.

Table 1.1 Basic SI units

Physical quantity	Name of unit	Symbol for unit
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Luminous intensity	candela	cd
Amount of substance	mole	mol

Table 1.2 Derived SI units with special names

Physical quantity	Name of unit	Symbol for unit	Definition of unit
Energy	joule	J	$\text{kg m}^2\text{s}^{-2}$
Force	newton	N	$\text{kg m s}^{-2} = \text{J m}^{-1}$
Power	watt	W	$\text{kg m}^2\text{s}^{-3} = \text{J s}^{-1}$
Pressure	pascal	Pa	$\text{kg m}^{-1}\text{s}^{-2} = \text{N m}^{-2}$
Electric charge	coulomb	C	A s
Electric potential difference	volt	V	$\text{kg m}^2\text{s}^{-3}\text{A}^{-1} = \text{J A}^{-1}\text{s}^{-1}$
Electric resistance	ohm	Ω	$\text{kg m}^2\text{s}^{-3}\text{A}^{-2} = \text{V A}^{-1}$
Electric capacitance	farad	F	$\text{A}^2\text{s}^4\text{kg}^{-1}\text{m}^{-2} = \text{A s V}^{-1}$
Magnetic flux	weber	Wb	$\text{kg m}^2\text{s}^{-2}\text{A}^{-1} = \text{V s}$
Inductance	henry	H	$\text{kg m}^2\text{s}^{-2}\text{A}^{-2} = \text{V s A}^{-1}$
Magnetic flux density	tesla	T	$\text{kg s}^{-2}\text{A}^{-1} = \text{V s m}^{-2}$
Luminous flux	lumen	lm	cd sr
Illumination	lux	lx	cd sr m^{-2}
Frequency	hertz	Hz	cycle per second : s^{-1}
Customary temperature, t	degree Celsius	$^{\circ}\text{C}$	$t [^{\circ}\text{C}] = T [\text{K}] - 273.15$
Plane angle	radian	rad	
Solid angle	steradian	sr	

Table 1.3 Derived SI units without special names

Physical quantity	SI Unit	Symbol for unit
Area	square meter	m^2
Volume	cubic meter	m^3
Density	kilogram per cubic meter	kg m^{-3}
Velocity	meter per second	m s^{-1}
Molar mass	kilogram per mole	kg mol^{-1}

Table 1.4 Fractions and multiples of SI units

Fraction	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10	deka	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

Prefixes for Fractions and Multiples of SI Units

Table 1.4 lists the internationally accepted prefixes for fractions and multiple of SI units.

These conform with the usual prefixes commonly used by scientists so that, for example, a frequency of 3.31×10^{10} Hz could equally well be expressed as 33.1 GHz (gigahertz) and 10^{-2} meter could be expressed as 1 cm (centimeter).

One awkward and as yet unresolved problem is that the basic SI unit for mass, the kilogram, already possesses a prefix. It is probably best to express 10^3 kg simply as one thousand kilograms or a megagram rather than a kilokilogram. Similarly, 10^{-3} kg is conveniently expressed as a gram rather than the absurd-sounding millikilogram!

Compound prefixes are taboo; for example, 10^{-9} meter is represented by

$$1 \text{ nm, not } 1 \text{ m}\mu\text{m.}$$

The attaching of a prefix to a unit in effect constitutes a new unit:

$$1 \text{ km}^2 = 1 (\text{km})^2 = 10^6 \text{ m}^2$$

and not

$$1 \text{ k(m)}^2 = 10^3 \text{ m}^2$$

Units Contrary to SI

You will encounter many units in various textbooks that are contrary to the SI rules. A few of these and their SI equivalents are given in Table 1.5.

In this book we endeavor to avoid use of units that are contrary to the SI codification such as those in Table 1.5. However, there are a few units very closely related to SI for which we make exceptions. Specifically, these few are listed in Table 1.6.

A table of physical constants is included for convenience inside the front cover.

Energy Units in Valency

Notice that there are two additional units of energy¹ in Table 1.6 aside from the SI joule. This is perhaps unfortunate, but nonetheless a fact. Chemists who classify themselves as having some degree of expertise in the field of valency are as much to blame for this state of affairs as anyone. The electron volt is the kinetic energy gained by an electron that has been accelerated through a potential difference of one volt. The electronvolt (eV) is simply the electronic charge e (see Chapter 2) times this potential difference V .

We have relaxed the SI principle in this book for the energy units of eV and cm^{-1} because not only are they all-pervading in other books and scientific articles, but also the magnitudes of the energy quantities are so minute when expressed in joules (we normally encounter molecular energies less than 1 aJ!). To assist in converting from one energy unit to another, Figure 1.1 gives a handy reference guide.

¹Frequency is proportional to energy via Planck's constant, $E = h\nu$, where E is the energy in joules, h is Planck's constant ($h = 6.626 \times 10^{-34}$ J s), and ν (Greek nu) is the frequency in Hertz (s^{-1}). The development of this important relationship between energy and frequency is further depicted in Chapter 3.

Table 1.5 Units contrary to SI

Physical quantity	Contrary unit	SI Equivalent
Length	Å	10^{-10} m = 100 pm
Energy	erg	10^{-7} J
	thermochemical calorie	4.184 J
Force	dyne	10^{-5} N
	kilogram-force	9.80665 N
Pressure	atmosphere	101.325 kPa
	torr—mm Hg	133.322 Pa
Magnetic flux density	gauss	10^{-4} T

Table 1.6 Units to be allowed in conjunction with SI in this book

Physical quantity	Name of unit	Symbol for unit	Definition of unit
Energy	Electronvolt	eV	1.602×10^{-19} J
Wavenumber	Centimeter to the minus one or loosely referred to as wavenumbers	cm^{-1}	100 m^{-1}

	from	→	to	Multiply by
1.240×10^{-4}	eV molecule ⁻¹		cm ⁻¹ molecule ⁻¹	8065.5
5.034×10^{22}	cm ⁻¹ molecule ⁻¹		joule molecule ⁻¹	1.986×10^{-23}
6.242×10^{18}	eV molecule ⁻¹		joule molecule ⁻¹	1.602×10^{-19}
2.390×10^{-4}	kcal mol ⁻¹		joule mol ⁻¹	4.184×10^3
Multiply by	to	←	from	

FIGURE 1.1. Energy conversion.

Classical Forms of Energy

Before leaving the topic of units and energy, it may be useful to review briefly a general classical classification of energy since much of our subsequent discussions are directly concerned with the energy of atoms and molecules. The *total mechanical energy* of a body is defined as the sum of its potential and kinetic energies.

$$E_{\text{tot}} = E_{\text{pot}} + E_{\text{kin}} = mgh + \frac{1}{2}mv^2$$

m being the mass of the object, g the Earth's gravitational constant = 9.80 m s^{-1} , h the height above a reference plane, and v the body's velocity. In addition to potential energy arising from gravity ($E_{\text{pot}} = mgh$), other forms of potential energy can arise. The one that we encounter most frequently in valency is electrostatic potential energy:

$$E_{\text{pot}} = \varphi Q$$

where Q is the electric charge on the object and φ is the electrostatic potential experienced by the object (e.g., when the object is a distance r meter from a charge q coulomb, it experiences a potential of $\varphi = (q/4\pi\epsilon_0 r) \text{ V}$).²

In addition, energy manifests itself thermally in terms of heat energy. The general study of the relations between other forms of energy and heat is known as thermodynamics. At the level that we discuss atomic structure and valency here we do not need to delve deeply into this subject but we use an energy principle:

The most stable state of an individual atom or molecule is that of lowest total potential energy. When there are external influences, such as collisions with other molecules or radiation, the atom or molecule may be found in some

² $1/4\pi\epsilon_0$ is a proportionality constant, ϵ_0 referred to as the *permittivity of vacuum* and having the value $\epsilon_0 = 8.855 \times 10^{-12} \text{ s}^2\text{C}^2 \text{ kg}^{-1} \text{ m}^{-3}$.

other energy state. Under normal laboratory conditions most atoms and molecules are encountered in their most stable state.

This is a principle where observation constitutes the proof, and for our purposes we accept it as being true:

Finally we also should realize that classically the transmission of energy can occur through the use of: (a) *projectiles* where mass is transferred and carries energy obtained at point *a* to point *b* and (b) *waves* where mass is not transferred.

An example of the former is a bowler who exerts himself to give kinetic energy to a cricket ball that then travels down the pitch carrying its energy (primarily kinetic energy) with it. The energy is expended on impact of the ball with the wicket, the bat, the stumps, or the gloves of the wicket keeper. Thus the ball acts as the projectile that transfers the energy. Transfer of energy via wave motion is more subtle in that the transportation of matter does not take place. For example, an earthquake in New Zealand causing a tidal wave to hit the eastern coast of Australia does not mean that water from New Zealand has been hurled against the shores of Australia, but simply that the ocean has been disturbed in one place, the disturbance has traveled across the surface of the water, and finally caused damage on the beaches of another shore. Other examples are seismic waves (earthquakes) and the cracking of a stock whip.

The two ways of classically transmitting energy historically were understood with the exception of one phenomenon known as light. Light is an energy form, but its propagation could not be explained using *either* a projectile model or wave model, and classical arguments appear to break down. As we see shortly, the significance of this is quite profound and has far-reaching implications in the currently accepted theories of atomic structure and valency.

Problems

- 1.1 Find the dimensions of action (energy \times time).
- 1.2 For the ideal gas equation, $PV = nRT$, find the SI units of R .
- 1.3 Express the weber units (see Table 1.2) in terms of J (joules) and A (amperes).
- 1.4 Complete the following equations:
 - a. $J \div C =$
 - b. $C \times \Omega = V \times$
 - c. $J \div N =$

1.5 Express the following:

- a. 2.562×10^{-7} m in nm
- b. 5685 g as kg
- c. 1.09×10^{-2} kV as mV
- d. 2.07×10^{-21} J as aJ

1.6 The electric permittivity of vacuum is defined by:

$$\epsilon_0 = \frac{1}{\mu_0 c^2}$$

where μ_0 is the magnetic permeability of vacuum and is by definition equal to $4\pi \times 10^{-7}$ H m⁻¹. Show that the units of ϵ_0 are s²C² kg⁻¹ m⁻³.

1.7 What is the conversion factor for eV molecule⁻¹ to J mol⁻¹?

2

Gross Atomic Structure

To begin our study of atomic structure and valency, we must ask a question that occurred to the earliest philosophers. If we examine a material body that appears homogeneous and then divide it into successively smaller pieces, can the division process go on indefinitely or will we eventually find a building block of matter that cannot be further subdivided without losing the characteristics of the material body? The answer, as postulated by Democritus (ca. 460 B.C.) and John Dalton (1766–1844), for example, is an emphatic “no.” We eventually reach an *atomic* or *molecular* state in which further degradation does alter the basic properties of our material.

We do not spend time here recounting the evidence (such as the proportions in which atoms combine to form compounds) that led to the atomic hypothesis. Rather, we trace the early development of the understanding of the gross structure of the atom from an experimental viewpoint. In Chapter 3 the explanations and theories of atomic structure are developed.

The Early Clues

It is difficult to impart to students in the 1970s the excitement and challenges that the early workers must have felt as they pieced together the structure of the atom. Facts that are taught nonchalantly today and accepted in the same manner defeated the world’s greatest intellects for centuries.

The first really significant insight was gained through Michael Faraday’s experiments on the electrolysis of substances in solution in the late nineteenth century. These