

# 1

## 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.<sup>1</sup>

<sup>1</sup> 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

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

## 1.1 Gas Properties

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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  $\text{H}_2\text{O}$ : 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	$\text{H}_2\text{O}$
Carbon dioxide	$\text{CO}_2$	$\text{CO}_2$
Ammonia	NH	$\text{NH}_3$
Sulfuric acid	$\text{SO}_2$	$\text{H}_2\text{SO}_4$

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*

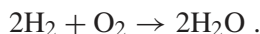
On December 31, 1808, Gay-Lussac read a paper to the Societe Philomathique in Paris, in which he announced his observation that gases at the same temperature and pressure always combine in definite proportions of *volumes*. For instance, two liters of hydrogen combine with one liter of oxygen to give 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  $\text{H}_2\text{O}$ , the reaction for producing molecules of water is



The use of Avogadro's principle rapidly provided the correct formulas for gases such as  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{NO}$ , 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  $\langle v^2 \rangle$ , the pressure is  $p = nm\langle v^2 \rangle/3$ . Using Charles' law, he concluded that  $\langle v^2 \rangle$  is proportional to absolute temperature. Writing this relation as  $m\langle v^2 \rangle/3 = kT$  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

$$pV = NkT . \quad (1.2.1)$$

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*  $\mu$  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:

$$m = \mu m_1 . \quad (1.2.2)$$

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  $\mu$  is defined as  $\mu$  grams, so in Eq. (1.2.3) the ratio  $M/\mu$  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  $6.02214 \times 10^{23}$  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.