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Early Atomic Theory

It is an old idea that matter consists of atoms, tiny indivisible particles moving in empty space. This theory can be traced to Democritus, working in the Greek city of Abdera, on the north shore of the Aegean sea. In the late 400s BC Democritus proclaimed that “atoms and void alone exist in reality.” He offered neither evidence for this hypothesis nor calculations on which to base predictions that could confirm it. Nevertheless, this idea was tremendously influential, if only as an example of how it might be possible to account for natural phenomena without invoking the gods. Atoms were brought into the materialistic philosophy of Epicurus of Samos, who a little after 300 BC founded one of the four great schools of Athens, the Garden. In turn, the idea of atoms and the philosophy of Epicurus were invoked in the poem *On the Nature of Things* by the Roman Lucretius. After this poem was rediscovered in 1417 it influenced Machiavelli, More, Shakespeare, Montaigne, and Newton, among others. Newton in his *Opticks* speculated that the properties of matter arise from the clustering of atoms into larger particles, which themselves cluster into larger particles, and so on. As we will see, Newton made a stab at an atomic theory of air pressure, but without significant success.

The serious scientific application of the atomic theory began in the eighteenth century, with calculations of the properties of gases, which had been studied experimentally since the century before. This is the topic with which we begin this chapter. Applications to chemistry and electrolysis followed in the nineteenth century and will be considered in subsequent sections. The final section of this chapter describes how the nature of atoms began to be clarified with the discovery of the electron. In the following chapter we will see how it became possible to estimate the atoms’ masses and sizes.¹

¹ Further historical details about some of these matters can be found in Weinberg, *The Discovery of Subatomic Particles*, listed in the bibliography.

1.1 Gas Properties

Experimental Relations

The upsurge of enthusiasm for experiment in the seventeenth century was largely concentrated on the properties of air. The execution and reports of these experiments did not depend on hypotheses regarding atoms, but we need to recall them here because their results provided the background for later theories of gas properties that did rely on assumptions about atoms.

It had been thought by Aristotle and his followers that the suction observed in pumps and bellows arises from nature's abhorrence of a vacuum. This notion was challenged in the 1640s by the invention of the barometer by the Florentine polymath Evangelista Torricelli (1608–1647). If nature abhors a vacuum, then when a long glass tube with one end closed is filled with mercury and set upright with the closed end on top, why does the mercury flow out of the bottom until the column is only 760 mm high, with empty space appearing above the mercury? Is there a limit to how much nature abhors a vacuum? Torricelli argued that the mercury is held up instead by the pressure of the air acting on the open end of the glass tube (or on the surface of a bath of mercury in which the open end of the tube is immersed), which is just sufficient to support a column of mercury 760 mm high. If so, then it should be possible to measure variations in air pressure using a column of mercury in a vertical glass tube, a device that we know as a barometer. Such measurements were made from 1648 to 1651 by Blaise Pascal (1623–1662), who found that the height of mercury in a barometer is decreased by moving to the top of a mountain, where less air extends above the barometer.

The quantitative properties of air pressure soon began to be studied experimentally, before there was any correct theoretical understanding of gas properties. In 1662, in the second edition of his book *New Experiments Physico-Mechanical Concerning the Spring of the Air and its Effects*, the Anglo-Irish aristocrat Robert Boyle (1627–1691) described experiments relating the pressure (the “spring of the air”) and volume of a fixed mass of air. He studied a sample of air enclosed at the end of a glass tube by a column of mercury in the tube. The air was compressed at constant temperature by pushing on the mercury's surface, revealing what came to be known as *Boyle's law*, that for constant temperature the volume of a gas of fixed mass and composition is inversely proportional to the pressure, now defined by Boyle as the force per area exerted on the gas.

Temperature Scales

A word must be said about the phrase “at constant temperature.” Boyle lived before the establishment of our modern Fahrenheit and Celsius scales, whose

forerunners go back respectively to 1724 and 1742. But, although in Boyle's time no meaningful numerical value could be given to the temperature of any given body, it was nevertheless possible to speak with precision of two bodies being at the *same* temperature: they are at the same temperature if when put in contact neither body is felt to grow appreciably hotter or colder. Boyle's glass tube could be kept at constant temperature by immersing it in a large bath, say of water from melting ice. Later the Fahrenheit temperature scale was established by defining the temperature of melting ice as 32 °F and the temperature of boiling water at mean atmospheric pressure as 212 °F, and defining a 1 °F increase of temperature by etching 212 – 32 equal divisions between 32 and 212 on the glass tube of a mercury thermometer. Likewise, in the Celsius scale, the temperatures of melting ice and boiling water are 0 °C and 100 °C, and 1 °C is the temperature difference required to increase the volume of mercury in a thermometer by 1% of the volume change in heating from melting ice to boiling water. As we will see in the next chapter, there is a more sophisticated universal definition of temperature, to which scales based on mercury thermometers provide only a good approximation.

After the temperature scale was established it became possible to carry out a quantitative study of the relation between volume and temperature, with pressure and mass kept fixed by enclosing the air in a vessel with flexible walls, which expand or contract to keep the pressure inside equal to the air pressure outside. This relation was announced in an 1802 lecture by Joseph Louis Gay-Lussac (1775–1850), who attributed it to unpublished work in the 1780s by Jacques Charles (1746–1823). The relation, subsequently known as *Charles' Law*, is that at constant pressure and mass the volume of gas is proportional to $\mathcal{T} - \mathcal{T}_0$, where \mathcal{T} is the temperature measured for instance with a mercury thermometer and \mathcal{T}_0 is a constant whose numerical value naturally depends on the units used for temperature: $\mathcal{T}_0 = -459.67\text{ °F} = -273.15\text{ °C}$. Thus \mathcal{T}_0 is absolute zero, the minimum possible temperature, at which the gas volume vanishes. Using Celsius units for temperature differences, the absolute temperature $T \equiv \mathcal{T} - \mathcal{T}_0$ is known today as the temperature in degrees Kelvin, denoted K.

Theoretical Explanations

In Proposition 23 of his great book, the *Principia*, Isaac Newton (1643–1727) made an attempt to account for Boyle's law by considering air to consist of particles repelling each other at a distance. Using little more than dimensional analysis, he showed that the pressure p of a fixed mass of air is inversely proportional to the volume V if the repulsive force between particles separated by a distance r falls off as $1/r$. But as he pointed out, if the repulsive force goes as $1/r^2$, then $p \propto V^{-4/3}$. He did not claim to offer any reason why the repulsive force should go as $1/r$ and, as we shall see, it is not forces that go as $1/r$ but

rather forces of very short range that act only in collisions that mostly account for the properties of gases.

It was the Swiss mathematical physicist Daniel Bernoulli (1700–1782) who made the first attempt to understand the properties of gases theoretically, on the assumption that a gas consists of many tiny particles moving freely except in very brief collisions. In 1738, in the chapter, “On the Properties and Motions of Elastic Fluids, Especially Air” of his book *Hydrodynamics*, he argued that in a gas (then called an “elastic fluid”) with n particles per unit volume moving with a velocity v that is the same (because of collisions) in all directions, the pressure is proportional to n and to v^2 , because the number of particles that hit any given area of the wall in a given time is proportional to the number in any given volume, to the rate at which they hit the wall, which is proportional to v , and to the force that each particle exerts on the wall, which is also proportional to v . For a fixed mass of gas n is inversely proportional to the volume V , so pV is proportional to v^2 . If (as Bernoulli thought) v^2 depends only on the temperature, this explains Boyle’s law. If v^2 is proportional to the absolute temperature, it also gives Charles’ law.

Bernoulli did not give much in the way of mathematical details, and did not try to say to what else the pressure might be proportional besides nv^2 , a matter crucial for the history of chemistry. These details were provided by Rudolf Clausius (1822–1888) in 1857, in an article entitled “The Nature of the Motion which We Call Heat.” Below is a more-or-less faithful description of Clausius’ derivation, in a somewhat different notation.

Suppose a particle hits the wall of a vessel and remains in contact with it for a small time t , during which it exerts a force with component F along the inward normal to the wall. Its momentum in the direction of the inward normal to the wall will decrease by an amount Ft , so if the component of the velocity of the particle before it strikes the wall is $v_{\perp} > 0$, and it bounces back elastically with normal velocity component $-v_{\perp}$, the change in the inward normal component of momentum is $-2mv_{\perp}$, where m is the particle mass, so

$$F = 2mv_{\perp}/t .$$

Now, suppose that this goes on with many particles hitting the wall over a time interval $T \gg t$, all particles with the same velocity vector \mathbf{v} . The number \mathcal{N} of particles that will hit an area A of the wall in this time is the number of particles in a cylinder with base A and height $v_{\perp}T$, or

$$\mathcal{N} = nAv_{\perp}T ,$$

where n is the number density, the number of particles per volume. Each of these particles is in contact with the wall for a fraction t/T of the time T , so the total force exerted on the wall is

$$F\mathcal{N}(t/T) = 2mv_{\perp}/t \times nAv_{\perp}T \times (t/T) = 2nmv_{\perp}^2 A .$$

We see that all dependence on the times t and T cancels. The pressure p is defined as the force per area, so this gives the relation

$$p = 2nmv_{\perp}^2 . \quad (1.1.1)$$

This is for the unphysical case in which every particle has the same value of v_{\perp} , positive in the sense that the particles are assumed to be going toward the wall. In the real world, different particles will be moving with different speeds in different directions, and Eq. (1.1.1) should be replaced with

$$p = 2nm \times \frac{1}{2} \langle v_{\perp}^2 \rangle = nm \langle v_{\perp}^2 \rangle , \quad (1.1.2)$$

the brackets indicating an average over all gas particles, with the factor $1/2$ inserted in the first expression because only 50% of these particles will be going toward any given wall area.

To express $\langle v_{\perp}^2 \rangle$ in terms of the root mean square velocity, Clausius assumed without proof that “on the average each direction [of the particle velocities] is equally represented.” In this case, the average square of each component of velocity equals $\langle v_{\perp}^2 \rangle$, and the average of the squared velocity vector is then

$$\langle \mathbf{v}^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle + \langle v_3^2 \rangle = 3 \langle v_{\perp}^2 \rangle$$

and therefore Eq. (1.1.2) reads

$$p = nm \langle \mathbf{v}^2 \rangle / 3 . \quad (1.1.3)$$

This is essentially the result $p \propto n \langle \mathbf{v}^2 \rangle$ of Bernoulli, except that, with the factor $m/3$, Eq. (1.1.3) is now an equality, not just a statement of proportionality. For a fixed mass M of gas occupying a volume V , the number density is $n = M/mV$, so Clausius could use Boyle’s law (which he called Mariotte’s law), which states that pV is constant for fixed temperature, to conclude that for a given gas $\langle \mathbf{v}^2 \rangle$ depends only on the temperature. Further, as Clausius remarked, Eq. (1.1.3) together with Charles’ law (which Clausius called the law of Gay-Lussac) indicates that $\langle \mathbf{v}^2 \rangle$ is proportional to the absolute temperature T . If we like, we can adopt a modern notation and write the constant of proportionality as $3k/m$, so that

$$m \langle \mathbf{v}^2 \rangle / 3 = kT , \quad (1.1.4)$$

and therefore Eq. (1.1.3) reads

$$p = nkT , \quad (1.1.5)$$

where k is a constant, in the sense of being independent of p , n , and T . But the choice of notation does not tell us whether k varies from one type of gas to another or whether it depends on the molecular mass m . Clausius could not answer this question, and did not offer any theoretical justification for Boyle’s

law or Charles' law. Clausius deserves to be called the founder of thermodynamics, discussed in Sections 2.2 and 2.3, but these are not questions that can be answered by thermodynamics alone. As we will see in the following section, experiments in the chemistry of gases indicated that k is the same for all gases, a universal constant now known as Boltzmann's constant, but the theoretical explanation for this and for Boyle's law and Charles' law had to wait for the development of kinetic theory and statistical mechanics, the subject of Section 2.4.

As indicated by the title of his article, "The Nature of the Motion which We Call Heat," Clausius was concerned to show that, at least in gases, the phenomenon of heat is explained by the motion of the particles of which gases are composed. He defended this view by using his theory to calculate the specific heat of gases, a topic to be considered in the next chapter.

1.2 Chemistry

Elements

The idea that all matter is composed of a limited number of elements goes back to the earliest speculations about the nature of matter. At first, in the century before Socrates, it was supposed that there is just one element: water (Thales) or air (Anaximenes) or fire (Heraclitus) or earth (perhaps Xenophanes). The idea of four elements was proposed around 450 BC by Empedocles of Acragas (modern Agrigento). In *On Nature* he identified the elements as "fire and water and earth and the endless height of air." Classical Chinese sources list five elements: water, fire, earth, wood, and metal.

Like the theory of atoms, these early proposals of elements did not come accompanied with any evidence that these really are elements, or any suggestion how such evidence might be gained. Plato in *Timaeus* even doubled down and stated that the difference between one element and another arises from the shapes of the atoms of which the elements are composed: earth atoms are tiny cubes, while the atoms of fire, air, and water are other regular polyhedra – solids bounded respectively by 4, 8, or 20 identical regular polygons, with every edge and every vertex of each solid the same as every other edge or vertex of that solid.

By the end of the middle ages this list of elements had come to seem implausible. It is difficult to identify any particular sample of dirt as the element earth, and fire seems more like a process than a substance. Alchemists narrowed the list of elements to just three: mercury, sulfur, and salt.

Modern chemistry began around the end of the eighteenth century, with careful experiments by Joseph Priestley (1733–1804), Henry Cavendish (1743–1810), Antoine Lavoisier (1743–1794), and others. By 1787 Lavoisier had

worked out a list of 55 elements. In place of air there were several gases: hydrogen, oxygen, and nitrogen; air was identified as a mixture of nitrogen and oxygen. There were other non-metals on the list of elements: sulfur, carbon, and phosphorus, and a number of common metals: iron, copper, tin, lead, silver, gold, mercury. Lavoisier also listed as elements some chemicals that we now know are tightly bound compounds: lime, soda, and potash. And the list also included heat and light, which of course are not substances at all.

Law of Combining Weights

Chemistry was first used to provide quantitative information about atoms by John Dalton (1766–1844), the son of a poor weaver. His laboratory notebooks from 1802 to 1804 describe careful measurements of the weights of elements combining in compounds. He discovered that these weights are always in fixed ratios. For instance, he found that when hydrogen burns in oxygen, 1 gram of hydrogen combines with 5.5 grams of oxygen, giving 6.5 grams of water, with nothing left over. Under the assumption that one particle of water consists of one atom of hydrogen and one atom of oxygen, one oxygen atom must weigh 5.5 times as much as one hydrogen atom.

As we will see, water was soon discovered to be H_2O : two atoms of hydrogen to each atom of oxygen. If Dalton had known this, he would have concluded that an oxygen atom weighs 5.5 times as much as *two* hydrogen atoms, i.e., 11 times the weight of one hydrogen atom. Of course, more accurate measurements later revealed that 1 gram of hydrogen combines with about 8 grams of oxygen, so one oxygen atom weighs eight times the weight of two hydrogen atoms, or 16 times as much as one hydrogen atom. Atomic weights soon became defined as the weights of atoms relative to the weight of one hydrogen atom, so the atomic weight of oxygen is 16. (This is only approximate. Today the atomic weight of the atoms of the most common isotope of carbon is defined to be precisely 12; with this definition, the atomic weights of the most common isotopes of hydrogen and oxygen are measured to be 1.007825 and 15.99491.)

The following table compares Dalton's assumed formulas for a few common compounds with the correct formulas:

<i>Compound</i>	<i>Dalton formula</i>	<i>True formula</i>
Water	HO	H_2O
Carbon dioxide	CO_2	CO_2
Ammonia	NH	NH_3
Sulfuric acid	SO_2	H_2SO_4

Here is a list of the approximate true atomic weights for a few elements, the weights deduced by Dalton, and (in the column marked with an asterisk) the weights Dalton would have calculated if he had known the true chemical formulas.

<i>Element</i>	<i>True</i>	<i>Dalton</i>	<i>Dalton*</i>
H	1	1	1
C	12	4.3	8.6
N	14	4.2	12.6
O	16	5.5	11
S	32	14.4	57.6

To make progress in measuring atomic weights, it was evidently necessary to find some way of working out the correct formulas for various chemical compounds. This was provided by the study of chemical reactions in gases.

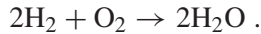
Law of Combining Volumes

On December 31, 1808, Gay-Lussac read a paper to the Societe Philomathique in Paris, in which he announced his observation that gases at the same temperature and pressure always combine in definite proportions of *volumes*. For instance, two liters of hydrogen combine with one liter of oxygen to give water vapor, with no hydrogen or oxygen left over. Likewise, one liter of nitrogen combines with three liters of hydrogen to give ammonia gas, with nothing left over. And so on.

The correct interpretation of this experimental result was given in 1811 by Count Amadeo Avogadro (1776–1856) in Turin. Avogadro's principle states that equal volumes of gases at the same temperature and pressure always contain equal numbers of the gas particles, which Avogadro called "molecules," particles that may consist of single atoms or of several atoms of the same or different elements joined together. The observation that water vapor is formed from a volume of oxygen combined with a volume of hydrogen twice as large shows, according to Avogadro's principle, that molecules of water are formed from twice as many molecules of hydrogen as molecules of oxygen, which is not what Dalton had assumed.

There was a further surprise in the data. Two liters of hydrogen combined with one liter of oxygen give not one but *two* liters of water vapor. This is not what one would expect if oxygen and hydrogen molecules consist of single atoms and water molecules consist of two atoms of hydrogen and one atom of oxygen. In that case two liters of hydrogen plus one liter of oxygen would produce *one* liter of water vapor. Avogadro could conclude that if, as seemed

plausible, molecules of water contain two atoms of hydrogen and one atom of oxygen, the molecules of oxygen and hydrogen must each contain two atoms. That is, taking water molecules as H_2O , the reaction for producing molecules of water is



The use of Avogadro's principle rapidly provided the correct formulas for gases such as CO_2 , NH_3 , NO , and so on. Knowing these formulas and measuring the *weights* of gases participating in various reactions, it was possible to correct Dalton's atomic weights and calculate more reliable values for the atomic weights of the atoms in gas molecules, relative to any one of them. Taking the atomic weight of hydrogen as unity, this gave atomic weights close to 12 for carbon, 14 for nitrogen, 16 for oxygen, 32 for sulfur, and so on. Then, knowing these atomic weights, it became possible to find atomic weights for many other elements, not just those commonly found in gases, by measuring the weights of elements combining in various chemical reactions.

The Gas Constant

As we saw in the previous section, in 1857 Clausius had shown that in a gas consisting of n particles of mass m per volume with mean square velocity $\langle \mathbf{v}^2 \rangle$, the pressure is $p = nm\langle \mathbf{v}^2 \rangle/3$. Using Charles' law, he concluded that $\langle \mathbf{v}^2 \rangle$ is proportional to absolute temperature. Writing this relation as $m\langle \mathbf{v}^2 \rangle/3 = kT$ with k some constant gives Eq. (1.1.5), $p = nkT$. But this in itself does not tell us how k varies from one gas to another. This is answered by Avogadro's principle. With N particles in a volume V , the number density is $n = N/V$, so Eq. (1.1.5) can be written

$$pV = NkT . \tag{1.2.1}$$

If as stated by Avogadro the number of molecules in a gas with a given pressure, volume, and temperature is the same for any gas, then $k = pV/NT$ must be the same for any gas. Clausius did not draw this conclusion, perhaps because there was then no known theoretical basis for Avogadro's principle. The universality of the constant k , and hence Avogadro's principle, were explained later by kinetic theory, to be covered in the next chapter. The constant k came to be called *Boltzmann's constant*, after Ludwig Boltzmann, who as we shall see was one of the chief founders of kinetic theory.

The *molecular weight* μ of any compound is defined as the sum of the atomic weights of the atoms in a single molecule. The actual mass m of a molecule is its molecular weight times the mass m_1 of a hypothetical atom with atomic weight unity:

$$m = \mu m_1 . \tag{1.2.2}$$

In the modern system of atomic weights, with the atomic weight of the most common isotope of carbon defined as precisely 12, $m_1 = 1.660539 \times 10^{-24}$ g, which of course was not known in Avogadro's time. A mass M contains $N = M/m = M/m_1\mu$ molecules, so the ideal gas law (1.2.1) can be written

$$pV = MkT/m_1\mu = (M/\mu)RT \quad (1.2.3)$$

where R is the gas constant

$$R = k/m_1 . \quad (1.2.4)$$

Physicists in the early nineteenth century could use Eq. (1.2.3) to measure R , and they found a value close to the modern value $R = 8.314$ J/K. This would have allowed a determination of m_1 and hence of the masses of all atoms of known atomic weight if k were known, but k did not become known until the developments described in Section 2.6.

Avogadro's Number

Incidentally, a mole of any element or compound of molecular weight μ is defined as μ grams, so in Eq. (1.2.3) the ratio M/μ expressed in grams equals the number of moles of gas. Since $N = M/m_1\mu$, one mole contains a number of molecules equal to $1/m_1$ with m_1 given in grams. This is known as *Avogadro's number*. But of course Avogadro did not know Avogadro's number. It is now known to be 6.02214×10^{23} molecules per mole, corresponding to unit molecular weight $m_1 = 1.66054 \times 10^{-24}$ grams. The measurement of Avogadro's number was widely recognized in the late nineteenth century as one of the great challenges facing physics.

1.3 Electrolysis

Early Electricity

Electricity was known in the ancient world, as what we now call static electricity. Amber rubbed with fur was seen to attract or repel small bits of light material. Plato in *Timaeus* mentions "marvels concerning the attraction of amber." (This is where the word electricity comes from; the Greek word for amber is "elektron.")

Electricity began to be studied scientifically in the eighteenth century. Two kinds of electricity were distinguished: resinous electricity is left on an amber rod when rubbed with fur, while vitreous electricity is left on a glass rod when rubbed with silk. Unlike charges were found to attract each other, while like charges repel each other. Benjamin Franklin (1706–1790) gave our modern terms positive and negative to vitreous and resinous electricity, respectively.

In 1785 Charles-Augustin de Coulomb (1736–1806) reported that the force F between two bodies carrying charges q_1 and q_2 separated by a distance r is

$$F = \frac{k_e q_1 q_2}{r^2} \quad (1.3.1)$$

where k_e is a universal constant. For like and unlike charges the product $q_1 q_2$ is positive or negative, respectively, indicating a repulsive or attractive force. Coulomb had no way of actually measuring these charges, but he could reduce the charge on a body by a factor 2 by touching it to an uncharged body of the same material and size, and observe that this reduces the force between it and any other charged body by the same factor 2. The introduction of our modern units of electric charge had to wait until the quantitative study of magnetism.

Early Magnetism

Magnetism too was known in the ancient world, as what we now call permanent magnetism. The Greeks knew of naturally occurring lodestones that could attract or repel small bits of iron. Plato's *Timaeus* refers to lodestones as "Heracleian stones." (Our word magnet comes from the city Magnesia in Asia Minor, near where lodestones were commonly found.)

Very early the Chinese also discovered the lodestone and used it as a magnetic compass (a "south-seeking stone") for purposes of geomancy and navigation. Each lodestone has a south-seeking pole at one end, attracted to a point near the South Pole of the Earth, and a north-seeking pole at the other end, attracted to a point near the Earth's North Pole. Magnetism was first studied scientifically by William Gilbert (1544–1603), court physician to Elizabeth I. It was observed that the south-seeking poles of different lodestones repel each other, and likewise for the north-seeking poles, while the south-seeking pole of one lodestone attracts the north-seeking pole of another lodestone. Gilbert concluded that one pole of a lodestone is pulled toward the north and the other toward the south because the Earth itself is a magnet, with what in a lodestone would be its south-seeking and north-seeking poles respectively near the Earth's North Pole and South Pole.

Electromagnetism

It began to be possible to explore the relations between electricity and magnetism quantitatively with the invention in 1809 of electric batteries by Count Alessandro Volta (1745–1827). These were stacks of disks of two different metals separated by cardboard disks soaked in salt water. Such batteries drive steady currents of electricity through wires attached to the ends of the stacks, with positive and negative terminals identified respectively as the ends of the stacks from which and towards which electric current flows.

In July 1820 Hans Christian Oersted (1777–1851) in Copenhagen noticed that turning on an electric current deflected a nearby compass needle, and concluded that electric currents exert force on magnets. Conversely, he found also that magnets exert force on wires carrying electric currents.

These discoveries were carried further in Paris a few months later by Andrè-Marie Ampère (1775–1836), who found that wires carrying electric current exert force on each other. For two parallel wires of length L carrying electric currents (charge per second) I_1 and I_2 , and separated by a distance $r \ll L$, the force is

$$F = \frac{k_m I_1 I_2 L}{r}, \quad (1.3.2)$$

where k_m is another universal constant. The force is repulsive if the currents are in the same direction; attractive if in opposite directions. One ampere is defined so that $F = 10^{-7} \times L/r$ newtons if $I_1 = I_2 = 1$ ampere. (That is, $k_m \equiv 10^{-7}$ N/ampere².) The electromagnetic unit of electric charge, the coulomb, is defined as the electric charge carried in one second by a current of one ampere. A modern ammeter measures electric currents by observing the magnetic force produced by current flowing through a wire loop.

The connection between electricity and magnetism was strengthened in 1831 by Michael Faraday (1791–1867), at the Royal Institution in London. He discovered that changing magnetic fields generate electric forces that can drive currents in conducting wires. This is the principle underlying the generation of electric currents today. Electricity began soon after to have important practical applications, with the invention in 1831 of the electric telegraph by the American painter Samuel F. B. Morse (1791–1872).

Finally, in the 1870s, the great Scottish physicist James Clerk Maxwell (1831–1879) showed that the consistency of the equation for the generation of magnetic fields by electric currents required that magnetic fields are also generated by changing electric fields. In particular, while oscillating magnetic fields produce oscillating electric fields, also oscillating electric fields produce oscillating magnetic fields, so a self-sustaining oscillation in both electric and magnetic fields can propagate in apparently empty space. Maxwell calculated the speed of its propagation and found it to equal $\sqrt{2k_e/k_m}$,² numerically about equal to the measured speed of light, suggesting strongly that light is such a self-sustaining oscillation in electric and magnetic fields. We will see more of Maxwell's equations in subsequent chapters, especially in Chapters 4 and 5.

² This quantity is independent of the units used for electric charge as long as the currents appearing in Eq. (1.3.2) are defined as the rates of flow of charge in the same units as used in Eq. (1.3.1). It is obviously also independent of the units used for force, as long as the same force units are used in Eqs. (1.3.1) and (1.3.2).

Discovery of Electrolysis

Electrolysis was discovered in 1800 by the chemist William Nicholson (1753–1815) and the surgeon Anthony Carlisle (1768–1840). They found that bubbles of hydrogen and oxygen would be produced where wires attached respectively to the negative and positive terminals of a Volta-style battery were inserted in water. Sir Humphrey Davy (1778–1829), Faraday's boss at the Royal Institution, carried out extensive experiments on the electrolysis of molten salts, finding for instance that, in the electrolysis of molten table salt, sodium, a previously unknown metal, was produced at the wire attached to the negative terminal of the battery and a greenish gas, chlorine, was produced at the wire attached to the other, positive, terminal. Davy's electrolysis experiments added several metals aside from sodium to Lavoisier's list of elements, including aluminum, potassium, calcium, and magnesium.

A theory of electrolysis was worked out by Faraday. In modern terms, a small fraction (1.8×10^{-9} at room temperature) of water molecules are normally dissociated into positive hydrogen ions (H^+), which are attracted to the wire attached to the negative terminal of a battery, and negative hydroxyl ions (OH^-), which are attracted to the wire attached to the positive terminal. At the wire attached to the negative terminal, two H^+ ions combine with two units of negative charge from the battery to form a neutral H_2 molecule. At the wire attached to the positive terminal, four OH^- ions give one O_2 molecule plus two H_2O molecules plus four units of negative charge, which flow through the battery to the negative terminal.³

Likewise, a small fraction of molten table salt (NaCl) molecules are normally dissociated into Na^+ ions and Cl^- ions. At the wire attached to the negative terminal of a battery, one Na^+ ion plus one unit of negative charge gives one atom of metallic sodium (Na); at the wire attached to the positive terminal, two Cl^- ions give one chlorine (Cl_2) molecule and two units of negative charge, which flow through the battery to the negative terminal.

In Faraday's theory, it takes one unit of electric charge to convert a singly charged ion such as H^+ or Cl^- to a neutral atom or molecule, so since molecules of molecular weight μ have mass μm_1 , it takes $M/m_1\mu$ units of electric charge to convert a mass M of singly charged ions to a mass M of neutral atoms or molecules of molecular weight μ . Experiment showed that it takes about 96 500 coulombs (e.g., one ampere for about 96 500 seconds) to convert μ grams (that is, one mole) of singly charged ions to neutral atoms or molecules. (This is called a faraday; the modern value is 96 486.3 coulombs/mole.) Hence

³ We now know that it is negative charge, i.e., electrons, that flows through a battery. As far as Faraday knew, it was equally possible that positive charges flow through a battery, in which case at the wire attached to the negative terminal two H^+ ions would give an H_2 molecule plus two units of positive charge, which would flow through the battery to the wire attached to the positive terminal, where four OH^- ions plus four units of positive charge would give an O_2 molecule and two H_2O molecules.

Faraday knew that $e/m_1 \simeq 96\,500$ coulombs/gram, where e is the unit of electric charge, which was called an “electrine” in 1874 by the Irish physicist George Johnstone Stoney (1826–1911). Having measured the faraday, if physicists knew the value of e then they would know m_1 , but they didn’t have this information until later. Also, no one then knew that e is the charge of an actual particle.

1.4 The Electron

As sometimes happens, in 1858 a new path in fundamental physics was opened with the invention of a practical device, in this case an improved air pump. In his pump the Bonn craftsman Heinrich Johann Geissler (1814–1879) used a column of mercury as a piston, in this way greatly reducing the leakage of air through the piston that had troubled all previous air pumps. With his pump Geissler was able to reduce the pressure in a closed glass tube to about a ten-thousandth of the typical air pressure on the Earth’s surface.

With such a near vacuum in a glass tube, electric currents could travel without wires through the tube. It was discovered that an electric current would flow from a cathode, a metal plate attached to the negative terminal of a powerful electric battery, fly through a hole in an anode, another metal plate attached to the positive pole of the battery, and light up a spot on the far wall of the tube. Adding small amounts of various gases to the interior of the tube caused these cathode rays to light up, with orange or pink or blue-green light emitted along the path of the ray, when neon, helium, or mercury vapor was added. Using Geissler’s pumps, Julius Plücker (1801–1868) in 1858–1859 found that cathode rays could be deflected by magnetic fields, thus moving the spot of light where the ray hits the glass at the tube end.

In 1897 Joseph John Thomson (1856–1940), the successor to Maxwell as Cavendish Professor at Cambridge, began a series of measurements of the deflection of cathode rays. In his experiments, after the ray particles pass through the anode they feel an electric or magnetic force F exerted at a right angle to their direction of motion for a distance d along the ray. They then drift in a force-free region for a distance $D \gg d$ until they hit the end of the tube. If a ray particle has velocity v along the direction of the ray, it feels the electric or magnetic force for a time d/v and then drifts for a longer time D/v . A force F normal to the ray gives ray particles of mass m a component of velocity perpendicular to the ray that is equal to the acceleration F/m times the time d/v , so by the time they hit the end of the tube they have been displaced by an amount

$$\text{displacement} = (F/m) \times (d/v) \times (D/v) = \frac{FdD}{mv^2} .$$

The forces exerted on a charge e by an electric field E or a magnetic field B at right angles to the ray are

$$F_{\text{elec}} = eE, \quad F_{\text{mag}} = evB$$

so

$$\text{electric displacement} = \frac{eEdD}{mv^2},$$

$$\text{magnetic displacement} = \frac{eBdD}{mv}.$$

Thomson wanted to measure e/m . He knew D , d , E , and B , but not v . He could eliminate v from these equations if he could measure both the electric and magnetic displacements, but the electric displacement was difficult to measure. A strong electric field tends to ionize any residual air in the tube, with positive and negative ions pulled to the negatively and positively charged plates that produce the electric fields, neutralizing their charges. Finally Thomson succeeded in measuring the electric as well as the magnetic deflection by using a cathode ray tube with very low air pressure. (Both the electric and magnetic displacements were only a few inches.) This gave results for the ratio of charge to mass ranging from 6×10^7 to 10^8 coulombs per gram.

Thomson compared this with the result that Faraday had found in measurements of electrolysis, that $e/m_1 \approx 10^5$ coulombs per gram, where e is the electric charge of a singly ionized atom or molecule (such as a sodium ion in the electrolysis of NaCl) and m_1 is the mass of a hypothetical atom of atomic weight unity, close to the mass of the hydrogen atom. He reasoned that if the particles in his cathode rays are the same as those transferred in electrolysis, then their charge must be the same as e , so their mass must be about $10^{-3}m_1$. Thomson concluded that since the cathode ray particles are so much lighter than ions or atoms, they must be the basic constituents of ions and atoms.

Thomson had still not measured e or m . He had not even shown that cathode rays are streams of particles; they might be streams of electrically charged fluid, with any volume of fluid having a ratio of charge to mass equal to his measured e/m . Nevertheless, in the following decade it became widely accepted that Thomson had indeed discovered a particle present in atoms, and the particle came to be called the electron.