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# **Principles of Physical Chemistry**

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# Principles of Physical Chemistry

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# Preface

We have adopted an approach to physical chemistry which, we believe, makes it easier to understand and more interesting than in conventional treatments. In the first place, we write from the viewpoint of the late twentieth century: we can be confident that the basic features are well established (even though there is still a great deal to understand). In the second place, we think the mathematics, while central to the subject, should be developed hand-in-hand with a physical understanding of what is going on. We always try to impart an insight into atomic and molecular behaviour, and then to use a little mathematics – hardly any is necessary at this level, and certainly none of any subtlety – to turn the insight into something that can be tested experimentally. Finally, we build on a sense of unity. We press home the idea that there is only a handful of basic concepts, and once they have been mastered much of chemistry can be explained simply by exploring their consequences. Physical chemistry should be easy to learn as soon as it is realized that there are only a few, but richly developed, concepts.

A book has to be written in a definite order, but it doesn't have to be used like that. While we have a view on what is the logical order, others will have different ideas, and there may be excellent practical reasons why the material should be presented in a different sequence: individuality is the essence of teaching. So, while we think that the order we use is a sensible one (for reasons we shall develop in a moment) we have tried to write the book so that it can be used readily in almost any order. We have written it so that the chapters fall into short, largely independent, sequences. Within each sequence there is first the presentation and then the development of a concept. This lets the book match a range of ideas on teaching, and minimizes the problem of interweaving the physical chemistry with the other parts of the syllabus.

We begin with something that is almost second nature to most students: the knowledge of the existence of atoms. We look at their properties, arrive at periodicity, and then see how they stick together to form compounds. The chapter on the determination of molecular structure is outside most syllabuses, but we think it appropriate to give a little insight into how, in modern laboratories, molecules are identified and their sizes determined. The next sequence looks at collections of particles, first at gases and then at solids. The third sequence looks at transitions between these states of matter, first of pure materials, and then of mixtures. One special kind of mixture is a solution of ions in water, and we spend a little time on examining their special characteristics, notably electrical conduction. At

this point another sequence begins: the study of energy in chemistry. We now move beyond simple physical change to the truly chemical transformation of matter. With the First law of Thermodynamics we begin to see how to use tabulated data to come to useful conclusions about the energy resources of reactions encountered in biology and industry (applications and illustrations from both areas are used throughout the text). The other major role of energy is in the determination of the position of chemical equilibrium, and a sequence of chapters develops this enormously important idea. In the first place we introduce the concept of an equilibrium constant as a quantity that comes from experiment and which characterizes the position of equilibrium. We explore its properties, and see how easy it is to make qualitative predictions about reactions. Then we go on to produce quantitative statements about the actual amounts of substance present in a reaction when it has reached equilibrium.

One entirely optional chapter (in some people's view, because it is outside most syllabuses), but one of central importance to understanding chemistry (in our view), is the chapter on entropy, Chapter 11. Entropy underlies the description of all chemical change, and its meaning is easy to grasp. Once the equilibrium constant has become established as a practically useful idea, it is a simple matter to apply it to a wide variety of systems, and in particular to sort out the processes that lead to the chemical generation of electricity in batteries and fuel cells. The position of equilibrium is independent of the rate at which chemical reactions take place – the confusion between rates and equilibria is something we try to avoid – and so the final chapter looks at this one subject. In this way we travel from topics that are almost pure physics (the structure of atoms) to subjects that are almost biology (the direction of change, and the rate of its occurrence).

We have written the book within severe constraints of length, but we cover the principal existing syllabuses in the UK and elsewhere and the various suggestions that have been put forward for a common core. We have used examination questions from a variety of sources covering (as does the text itself) a broad range of academic ability. We have supplied a summary of each chapter in the hope that if these ideas are remembered the reader will have a framework for answering most questions that are likely to be asked. Since we recognize that science does have a human side, and that readers are often interested both in the way that concepts developed and in the personalities of their discoverers, we have interspersed the text with Boxes containing some historical and biographical details.

We have tried to present a modern book, which is not only pleasant and easy to use, but teaches a great deal about physical chemistry in a lucid and comprehensible way. We could not possibly have done so without the detailed advice of a large number of very experienced teachers. Among them we should like to make special mention of Dr T. P. Borrows, Dr J. N. King, Dr F. J. Marsden, Dr C. L. Mason, Mr P. McManus, Mr D. M. Robins, Mr N. Rowbotham, and Dr J. Spice, who read the manuscript in detail, controlled our wilder impulses, contributed suggestions, and encouraged us to be original where originality was

needed. We also wish to thank Professor M. J. Frazer for contributing in invisible but tangible ways. Our thanks are due to Corinne Clugston for reading through the manuscript and to Caron Crisp for typing it. Finally, we should like to thank our publishers for their commitment to the book and for all they have done for its development and production.

P.W.A. M.J.C.

Oxford and Tonbridge, 1981

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We are grateful to the following boards for permission to use examination questions: The Associated Examining Board, Joint Matriculation Board, Oxford and Cambridge Schools Examination Board, Oxford (Local) Examination Board, Southern Universities Joint Board, The University of London Board, The Welsh Joint Education Committee. We are grateful to the following individuals for permission to reproduce photographs: Professor B. J. Alder, Lawrence Radiation Laboratory, University of California (Fig. 6.1), Professor A. V. Crewe, Enrico Fermi Institute, University of Chicago (Figs 1.1 and 2.1), and Professor M. H. F. Wilkins, Department of Biophysics, King's College, University of London (Fig. 2.2, DNA).

PERIODIC TABLE

IA		IIA		IIIA		IVA		VA		VIA		VIIA		VIII		IB		IIB		IIIB		IVB		VB		VIB		VIIB		VIIIB		O																																																																																																																																																			
<sup>1</sup> H	1.008	<sup>2</sup> He	4.003	<sup>3</sup> Li	6.941	<sup>4</sup> Be	9.012	<sup>11</sup> Na	22.99	<sup>12</sup> Mg	24.31	<sup>19</sup> K	39.10	<sup>20</sup> Ca	40.08	<sup>21</sup> Sc	44.96	<sup>22</sup> Ti	47.90	<sup>23</sup> V	50.94	<sup>24</sup> Cr	52.00	<sup>25</sup> Mn	54.94	<sup>26</sup> Fe	55.85	<sup>27</sup> Co	58.93	<sup>28</sup> Ni	58.71	<sup>29</sup> Cu	63.55	<sup>30</sup> Zn	65.37	<sup>31</sup> Ga	69.72	<sup>32</sup> Ge	72.60	<sup>33</sup> As	74.92	<sup>34</sup> Se	78.96	<sup>35</sup> Br	79.90	<sup>36</sup> Kr	83.80	<sup>37</sup> Rb	85.47	<sup>38</sup> Sr	87.62	<sup>39</sup> Y	88.91	<sup>40</sup> Zr	91.22	<sup>41</sup> Nb	92.91	<sup>42</sup> Mo	95.94	<sup>43</sup> Tc	(99)	<sup>44</sup> Ru	101.1	<sup>45</sup> Rh	102.9	<sup>46</sup> Pd	106.4	<sup>47</sup> Ag	107.9	<sup>48</sup> Cd	112.4	<sup>49</sup> In	114.8	<sup>50</sup> Sn	118.7	<sup>51</sup> Sb	121.8	<sup>52</sup> Te	127.6	<sup>53</sup> I	126.9	<sup>54</sup> Xe	131.3	<sup>55</sup> Cs	132.9	<sup>56</sup> Ba	137.3	<sup>57</sup> La	138.9	<sup>72</sup> Hf	178.5	<sup>73</sup> Ta	180.9	<sup>74</sup> W	183.9	<sup>75</sup> Re	186.2	<sup>76</sup> Os	190.2	<sup>77</sup> Ir	192.2	<sup>78</sup> Pt	195.1	<sup>79</sup> Au	197.0	<sup>80</sup> Hg	200.6	<sup>81</sup> Tl	204.4	<sup>82</sup> Pb	207.2	<sup>83</sup> Bi	209.0	<sup>84</sup> Po	(210)	<sup>85</sup> At	(210)	<sup>86</sup> Rn	(222)	<sup>87</sup> Fr	(223)	<sup>88</sup> Ra	(226)	<sup>89</sup> Ac	(227)	<sup>59</sup> Ce	140.1	<sup>60</sup> Nd	144.2	<sup>61</sup> Pm	(147)	<sup>62</sup> Sm	150.4	<sup>63</sup> Eu	152.0	<sup>64</sup> Gd	157.3	<sup>65</sup> Tb	158.9	<sup>66</sup> Dy	162.5	<sup>67</sup> Ho	164.9	<sup>68</sup> Er	167.3	<sup>69</sup> Tm	168.9	<sup>70</sup> Yb	173.0	<sup>71</sup> Lu	175.0	<sup>90</sup> Th	232.0	<sup>91</sup> Pa	(231)	<sup>92</sup> U	238.0	<sup>93</sup> Np	(237)	<sup>94</sup> Pu	(242)	<sup>95</sup> Am	(247)	<sup>96</sup> Cm	(248)	<sup>97</sup> Bk	(247)	<sup>98</sup> Cf	(251)	<sup>99</sup> Bh	(254)	<sup>100</sup> Fm	(253)	<sup>101</sup> Md	(256)	<sup>102</sup> No	(254)	<sup>103</sup> Lr	(257)

Lanthanides

Actinides

### Fundamental physical constants

Charge of proton	$e$	$1.602 \times 10^{-19} \text{ C}$
Avogadro constant	$L$	$6.022 \times 10^{23} \text{ mol}^{-1}$
Faraday constant	$F = Le$	$9.648 \times 10^4 \text{ C mol}^{-1}$
Speed of light	$c$	$2.998 \times 10^8 \text{ m s}^{-1}$
Mass of electron	$m_e$	$9.110 \times 10^{-31} \text{ kg}$
Mass of proton	$m_p$	$1.673 \times 10^{-27} \text{ kg}$
Atomic mass unit	$m_u$	$1.661 \times 10^{-27} \text{ kg}$
Molar gas constant	$R$	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Planck constant	$h$	$6.626 \times 10^{-34} \text{ J s}$

### Useful data

0 °C corresponds to 273.15 K

1 atm corresponds to 101.325 kPa and can support a 760 mm column of mercury (that is, 1 atm corresponds to 760 mmHg)

1 eV (1 electronvolt) corresponds to  $1.602 \times 10^{-19} \text{ J}$  or  $96.48 \text{ kJ mol}^{-1}$

1 Å (1 angstrom) corresponds to  $1 \times 10^{-10} \text{ m}$

1 D (1 debye) corresponds to  $3.336 \times 10^{-30} \text{ C m}$

When pressures are expressed in atmospheres, a convenient form of the molar gas constant is  $R = 8.206 \times 10^{-2} \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ .



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# 1

# Inside atoms

In this chapter we meet the evidence for the modern view of an atom as a central massive nucleus surrounded by a cloud of electrons. We see how the electrons are arranged, and meet the modern description of atomic structure in terms of orbitals. The basis of the periodic classification of the elements is explained in terms of these ideas. We see how atomic spectroscopy is used to identify atoms and explore their structures, and how mass spectrometry is used to determine their masses. Finally we examine the nucleus more closely, and see how it gives rise to the three kinds of radioactivity.

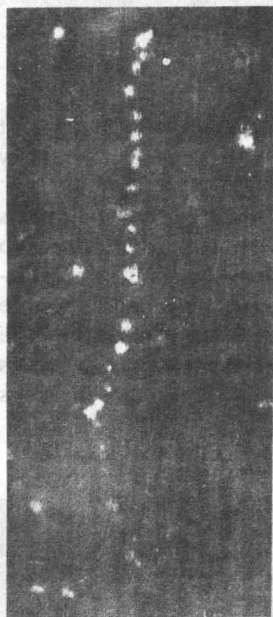
## Introduction

The bright dots lying in a line down the photograph in Fig. 1.1 are images of atoms. The idea that matter is built up from these fundamental building blocks is now almost second nature to us, but it is only recently that such direct evidence for their existence has become available. In the late eighteenth and early nineteenth centuries Dalton assembled indirect evidence in favour of the existence of atoms, Box 1.1. Now, in the late twentieth century, we can actually see them.

Dalton thought that atoms were indivisible (which is what *atomos* means in Greek). This view could not be held once electrons were discovered, for if electrons could be knocked out of atoms, atoms had to have an internal structure. Modern chemistry began when it was understood how atoms are built up, because understanding atoms is the key to understanding chemistry.

### Box 1.1: The origins of the atomic hypothesis

The concept of 'atom' was originated by the Greeks, especially Democritus and Leucippus, and Lucretius's poem 'On the nature of the world', which was written in about 56 B.C., uses images that bear a striking resemblance to our modern view. Nevertheless, while it is true that the Greeks put forward the idea that matter is composed of atoms, it was only a speculation. The scientific, as



1.1 Electron microscope images of atoms

distinct from the philosophical, evidence for the existence of atoms was accumulated about 200 years ago. There were three principal contributions. The *Law of conservation of mass* (expressed by Lavoisier in 1789 just before he fell to the guillotine in 1794) states that matter is neither created nor destroyed in a chemical reaction. The *Law of constant composition* (expressed by Proust in 1799; Proust was the son of an apothecary, and so was surrounded by chemistry throughout his childhood) states that all pure samples of the same compound contain the same elements combined in the same proportion by mass. The *Law of multiple proportions* (Dalton, 1803) states that when the elements A and B combine together to form more than one compound, the various masses of A that combine with a fixed mass of B are in a simple ratio. (Dalton, who worked in Manchester, came to chemistry through his interest in meteorology. He was kindly, socially uncouth, and learned – until he grew tired of reading what others had written.)

The first of these laws suggests that chemical reactions involve the reorganization of things, not their destruction or creation. The second suggests that, since mass characterizes the nature of a compound, the things that are reorganized have characteristic masses. The third suggests that the things are indivisible, so that a compound consists of 1, 2, 3, ... and not some intermediate, non-integral number of them. Dalton accounted for all these observations by proposing the existence of atoms, the indivisible fundamental units of elements.

### 1.1 The nuclear atom

The first sub-atomic particle to be discovered was the *electron*, Box 1.2. It is negatively charged, and its charge and mass have been measured by observing its deflection in electric and magnetic fields.

When a hydrogen atom loses its single electron a *proton* is left. This is the other fundamental sub-atomic particle of central importance to chemistry. The proton is positively charged (exactly balancing the electron's charge, so that the atom itself is electrically neutral), and its charge and mass can be measured in the same way as for the electron. The proton is about 1840 times heavier than the electron, and so protons (together with the neutrons we meet shortly) account for most of the mass of an atom.

#### Box 1.2: The discovery of the electron

The discovery of the electron depended on the technological advance of being able to produce high vacua. When that had been achieved in the middle of the 19th century it was not long before *cathode rays* were discovered by passing an electric discharge

through a low pressure gas. By 1895 it was known that the cathode rays were negatively charged, but their nature was unknown. The Germans argued that they were waves of some kind; the French and the British thought they were streams of particles. In 1897 J. J. Thomson scored a resounding victory for the latter view by showing that the rays were deflected by electric and magnetic fields, and that the deflection led to a value of charge/mass. Since it had been shown that the rays were absorbed by all materials (by Lenard), Thomson put forward the view that these negatively charged particles, or *electrons* as they became known (the name was coined in 1891 by Stoney), were universal constituents of matter. The charge of the electron was later measured (using Millikan's experiment and the photoelectric effect), and hence the mass itself could be determined. The victorious British-French view survived until 1927, when it was shown that electrons could be diffracted, and hence were waves after all! The crucial experiments were performed by Davisson and Germer and by G. P. Thomson, the son of J. J. Indeed, J. J. Thomson won the Nobel prize for proving that the electron is a particle and his son, G. P. Thomson, received it for proving that the electron is a wave. The resolution of the paradox was achieved with quantum mechanics, which shows how to regard objects, including electrons, as both particles and waves: this is the particle-wave *duality* of matter.

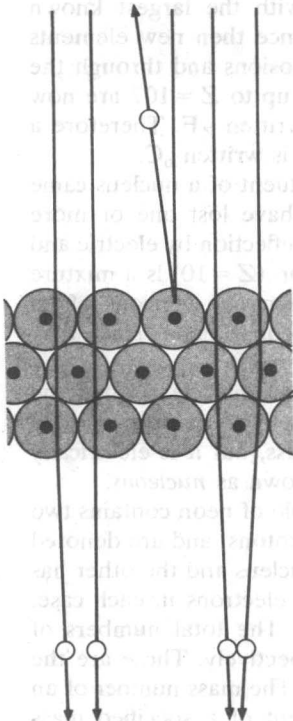
### The Geiger-Marsden experiment

In the early years of this century there was a lot of argument about the way protons and electrons were arranged in atoms. The model that originally attracted attention was the 'plum pudding', in which the electrons were pictured as lumps in a jelly-like background of positive charge. This was dismissed by the results of a classic experiment carried out by Geiger and Marsden (in 1909) working under the guidance of Rutherford.

The experiment involved shooting projectiles at atoms and measuring their deflection. As projectiles Geiger and Marsden used  $\alpha$ -particles (alpha-particles, the nuclei of helium atoms) generated by the radioactive decay of radon. As a target they used a very thin gold foil about 1000 atoms thick. The deflection of the particles by the atoms in the metal foil was detected by observing the bright flashes of light where they struck a fluorescent screen.

They found that most of the  $\alpha$ -particles were deflected through angles of less than  $1^\circ$ . Some - about 1 in 20 000 - were deflected through  $90^\circ$  or more, Fig. 1.2. These big deflections eliminated the plum pudding from science. Rutherford expressed his surprise at the result with the remark that "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you".

Rutherford went on to argue (in 1911) that (a) an atom is mostly empty space (to account for the undeflected passage of most particles) but



1.2 The Geiger-Marsden experiment



(b) most of the mass, and all the positive charge, is in a minute central *nucleus* (to account for the large deflections observed when the  $\alpha$ -particle scored an occasional direct hit). The *nuclear atom*, a positive nucleus surrounded by electrons, the former accounting for the atom's mass and the latter for its size, had entered science.

### Atomic numbers and atomic masses

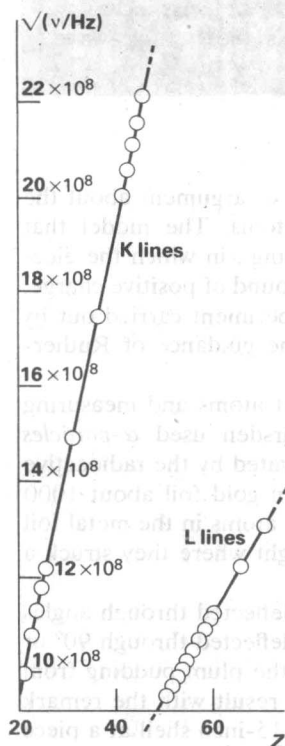
The *atomic number* ( $Z$ ) was originally a label indicating the place of the element in the periodic table. Now it is defined as *the number of protons in the nucleus* of an atom of the element (and so it is also sometimes called the *proton number*). The determination of the value of  $Z$  was made possible by Moseley's work on X-rays (in 1913, shortly before he fell in action at Gallipoli). It was known that when elements are bombarded with fast electrons they emit X-rays, and that there are two intense components, the *K and L lines*. Moseley measured their frequencies, and found that when the square root of the frequency is plotted against atomic number, a straight line is obtained, Fig. 1.3. This meant that  $Z$  could be found simply by measuring an element's characteristic X-ray frequency and reading off the appropriate value of  $Z$  from his graph.

Hydrogen has  $Z = 1$  and so it has one proton (and one electron around it). Carbon has  $Z = 6$ , and its nucleus contains six protons (with six electrons around it). Until 1940 the element with the largest known atomic number was uranium with  $Z = 92$ , but since then new elements have been made both as a result of nuclear explosions and through the use of particle accelerators, and all the elements up to  $Z = 107$  are now known. In general an atom of an element  $E$  is written  ${}_Z E$ . Therefore a hydrogen atom is written  ${}_1 H$  and a carbon atom is written  ${}_6 C$ .

Evidence that the proton is not the only constituent of a nucleus came when the masses of *ionized atoms* (atoms that have lost one or more electrons) were measured using the technique of deflection by electric and magnetic fields. In 1912 Thomson found that neon ( $Z = 10$ ) is a mixture of atoms of different masses. These various alternative versions of an element are called *isotopes* (after the Greek for 'equal place', since they all correspond to the same place in the periodic table).

The explanation of the existence of isotopes became clear when the *neutron* was discovered (by Chadwick in 1932). The neutron is very similar to the proton, having almost the same mass, but it is electrically neutral. Protons and neutrons are collectively known as *nucleons*.

Thomson's observations are explained if a sample of neon contains two types of atom. Both have  $Z = 10$  (and hence 10 protons) and are denoted  ${}_{10} Ne$ . One type of atom has 10 neutrons in the nucleus and the other has 12. Since there are 10 protons there are also 10 electrons in each case, and so the chemistry of the atoms is the same. The total numbers of nucleons in the two isotopes are 20 and 22, respectively. These are the *mass numbers* (or *nucleon numbers*) of the atoms. The mass number of an element is written  $A$ , and an atom of an element of a specified mass number is called a *nuclide* and denoted  ${}_Z^A E$ . The isotopes of neon are therefore the two nuclides  ${}_{10}^{20} Ne$  and  ${}_{10}^{22} Ne$ .



1.3 Some of Moseley's X-ray results