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Chapter 6

A brief history of the unit of chemical amount

Juris Meija

Humans have been making measurements of chemical nature for a long time. The use of gold and silver as a currency has created the need for analyzing the purity of the precious metals. Amarna letters, written on clay tablets over 3000 years ago, detail the complaint of the king of Babylon to Amenhotep III (Rainey 2015):

As for the forty minas of gold that they brought, when I cast it into the kiln, for sure only ten minas came forth

Thus, gold was tested for its purity by the fire-assay, a process also known as cupellation. Roman emperor Nero required that taxes should be paid with gold that was tested using such method. This process is described in full detail for the first time only in the 16th century in one of the first textbooks of quantitative analytical chemistry—*De re metallica* by Georgius Agricola (1556)¹.

In his book *On Stones* (circa 300 BC), Greek philosopher Theophrastus describes a smooth stone that imparts a colour of metal alloys when rubbed (Wälchli 1981). A few centuries later, Pliny the Elder writes in his *Natural History* that with this method one can ‘tell in a moment the proportion of gold there is in it, how much silver, or how much copper; [...] their accuracy being so marvelous that they are never mistaken’ (Pliny the Elder). Because the colour of precious alloys depends largely on the gold content, their colour can be compared to samples of known purity. This early form of colorimetric touchstone comparison method was used by Romans and Egyptians alike and this practice continues to this day.

¹ As an interesting historical note, this book was first translated into English in 1912 by Lou Henry Hoover and her husband Herbert Hoover who later became the 31st President of the United States of America.

6.1 Comparative measurements

In 1663, Robert Boyle noted that acids and bases can destroy and restore the blue colour of some plant dyes such as the syrup of violets. This enabled him to ‘guess at the strength of the liquors, thus examined, by the quantity of them; which is sufficient to destroy, or restore the blue colour of our tincture’ (Boyle 1725). In 1699, Wilhelm Homberg, who had worked with Boyle in his laboratory, reported quantitative measurements on neutralization of acids and bases. He measured the strength of acids by neutralizing them with potassium carbonate and then weighing the dried residue (Homberg 1699). Similar experiments were done in 1729 by Claude Francois Geoffroy who determined the strength of vinegar by adding a powder of potassium carbonate until no further effervescence took place. These three early studies seem trivial to us but they paved a way for entirely new kinds of chemical measurements which enable determining the amounts of several substances by chemical means. Furthermore, the analysis methods of Boyle, Homberg, and Geoffroy differ from those described by Pliny the Elder and Agricola because they enabled chemists, for the first time, to chemically *compare* the quantities of various substances. Before the 18th century, measurements of different chemical quantities were seen as unrelated. One can determine the mass of copper and gold in a coin but a direct comparison of these two values does not seem to be of much value. However, comparing the amount of vinegar with that of potash enables us to express the strength of vinegar in terms of a universal unit, for example, a teaspoon of potash. The idea of comparing amounts of chemical substances thus emerged in the 17th and 18th century. In 1767, British chemist Henry Cavendish described a fixed mass of potassium carbonate as ‘equivalent’ to a fixed mass of calcium oxide if they would both saturate (neutralize) equal amounts of acid.

6.2 Quantitative measurements

In the late 18th century, French chemist Antoine-Laurent Lavoisier revolutionized chemistry through his experiments and ideas. In his seminal book *Traité élémentaire de Chimie* (1789), Lavoisier put forward that both the mass and matter is conserved in chemical reactions (Lavoisier 1790, Smartt Bel 2005):

We may lay it down as an incontestible axiom, that, in all the operations of art and nature, nothing is created; an equal quantity of matter exists both before and after the experiment; the quality and quantity of the elements remain precisely the same; and nothing takes place beyond changes and modifications in the combination of these elements. Upon this principle the whole art of performing chemical experiments depends.

Lavoisier was certainly not the first to recognize this fundamental law, but he is credited as its discoverer because he applied the permanency of mass to chemistry and all chemical processes alike. As Thomas Kuhn has noted (Kuhn 1961), Lavoisier’s contemporaries felt that his theory of combustion deprived chemistry of one of its principal traditional functions—the explanation of the qualitative

properties of bodies. In addition to introducing chemists to quantitative thought, a striking feature of the *Traité* was the first modern definition of chemical elements. These advances prompted chemists to further study the relationship between the masses of various substances that combine with one another, known as the equivalent or combining weights. In the 1790s, his fellow countryman Jeremias Benjamin Richter called this study ‘stoichiometry’ or ‘the art of measuring chemical elements’. Richter found that the mass ratio of the compounds consumed in a chemical reaction was always the same: when two substances combine with a third in a certain proportion, they will combine with each other in the same proportion. Today we know this as the law of reciprocal proportions. The same conclusion was reached by the French chemist Joseph-Louis Proust who observed that substances always contain their component elements in fixed mass ratio regardless of method of preparation. Richter compiled a list of values for various common chemicals which were ‘equivalent’ to one another. For example, 1000 parts of hydrochloric acid were equivalent to 858, 1107, and 3099 parts of magnesium, calcium, and barium oxides, respectively. Likewise, 1000 parts of sulphuric acid were equivalent to 616, 796, and 2226 parts of magnesium, calcium, and barium oxides, respectively. By comparing the numerical values in these two series, Richter thus found a way not only to compare amounts of substances that react directly with one another, such as acids and bases, but also a way to compare amounts of substances that do not react with one another, such as sulphuric and hydrochloric acids. Richter showed that 1394 parts of sulphuric acid and 1000 parts of hydrochloric acid were distinct yet equivalent quantities². In other words, 1394 parts of sulphuric acid will neutralize the same amount of other bases as 1000 parts of hydrochloric acid.

In contrast to the view that chemical substances unite in definite proportions, some prominent chemists of the time thought that in most cases substances could combine chemically in an infinite number of ratios varying continuously between certain limits (Hartog 1894), a notion that was soon disproved by the precise experimental work of the Swedish chemist Jöns Jacob Berzelius (1779–1848).

The general aptitude for quantitative work by chemists was in its infancy in the late 18th century. In 1786, Immanuel Kant famously denied chemistry the status of ‘proper’ science largely because of the lack of application of mathematics in its teachings (McNulty 2014). To Kant, there could be only as much proper science as there is mathematics therein. Perhaps this explains the rudimentary level of Richter’s explanations in his *Stoichiometry* where he famously explains how to add two numbers ‘19 + 424 means that we add 19 to 424’ (Szabadváry 1966). A century later, similar sentiments were raised by Sir Edward Frankland, one of the leading chemists of his time, in a letter to James Joseph Sylvester, a leading mathematician of his time: ‘I am convinced that the future progress of chemistry, as an exact science, depends very much indeed upon the alliance of mathematics’ (Frankland 1878).

Richter spent a significant amount of time trying to explain the numerical patterns in the values of equivalent weights. For example, he noted that the

² Equivalent weights are often wrongly attributed to C F Wenzel (1777). See *A Short History of Chemistry* By James Riddick Partington.

equivalent weights of magnesium, calcium, and barium oxides (in a scale $\text{HCl} = 1000$) can be represented in a mathematical progression $a + b$, $a + 3b$, and $a + 19b$ where $a = 734$ and $b = 124.5$ ³. Richter was, however, not alone in trying to find patterns in the equivalent weights of the various elements. In fact, throughout a large part of the 19th century chemists would search for meaning in the atomic weights in order to find universal relationships between these values. Most notably, this led the English chemist William Prout (1785–1850) to suggest in 1815 that atomic weights of all the elements are exact multiples of hydrogen (Prout 1815).

In 1808 French chemist Joseph Louis Gay-Lussac published his observations on the combining volumes of gases, namely that they react with one another in very simple proportions of their volumes. Moreover, if the product is also a gas, its volume too is in simple proportion of the reactants. Armed with the results of Gay-Lussac, Amedeo Avogadro postulated in 1811 that gases at the same temperature and pressure contain the same number of molecules. Avogadro saw his postulate as a practical way to establish accurate relative masses of atoms based on the density of gases.

6.3 The mass unit of the chemist: the gram-molecule

One of the fundamental laws of chemistry is that of discontinuity. The discontinuous variation according to the law of multiple proportions in the composition of various substances made from the same atoms becomes immediately clear: it arises solely due to the condition that the molecule constituting a compound contains necessarily a whole number of atoms of each kind. Indeed, John Dalton (1803) noted that ‘when elements combine, they do so in a ratio of small whole numbers’. This was a culmination of the work of scientists such as Wenzel, Richter, and Prout. Here Dalton meant not the mass but rather the number of atoms. Thus began the paradigm shift away from inertial descriptors of chemical processes (such as the mass or the volume of the reacting substances) to the particulate descriptors (such as the number of atoms or derived quantities directly proportional to them). After all, not everything depends on the mass of substance. Fill equal masses of two gases in two identical cylinders and they will exert different pressure. Combine equal masses of sulphuric acid and sodium hydroxide and the resulting mixture will be far from neutral.

Chemists accepted that the amount of substance is characterized by the number of elementary entities and not their mass. Although there was no means to ascertain this number directly, Dalton put forward the idea that chemical elements are made of atoms of differing mass. Combined with the idea that elements combine with one another in a ratio of small whole numbers, Dalton could deduce the relative masses of the various atoms using hydrogen as the unit (Dalton 1808). For example, oxygen and hydrogen unite in a mass ratio of 8:1 to form water. If we assume that water contains 1 atom of hydrogen and 1 atom of oxygen, as Dalton did, then the 8:1

³To Richter, the unfilled sequences in the series from $a+3b$... $a+19b$ represented still undiscovered elements. See Szabadváry (1966) for more discussion.

combining mass ratio is a direct consequence of the fact that oxygen atoms are eight times heavier than hydrogen atoms.

Since the introduction of the atomic weight concept by Dalton, chemists are able to express their observations in a quantity that is proportional to the number of elementary entities. It became possible, for the first time, to establish a practical connection between mass measurements and chemical stoichiometry. The use of atomic weights, in conjunction with the mass measurements of substances, still remains a common means for stoichiometric calculations in chemistry (Meija 2014). A problem inherent to Dalton's approach, however, was the assumption of the chemical composition. For, if a water molecule contained *two* atoms of hydrogen and one oxygen atom, then the observed 8:1 combining mass ratio of oxygen and hydrogen gases corresponds, means that oxygen atoms are sixteen times heavier than hydrogen atoms. Thus, proper determination of atomic weights necessitated knowledge of chemical composition yet one could not determine chemical composition without proper atomic weights. This *catch-22* plagued chemistry for almost all of the 19th century despite the fact that 32 year old Italian chemist Stanislao Cannizzaro noted during the 1860 Karlsruhe Congress that the long-forgotten Avogadro hypothesis enables the breaking of this logical circle (Mönnich 2010).

Central to these developments in analytical chemistry was the discovery that matter reacting chemically does not do so simply between equal masses of the samples involved. We now refer to the study of this phenomenon by using Richter's term 'stoichiometry', now defined as the relationship between the amounts of substance that react together, and the products that are formed. Hence, chemists still carried out their measurements using an analytical balance, as they did before, but they now rationalized all combining masses through the corresponding relative atomic masses. The *Encyclopaedia Britannica* (1883, 9th edn, vol 16) explained this practice as follows:

When a chemist speaks of acting on a molecule of succinic acid with two molecules of pentachloride of phosphorus, he means that he mixes them in the proportion of 118 parts of the former to 2×177.5 of the latter. For the sake of precision we sometimes speak of a molecule of water (or other substance) in grammes, or even of a *gramme-molecule*, a *grain-molecule*, &c. Thus, in the case just mentioned a gramme-molecule of succinic acid means 118 grammes of succinic acid, &c.

6.4 The many atomic weight scales

Indeed, throughout most of the 19th century chemistry was plagued with inaccurate atomic weights largely because of the differing opinions regarding the underlying constitution of the molecules. One also has to bear in mind the difficulty in accurate measurements of these values, which was eventually recognized with the 1914 Nobel Prize for chemistry to Theodore W Richards. There was, however, an additional source of discontent. While Dalton used hydrogen as the basis for the atomic weight

Table 6.1. Relative atomic mass scales through the centuries (Jensen and Meija 2010).

19th century: average mass scale	
H = 1 (O = 5.5)	Dalton, 1803–1805
H = 1 (O = 16)	Davy, 1812
O = 10	Wollaston, 1813
O = 1	Thomson, 1813, 1825
O = 100	Berzelius, 1814
O = 4	Griffin, 1834
O = 16	Brauner 1889; Clarke, 1893
C = 12	Hinrichs, 1893
20th century: isotopic mass scale	
¹⁶ O = 16	Aston, 1931
¹² C = 12	IUPAC, 1961

scale, chemists were split on the merit of this choice for a long time. In fact, there have been numerous other scales used since Dalton, many of these alternative atomic weight scales used oxygen as the basis following a suggestion by Wollaston (see table 6.1).

By the end of the 19th century, two scales gained popular support: H = 1 and O = 16. This duality was undesired in science and one of the inaugural tasks of the newly-formed International Commission on Atomic Weights was to decide (in 1899) whether ‘O = 16 shall be fixed as the future standard for the calculation of atomic weights’⁴. The Commission did side with oxygen but the debate was not over. In 1901, Theodore W Richards summarized the debate over the choice of hydrogen or oxygen as the atomic weight unit as follows (Richards 1901):

One regrets that so much time should have been spent in discussing a matter which involves no fundamental principle, but is simply a question of form and of convenience.

In addition to educational features, the choice between hydrogen and oxygen as the atomic weight unit had significant practical implications. Czech chemist Bohuslav Brauner (1855–1935) showed that the measurements of the O:H ratio varied from 15.87 to 16.01 (Brauner 1889). Each new determination of this ratio gave a new value for oxygen because hydrogen was set to H = 1 by definition. Since most atomic weights were measured in relation to oxygen, and not hydrogen—owing to the trivial fact that oxides are more stable than hydrides—atomic weights of most elements could not be established to better than 0.5% uncertainty. To avoid this problem, Brauner suggested to return to the oxygen scale by setting O = 16.

⁴ Not unlike the undergoing debates regarding the redefinition of the mole, one of the main oppositions to O = 16 scale was pedagogical. People claimed that it would be confusing to see the atomic weight of the lightest element, hydrogen, as 1.008, and not 1 exactly. For more discussion on this matter refer to (Richards 1900).

In 1920, during the first General Assembly of the International Union of Pure and Applied Chemistry (IUPAC) the question to reintroduce $H = 1$ was back on the agenda but was rejected by the International Atomic Weights Commission.

With the discovery of oxygen isotopes in the late 1920s, scientists realized that physicists have been, in fact, using the oxygen-16 as the mass standard, whereas chemists relied on the average atomic mass of all its isotopes. The difference was tiny (0.03%) but it was soon discovered that oxygen isotopic abundances were not constant in nature. As a result of the inherent uncertainty in the atomic weight scale, no chemical measurement could have been done to a precision better than a few parts in 10^5 . With no obvious solution at hand, chemists continued using the $O = 16$ scale and physicists retained $^{16}O = 16$. This schism ended in 1961 when physicists and chemists both agreed to adopt a carbon-12 based scale for atomic masses through their respective International Unions⁵.

6.5 The name: mole

Chemists did not have a proper name for the quantity that refers to the size of an ensemble of entities. As is often the case in science, developments in terminology and the symbolic language come second to technical advances. Only after the World War II the international interest in the symbols of physics became mature and scientists realized that ‘gram-molecular weight’ has the nature of a base quantity as it measures the size of the ensemble of atoms and molecules.

During the 1950s it became apparent that the mole was understood by chemists in two different meanings: as a certain *mass* of a substance (1 mol of potassium = 39 g) and as a certain *number of entities* (1 mol of potassium = 6.02×10^{23} atoms) (Milton and Mills 2009). Indeed, the word mole was introduced by two future Nobel laureates—Walther Nernst and Wilhelm Ostwald—as a practical way to compare the number of entities contained in a given bulk mass of a substance. The purpose of this mathematical construct has always been to compare the number of entities and this eventually became the official interpretation of the ‘amount of substance’ as was explained in the 1957 German Standard DIN 5484:

Unter Stoffmenge wird im folgenden eine physikalische Großenart verstanden, die dazu dient, einen aus bestimmten unter sich gleichen [...] Teilchen bestehenden Körper oder eine sonstige Gesamtheit solcher nach der Anzahl dieser Teilchen zu bewerten. [...] Demnach haben zwei Körper oder Gesamtheiten die gleiche Stoffmenge, wenn sie gleiche Anzahlen der jeweils gemeinten Teilchen enthalten.

In the following text, the term ‘quantity of substance’ is understood to mean a physical quantity which is used to evaluate a body consisting of identical [...] particles or aggregates of particles according to the number of these particles.

⁵ These developments are recounted by Henry E Duckworth in his memoir (Duckworth 2000).

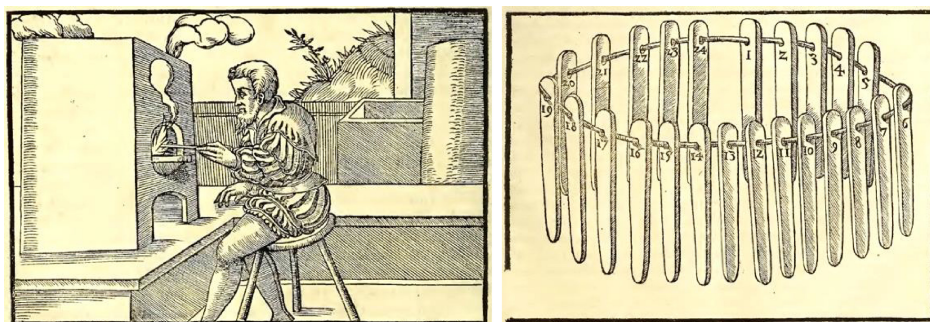


Figure 6.1. Two methods to determine the purity of precious metals which have been used since antiquity. (Left) The cupellation process, in which the object to be tested is melted down in a special manner and the mass of the purified residue is compared to the initial value. (Right) The purity of gold can be determined by comparing the colour of the material to that of a standard set of needles containing gold of known purity. Woodcuts from Georg Agricola's *De re metallica* (2nd edn, Basil, 1561).

[...] Accordingly, two bodies or aggregates have the same amount of substance if they contain equal numbers of particles.

After more than a century in use, in 1971, the 'gram molecule' was to become a full-fledged unit with a proper name: the mole. This quantity was eventually called the 'amount of substance' and, in keeping with the long-held tradition of chemists, a quantity corresponding to 1 gram-molecule was chosen as the SI base unit with the name 'mole'. Following the advice of the International Union of Pure and Applied Physics, the International Union of Pure and Applied Chemistry, and of the International Organization for Standardization, the mole was officially adopted as a base unit of the SI by the 14th CGPM in October 1971⁶.

The English name 'amount of substance' was derived from the German word *Stoffmenge* and it is not a well-liked name (Mills and Milton 2009). One problem with this quantity name is its unwieldy application by some, as in the 'amount of substance of benzene'. IUPAC notes that the word 'substance' in the 'amount of substance' is a placeholder for the actual substance which therefore renders 'amount of benzene'. This leads to another difficulty since the word 'amount' is too universal to be understood only in the chemical context. For this reason, many prefer a two-word 'chemical amount' which is similar to 'electric current' and also adds the word chemistry explicitly in the list of base quantities (Marquardt *et al* 2017). In fact, 'chemical amount' appears as an alternative name for 'amount of substance' in the IUPAC Green Book since 1993.

The word 'moles' is Latin for 'mass' and its modern diminutive 'molecula' has been used by many chemists to designate a particulate matter of 'little mass'. Thus, when Avogadro spoke of molecules in his seminal 1811 manuscript he meant the

⁶ Three delegations (of nearly 40) cast votes against this Resolution: Poland, Czech Republic and USSR. See, for example, the article by Aleksandrov Yu I for further discussion about the mole.

smallest particles. Much like the Greek philosophers of antiquity, we use the word ‘atom’ to describe the same concept.

With the advent of the atomic theory during the 19th century, chemists were progressively distinguishing and describing matter at two levels: molar and molecular. August Wilhelm von Hofmann made use of the word ‘moles’ and in his 1865 textbook *An Introduction to Modern Chemistry* he introduced the adjectival form ‘molar’ which since has become synonymous with chemistry:

the reciprocal actions of minute particles through insensible intervals of space are distinguished as *molecular*. We may fairly therefore contradistinguish, by the epithet *molar*, the reciprocal actions of measurable masses through measurable intervals of space. [p 140; emphases in the original]

The adjectival form ‘molar’ has become commonplace in chemistry and is joined with decimal prefixes as in ‘decimolar’ or ‘millimolar’. In the mid-nineteenth century it was common to use the phrase ‘gram-molecular weight’ in chemistry to denote the mass of a substance that is equal to its molecular weight. As time went by, this unwieldy phrase was variously shortened to ‘gr.mol.wt, gr.mol, or g-mol. which eventually became abbreviated to ‘mol.’ or ‘Mol.’. In the late 1890s, Ostwald and Nernst’s proposal was to change this abbreviation into a stand-alone word ‘Mol’ while retaining the same historical meaning of gram-molecule. Ostwald wrote in 1893 (Ostwald 1893):

Nennen wir allgemein das Gewicht in Grammen, welches dem Molekulargewicht eines gegebenen Stoffes numerisch gleich ist, ein Mol [...]

Let us generally refer to the weight in grams that is numerically identical to the molecular weight of that substance, as one mole [...]

In addition to ‘Mol’, Nernst also used the word ‘Mole’. Although mole can be seen as a logical simplification of the gram-molecule, the acceptance of this term was not swift. The early English translations of Ostwald’s and Nernst’s textbooks omitted this terminological proposal and generally reverted ‘Mol’ back to ‘g.-mol.’ (Ostwald 1894, Nernst 1895). It was not until Alexander Findley’s translation of Ostwald’s *Inorganic Chemistry* in 1902 when ‘mole’ first appeared in English texts. IUPAC recommended ‘mol’ as the symbol for mole in 1963 (Comptes Rendus XXII Conference 1963).

6.6 Molar measurements in practice

In the early 19th century, the results of chemical analyses and calculations were done on the mass basis. Hence, different scales were required to compare, say, the amount of soda or potash. A prominent science writer of his time, Scottish chemist Andrew Ure (1778–1857), describes, for example, a ‘normal solution of sea salt’ as a solution

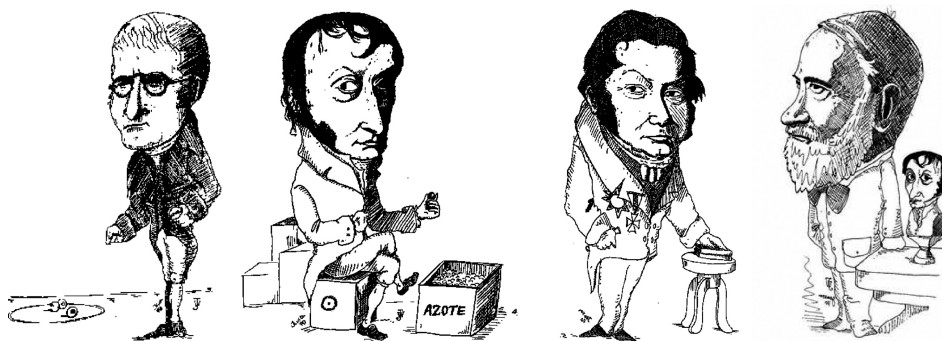


Figure 6.2. (from left) Dalton, Avogadro, Berzelius, and Cannizzaro: four key figures in the advancement of chemical measurements in 19th century. Although Dalton was not the first to propose the atomic theory, he put forward that atoms come in different weights. Dalton also formulated the law of multiple proportions which could be easily explained with the help of the atomic theory. Avogadro noted that equal volumes of gases must contain equal number of atoms. Hence, elucidation of stoichiometry and atomic weights could be greatly facilitated by measurements of combining volumes of substances and not just their masses. Berzelius is especially noted for the development of classical analytical techniques and precise determinations of atomic weights. ‘Berzelius gave order to everything he touched’, as Ronald G W Norrish noted in his Nobel Prize acceptance speech. With Cannizzaro’s advance, chemists finally acquired a standard set of atomic weights and were able to determine unambiguous and universally accepted compositional formulas for their compounds. Caricatures courtesy of William B Jensen (University of Cincinnati).

‘of which 100 grammes will precipitate exactly one gramme of silver’ (Ure 1848). Such an approach to chemical analysis generally required that each substance to be tested had its own reagent prepared in a concentration that would provide conveniently the analysis results as the mass fraction (percent).

The English chemist John Joseph Griffin noted another shortcoming to many 19th century chemical measurements: the common use of density of a chemical solution to ascertain its strength is an unacceptable proxy (Griffin 1848, p 103, Griffin 1851). He noted that for many common chemicals the density of their solutions is simply a poor and ambiguous substitute for ‘chemical strength’

All who have mastered the elements of theoretical chemistry know, that the *power* of chemical solution depends upon the *number* of atoms or equivalents it contains, and not upon the *absolute weight* of those atoms. Diluted nitric acid of 300° is twice as strong as diluted sulphuric acid of 150°, because there are twice as many chemical atoms present in it, not because the atoms of the nitric acid weigh twice as much as those of the sulphuric acid.

Due to the peculiar relationship between the concentration and density of its solutions, acetic acid of density 1.065 to 1.066 g mL⁻¹, for example, can be either 60% or 90% strength. In addition, 1% difference in the densities of ammonia solutions (0.95 vs 0.96 g mL⁻¹) corresponds to nearly 30% difference in the mass fraction of ammonia. Griffin advocated the use of ‘chemical strength’ to achieve greater uniformity and clarity. His ‘centigrade testing’ relied on preparation of

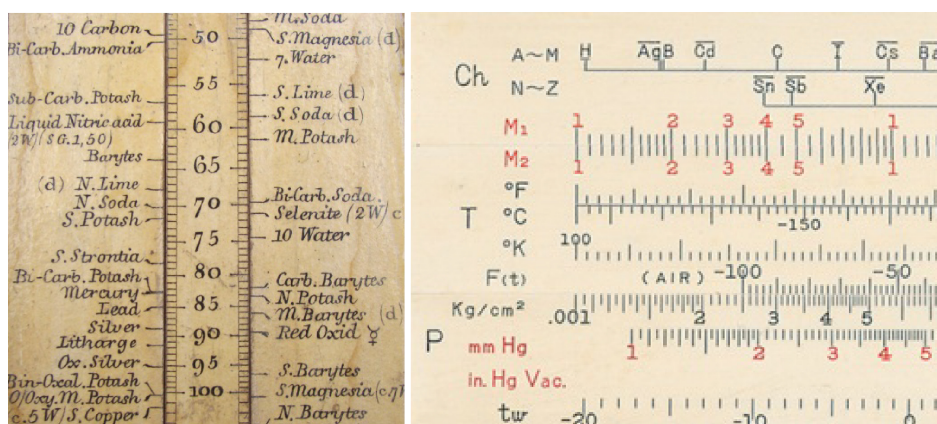


Figure 6.3. Wollaston's 1814 slide rule for calculating molecular weights (left). Only six original slide rules are believed to exist today. Similar slide rules were still being manufactured during the 1950s such as the Sun Hemmi 257—For Chemical Engineer (right). In Hemmi 257, placing the cursor over an element or chemical group on the upper scale allows the molecular weight to be read on the scale located on the other side of the slide rule. Courtesy of Tesseract—Early Scientific Instruments.

chemical solutions of 'equivalent strength' (Griffin used the centigrade notation as in '100° strong'). Such solutions were prepared by dissolving 'one test atom of the chemical preparation in so much water as will make a decigallon of solution at 62° Fahr'. The success of this approach was in its inherent feature that equally strong acids and bases will neutralize one another in equal volumes. The use of atomic weights (chemical equivalents) in reporting chemical results was further popularized by Karl Friedrich Mohr in his seminal 1855 textbook which formed the basis for volumetric chemical analysis (Mohr 1855).

The use of the term 'molarity' was preceded in time and popularity by 'normality'. In fact, since the mid-19th century chemists frequently applied the phrase 'normal solution' to denote solutions that 'contain one atomic weight of the active chemical, weighed in Grammes, and dissolved in a Litre of solution'. Later, the normality would also be adjusted for the stoichiometry of the chemical reaction for which such solution is intended (Haynes 1895). Chemists have been, in fact, using the term 'normal' to describe solutions containing one 'equivalent' of substance in a litre of solution.

Both systems had their advantages and disadvantages. In the old, mass-based, system, a statement '7.1 mg of phosphorus oxide' is timeless and unambiguous. In the new, amount-based, system, however, the results of chemical measurements were no longer based solely on the actual masses of reactants. Instead, the comparison of the various substances was achieved from their mass via atomic weights. This becomes problematic if unreliable atomic weights are employed. Indeed, the atomic weights themselves did not become reliable until the late 19th century. Fleischer's *A System of Volumetric Analysis* (Fleischer 1877) illustrates the unwanted consequences of a theory-laden with reliance on atomic weights:

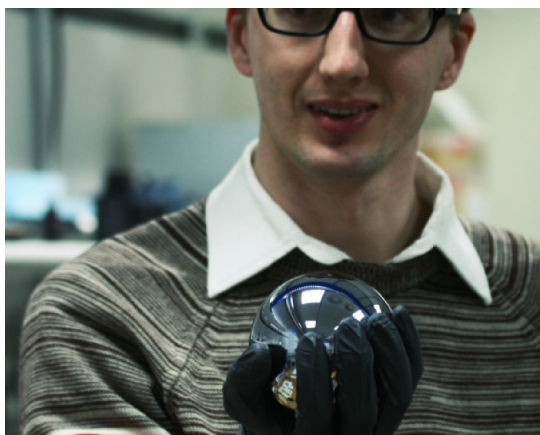


Figure 6.4. Grapefruit-sized sphere made from a single crystal of nearly pure silicon-28. The sphere weighs 1 kilogram and was used to determine the Avogadro constant (and the Avogadro number) with an unmatched accuracy. Photo credit: Olaf Rienitz, PTB.

Thus, 1 cb.c. [mL] of normal hydrochloric acid containing 36.5 m.gm [mg] HCl neutralizes an equivalent of caustic soda in m.gms.—i.e., 40 m.gm.; 2 cb. c. neutralize 80 m.gm. NaHO, and so on. (In old notation 1 cb.c. normal acid neutralizes 32 m.gm. NaHO.)

If the amount of HCl is used as a measure of NaOH, we witness here a 20% error based on the change of the atomic weight of oxygen from $O = 8$ to $O = 16$ which subsequently changed the relative molecular weight of NaOH from 32 to 40 (in the scale $H = 1$). Problems with amount-based notation did not stop with atomic weights. The use of ‘normality’ has been deprecated for many decades largely due to its core ambiguity: 1 N $BaCl_2$ solution could refer to a 1 N barium(II) solution or 1 N chloride solution. The former corresponds to 0.05 M $BaCl_2$, whereas the latter equates to 1 M $BaCl_2$.

Although Dalton put forward the atomic theory, his theoretical views were not readily met with acceptance. Interestingly enough, Dalton’s atomic theory owes much of its success to a wooden slide rule—a mechanical calculator of its time—which was introduced by English chemist William Hyde Wollaston in 1814 (Wollaston 1814). Wollaston’s slide rule contained the chemical equivalents (relative combining weights of elements) on the base of the rule and on the sliding part of it. Because both scales were logarithmically spaced, the slide rule allowed for a quick calculation of the relative masses of substances reacting with one another, the quantity of products, or the relative proportion of elements in a compound (Williams 1992). Wollaston’s slide rule soon became an indispensable item of laboratory equipment which has prompted some chemists even to proclaim that it has facilitated the development of chemical analysis more than any other invention (Comstock 1834).

6.7 Amount of substance as a dimensional quantity

Discussions on ‘dimensions’ are quite controversial and often subjective (Emerson 2005). Edward A Guggenheim noted in 1942 that ‘for special problems it may be advantageous to increase the number of fundamental quantities above the usual number. It can sometimes be useful in dimensional analysis to regard the number of atoms as having dimensions different from a pure number’ (Guggenheim 1942). Thus, conferring a unique ‘dimensionality’ to the amount of substance marks parallels to temperature which we do distinguish from thermal energy as a matter of convenience.

Nevertheless, the mole is often said to be an arbitrary unit. Such comments are unhelpful because all units are arbitrary. The kilogram did not have to be tied to the mass of one litre of water, the metre did not have to be tied to a quadrant of Earth, and the kelvin did not have to be tied to the triple point of water. Likewise, the mole did not have to be tied to the mass of carbon-12. All decisions that have set the magnitude of base units are results of practical, albeit arbitrary, decisions.

6.8 The Avogadro number

Scientists had been wondering about the size of atoms and molecules for a long time. Since gram-molecule had been established as a natural unit of mass when dealing with chemical substances, it was natural to wonder about ‘the number of actual molecules contained in one gram-molecule’, as Einstein did in 1905. In 1909, the future Nobel laureate Jean Perrin proposed calling this number in honour of Amedeo Avogadro (Perrin 1909):

Ce nombre invariable N est une constante universelle qu’il semble juste d’appeler *constant d’Avogadro*.

This invariable number N is a universal constant and it seems fair to name it *Avogadro’s constant*.

While today we distinguish carefully between the Avogadro constant and the Avogadro number, this terminological and conceptual distinction is rather new. Many have argued that this number (or constant) is not a fully-fledged physical constant; rather, a man-made arbitrary scaling factor or a ‘constant of a lesser breed’ (Mills 2010). On the contrary, some have called it ‘the most important of all physical constants’ (Hinshelwood 1956) During the 1926 Nobel Prize Award Ceremony Speech, Professor Carl Wilhelm Oseen, member of the Nobel Committee for Physics⁷, had this to say: *Perrin was able to determine one of the most important physical constants, Avogadro’s number*. Whether we like it or not, Avogadro number is an important aspect of modern science. One of Einstein’s three *annus mirabilis*

⁷ Among many other nominators, Oseen successfully nominated Albert Einstein for the 1921 Nobel Prize for Physics.

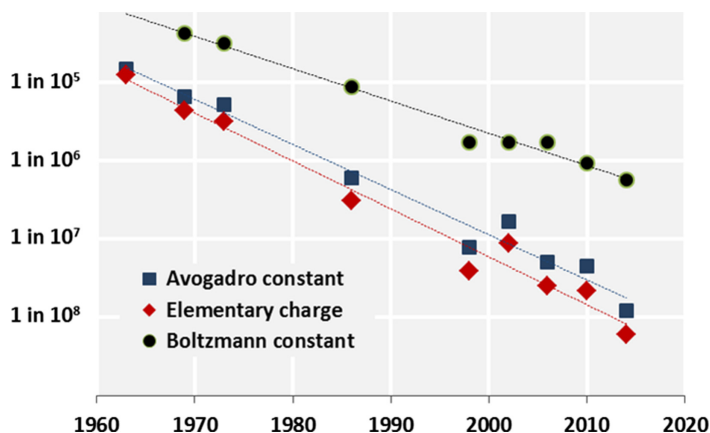


Figure 6.5. Advances in science manifest as ten-fold reduction in the uncertainty of most fundamental physical constants in every two decades or so, as shown here in the case of the Avogadro constant (N_A), the elementary charge (e), and the Boltzmann constant (k_B). Today, fundamental physical constants are now known with sufficient certainty to redefine the International System of Units in terms of some of these constants.

papers dealt with Brownian motion and ways to best determine the Avogadro number.

The Avogadro number remains relevant in science because it is a scaling factor between two mass units still used in science: the kilogram and the dalton, the latter being the 1/12 mass of a single carbon-12 atom. Determination of the Avogadro constant plays an important role in science because it enables a comparison of disparate experiments of other constants. For example, the Rydberg constant relates the Avogadro and Planck constants through several other well-known physical constants. Because of this, the value of the molar Planck constant ($N_A h$) is known better than either N_A or h and therefore determination of the Avogadro constant indirectly provides a value of the Planck constant (Becker and Bettin 2011). In the early 1990s, several of the world's leading metrology institutes started the work on determining the value of the Avogadro number using x-ray crystal density method. Here, the density of a material is measured in two ways, at the macroscopic and atomic levels:

$$\rho_1 = m_{\text{sphere}}/V_{\text{sphere}} \text{ [kg/m}^{-3}\text{]}$$

$$\rho_2 = m_{\text{unit cell}}/V_{\text{unit cell}} \text{ [Da/m}^{-3}\text{]}$$

Equating these two density measurements provides the value of the Avogadro number, $\{N_A\} = \text{kg/Da}$, which is the numerical value of the Avogadro constant. This expensive experiment remains the most accurate realization of the definition of the mole to date.

6.9 Proposed new definition of the mole

Chemists rely on mass measurements and relative atomic masses (atomic weights) of atoms to enable them to conceptually realize the amount of substance. This is why

chemical measurements are almost invariably traceable to the relative atomic masses.

In the early 20th century the Avogadro number was viewed as a scaling factor for mass. When referring to the Avogadro number, for example, Percy Williams Bridgeman notes that ‘its dimensions are evidently the reciprocal of a mass’ (Bridgeman 1922). Today, we view its dimension as the reciprocal of the amount of substance. This paradigm shift aligns with the common view among chemists that ‘the mole is the Avogadro number of entities’ as it was summarized by the IUPAC ICTNS in 2009. It is not easy to gauge public opinion on a broad technical matter such as the redefinition of the mole. However, in the last two decades, significant support has been generated for a definition of the mole based on a fixed number of entities (Mills 2006, Milton and Mills 2009).

The mole is the amount of substance of a system that contains exactly $6.022\,1415 \times 10^{23}$ specified elementary entities, which may be atoms, molecules, ions, electrons, other particles or specified groups of such particles.

(The precise value for the Avogadro number to be used in the definition of the mole will be set by the CODATA Task Group on Fundamental Constants prior to the 26th CGPM in 2018.) At core, the redefinition of the mole centred on the question of whether it should be defined as an amount of substance contained in a certain *mass* of unbound carbon-12 atoms or a certain *number* of entities. In both cases, the magnitude of the mole remains unchanged.

6.10 Consequences of the entity-based definition

Chemists enjoy the relationship $1\text{ g mol}^{-1} = 1\text{ Da/ent}$ which states that the atomic mass of entities (atomic weight) is numerically identical to the mass of one mole of such entities when it is expressed in grams. This relationship is true because the current definition of the mole has the effect of setting the molar mass of carbon-12 to 0.012 kg mol^{-1} and because the current definition of the dalton is based on the mass of the carbon-12 atom, $m_a(^{12}\text{C}) = 12\text{ Da}$. Once the mole is no longer tied to carbon-12, the exact link between the atomic weights and molar masses will no longer be there. In other words, 12 g of carbon-12 will no longer be exactly 1 mol (of carbon-12).

The molar mass of a substance is related to its molecular weight via $M(X) = A_r(X) M_u$ where M_u is the molar mass constant with an exact value of $10^{-3}\text{ kg mol}^{-1}$. In the new SI, M_u will no longer have an exact value but rather will be set via the dalton as $M_u = N_A m_u$. CODATA-2014 puts the uncertainty of M_u to 1.2 parts in 10^{10} . A discrepancy in the molar mass at the level of one part in 10^{10} is not in the realm of concern for chemists. In fact, there are only two elements whose standard atomic weights are currently known with precision below a few parts in 10^{10} : fluorine and phosphorus. Hence, the fact that the molar mass of carbon-12 will now have an uncertainty of one part in 10^{10} will have a marginal impact on the molar masses of only a handful of substances such as F_2 , P_4 , or PF_3 .

The above comments notwithstanding, many are surprised to find out that there is actually no *exact* link between molar masses and atomic weights. In other words, 0.012 kg of pure carbon-12 is, in fact, not exactly 1 mol under the 1971 definition of the mole if the carbon is in solid form, and at room temperature. This is because in the definition of the mole, it is understood that unbound atoms of carbon-12, at rest and in their ground state, are referred to. Chemists do not work with unbound atoms; and atoms are at rest and in their ground state only at zero kelvin temperature, whereas chemists normally perform their measurements at room temperature. In fact, the molar mass of crystalline substances is given by

$$M(\mathbf{X}) = A_r(\mathbf{X})M_u - \Delta_f H_c^0(\mathbf{X})/c_0^2$$

where $A_r(\mathbf{X})$ is the molecular weight (sum of all relevant atomic weights), M_u is the molar mass constant, $\Delta_f H_c^0(\mathbf{X})$ is the cohesive energy of the crystal, and c_0 is the speed of light in vacuum. For a graphite crystal, $\Delta_f H_c^0(\mathbf{X}) = 711$ kJ/mol which corresponds to a difference between the molar mass of bound and unbound graphite of almost one part in 10^9 (equivalent to 1 μg in 1 kg). Currently, chemists mostly ignore the discrepancy between 1 g/mol and 1 Da at the level of one part in 10^9 so there is no reason to believe that a ten-fold smaller discrepancy will become problematic. Thus, while 1 mol of substance always contains the same number of specified entities, the 1971 definition requires corrections to be made for bonding energy, whereas the entity-based definition does not (Davis and Milton 2014). In this sense, the definition of the mole in the new SI is more fundamental, than the 1971 definition.

Atomic weights and chemical calculations have become so intertwined with chemical measurements that it becomes natural to wonder if there is a way to realize the new definition of the mole without invoking the atomic weights. In 2010, for example, Schlegel and coworkers described an experiment where bismuth ions were accumulated on a metal disk (Schlegel *et al* 2010). A total of 323.1 mg of bismuth was accumulated over 24 h requiring a total electric charge of 149.2 coulomb (ampere seconds). Since one mole of electrons corresponds to a charge of $F = N_A e = 96\,485$ A s, the 323.1 mg of bismuth therefore corresponds to 1.55 mmol of bismuth. In this experiment, the mole is effectively realized from definitions of the ampere and second. Alternatively, we find that for bismuth the ratio of its mass and chemical amount is $323.1 \text{ mg}/1.55 \text{ mmol} = 209.0 \text{ g mol}^{-1}$ from this experiment.

6.11 Outlook

The mole is thought of by many chemists as a quantity that contains the Avogadro number of entities. The upcoming revision of the International System of Units will align the official definition of the mole with this commonly held view. While the new definition does offer technical improvements over the 1971 definition, virtually no chemist will be able to take advantage of it in the foreseeable future. To them, the biggest advantage will certainly be in the formulation of the mole which will specify the exact number of entities. The techniques that can be used for realization and dissemination of the mole will remain the same as before. These include gravimetry

(with corrections for chemical purity), electrolysis, and use of the ideal gas law (with corrections for non-ideality). Under best practices, these three methods can achieve precision from few parts in 10^4 to few parts in 10^6 for realizing the amount of substance (although some state-of-the-art measurements can do better, as described in the above x-ray crystal density method for silicon). In the new SI, Faraday constant and the universal gas constant will acquire fixed numerical values, whereas the molar mass of carbon-12 will no longer be exact. However, the uncertainty on this value will be less than one part in 10^9 with no consequence to chemists, thereby allowing continuity with the previous definition.

References

- Becker P and Bettin H 2011 *Philos. Trans. A Math. Phys. Eng. Sci.* **369** 3925–35
- Boyle R 1725 *The Philosophical Works of the Honourable Robert Boyle. Vol. II, ed Peter Shaw (London 1725)* Experiments and observations upon colours (W and J Innys)
- Brauner B 1889 Die Basis der Atomgewichte *Ber. Dtsch. Chem. Ges.* **22** 1186–92 See also *Chem. News* 1888, 58, 307–8
- Bridgman P W 1922 *Dimensional analysis* (New Haven, CT: Yale University Press)
- Comptes Rendus XXII Conference* London 1963 (London: Butterworths Scientific)
- Comstock J L 1834 *Elements of Chemistry*, reprint 2016 (Wentworth Press)
- Dalton J 1808 *A New System of Chemical Philosophy*
- Davis R S and Milton M J T 2014 *Metrologia* **51** 169–73
- Duckworth H E 2000 *One Version of the Facts: My Life in the Ivory Tower* (Winnipeg: University of Manitoba Press)
- Emerson W H 2005 On the concept of dimension *Metrologia* **42** L01
- Fleischer E 1877 *A System of Volumetric Analysis* reprint 2016 (Wentworth Press)
- Frankland E 1878 Extract from a Letter of Dr Frankland to Mr Sylvester *Am. J. Math.* **1** 345–9
- Griffin J 1848 *Chemical Reactions: a Popular Manual of Experimental Chemistry* (London: John Joseph Griffin)
- Griffin J 1851 On the use of Centigrade testing in pharmacy *Pharmaceut. J.* Jan **1851**
- Guggenheim E A 1942 Units and Dimensions *Philos. Mag.* **33** 479–96
- Hartog P J 1894 *Nature* **50** 149–50
- Haynes D O 1895 *The Pharmaceutical Era* vol 14 (D O Haynes and Co.)
- Hinshelwood C N 1956 Amedeo Avogadro *Science* **124** 708–13
- Homberg 1699 Observation sur le quantité exacte des Sels Volatils Acides contenus dans les differens Esprits Acides *Histoire de l'Academie Royale des Sciences* **1** 44
- Jensen W B and Meija J 2010 *Anal Bioanal. Chem.* **398** 11–2
- Kuhn T S 1961 The Function of Measurement in Modern Physical Science *Isis* **52** 161–93
- Lavoisier 1790 *Elements of Chemistry*, Engl. transl. R.Kerr
- Marquard R *et al* 2017 A critical review of the proposed definitions of fundamental chemical quantities and their impact on chemical communities (IUPAC Technical Report) *Pure Appl. Chem.* <https://doi.org/10.1515/pac-2016-0808>
- McNulty M B 2014 Kant's Philosophy of Chemistry *Doctor of Philosophy dissertation* (Irvine: University of California)
- Meija J 2014 An ode the atomic weights *Nat. Chem.* **6** 749–50
- Mills I and Milton M 2009 Amount of substance and the mole *Chem. Int.* **31** 3–7
- Mills I M 2010 What is a mole?: old concepts and new *Chem. Int.* **32** 1

- Mills I M *et al* 2006 Redefinition of the kilogram, ampere, kelvin and mole: a proposed approach to implementing CIPM recommendation 1 (CI-2005) *Metrologia* **43** 227
- Milton M J T and Mills I M 2009 Amount of substance and the proposed redefinition of the mole *Metrologia* **46** 332–8
- Mohr F 1855 *Lehrbuch der chemisch-analytischen Titrimethode* (Berlin: F Vieweg)
- Mönnich M W 2010 Thriving for unity in chemistry: the first international gathering of chemists *Chem. Inter.* **32** 10–4
- Nernst W 1895 *Theoretical Chemistry* (transl.) ed C S Palmer (London: Macmillan)
- Ostwald W 1893 *Hand- und Hilfsbuch zur Ausführung Physiko-Chemischer Messungen* (Leipzig: Engelmann) p 119
- Ostwald W 1894 *Manual of physico-chemical measurements transl.* ed J Walker (London: Macmillan)
- Perrin J 1909 Mouvement brownien et réalité moléculaire *Ann. Chim. Physique* **18** 5–114
- Pliny the Elder *The Natural History Book XXXIII* ch 43 ed J Bostock
- Prout W 1815 On the relation between the specific gravities of bodies in their gaseous state and the weights of their atoms *Ann. Philos.* **6** 321–30
- Rainey A F Z L 2015 Amarna Letter EA7. *The El-Amarna Correspondence vol 1* (Leiden, Boston: Brill)
- Richards T W 1900 International atomic weights *Proc. Am. Acad. Arts Sci.* **36** 171–6
- Richards T W 1901 The standard of atomic weights *Proc. Am. Acad. Arts Sci.* **37** 177–81
- Schlegel C *et al* 2010 The determination of the atomic mass constant with ion accumulation: status and perspectives *Metrologia* **47** 146
- Smartt Bel M 2005 *Lavoisier in the Year One: The Birth of a New Science in an Age of Revolution* (New York: Norton)
- Szabadváry F 1966 *History of Analytical Chemistry: International Series of Monographs in Analytical Chemistry vol 26* (Oxford: Pergamon)
- Ure A 1848 *A Dictionary of Arts, Manufactures, and Mines* (New York: D Appleton and Co.)
- Wälchli W 1981 Touching Precious Metals *Gold Bull.* **14** 154–9
- Williams W D 1992 Some early chemical slide rules *Bull. Hist. Chem.* **12** 24–9
- Wollaston W H 1814 A Synoptic Scale of Chemical Equivalents *Philos. Trans. R. Soc.* **104** 1–22