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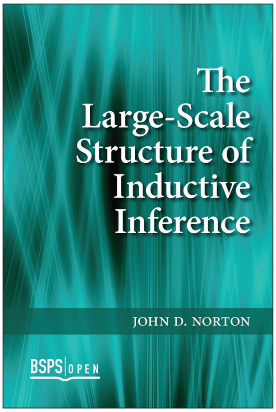

THE LARGE-SCALE STRUCTURE OF INDUCTIVE INFERENCE

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ISBN 978-1-77385-541-7

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11

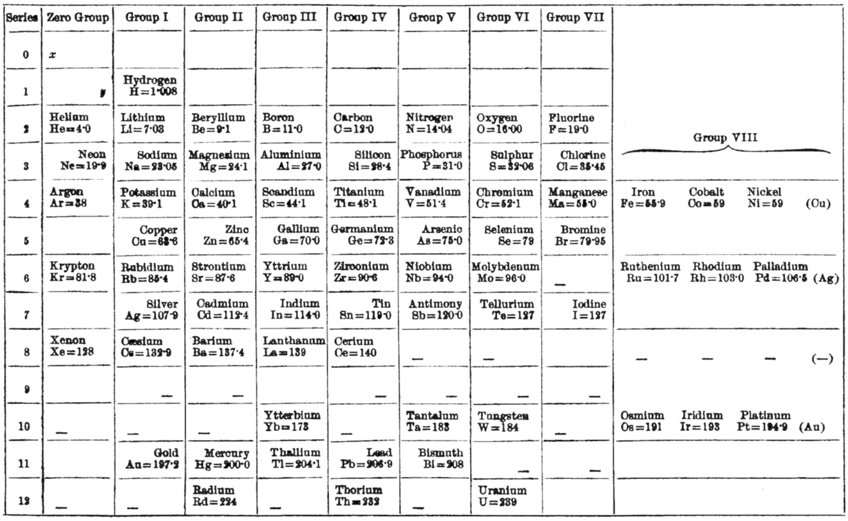
The Determination of Atomic Weights

1. Introduction

A table of the weights of the atoms of the elements of chemistry is commonly on display in high school science classrooms. Figure 11.1 shows an early example of the table, drawn from the work of Dmitri Mendeleev, the chemist most associated with the introduction of the table. We read familiar facts from it. A hydrogen atom has a weight of 1, near enough. An atom of carbon has a weight of 12. An atom of oxygen has a weight of 16. And so on. We then easily compute the weight of a molecule of water, whose composition is specified by the familiar formula H_2O. A water molecule has two atoms of hydrogen and one atom of oxygen. Its weight is 2 x 1 + 16 = 18.

Familiar as these facts are now, they did not spring into our textbooks the moment that Dalton (1808) proposed that ordinary matter consists of atoms of the elements hydrogen, carbon, oxygen, and so on. Rather, these were details that Dalton's theory failed to specify adequately. The omission was no oversight. The evidence that Dalton marshaled for his theory was too weak to pin down the relative weights of his atoms and the molecular formulae of simple substances such as water. These facts were hidden behind an evidential circle. Dalton could not know the correct molecular formulae until he had determined the correct atomic weights. But he could not determine the correct atomic weights until he had found the correct molecular formulae. He had no means adequate to break the evidential circle.

The determination of the weights of his atoms proved to be a recalcitrant problem whose solution required half a century of concerted efforts by chemists. That half century provides us with an illuminating study of a tangle of mutual relations of inductive support. Because of the great complexity of the facts of chemistry with its many elements, we shall see that these relations of support are far more complicated than, in the architectural analogy, two sides of an arch supporting each other. They are closer to the multiplicity of mutual support relations of an intricate vaulted ceiling, such as displayed in Chapter 2. We shall also see that higher-level hypotheses proved to be essential in the efforts to break the circularity that defeated Dalton. The most familiar of them is Avogadro's hypothesis. Its content is now taught to high school students, who memorize it as they did the lines of nursery rhymes. It already merited only a perfunctory statement in the 1911 eleventh edition of the *Encyclopaedia Britannica*, buried in the short entry for "Amedeo Avogadro": ". . . [U]nder the same conditions of temperature and pressure equal volumes of all gases contain the same number of smallest particles or molecules. . . ." In its time, however, it was an adventurous speculation, indulged only cautiously since it allowed chemists to determine atomic weights and molecular formulae. Adopting hypotheses such as Avogadro's incurred an evidential debt. We shall see that this debt was discharged through still more entangled relations of mutual inductive support at the corresponding higher levels of generalization.



Series	Zero Group	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
0	x								
1	y	Hydrogen H=1·008							
2	Helium He=4·0	Lithium Li=7·03	Beryllium Be=9·1	Boron B=11·0	Carbon C=12·0	Nitrogen N=14·04	Oxygen O=16·00	Fluorine F=19·0	
3	Neon Ne=19·9	Sodium Na=23·05	Magnesium Mg=24·1	Aluminium Al=27·0	Silicon Si=28·4	Phosphorus P=31·0	Sulphur S=32·06	Chlorine Cl=35·45	
4	Argon Ar=38	Potassium K=39·1	Calcium Ca=40·1	Scandium Sc=44·1	Titanium Ti=48·1	Vanadium V=51·4	Chromium Cr=52·1	Manganese Mn=55·0	Iron Fe=55·9 Cobalt Co=59 Nickel Ni=59 (Cu)
5		Copper Cu=63·6	Zinc Zn=65·4	Gallium Ga=70·0	Germanium Ge=72·3	Arsenic As=75·0	Selenium Se=79	Bromine Br=79·95	
6	Krypton Kr=81·8	Rubidium Rb=85·4	Strontium Sr=87·6	Yttrium Y=89·0	Zirconium Zr=90·6	Niobium Nb=94·0	Molybdenum Mo=96·0	—	Ruthenium Ru=101·7 Rhodium Rh=103·0 Palladium Pd=106·5 (Ag)
7		Silver Ag=107·9	Cadmium Cd=112·4	Indium In=114·0	Tin Sn=119·0	Antimony Sb=120·0	Tellurium Te=127	Iodine I=127	
8	Xenon Xe=128	Cæsium Cs=132·9	Barium Ba=137·4	Lanthanum La=139	Cerium Ce=140	—	—		— — — (—)
9		—	—		—	—	—	—	
10	—	—	—	Ytterbium Yb=173	—	Tantalum Ta=183	Tungsten W=184	—	Osmium Os=191 Iridium Ir=193 Platinum Pt=194·9 (Au)
11		Gold Au=197·2	Mercury Hg=200·0	Thallium Tl=204·1	Lead Pb=206·9	Bismuth Bi=208	—	—	
12	—	—	Radium Rd=224	—	Thorium Th=232	—	Uranium U=239		

Figure 11.1. A periodic table of the elements; from Mendeleev (1904, 26)

In Sections 2 and 3 of this chapter, I will review Dalton's "new system" of 1808 and how it is troubled by an evidential circularity in atomic weights and molecular formulae. Such circularities can be broken by an aptly chosen hypothesis. In Section 4, I review Dalton's failed attempt, guided by notions of simplicity, to select such a hypothesis. In Section 5, I review three hypotheses that came to guide work on atomic weights and molecular formulae over the next half century: Avogadro's hypothesis, Dulong and Petit's law of specific heats, and Mitscherlich's law of isomorphism. The ensuing analysis culminated in a celebrated synthesis of the chemical evidence and the support relations among them by Stanislao Cannizzaro (1858). In Sections 6–8, I review the evidential case presented by Cannizzaro. It emphasizes the interconnectedness of the relations at multiple levels. In Section 9, I review another relation of mutual support, this time between two sciences. For the chemists, Avogadro's hypothesis was supported by the equipartition theorem of the new physics of the kinetic theory of gases. For the physicists, the direction of the support was reversed. Finally, in Section 10, I record the transition of Avogadro's hypothesis from a useful speculation to an established rule. Dulong and Petit's law of specific heats was similarly established but with a crucial amendment that quantum effects lead it to fail at low temperatures.

2. Dalton's Atomic Theory

The atomic theory of matter has a venerable history, extending back to antiquity. Although it is easy to praise the early atomists as far-sighted visionaries, struggling to free themselves from the prejudices of their eras, a better assessment is less celebratory. Alan Chalmers (2009) has documented thoroughly how, for most of its life, the atomic theory was highly speculative. It had little empirical grounding and was thus rightly regarded with reserve or suspicion by those who practiced empirical science.

The turning point came in the early nineteenth century with Dalton's (1808) new proposal of a specific atomic constitution for matter in his *New System of Chemical Philosophy*. Curiously, though, his proposal was not the decisive factor in turning atomism from potentially fertile speculation to successful empirical science. The success of his proposal depended essentially on Antoine Lavoisier's work in chemistry a few decades earlier. Before it, just which were the elements of chemistry was unsettled. Was it to be the ancient choice of earth, air, fire, or water? Or was it the *tria prima* of the three principles of mercury, sulfur, and salt of Paracelsus? Or should we follow Boyle and discard the notion of elements entirely? Lavoisier had settled the matter when he collected his table of elements, as presented in his *Elements of Chemistry* ([1789] 1965). There he gave a subset of the familiar modern table of elements (175). It included hydrogen, oxygen, "azote" (nitrogen), sulfur, phosphorus, charcoal (carbon), and many more. Air and water, it was now found, are not elements after all. Air is a mixture of oxygen and azote. Water is a compound of oxygen and hydrogen. Combustion is not the release of phlogiston but the consumption of oxygen.[1]

Prior to Lavoisier's discoveries, an atomic theory had little hope of bridging the gap between specific properties attributed to atoms and the chemical properties of matter seen in the laboratory. One could speculate *ad nauseam* about the properties and behaviors of the most fundamental atoms or (breakable) corpuscles of matter. However, as long as these were atoms or corpuscles of air, water, fire, or earth, recovering the rich repertoire of chemical change then known to the chemists was precluded.

After Lavoisier, the prospects were quite different. Speculate that the simple bodies of Lavoisier's system are constituted of atoms peculiar to each and the pieces fall rapidly and easily into place. Dalton's good fortune was that his was the first prominent attempt at this speculation. Dalton associated a definite atom with each of Lavoisier's elements. The theory of chemical composition then became beautifully simple. The elements form compounds when their atoms combine in simple ratios. One carbon atom combines with one oxygen atom to make "carbonic oxide" (modern carbon monoxide CO). One carbon atom combines with two atoms of oxygen to make "carbonic acid" (modern carbon dioxide CO_2) (Dalton 1808, 215). We now take this simple idea for granted. However, its use with Lavoisier's table of elements is profound; the constancy of proportions in chemical composition is now explained at the atomic level.

Dalton was dependent on Lavoisier's proclamations of which are the elements. This dependence is shown by Dalton's retention of Lavoisier's identification of heat as a material substance. For Dalton, gases, liquids, and solids

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[1] There are also a few unexpected entries in Lavoisier's ([1789] 1965) table of "simple substances." It includes light and caloric, in which caloric is a material substance comprising heat. A "gas" for Lavoisier is defined as a body fully saturated with caloric (50). The oxygen that he prepared in his laboratory was for him really "oxygen gas" (52), elemental oxygen saturated with caloric.

were all quiescent at the atomic level. He had no kinetic conception of heat as atomic or molecular motion. Rather, the fundamental particles of matter were surrounded by atmospheres of heat. The expansion and contraction of matter with heating and cooling were explained by the addition to or subtraction of the substance of heat in these atmospheres, which would then enlarge or diminish.

3. A Circularity: Atomic Weights and Molecular Formulae

I now turn to the awkwardness that will govern the discussion to follow. Dalton's theory required atoms to combine in simple ratios when forming compounds: 1:1, 1:2, et cetera. However, Dalton had real difficulty in determining just which of those ratios should be for specific compounds. Famously, he decided that water is formed from one atom of hydrogen and one atom of oxygen, so that we would now write its molecular formula as HO rather than the familiar H_2O. This was just one of many molecular formulae that would require subsequent correction. Ammonia, for example, is NH in his account, not the modern NH_3.

I should note, as a matter of historical fidelity, that neither the term "molecular formula" nor the notation "HO" is Dalton's. I use them here for descriptive continuity with later work. Dalton drew circles representing each element and its compounds. The representation from his *New System* shown in Figure 11.2 is much reproduced and has near-iconic status. In it, hydrogen is "simple" 1 and drawn as a circle with a dot. Oxygen is "simple" 4 and drawn as a plain circle. The first "binary" (compound) 21 is water and represented by the two circles, one each for hydrogen and oxygen, side by side.

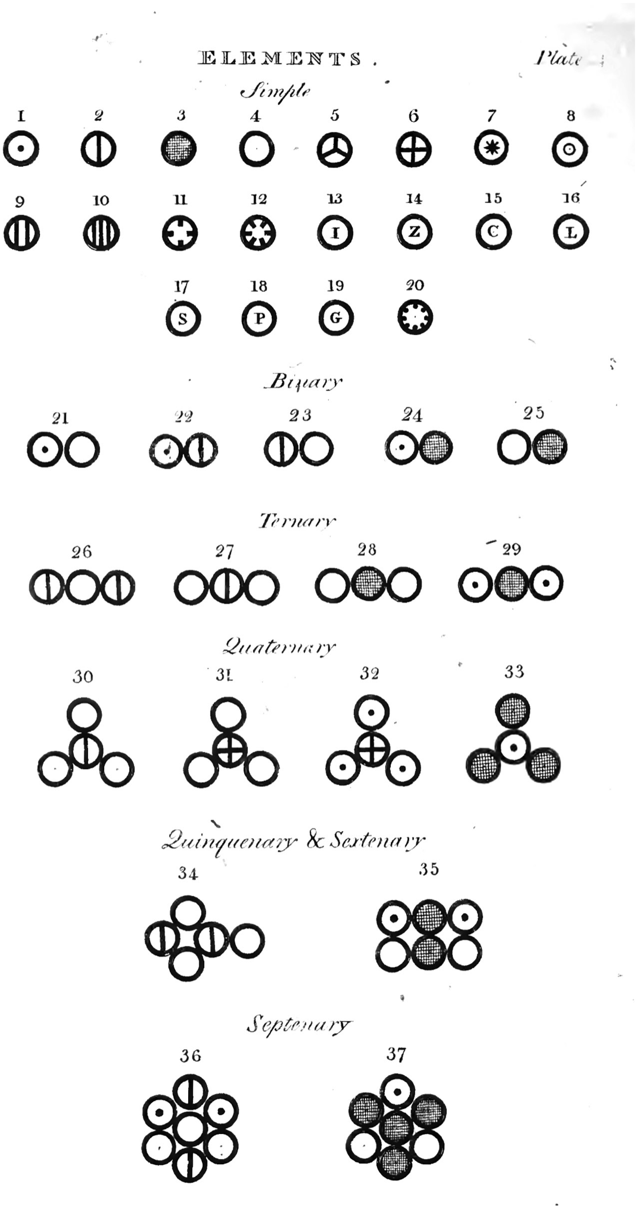

Figure 11.2. Dalton's illustration of the atomic elements and their compounds; from Dalton (1808, Plate 4, near 219)

The misidentification of the molecular formula of water and other compounds lay in no oversight or inattentiveness by Dalton. It lay in a serious incompleteness in his theory. One might know that 1g of hydrogen combines with exactly 8g of oxygen to produce water.[2] But how is one to know that this reaction involves two hydrogen atoms for each oxygen atom? That is, how can one know the correct molecular formula for water from the ratios of weights of the elements in it?

The problem would be solved by knowledge of the ratio of the weights of individual atoms. If we set the atomic weight of a hydrogen atom as the unit, then what would result if an oxygen atom has atomic weight 8? From the fact that 1g of hydrogen combines with 8g of oxygen to make water, we might propose that one atom of hydrogen has combined with one atom of oxygen to make water. That is, we find that water is HO.

However, what if the atomic weight of oxygen is really 16? Then, from the fact that 1g of hydrogen combines with 8g of oxygen to make water, we might propose that water forms by combining two atoms of hydrogen with one atom of oxygen. That is, water is H_2O. These possibilities can be multiplied indefinitely, and Table 11.1 shows some of them.

Table 11.1. Underdetermination of molecular formulae by combining weights

Combining weights to make water	**Atomic weights**	**Molecular formula for water***
1g hydrogen : 8g oxygen	hydrogen = 1; oxygen = 1	HO_8
1g hydrogen : 8g oxygen	hydrogen = 1; oxygen = 2	HO_4
1g hydrogen : 8g oxygen	hydrogen = 1; oxygen = 4	HO_2
1g hydrogen : 8g oxygen	hydrogen = 1; oxygen = 8	HO
1g hydrogen : 8g oxygen	hydrogen = 1; oxygen = 16	H_2O
1g hydrogen : 8g oxygen	hydrogen = 1; oxygen = 32	H_4O
1g hydrogen : 8g oxygen	hydrogen = 1; oxygen = 64	H_8O

* More generally, each of these formulae belongs to an infinite class with the same ratio of atoms. If hydrogen has atomic weight 1 and oxygen has atomic weight 8, then the compound molecule could be HO, H_2O_2, H_3O_3, H_4O_4, et cetera.

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[2] This is the modern figure. Dalton (1808, 215) reports the ratio as "1:7, nearly."

The molecular formula for water is left underdetermined by the observed combining weights. Rather, these weights merely give us an infinite set of possible pairings of component atomic weights and molecular formulae. If we knew one member of the pair, then we would know the other. If we knew the atomic weights, then we would know the molecular formulae. If we knew the molecular formulae, then we would know the atomic weights. There is a tight circularity in these pairings. To know one, we need to know the other. But we cannot know the second unless we already know the first. Because of this circularity, the molecular formula for water and the atomic weights of its constituent atoms remain underdetermined.

4. A Failed Hypothesis of Simplicity

This circularity can be broken by an aptly chosen hypothesis. We shall soon investigate cases of hypotheses that were introduced speculatively and eventually found solid inductive support. They are the success stories. Hypotheses do not always fare well. A clear instance is the hypothesis that Dalton himself introduced to solve the problem of determining "the number of simple elementary particles which constitute one compound particle" (1808, 213) or the correct molecular formulae (to use the more modern expression). He defined compounds as binary, ternary, and so on by equations (213).

> 1 atom of A + 1 atom of B = 1 atom of C, binary.
>
> 1 atom of A + 2 atoms of B = 1 atom of D, ternary.
>
> 2 atoms of A + 1 atom of B = 1 atom of E, ternary.
>
> 1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
>
> 3 atoms of A + 1 atom of B = 1 atom of G, quaternary.
>
> &c., &c.

With these terms in place, Dalton made the elaborate, multi-part hypothesis that would enable him to determine molecular formulae independently of the relative atomic weights.

> The following general rules may be adopted as guides in all our investigations respecting chemical synthesis.

> 1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary.
>
> 2nd. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.
>
> 3rd. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.
>
> 4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, &c.
>
> 5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.
>
> 6th. A *ternary* compound should be specifically heavier than the mixture of a binary and a simple, which would, if combined, constitute it; &c.
>
> 7th. The above rules and observations equally apply, when two bodies, such as C and D, D and E, &c., are combined. (214; Dalton's emphasis)

In the briefest terms, this compound hypothesis amounted to the assertion that one should choose the simplest molecular formula or formulae available. These rules were not entirely arbitrary. They fit comfortably with the mechanical picture that Dalton had developed of how compounds form. (It would take us too far afield for me to explain how.)

For my purposes here, it was a hypothesis nonetheless and introduced provisionally. To remain in chemistry, eventually it had to accrue inductive support. This is a story of failure, not success. It did not find this support. The hypothesis led Dalton to incorrect molecular formulae, such as that water is HO. Thus, it proved to be incompatible with the other hypotheses introduced to determine the molecular formulae. These other hypotheses mutually supported one another and survived into standard chemistry. Dalton's hypothesis did not find support and was discarded.

5. Breaking the Circularity

Dalton was trapped in a circularity. To know the correct molecular formulae, he needed to know the correct, relative atomic weights. Yet to know the correct, relative atomic weights, he needed to know the correct molecular formulae. This circularity presented a serious challenge to chemists in the first half of the nineteenth century. It was broken and decisively so by the efforts of some of the greatest chemists of the era. They found other means for ascertaining molecular formulae or atomic weights. No one of them was decisive, but their accumulated import was.

Following are three of the most important.[3]

5.1. Avogadro's Hypothesis

When compounds form from elements, their weights combine in fixed ratios. One gram of hydrogen combines with exactly 8g of oxygen to produce water. This fact is explained elegantly in Dalton's atomic theory by his supposition that compounds form when elemental atoms combine in simple, whole number ratios.

Gay-Lussac had remarked in a memoir read in 1808 on a second fixed ratio that proved to be just as important. When gaseous elements combine, they also do so in fixed volume ratios.[4] Two volumes of hydrogen (under the same conditions of temperature and pressure) always combine with just one volume of oxygen to make water. An appealing explanation of this fixity of volume ratios is that each of the volumes contains the same number of atoms. We could then read directly from the 2:1 ratio of volumes that water forms when two atoms of hydrogen combine with one atom of oxygen to make water. The circularity is broken. Water is H_2O and not HO.

There is an initial plausibility to the idea. Although atoms of different elements might have different weights, we would be merely supposing that each atom occupies the same space.[5] It is natural to extend the hypothesis

---

[3] They are selected since they play major roles in standard accounts of the determination of atomic weights written around the end of the nineteenth century: Meyer (1888, Part I, 1892), Pattison Muir (1890), and Wurtz (1881).

[4] For a convenient compendium of Gay-Lussac's, Dalton's, and Avogadro's writings on the topic, see Dalton, Gay-Lussac, and Avogadro (1893).

[5] At this time, prior to the kinetic theory of gases, the discussion proceeded with Dalton's model of gases as quiescent piles of atoms. Each atom was surrounded by a halo of caloric or heat.

to molecules compounded of atoms: a fixed volume of gas or vapor holds the same number of free atoms (if atomic) or molecules (if a molecular compound). However, the hypothesis then runs immediately into serious difficulties. Using modern notation not then in use, we represent the formation of water as

$$2H + O \rightarrow H_2O$$

$$\text{2 vol. hydrogen + 1 vol. oxygen} \rightarrow \text{1 vol. water vapor}$$

This contradicts laboratory observations. Two volumes of hydrogen combine with one volume of oxygen to make *two* volumes of water vapor.

The solution to the puzzle was given by Avogadro (1811).[6] One had to give up the assumption that hydrogen gas and oxygen gas consist simply of free atoms of hydrogen and oxygen. Rather, both gases consist of molecules that, in this case, contain two atoms of hydrogen and two atoms of oxygen.[7] Using modern notation, the formation of water is represented by

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$\text{2 vol. hydrogen + 1 vol. oxygen} \rightarrow \text{2 vol. water vapor}$$

What resulted was a powerful new principle for the determination of molecular formulae. It is given a complete and canonical formulation by Cannizzaro (1858, 1):

> I believe that the progress of science made in these last years has confirmed the hypothesis of Avogadro, of Ampere, and of Dumas on the similar constitution of substances in the gaseous state; that is, that equal volumes of these substances, whether

---

Heating the gas increased the size of the halo, and that explained why heating a gas leads it to expand.

[6] Translated as "Essay on a Manner of Determining the Relative Masses of the Elementary Molecules of Bodies, and the Proportions in Which They Enter into These Compounds" in Dalton, Gay-Lussac, and Avogadro (1893). An editor, "J. W.," remarks in the preface that "the English version of the French original will probably be found more faithful than elegant, especially so in the case of Avogadro's paper, where the French is always clumsy and occasionally obscure."

[7] Avogadro's use of the term "molecule" in 1811 did not match modern usage. Avogadro used the term for what we would now label either an atom or a molecule. What we now distinguish as an atom he labeled *molecule élémentaire* ("elementary molecule").

> simple or compound, contain an equal number of molecules: not however an equal number of atoms, since the molecules of the different substances, or those of the same substance in its different states, may contain a different number of atoms, whether of the same or of diverse nature.

Powerful as this hypothesis would prove to be, its early history was troubled. It did not gain ready acceptance for decades. Dalton himself had come out early against the hypothesis. An appendix to *Part II* of his *New System* contained a survey of some experiments on the combining volumes of gases. He found the results to contradict Gay-Lussac's claim that gas volumes combine chemically in simple, whole number ratios. Dalton concluded that

> The truth is, I believe, that gases do not unite in equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments. . . . (1810, 559)

If Gay-Lussac's claim fails, then so must the stronger hypothesis of Avogadro.

5.2. Dulong and Petit's Law of Specific Heats

Avogadro's hypothesis provided independent access to atomic and molecular weights of gaseous substances. It also indirectly opened access to the atomic weights of nongaseous elements as long as they enter into compounds with elements that elsewhere take the gaseous state. However, the scope of this indirect access is limited.

Dulong and Petit (1819) reported quite a different method of determining the atomic weights of solid elements. In his atomic theory, Dalton had represented solid elements as consisting of quiescent atoms surrounded by halos of caloric (heat). Dulong and Petit reported that Dalton had supposed that the quantity of heat associated with each atom was the same, no matter the element. It would then follow that the atomic heat capacity — the amount of heat needed to raise each atom by one degree of temperature — would be the same for all elements. However, Dulong and Petit continued to note that the results that Dalton had derived from this hypothesis were "so inconsistent with experiment that it is impossible for us not to reject the principle upon which such determinations are founded" (190). They attributed the difficulty to the inaccuracy in data then available to Dalton. They proceeded to show that more careful measurements led to vindication of the law. It is asserted as

The atoms of all simple bodies have exactly the same capacity for heat.

In other words, the atomic heat capacity is the same for all elements.

The expression of the law in measurable quantities was not so simple. We cannot measure the atomic heat capacity directly. What we can measure is the specific heat. It is the heat needed to raise a unit weight (1g) of a body by one degree of temperature. It must be multiplied by the true atomic weight, expressed as grams per atom, to recover the atomic heat capacity.

(specific heat) x (true atomic weight) = (atomic heat capacity)

However, we do not know the atomic weights in grams per atom. All that we know is the relative atomic weights, taking some atom as an arbitrary unit. That is, we have

(relative atomic weight) = (unknown conversion factor) x (true atomic weight)

So the best quantitative expression for the law is that

(specific heat) x (relative atomic weight) = constant

where the constant must come out the same for all elements. Using the best values that they could find for both specific heats and relative atomic weights, Dulong and Petit (1819) proceeded to show that this relation returns the same constant for a list of elements. Table 11.2 shows the data that they reported.

Table 11.2. Dulong and Petit's data

	Specific heats	**Relative weights of the atoms***	**Products of the weight of each atom by the corresponding capacity**
bismuth	0.0288	13.30	0.3830
lead	0.0293	12.95	0.3794
gold	0.0298	12.43	0.3704
platinum	0.0314	11.16	0.3740
tin	0.0514	7.35	0.3779
silver	0.0557	6.75	0.3759
zinc	0.0927	4.03	0.3736
tellurium	0.0912	4.03	0.3675
copper	0.0949	3.957	0.3755
nickel	0.1035	3.69	0.3819
iron	0.1100	3.392	0.3731
cobalt	0.1498	2.46	0.3685
sulfur	0.1880	2.011	0.3780

* The weights are relative to the atomic weight of oxygen. Multiplying them by 16 gives roughly the modern values, except for tellurium and cobalt.

The near constancy of the product in the final column indicates that the relative atomic weights are correct, at least relative to the elements in the table.

This constant is the atomic heat capacity of all atoms but expressed in some arbitrary system of units dependent on the unknown conversion factor mentioned above.

5.3. Mitscherlich's Law of Isomorphism

These two methods seem to have been the most important in breaking the circularity of atomic weights and molecular formulae. Other methods were also brought to bear. Mitscherlich's 1821 "law of isomorphism" is routinely mentioned in contemporary accounts (Meyer 1888, Part I, Section IV; Pattison Muir 1890, 345–47; Wurtz 1881, 55–60). In Mitscherlich's formulation, it asserts that

> Equal numbers of atoms similarly combined exhibit the same crystalline form; identity of crystalline form is independent of

> the chemical nature of the atoms, and is conditioned only by the number and configuration of the atoms. (quoted in Pattison Muir 1890, 345)

The law connects crystalline form with molecular formula so that a similarity of crystalline form suggests a similarity of molecular formula. A celebrated case — mentioned in both Pattison Muir (1890, 346) and Ramsay (1900, 17–18) — is gallium alum. So-called alums are sulfates of two metals. Potassium alum or potash alum, otherwise common alum, is a sulfate of potassium and aluminum. Gallium also forms an alum-like compound of sulfates of gallium and potassium and has a crystalline form similar to common alum. By invoking Mitscherlich's law of isomorphism, one can assume that the gallium merely replaced the potassium in the crystalline structure, and one can then determine gallium's atomic weight.

Despite its virtues, accounts of Mitscherlich's law are notable for their qualifications and warnings of the law's limited scope and fragility. Cannizzaro (1858) did not use it, as far as I can see.

6. The Vaulted Inductive Structure of Atomic Weights and Molecular Formulae

The methods just described are powerful and enable a complete determination of the atomic weights of the elements and thus the correct molecular formulae. Nevertheless, half a century after Dalton proposed his atomic theory, there was still a chaos of competing proposals. The Karlsruhe Congress of 1860 gathered about 140 of the leading chemists of Europe with the purpose of resolving the problem. The events of the congress have become a matter of legend in the history of chemistry.[8] Two years earlier Stanislao Cannizzaro had already published a solution to the problem. Relying heavily on Avogadro's hypothesis, he had successfully pieced together all of the parts of the puzzle and found a consistent set of atomic weights and molecular formulae. He had reported his success to *Il nuovo cimento* (Cannizzaro 1858), in which he sketched how he had led his students through his solution.

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[8] See Hartley (1966) and Ihde (1961) for accounts.

That set Cannizzaro outside the mainstream of work in chemistry, which remained skeptical of Avogadro's hypothesis.[9] He needed to mount a sustained defense of Avogadro's hypothesis even in 1860 at the Karlsruhe Congress. In spite of his efforts and the earlier publication of his solution, no agreement was reached at the congress. Rather, the decisive moment came at its close when Angelo Pavesi distributed copies of Cannizzaro's paper. When key participants, including Lothar Meyer and Dmitri Mendeleev, later studied Cannizzaro's paper, they were convinced, and his system was established as the standard.

This, at least, is the standard history. Chalmers (2009, Chapter 10) has argued that Cannizzaro's achievement is overrated. What is not acknowledged is his debt to the successes in prior work by organic chemists able to arrive at structural formulae for organic substances. Cannizzaro's methods, however, could yield atomic weights and molecular formulae but not the structural formulae.

My concern here, however, is narrower. It is the inductive structure of the case that Cannizzaro laid out for his values of atomic weights and molecular formulae and its later development. In short, that case exemplifies the massively complex interconnections suggested by the analogy with a vaulted ceiling. In the sections that follow, we shall see just a small portion of these interconnections.

- Section 7 will review relations of mutual support at the level of finest detail: that is, interrelations among the atomic weights and molecular formulae of specific substances.
- Section 8 will review relations of mutual support among the methods used. Specifically, there are relations of mutual support between Avogadro's hypothesis and the law of Dulong and Petit.
- Section 9 will review relations of support at the level of theory. That is, Avogadro's hypothesis in chemistry lends

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[9] Thorpe (1910, 64–65) recalls the situation:

> By the middle of the nineteenth century the hypothesis of Avogadro was practically forgotten and the law of volumes ignored. The atomic weights of the elements and the system of notation universally employed in England and Germany were based wholly upon equivalents.

support to an analogous hypothesis in statistical physics and conversely.

7. Mutual Support of Atomic Weights and Molecular Formulae

Cannizzaro's (1858) analysis depends heavily on Avogadro's hypothesis and the associated notion that elemental gases have molecular compositions, such as H_2, O_2, et cetera. The hypothesis requires that equal volumes of gases contain the same number of molecules. As a result, the mass density of a gas is directly proportional to the molecular weight of its constituent molecules. This observation provided the starting point for Cannizzaro's analysis. Cannizzaro prepared a large table of the densities of many gases of both elements and compounds. Table 11.3 lists just some of the densities from his large table (9). The units for mass density are selected so that molecular hydrogen gas has a density of 2.

The third column of the table includes further information of great importance. It divides the gas densities of compounds in proportion to the mass ratios of the constituent elements. For example, hydrochloric acid — hydrogen chloride HCl — forms from chlorine and hydrogen in the mass ratio of 35.5:1. Thus, the gas density of 36.5 for hydrochloric acid is broken up as deriving from a density of 35.5 of chlorine and 1 of hydrogen.

Table 11.3. Some of Cannizzaro's gas density data

Substance	**Density**	**Component densities**
hydrogen (H_2)	2	2 hydrogen
oxygen (O_2)	32	32 oxygen
chlorine (Cl_2)	71	71 chlorine
bromine (Br_2)	160	160 bromine
iodine (I_2)	254	254 iodine
mercury (Hg)	200	200 mercury
hydrochloric acid (HCl)	36.6	35.5 chlorine + 1 hydrogen
hydrobromic acid (HBr)	81	80 bromine + 1 hydrogen
hydroiodic acid (HI)	128	127 iodine + 1 hydrogen
water (H_2O)	18	16 oxygen + 2 hydrogen
calomel (mercurous chloride HgCl)*	235.5	35.5 chlorine + 200 mercury
corrosive sublimate (mercuric chloride $HgCl_2$)	271	70 chlorine + 200 mercury

* The modern formula is Hg_2Cl_2. However, above 400°C, calomel yields a vapor with the density that Cannizzaro indicated, now understood to result from a mixture of Hg and $HgCl_2$. See Selwood and Preckel (1940).

The table (unlike Cannizzaro's) includes the resulting molecular formulae for ease of reference. It is straightforward to arrive at them. A brief inspection of the table shows that the atomic weights of the elements present are overdetermined as the values of Table 11.4.

Table 11.4. Atomic weights inferred

Element	**Atomic weight**
hydrogen	1
oxygen	8
chlorine	35.5
bromine	80
iodine	127
mercury	200

To recapitulate Cannizzaro's analysis, recall that Avogadro's hypothesis tells us that the gas density is a surrogate for the molecular weight. Cannizzaro had conveniently chosen the unit for the gas density so that the gas density numerically equals the molecular weight. All that remains now is to find the combination of molecular formulae and atomic weights that returns the gas densities of Table 11.3.

Cannizzaro arrived at these combinations by noting how the component density of each element always appears as a multiple of some smallest unit. This smallest unit is the atomic weight. The simplest case is hydrogen, whose component densities are all multiples of 1. So we infer that the atomic weight of hydrogen is 1. We now read directly from the densities of Table 11.3 that the molecular formulae for hydrochloric, hydrobromic, and hydroiodic acids each have just one hydrogen atom. So their molecular formulae are HCl_x, HBr_y, and HI_z, where x, y, and z are unknown whole numbers. We also see that gaseous hydrogen is composed of molecules of two atoms, H_2. Water also has two atoms of hydrogen, so it is H_2O_w where w is some unknown whole number.

Proceeding in this way for the remaining elements completes the entries in Table 11.4 for the atomic weights and justifies the molecular formulae added to Table 11.3. Chlorine's component densities are multiples of 35.5, so that is its atomic weight. Chlorine gas is diatomic, Cl_2, and hydrochloric acid is HCl. Oxygen's component densities are multiples of 16, so that is its atomic weight. And so on.

For my purposes here, the important point is that the results are overdetermined. That means that only a portion of the data is needed to arrive at the full results. For example, the results for the remaining elements would remain the same if we dropped iodine and its compounds from the analysis. It would then follow that, if we reintroduce the data for iodine, the resulting assessment must agree with the earlier results. The atomic weight of hydrogen in iodine compounds must be the same as in water and hydrochloric and hydrobromic acids.

This overdetermination leads to multiple relations of mutual support. It means that we can take some subset of the results and find that it supports other parts of the results, and there is support in the converse direction.[10] For example, take the propositions that hydrogen gas and the halogen gases are diatomic: H_2, Cl_2, Br_2, and I_2. Using Avogadro's hypothesis and the gas density data, we now infer the atomic weights of these elements and from them that the hydro-halogenic acids have monovalent formulae, HCl, HBr, and HI. Or

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[10] An analogy to the overdetermination of two agreeing eyewitness accounts of some event might make this clearer. Each account provides support for the veracity of the other.

we can reverse the inference. From the monovalent formulae for the acids, we arrive at the diatomic molecular formulae of hydrogen and the halogens. These inferences can be represented as follows.

Hydrogen and the halogens are diatomic.

$$\frac{\text{gas density data}}{\text{Hydro-halogenic acids are monovalent.}}\quad \text{(Avogadro's hypothesis)}$$

Hydro-halogenic acids are monovalent.

$$\frac{\text{gas density data}}{\text{Hydrogen and the halogens are diatomic.}}\quad \text{(Avogadro's hypothesis)}$$

As before, we can depict these relations of support as an arch (shown in Figure 11.3).

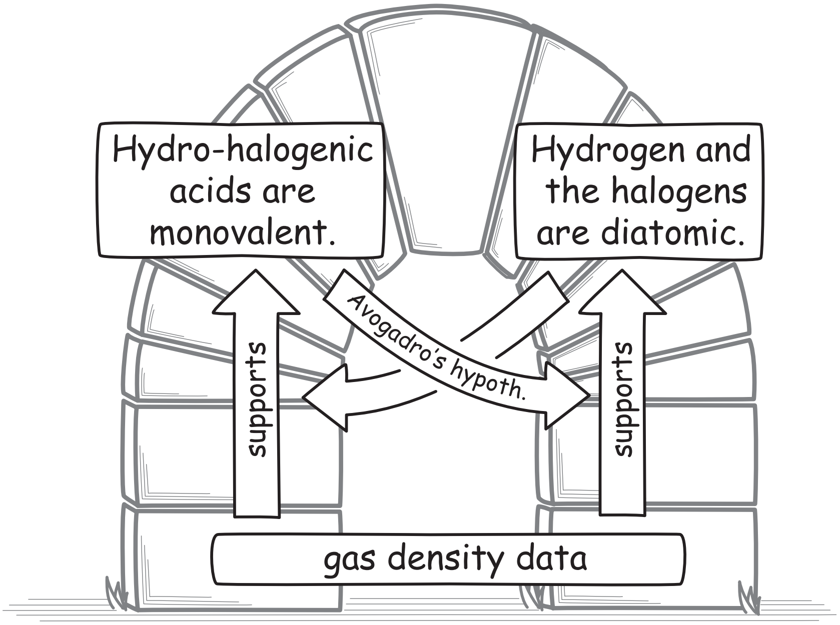

Figure 11.3. Mutual support of molecular formulae

The examples of mutual support are readily multiplied. For example, the diatomic composition of hydrogen and oxygen supports the molecular formula H_2O for water, and that formula supports the diatomic composition of hydrogen and oxygen. That is, we have the following inferences.

$$\dfrac{\begin{array}{c}\text{Hydrogen and oxygen are diatomic.}\\[2em] \text{gas density data}\end{array}}{\text{Water is } H_2O.}\ \text{(Avogadro's hypothesis)} \qquad \dfrac{\begin{array}{c}\text{Water is } H_2O.\\[2em] \text{gas density data}\end{array}}{\text{Hydrogen and oxygen are diatomic.}}\ \text{(Avogadro's hypothesis)}$$

These further relations of mutual support, and many more of greater complexity, combine to form a vaulted structure of many entangled relations of support.

These two sets of inferences illustrate how hypotheses function at this fine-grained level. Avogadro assumed that hydrogen gas is diatomic as a provisional hypothesis while he pursued his main hypothesis concerning gas density. It followed that water is H_2O. However, the diatomic hypotheses need further support from elsewhere before their provisional status can be discharged. That is now provided by the other inferences concerning the hydro-halogenic acids.

This support for the diatomic hypothesis was already included in Avogadro's original essay. There Avogadro[11] noted the essential fact that hydrochloric acid gas (then still called "muriatic acid gas") is formed by combining unit volumes of hydrogen and chlorine to form *two* volumes of hydrochloric acid gas. This is incompatible with a monatomic constitution for hydrogen and chlorine, for then we have

$$H + Cl \rightarrow HCl$$

$$\text{1 vol. hydrogen} + \text{1 vol. chlorine} \rightarrow \text{1 vol. hydrochloric acid gas}$$

---

[11] Avogadro (1811), as translated in Dalton, Gay-Lussac, and Avogadro (1893, 45).

If both hydrogen and chlorine are diatomic, however, then compatibility with the observed volumes is restored:

$$H_2 + Cl_2 \rightarrow 2HCl$$

1 vol. hydrogen + 1 vol. chlorine → 2 vol. hydrochloric acid gas

Hydrogen enters into many more compounds. As the molecular formulae of these further compounds are found, the original hypothesis of the diatomic character of hydrogen receives correspondingly more support. What was a provisional hypothesis initially becomes a fixed part of a much larger network of relations of mutual support. Eventually, the diatomic hypothesis cannot be discarded without also having to discard the full set of atomic weights and molecular formulae developed in modern chemistry.

The density of the relations of mutual support is greater than can be seen in the above analysis. Table 11.3 reports only some of Cannizzaro's density data. His full set is larger, and as a result the number of compounds is still larger,[12] which in turn provides many more relations of mutual support.

8. Mutual Support of Avogadro's Hypothesis and the Law of Dulong and Petit

The inferences of the previous section depend on Avogadro's hypothesis. It is the material fact that warrants them. What grounds do we have for Avogadro's hypothesis? When it was introduced, its support in background theory was meager. His original suggestion was dependent on rather fragile suppositions about the nature of Daltonian atoms: the hypothesis follows from the assumption that the volume of caloric associated with each atom is independent of the type of element.

Cannizzaro had urged much more convincingly that the very success of the inferences of the previous section is already strong support for the hypotheses:

> Now, since all chemical reactions take place between equal volumes, or integral multiples of them, it is possible to express

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[12] Crudely, if one has *n* elements, then the number of binary pairings of elements increases as n^2. Although not all pairing will produce a new compound, the possibilities are still growing faster than *n*.

> all chemical reactions by means of the same numerical values and integral coefficients. The law enunciated in the form just indicated is a direct deduction from the facts: but who is not led to assume from this same law that the weights of equal volumes represent the molecular weights, although other proofs are wanting? I thus prefer to substitute in the expression of the law the word molecule instead of volume. (1858, 13)

However, other proofs were not wanting. They could be found both in other parts of Cannizzaro's sketch (as we shall see in this section) and in relations to physical theories of gases (as we shall see in the next section).

His earlier analysis had suggested an atomic weight of 200 for mercury. However, Cannizzaro reported (1858, 22) that an incorrect atomic weight of 100 had been supposed elsewhere. To show the error, he now turned to a second method of determining atomic weights, by means of their elemental specific heats. The method is that of Dulong and Petit (1819), although they are not mentioned by name. To begin, Cannizzaro showed that the atomic weights found earlier for mercury, bromine, and iodine yield the constant atomic heat capacity required by Dulong and Petit. His data and computation are shown in Table 11.5.

Table 11.5. Cannizzaro's specific heat calculations for elements

Substance	**Atomic weight**	**Specific heat**	**Atomic heat capacity***
solid bromine	80	0.08432	6.74560
iodine	127	0.05412	6.87324
solid mercury	200	0.03241	6.48200

* This atomic heat capacity of roughly 6.8 differs from that of Dulong and Petit (1819) of roughly 0.38 since Cannizzaro's atomic weights are taken in units in which the atomic weight of hydrogen is 1, whereas Dulong and Petit's Table 2 takes the atomic weight of oxygen to be 1. They both measure specific heat with the same units, however.

Cannizzaro (1858, 22–24) then extended the method to compounds. He supposed that the heat capacity of each atom remained the same, even when the atom is in a compound. That meant that the atomic heat capacity of each atom in some molecule was to be calculated by the new formula

$$\text{specific heat of compound} \times \text{compound molecular weight} \,/\, \text{number of atoms per molecule} = \text{constant}$$

where the constant was once again the atomic heat capacity in the same system of units as used in Table 11.5.

Using that assumption, Cannizzaro (1858) sought the atomic weight of mercury from the measured heat capacities of four halides of mercury: HgCl, $HgCl_2$, HgI, and HgI_2. Assuming that these were the correct molecular formulae and using the atomic weights already determined, Cannizzaro arrived at the results presented in Table 11.6.

Table 11.6. Cannizzaro's specific heat computation for some mercury halides

Formula	Molecular weight	Specific heat	Number of atoms per molecules	Atomic heat capacity
HgCl	235.5	0.05205	2	6.128872
HgI	327	0.03949	2	6.45661
$HgCl_2$	271	0.06889	3	6.22306
HgI_2	454	0.04197	3	6.35146

Once again the computed atomic heat capacities of the elements in the compounds come out to be almost the same constant. They are also not too distant from the atomic heat capacity for the elements computed in Table 11.5. This affirms the correctness of the formula and atomic weights of Tables 11.5 and 11.6.

For my purposes here, the important point is that the two principal methods employed — Avogadro's hypothesis and the constancy of atomic heat capacity — agree in the atomic weights and molecular formulae that they deliver for the subset of the substances to which they both apply.

$$\text{Atomic and molecular weights and molecular formulae for mercury, chlorine, and mercury chlorides determined by Avogadro's hypothesis} = \text{Atomic and molecular weights and molecular formulae for mercury, chlorine, and mercury chlorides determined by atomic specific heats}$$

This agreement is another manifestation of the overdetermination of Cannizzaro's results. However, as before, it can be expressed in terms of relations of mutual support. The correctness of the results delivered by atomic heat capacities for mercury chlorides is supported by the results of applying Avogadro's hypotheses to the same substances. The converse relation of support holds as well. These mutual relations of support can be represented in the arch analogy shown in Figure 11.4.

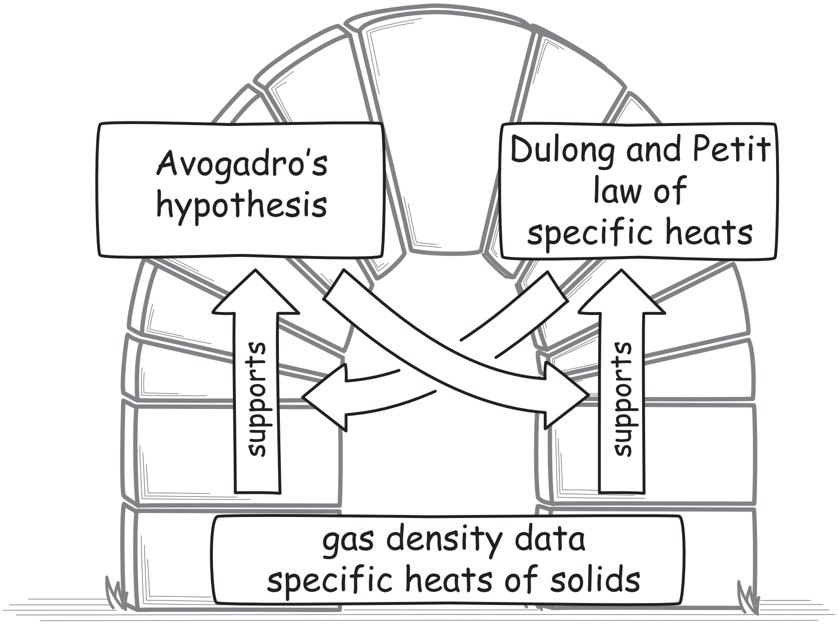

Figure 11.4. Mutual relations of support among Avogadro's hypothesis and Dulong and Petit's law

9. Mutual Support of Avogadro's Hypothesis in Chemistry and the Kinetic Theory of Gases

At the same time as Cannizzaro was using Avogadro's hypothesis to determine the correct atomic weights, a new science was emerging that would provide support for Avogadro's hypothesis. This was the kinetic theory of gases. It was advancing rapidly in the mid-1850s through the work of Krönig (1856), Clausius (1857), and Maxwell (1860). The theory sought to recover the mechanical properties of gases from the assumption that a gas consists of many molecules in rapid motion. In that theory, the pressure exerted by a gas on the walls of a containing vessel results from many collisions of the gas molecules with the wall. The heat energy of the gas corresponds to the kinetic energy of its molecules, and its temperature is proportional to the kinetic energy of each of its molecules.

An early and important achievement of kinetic theory was the recovery of the ideal gas law. According to it, the pressure P exerted by a volume V of gas at temperature T is given by

$$PV = n_m RT = nkT$$

The gas consists of n_m moles, that is, $n = n_m N$ molecules, where N is Avogadro's number, R is the ideal gas constant, k is Boltzmann's constant, and $R = Nk$.

This law already contains Avogadro's hypothesis. To see this, we merely rewrite the law as

$$n = PV/kT$$

It follows immediately that, if two samples of a gas have the same pressure P, volume V, and temperature T, then they contain the same number of molecules n.

It is possible, following Maxwell's later (1871, 295–96) development,[13] to isolate the assumptions used to arrive at Avogadro's hypothesis. First is a purely mechanical result about the pressure P exerted by n molecules of weight m:

$$(2/3)\ P = (1/2)\ nmv_{\mathrm{rms}}{}^2$$

where v_{rms} is the square root of the mean of the squared molecular velocities (rms = "root-mean-square"). Second is a result that Maxwell sought to prove in 1860: if two gases are at thermal equilibrium — that is, at the same temperature — then the mean kinetic energy of their molecules is the same. That is, they agree in the quantity $(1/2)\ mv_{\mathrm{rms}}{}^2$.

These two results are now applied to two volumes of gases of the same pressure, volume, and temperature. Respectively, they consist of n_1 and n_2 molecules, of molecular weight m_1 and m_2, and have rms velocities v_{rms1} and v_{rms2}. The condition of sameness of pressure entails

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[13] Curiously, Maxwell misattributes the hypothesis as the "Law of Gay-Lussac."

$$\text{(pressure)} \qquad (1/2)\, n_1 m_1 v_{\text{rms}1}^{\;2} = (1/2)\, n_2 m_2 v_{\text{rms}2}^{\;2} \tag{1}$$

The condition of thermal equilibrium entails that their kinetic energies are equal:

$$\text{(thermal equilibrium)} \qquad (1/2)\, m_1 v_{\text{rms}1}^{\;2} = (1/2)\, m_2 v_{\text{rms}2}^{\;2} \tag{2}$$

It follows immediately from (1) and (2) that

$$\text{(Avogadro's hypothesis)} \qquad n_1 = n_2 \tag{3}$$

asserts that the two volumes of gases hold the same number of molecules. I have labeled the three equations so that we can summarize this last inference as

$$\begin{array}{l}\text{(pressure)}\\ \text{(thermal equilibrium)}\\ \hline \text{(Avogadro's hypothesis)}\end{array}$$

Needless to say, chemists such as Cannizzaro were delighted with this affirmation of a core assumption of their analysis by physicists, especially given the doubts still prevailing about Avogadro’s hypothesis. Cannizzaro (1858, 4) mentions confirmation by Clausius (1857). He was far more buoyant, however, about the significance of this independent support for Avogadro’s hypothesis when he gave the Faraday Lecture at the Chemical Society on May 30, 1872:

> . . . [A]t the same time physicists, by considering the constitution of gases under a new point of view, have been brought, independently of chemical considerations, to the supposition of equal numbers of molecules in equal volumes of perfect gases, to which Avogadro and Ampère had previously been led by different modes of interpreting physical phenomena.
>
> Who can fail to see in this long and unconscious march of the science, around and towards a fixed point, the decisive proof of the theory of Avogadro and Ampère? A theory to which we have been led by setting out from different and even opposite points — a theory which has enabled us to forsee several facts which experience has confirmed, must be something more than a mere scientific fiction. It must indeed be either the

> actual truth, or the image of that truth, seen through media interposed between our intelligence and the reality. (947–48)

Lothar Meyer was one of the chemists who turned to Cannizzaro's views after the congress in 1860. He also reported with enthusiasm that the physicists had found independent support for Avogadro's hypothesis. In his more popular *Outlines of Theoretical Chemistry* (1892, 32–33), he noted that "this idea of Avogadro has received decisive confirmation as a result of the new development of the mechanical theory of heat." After a qualitative review of how the confirmation arises, he concluded that "this is one of the most powerful arguments in support of Avogadro's hypothesis. Its truth is now no longer disputed."[14]

The chemists were eager to show that Avogadro's hypothesis gains support from the kinetic theory of gases. The physicists, however, were happy to display the relation of support proceeding in the other direction: that is, *from* the chemists' establishment of Avogadro's hypothesis by chemical means *to* key results in the kinetic theory. Since Avogadro's hypothesis in physics had neither the central role nor the controversial history that it had in chemistry, the display of this reverse inference was less prominent in physics. However, it was present.

In its simplest form, it is as follows. The chemists were eager to report that (1) ("pressure") and (2) ("thermal equilibrium") entailed (3) (Avogadro's hypothesis). However, a quick inspection of the algebra relating (1), (2), and (3) shows that (2) could be inferred from (1) and (3). That is,

(pressure)

(Avogadro's hypothesis)

____

(thermal equilibrium)

This inversion of the chemists' inference was actually the one first reported by Clausius in his paper in 1857 on the kinetic theory of gases. Clausius first

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[14] Meyer's more technical text (1888, 23) gives more details of the reasoning sketched in equations (1)–(3) and concludes that ". . . Avogadro's hypothesis attains the same degree of probability which the kinetic theory of gases has obtained."

reported Krönig's (1856) derivation of the pressure formula (1) and then continued that

> If we apply this [(1) (pressure)] to simple gases, and assume that, when pressure and temperature are the same, equal volumes contain the same number of atoms — a hypothesis which for other reasons is very probable, — it follows that, in reference to their translatory motion, the atoms of different gases must have the same *vis viva* [kinetic energy]. (Section 11)

One might wonder why Clausius wanted to proceed in this reverse direction. The reason is that the result (2) ("thermal equilibrium") is not easy to attain by purely dynamic arguments concerning the collisions of molecules. Maxwell's (1860) paper offered a demonstration of it in conjunction with his derivation of the Maxwell velocity distribution for the gas molecules.

However, even Maxwell was happy to claim independent support for the results of the kinetic theory of gases from the research of the chemists. In his *Encyclopaedia Britannica* article "Atom," Maxwell (1875, 455–56) reviewed briefly the inference to Avogadro's hypothesis (3) from the assumptions (1) (pressure) and (2) (thermal equilibrium). He then noted that the same hypothesis[15] had been recovered by the chemists in their investigations of chemical combinations. He continued that

> This kind of reasoning, when presented in a proper form and sustained by proper evidence, has a high degree of cogency. But it is purely chemical reasoning; it is not dynamical reasoning. It is founded on chemical experience, not on the laws of motion.
>
> Our definition of a molecule is purely dynamical. A molecule is that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas. The result of the kinetic theory, therefore, is to give us information about the relative masses of molecules considered as moving bodies. The consistency of this information with the deductions

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[15] Once again misattributed to Gay-Lussac.

> of chemists from the phenomena of combination, greatly strengthens the evidence in favour of the actual existence and motion of gaseous molecules. (456)

These relations of mutual support are made possible by the logical interdependence of the relations (1), (2), and (3). Hence, Andrew Meldrum (1904, 24), adopting a skeptical stance, could review the logic of the demonstration of Avogadro's hypothesis in the kinetic theory and conclude that

> This puts the proof of Avogadro's hypothesis from the kinetic theory of gases in its true light. The hypothesis is but one out of two hypotheses which are contingent on one another. Either granted, the other can be proved.

10. Hypothesis No More

The appeal of Avogadro's hypothesis was that it provided an independent way to determine molecular weights and thereby defeat the circularity that had trapped Dalton. It was introduced provisionally in 1811 and faced what amounted to Dalton's claim of incompatibility with experiment. It languished for decades until Cannizzaro found it to be just the vehicle that he needed to determine the true molecular formulae and atomic weights.

At this point, Avogadro's hypothesis was being used as just the sort of provisional warrant for inference described in Chapter 2. It was indulged because of its great utility. Starting with the ratio of the densities of two gases, the hypothesis warranted an inference to the ratios of their molecular weights. It is the analog of the stone supported by scaffolding while the remaining stones of the arch are put in place.

The provisional status of the hypothesis had to be discharged, however, just as the scaffolding supporting the stones of an arch or vault eventually has to be removed. This burden was taken seriously. We have seen above how support for the hypothesis gradually accrued through the success of the overall project. Its results are overdetermined. That means that a part can become support for another part and conversely. Just this happened with the agreement of the results derived through Avogadro's hypothesis and through Dulong and Petit's law of specific heats. That allowed each to support the other. For Cannizzaro, the derivation of Avogadro's hypothesis from the kinetic theory of gases supplied what he called above the "decisive proof."

As the supports mounted, Avogadro's hypothesis lost its hypothetical character. It became a *rule*, a certainty of textbook chemistry. In his *Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics*,[16] Nernst (1904, 39–40) reported that ". . . Avogadro (1811) advanced a hypothesis which, after much opposition, has come to be recognized as an important foundation of molecular physics, as well as of all chemical investigations." Nernst proceeded to list four types of support. The hypothesis explains Gay-Lussac's result about combining volumes. It supplies molecular weights that agree with those derived from purely chemical investigations. It is derived independently from the kinetic theory of gases. It is able to deal successfully with a challenge from abnormal vapor densities.

In this chapter, I have traced the development and use of Avogadro's hypothesis as an illustration of how hypotheses are used in inductive inference in science. A second illustration could be provided by Dulong and Petit's law of specific heats. In brief, it warrants an inference from observed properties (specific heats of solids) to relative atomic weights. The law had a provisional status originally. One serious problem was that the constancy of the atomic heat capacity of the law was found to hold only in certain temperature ranges, notably failing for low temperatures. However, it gained support through its successful application. It also gained support from the new statistical physics that developed from the kinetic theory of gases. In brief, a simple model for a crystalline solid is a lattice of atoms held in place with spring-like forces. Statistical physics entails a constant molar heat capacity for such a system.[17] Perhaps the greatest triumph of the analysis came when Einstein (1907) explained the deviations from constancy of the molar heat capacity at low temperatures as deriving from the quantization of energy.

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[16] The German word is *Regel*: *Theoretische Chemie vom Standpunkte der Avogadro'schen Regel und der Thermodynamik*.

[17] Each atom has three translational degrees of freedom and three position degrees of freedom associated with the conservative forces holding it in place in the lattice. The equipartition theorem assigns mean energy $kT/2$ to each degree of freedom so that there is a mean energy $6kT/2 = 3kT$ per molecule or $3RT$ per mole. It follows immediately that the atomic heat capacity is the constant $3k$ and that the molar heat capacity is the constant $3R$.

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