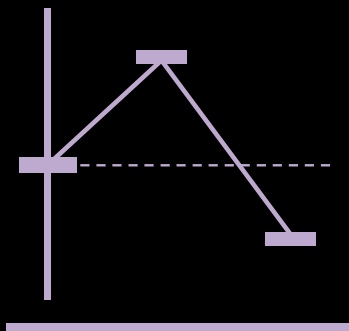
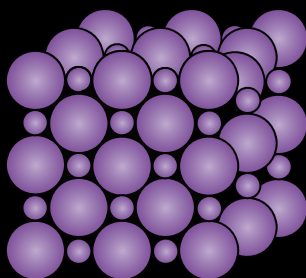
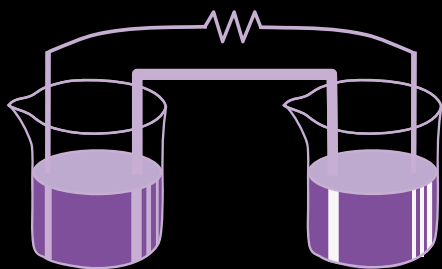


The Chemistry Companion

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This book is dedicated to Bill Cripps
— industrial chemist

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Preface

This book is similar to previous Companion style books where each topic is covered in a single page outline format with enough detail to provide a good understanding of the subject.

This book emphasises the physics underlying chemistry, especially in the first chapter. I hope that by understanding what is happening from a physics point of view, the reader may better appreciate what is happening from the chemical perspective that is usually found in a traditional chemistry book.

I am indebted to Dr. Ray Sleet of the University of Technology, Sydney, an exemplary teacher who taught me that anything can be learned if it is broken down into manageable pieces with attainable goals. Many of the presentations in this book have their origin in Dr. Sleet's excellent undergraduate lectures.

I also thank Hilary Rowe for her persistence in getting this book into print and the editorial and production team at Taylor & Francis for their very professional and helpful approach to the whole publication process.

Tony Fischer-Cripps,
Killarney Heights, Australia

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1. Structure of Matter

Summary

Energy levels Bohr H-like atom:

$$E_n = -\frac{m_e Z^2 q_e^4}{8\epsilon_o^2 \hbar^2 n^2}$$

Energy levels Schrödinger equation,
Coulomb potential:

$$E_n = -\frac{Z^2 q_e^4 m}{(4\pi\epsilon_o)^2 2\hbar^2 n^2}$$

Covalent bond: the co-sharing of valence electrons.

Ionic bond: the electrostatic attraction between ions formed after electrons are transferred from one atom to another.

Metallic bond: free electrons in the valence band reduce the energy of the system and so act to hold atoms together.

The electronegativity describes the relative ability of an atom, when it combines with another atom, to become “more negative” by more strongly capturing a shared electron or electron pair.

1.1 Atoms

Sixth century BC Thales of Miletos proposes that the basic element from which all things are made is water. 450 BC Empedocles teaches that all matter is composed of earth, air, water and fire. Around 400 BC, Greek philosophers (Leucippus, **Democritus**, Epicurus) proposed that if one could divide a piece of matter again and again, eventually a limit would be reached where no further subdivision could take place, this limiting amount of matter was called the **atom**. About 300 BC, **Aristotle** rejects the atomistic view and argues that matter is based upon the four basic elements of Empedocles but adds the qualities of coldness, hotness, dryness and moistness. Aristotle's considerable reputation ensured that his ideas became embodied in religious teaching for many hundreds of years.

In the fifteenth century, new advances in physics suggested that matter was made from particles, in agreement with the ancient Greek atomists. Robert **Boyle** taught that matter consists of different types of **elements** that were composed of atoms of the same type. Different elements could join together in fixed proportions to form **compounds**. Later, in 1803, John **Dalton** proposed the **atomic theory of matter** that was based on quantitative experimental evidence from the weighing of different elements in combination. He created a scale atomic mass for the different elements that were then known. Dalton's reference atom was the lightest element known, hydrogen, which was assigned an atomic mass of one. Other elements were given atomic masses according to how heavy they were compared to a hydrogen atom.

In 1807, Humphry Davy decomposed potash into sodium and potassium metals using electrolysis. In 1832, Michael **Faraday** discovered a quantitative connection between electricity and the separation of compounds into elements in electrolysis. These observations suggested that atoms themselves contain electric charge. Experiments by William Crookes demonstrated visible "cathode rays" that emanated from a negatively charged electrode (cathode) and travelled towards the positive electrode (anode) in an evacuated tube.

In 1872, **Mendeleev** arranged elements in increasing order of atomic mass and discovered that the properties of certain elements were repeated at regular intervals. When elements were ordered in columns with the atomic mass going across from left to right, and similar chemical properties going down, a **periodic table** was formed whereby, using the known elements at the time, Mendeleev was able to predict the properties of some as-yet undiscovered elements from gaps in the table.

1.2 Bohr Atom

In 1897, **Thomson** demonstrated that the rays observed to be emitted from the cathodes of vacuum tubes were in fact charged particles which he called **electrons**. Thomson proposed that atoms consisted of a positively charged sphere within which were embedded negatively charged electrons.

Rutherford found in 1911 that the electrons were actually located at some distance from a central positively charged **nucleus**. He proposed that electrons orbited the nucleus and the electrostatic attraction between the nucleus and the electron was balanced by the centrifugal force arising from the orbital motion. However, a major problem with this was that if this were the case, then the electrons would continuously radiate all their energy as **electromagnetic waves** and very quickly fall into the nucleus.

In 1913, **Bohr** postulated two important additions to Rutherford's theory of atomic structure:

1. Electrons of mass m_e can orbit the nucleus at radius r with velocity v in what are called **stationary states** in which no emission of radiation occurs and in which the **angular momentum** L is constrained to have values:

$$L = m_e v r = \frac{nh}{2\pi}$$

The 2π appears because L is expressed in terms of ω rather than f .

2. Electrons can make transitions from one state to another accompanied by the emission or absorption of a single **photon** of energy $E = hf$, this being the absorption and emission spectra observed experimentally.

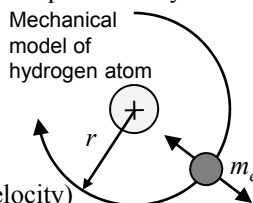
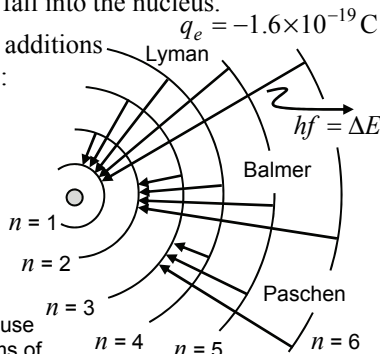
As in the Rutherford atom, the centrifugal force is balanced by Coulomb attraction:

$$\frac{1}{4\pi\epsilon_0} \frac{q_e^2}{r^2} = \frac{m_e v^2}{r} \quad \text{with the addition that: } m_e v r = \frac{nh}{2\pi}$$

By summing the **kinetic energy** (from the orbital velocity) and the **potential energy** from the electrostatic force, the **total energy** of an electron at a given energy level n is given by:

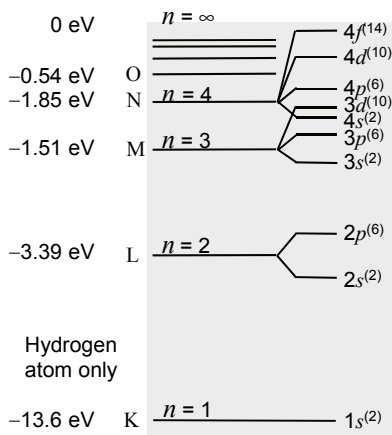
$$E_n = -\frac{m_e Z^2 q_e^4}{8\epsilon_0^2 h^2 n^2}$$

Note: **atomic number** $Z = 1$ for the hydrogen atom where the energy of the ground state is -13.6 eV. The energy levels for each state n rise as Z^2 . Thus, according to the Bohr model, the energy level of the innermost shell for multi-electron atoms can in principle be several thousand eV.



1.3 Energy Levels

The stationary states or energy levels allowed by the Bohr model are called **electron shells** or orbitals, and are labelled K, L, M, N, etc. with K corresponding to $n = 1$. The number n is called the **principal quantum number**. According to the Bohr model, the electron energy only depends on n , but experiments show that in multi-electron atoms, electron shells consist of sub-levels (evidenced by fine splitting of spectral lines). For example, the L shell $n=2$ has two **sub-shells**, $2s$ and $2p$.



It is convenient to assign the energy at infinity as being 0 since as an electron moves closer to the nucleus, which is positively charged, its potential to do work is less and thus the energy levels for each shell shown are negative. In hydrogen, a single-electron atom, the energies for each shell are given by:

$$E = -\frac{13.6}{n^2} \quad \text{for hydrogen}$$

The electron-volt is a unit of energy.
 $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

Sometimes the splitting of principal shells into sub-shells results in some overlap (e.g. $4s$ is lower in energy than $3d$).

At each value of n the **angular momentum** can take on several distinct values. The number of values is described by the second quantum number l . The allowed values of l are 0, 1, ... ($n-1$). Each value of l is indicated by a letter that indicates the sub-shell:

A third quantum number m describes the allowable changes in angle of the **angular momentum** vector in the presence of an electric field. It takes the values $-l$ to 0 to $+l$.

A fourth quantum number describes the **spin** of an electron where the spin can be either $-1/2$ or $+1/2$.

According to the **Pauli exclusion principle**, no electron in any one atom can have the same combination of quantum numbers. When all the electrons in an atom are in the lowest possible energy levels, the atom is said to be in its **ground state**. The outermost electrons in an atom are called the **valence electrons**.

$l = 0$	s
$l = 1$	p
$l = 2$	d
$l = 3$	f
$l = 4$	g
$l = 5$	h

For example, the $3d$ sub-shell can hold up to 10 electrons:

$$n = 3$$

thus: $l = 0, 1, 2$ (s, p, d)

and: $m = -2, -1, 0, 1, 2$

5 values of m times 2 for spin,
 thus 10 possible electrons

1.4 Schrödinger Equation

The total energy E of an electron in an atom is the sum of the potential and kinetic energies. Expressed in terms of **momentum**, p , and mass of electron m , this is stated:

$$E = \frac{p^2}{2m} + V$$

Thus: $hf = \frac{p^2}{2m} + V(x, t)$

since $E = hf$

Let $p = -i\hbar \frac{\partial \Psi}{\partial x}$ $\left. \begin{array}{l} \Psi \text{ is a variable, the form} \\ \text{and value of which provide} \\ \text{information about the} \\ \text{motion of a wave/particle.} \end{array} \right\}$

$E = i\hbar \frac{\partial \Psi}{\partial t}$

Thus:

$$\boxed{-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x, t)\Psi = i\hbar \frac{\partial \Psi}{\partial t}} \quad \text{Schrödinger equation}$$

The solution to the Schrödinger wave equation is the **wave function** Ψ . If V is a function of x only, then the wave equation can be separated into time-independent and time-dependent equations that can be readily solved.

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(\psi) = E\psi \quad \phi(t) = e^{i\frac{E}{\hbar}t}$$

The resulting solutions of these equations, when multiplied together, give the **wave function**: $\Psi(x, t) = \psi(x)\phi(t)$

The wave function gives all the information about the motion of an electron in an atom. Ψ is a complex quantity, the magnitude of which $|\Psi|$ is interpreted as a **probability density function** which in turn can be used to determine the probability of an electron being at some position between x and Δx .

Quantum mechanics is concerned with determining the wave function (i.e. solving the Schrödinger equation) for particular potential energy functions such as those inside atoms. It is found that valid solutions to the time-independent wave equation occur only when the total energy is quantised. The solutions correspond to **stationary states**.

Solutions to the Schrödinger equation can be found for potential functions which are a function of both x and t . This enables time-dependent phenomena (e.g. the probability of transitions of electrons between energy levels in an atom) to be calculated and hence the intensity of spectral lines.