

Looking in Freshman Lab III – Looking into *The Constitution of Bodies*:  
How does the supposition of particles help us to see?<sup>1</sup>

**LAVOISIER'S PROGRAM FOR GENERATING SEQUENCES OF EXPERIMENTS LEADING TO FACTS AND IDEAS, BASED ON MEASURING WEIGHTS (1789)**

In his “Preliminary Discourse”<sup>2</sup> Lavoisier lays out guidelines for how to arrive at knowledge in the physical sciences in general and in chemistry in particular. Students should follow the same course as “nature follows in the formation of a child’s ideas ... [T]heir ideas ought to be only the consequence, the immediate continuation (*suite*) of an experiment or observation” (0.6). According to Lavoisier the child’s first ideas, engendered by its sensations of its needs, are of objects appropriate for satisfying those needs. Insensibly over time, as a result of a sequence (*suite*) of such sensations and observations of suitable objects, the child generates a succession “of ideas, all bound to one another.” As with the child so in chemistry, if one were “an attentive observer,” one “could, up to a certain point, even find again” in the sequence of sensations, observations, and analyses “the thread and the linking (*enchaînement*) of those ideas, bound to one another, which constitute the totality of what we know” in chemistry (0.5).<sup>3</sup>

In accord with this account, we might say that Lavoisier will aim to show us a sequence of sensations and observations of experiments and a corresponding sequence of ideas, which he generated from them. In his case following “the course that nature follows” appears to consist: i) in linking “the facts and the truths of chemistry in the order most appropriate for facilitating the insight (*intelligence*)

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<sup>1</sup> A Wednesday Afternoon Lecture, delivered at St. John’s College, Annapolis, on April 13<sup>th</sup>, 2022.

<sup>2</sup> For all translations from the first chapters of Lavoisier, Antoine Lavoisier, *Oxygen, Acids, and Water*, H. Fisher, ed., C. Burke and M. Holtzman, trls. (Santa Fe: Green Lion Press, 2019) was consulted and often followed word for word. The references in parentheses are to chapter and paragraph number in that translation.

<sup>3</sup> *Dans notre première enfance nos idées viennent de nos besoins; la sensation de nos besoins fait naître l'idée des objets propres à les satisfaire, & insensiblement par une suite de sensations, d'observations & d'analyses, il se forme une génération successive d'idées toutes liées les unes aux autres, dont un observateur attentif peut même jusqu'à un certain point y retrouver le fil & l'enchaînement, & qui constituent l'ensemble de ce que nous savons.*

of beginners” and ii) in ensuring that the consequent ideas “derive immediately from the facts” and “from experiments and observations.” This arrangement would be “the natural linking of experiences and observations” “from the known to the unknown” (0.5, .6, .8, .10, .11).

As with the child our “sensations give birth to ideas” and “ideas ought to be only what ... follows immediately an experiment or observation” (0.6). Then we are not led “to draw conclusions which by no means derive immediately from the facts,” (0.8). By presenting the facts and ideas in this way, Lavoisier will enable us, if we are attentive, to find for ourselves the thread binding those ideas to one another. In coming to see this connection, we should be in a situation somewhat like that of Goethe’s reader—mentioned in the first lecture on looking in Freshman Laboratory—who can follow similarity through its transitions, by holding in her imagination a temporal sequence of appearances, until she can derive them from one another.

Based upon our experience in the lab up to this point, the interpretation of “derive immediately from the facts” is that our awareness of an experiment, whether we performed it or read Lavoisier’s account of it, gives birth to an idea in us. The experiment suddenly “makes sense” to us. But it wouldn’t have done so absent the foreknowledge we had acquired through experience. In this respect there is an analogy with Euclid’s sequence of propositions. A given proposition at the place where it is enunciated appears to derive immediately from the preceding propositions in the sense that given our familiarity with the earlier ones, in some cases, insight into the truth of the later one may be born in us as we read it.<sup>4</sup>

Following Lavoisier’s course involves, first, describing all the equipment used in each experiment and telling the step-by-step story of what was done and what occurred throughout. That story includes both observations and notes of the *qualities* of the substances involved in the experiment and of the

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<sup>4</sup> The analogy could be extended to include Euclid’s postulates. Just as Euclid needs to request that we admit them, if we are to have the sequence of insights generated by his propositions, so Lavoisier has to ask that we admit his “principle” “that, in every operation, there is an equal quantity of matter before and after the operation” (see below), as a condition for the possibility of ideas being born in us immediately in response to his experiments.

*weights* of all of those substances. Other relevant *quantities*, such as temperature, pressure, and volume of gases must also be recorded.<sup>5</sup> In addition, one experiment, even if repeated several times, would not be sufficient:

Chemistry furnishes two means for determining the nature of the constituent parts of bodies: composition and decomposition. When, for example, water and ... alcohol... are combined, creating ... eau-de-vie, we are entitled to conclude therefrom that eau-de-vie is composed of alcohol and water. But the same conclusion can be reached through decomposition, and we ought to be fully satisfied in chemistry only as far as we have been able to bring together both kinds of proof (3.3).

Much of Lavoisier's focus will be on concluding—from experiments in which he observes and measures especially the weights of the substances before and after the experiment—to a fact that a particular substance, having weight  $W$ , has been composed from two (or more) other substances, having respective weights  $w_1$  and  $w_2$ . For instance, after his first description of a pair of decomposition-recomposition experiments, Lavoisier writes that it “does not give us exact ideas about the proportion” of the weights of the component substances (3.14). So, he goes on to perform a further experiment in the same series, as a result of which one can determine that the one substance “diminishes by an amount in weight exactly equal to that by which [the other] is increased” (3.25).

In the course of describing the next set of experiments, having noted that “since nothing with weight passes through the glass,” Lavoisier writes, “we are entitled to conclude from them that the weight of whatever substance has resulted from this combination ... had to be the same as the sum of the weights” of the substances that were there before the combination (5.7).

He only later<sup>6</sup> states the “principle” upon which he bases this claim: “Nothing is created, ...; we may posit in principle (*poser en principe*) that, in every” experiment, “there is an equal quantity of matter before and after” the experiment, “and that there are only changes, modifications” of matter.<sup>7</sup> He is

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<sup>5</sup> In their papers at the end of *Equilibrium and Measurement*, Marotte and Gay-Lussac reported having done this.

<sup>6</sup> Antoine Lavoisier, *Oxygen, Acids, and Water*, H. Fisher, ed., C. Burke and M. Holtzman, trls. (Santa Fe: Green Lion Press, 2019), p. 57, note to 5.7.

<sup>7</sup> *Traité Élémentaire de Chimie*, T. 1<sup>er</sup> (Paris : Cuchet, Libraire, 1789), Ch. 13.

positing this principle underneath his feet, as it were, like a foundation on which to stand, in order to be able to investigate. A student<sup>8</sup> put it this way: “you have to find a foundation—which does not shift around as much as what you are trying to see—on which to discover something new amid what is shifting.” In this respect Lavoisier seems to be illustrating the following words of Socrates to Glaucon: “a soul ... is forced to seek on the basis of sup-positions (ἐξ ὑποθέσεων)” (*Rep* 510b). At a minimum Lavoisier has recognized that such a sup-posit-ion is a necessary condition for being able to learn anything from chemical experiments by keeping tally of the weights involved in them.

In spite of the support provided by the principle, however, just after having concluded to the sameness of weights before and after the above experiment, Lavoisier goes on to write that “no matter how conclusive this experiment may have been, it was not yet sufficiently rigorous,” due to the fact that it was “not possible to verify the weight” of the resultant compound. “We can only conclude to it by way of calculation, in supposing it equal to the weights of” the ingredient substances. “But however evident this conclusion may be, in chemistry and physics it is never allowable to suppose something that can be determined through direct experiments” (5.9). So, as long as all the weights involved in an experiment are determinable by some experiment, he does not rely on what he can conclude by standing on the principle he has posited. For physical scientists have “often supposed instead of concluding,” and “these suppositions, from one age to the next, ... acquire the weight of authority” (0.9).

We might say that when he *concludes*, Lavoisier encloses together all that he’s observed, measured, and noted throughout an experiment, in order to come to a *fact*, which would be the conclusion, or end, of the experiment. The act of concluding would then be a shift from taking “composition” as meaning the *process of putting (poser) two substances together (com)* during an experiment to viewing it as signifying the qualitative and quantitative *make-up, or composition*, of the outcome of an experiment.

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<sup>8</sup> Katherine Bates in Freshman Lab class, 2020.

For instance, from *having* made (*ayant fait*) a certain weight of white flakes out of a given weight of oxygen and another of phosphorous, one is entitled to conclude to the fact (*fait, factum*) that a certain weight of white flakes *is* made (*est fait*) of a given weight of oxygen and another of phosphorous. A decomposition experiment of unmaking the white flakes would allow concluding to the fact from an un-making. On this literal understanding of “fact,” it would not be correct to say it’s a fact that a given substance is elementary, since no making or unmaking has shown that to be the case.

However, in view of the principle, such an enclosing-together is possible only if the “walls” of the “enclosing room” let nothing come in or out, at least in the course of the experiment. That is, we would have to suppose something which could not be determined through direct experiments, namely, that “the great walls of the capacious world” are closed, in the sense that they cannot, “suddenly torn asunder, have burst apart”<sup>9</sup> and have allowed material substances to pass through them in either direction.

An example of *particular* ideas that derive immediately from a sequence of facts, each like the one in the above example of white flakes, might be the idea that this *kind* of white flakes, which is found to have various acidic properties (5.18), is a compound substance, or, to take another case, the idea that water is a compound substance, composed of hydrogen and oxygen, approximately in the ratio of 1g : 5.2555g (8.12). In Lavoisier’s usage such ideas are “consequences” that we “draw” (0.8). An example of a *general* idea would then be *compound substance*.

Perhaps, in the case of *compound substance*, it is as if we now not only were looking at *these* white flakes and remembering them as the concluding frame of a “film strip” of the just performed composition experiment, but also were seeing, as such a frame of a *generalized* film strip, any substance for which such a sequence of experiments had revealed that instances of it were made of two or more component substances.

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<sup>9</sup> Lucretius, *De rerum naturae*, VI.122-23: *divolsa repente maxima dissiluisse capacis moenia mundi*.

We may take Lavoisier's figures along with the accompanying text as a musical score in two different ways. In one way they tell us how to "play" each experiment in our imaginations, picturing the equipment, the ingredient substances, the sequence of steps and events, and the outcome. We may write down his numbers for height of mercury, volume of a container, and weights of substances and then do the calculations. Finally, based upon trust in his report and in his results, we may see that the burning of phosphorus, which we had considered an *alteration* of one substance, can be analyzed as the composition of one substance from two others.

Moreover, we may also see that having kept track of the change in volume and of the weights of the substances we can conclude to the *fact* that, for example, 45 gr of phosphorus and 69.375 gr of oxygen *composed* to make 114.375 gr of white flakes (5.7). Furthermore, based upon trust that Lavoisier has done many repetitions of this experiment, we can draw the consequence that such white flakes *are composed* of phosphorous and oxygen, roughly in the ratio 1 : 1.54 by weight. So, we now have the *idea* of such white flakes as a substance composed of two other substances in this weight ratio.

In the other way of taking the musical score, we "play" Lavoisier's score in our laboratory, with equipment similar to his. Here we trust only what we observe, that is, see and measure. Thus—it is hoped—we arrive at the same conclusion, consequence, and idea, but upon a different basis. In either way through his "score" Lavoisier has given any human being access to the facts and ideas he has generated. In that sense these latter are objective.

We also recognize that in addition to the resultant general insight that, in some cases, at least, apparent alteration might be analyzable as the composition or decomposition of substances, Lavoisier must have relied, in advance, upon three supplementary insights: 1) that this analysis could be most productively carried out by keeping track of the weights of the substances involved, 2) that a condition for the possibility of this keeping-track is the supposition of the principle that, in every operation, there is an equal quantity of matter before and after the operation, and 3) that another condition for the

possibility of this keeping-track is the supposition that the vessels used in the experiments are impermeable to the passage of the substances involved.

One way to imagine the generation of these insights would be as follows. Suppose we had left a piece of moistened steel wool in a jar with a top on it. When we return after several days, we notice not only the rusting of the steel wool but also a sensation of air being sucked into the jar as we unscrew the top. It would seem as if something had happened to the air, a reduction in amount, simultaneously with the rusting. Perhaps we could repeat this experience on a larger scale, using a bell jar, inverted over mercury, weighing some dry steel wool, before and after the period of several days, etc. If when we calculated we found a significant reduction in the amount of air and a significant increase in the weight of the steel wool, we might think that the rusting might be a combining of the steel wool with something in the air. We could then go on to figure out *how much* of a reduction by weight the air underwent and compare that with the weight gain of the steel wool (cp. CB 6).<sup>10</sup> We could note along the way that our calculations would not be valid, unless we had made Lavoisier's suppositions.

#### ***INTERLUDE: GAY-LUSSAC'S RECOLLECTION OF IDEALLY EXACT LIMIT-NUMBERS (1808)***

Before returning to Lavoisier, we shall glance at a paper<sup>11</sup> by Gay-Lussac, which is read about a week after Lavoisier is finished. Gay-Lussac generally proceeds in accord with the course recommended by Lavoisier, of beginning with observations and experiments, concluding from them to facts, and deriving ideas immediately from the latter. He did, however, introduce a new feature. The students sometimes claim that Gay-Lussac introduced mathematics into Lavoisier-style chemistry. What are they thinking of?

Gay-Lussac began by noting a contrast between the behavior of gases, on the one hand, and, on the other, that of liquids and solids, which had been revealed by the experimental work of Edme

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<sup>10</sup> *The Constitution of Bodies* (Annapolis, MD: St. John's College, Printed Spring 2021), p. 6. Future references to this manual will be noted "CB," followed by the page number.

<sup>11</sup> "Memoire on the Combination of Gaseous Substances with Each Other" (1808), CB 37-42, translation modified in places.

Mariotte. Mariotte showed that the same reduction in pressure, say, by  $2/3$ , applied to volumes of any two different gases, say, hydrogen and oxygen, would produce the same expansion of an increase by  $2/3$  in each of the two volumes, so that for an expansible container of a gas at any given fixed temperature the product of the pressure-number and the volume-number remains the same, as its pressure and volume vary. In contrast, as Gay-Lussac noted, “the same compression applied to all solid or liquid substances would produce a diminution of volume differing in each case” (CB 37).

Thus, while the variations in volume of liquids and solids, with changes in pressure, “have hitherto presented no regular law,” *independent* of the nature of the liquid or solid in question, the laws of the variations in volume of gases *are* “equal and independent of the nature of each gas.” This recognition probably led Gay-Lussac to the intuition that he could see something new by simultaneously narrowing his gaze to experiments involving only ingredient *gases* and shifting his focus from Lavoisier’s weight-experiments to *volume*-experiments. He writes that it is his intention to show thereby that gases “combine amongst themselves in very simple ratios” (CB 37).

Gay-Lussac thinks that the cause of this key difference between liquids and solids, on the one hand, and gases, on the other, is that the particles of the former are drawn close to each other by an attractive force, which is not present in the case of gases (CB 37). Imagining the particular attractions between particles makes for a complicated picture when we look at volumes of solids and liquids. In addition, it is a picture which we cannot actually see because we don’t know anything about the small-scale details of the attractions which would allow us to predict any determinate experimental outcome. So, in effect, Gay-Lussac “hears” attractions between particles as “noise.” That noise is silenced when he listens only to gases and their volumes. Then, Gay-Lussac “listens” to the regularity Mariotte had found to be independent of the natures of particular gases.

Gay-Lussac presents the facts from which his idea arose. He performed an experiment with a colleague in which they found an “exact ratio of 100 of oxygen gas to 200 of hydrogen gas for the

[volume] proportion of water.” This result led him to suspect “that the other gases might also combine in simple ratios” by volume. In the next four experiments he performed, Gay-Lussac found that in two of them the volume ratios of the combining substances were 100 : 100 and, in the other two, 100 : 200 (CB 38-39).

He goes on to offer “some fresh proofs, after which he states:

Thus it appears evident to me that gases always combine in the simplest proportions when they act on one another; and we have seen in reality in all the preceding examples that the ratio of combination is 1 to 1, 1 to 2, or 1 to 3 (CB 41).

He adds that when the result of the combination of two gases is a gas, its volume is also in a very simple whole-number ratio with that of each of the components (CB 41; cp. Avogadro, CB 43).

Analogous to Archimedes in his first treatise, Gay-Lussac has found a way to see ideal-exact limit-formations—in his case, to see, in chemical experiments, the unit and assemblages of units (*ἀριθμοί*). When he looked at the ingredient and resultant gas volumes in his and others’ experiments, “the thought occurred to him of another thing”—a unit or two units or three units—a thing not found in his sensory experience, something as if he knew it “from before.” Socrates would have said that Gay-Lussac “is recollecting that of which he grasped the thought” (*Ph* 72e-73cd). For instance, Gay-Lussac saw the volumes of nitrogen gas and oxygen gas that combined to form nitric acid gas as “reaching after” the One and the Two, respectively, but “in a condition of falling short” of them (*Ph* 74c-75b; italics added). Edmund Husserl would have claimed that the unit volumes that Gay-Lussac saw were examples of ideally exact limit-formations, like those encountered in Lecture II.<sup>12</sup>

The last three of Gay-Lussac’s proofs are based upon the results of experiments performed by Davy, in which the *weights* of the combining substances and of the resultant substances were given. In order to “hear” the corresponding *volumes*, Gay-Lussac must reduce the weight ratios in each case to volume ratios. He reverses Lavoisier’s procedure (see, for example, Lavoisier 3.25) for translating a

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<sup>12</sup> Husserl, *op. cit.*, pp. 22-23; *The Crisis of European Sciences and Transcendental Phenomenology: An Introduction to Phenomenological Philosophy*, tr. D. Carr (Northwestern: 1970), pp. 25-26.

measured diminution in volume into the corresponding diminution in weight. Gay-Lussac divides the observed weights by the known densities of the gases in order to determine the volume ratios of the experiments.

For instance, Gay-Lussac then heard, or, to shift metaphors, saw, the volumes of nitrogen gas and oxygen gas that combined to form three nitrogen compounds as “reaching after” the One and the Two, respectively, but “in a condition of falling short” of them (Ph 74c-75b; italics added)—like a chalk mark reaching after the Straight. For the actual experimental results for these three compounds were that the nitrogen volume was to the oxygen volume as - 2 : 0.99 and 1 : 1.089 and 1 : 2.047, respectively.

Gay-Lussac comments:

The first and the last of these [ratios] differ only slightly from [2 to 1], and [1 to 2]; it is only the second which diverges somewhat from [1 to 1]. The difference, however, is not very great, and is such as we might expect in experiments of this sort; and I have assured myself that it is actually nil (CB40).<sup>13</sup>

This assurance suggests that hearing, or seeing, ideal-exact volume-units can allow us to *correct* values arrived at by measuring weights. In an application of his new approach—without having to perform any experiments, but simply by viewing a weight-experiment, through the lens of volume—Gay-Lussac corrected the accepted density of carbonic acid gas.

Cruikshanks had experimentally determined its value to be 0.9569. When Gay-Lussac looked at the volume results of an experiment by Berthollet, in which 200 carbonic oxide + 100 oxygen → 200 carbonic acid, he concluded that the relation of the densities is  $d_{\text{coxide}} = d_{\text{cacid}} - \frac{1}{2}d_{\text{oxy}}$ . Since the latter two densities had been well established<sup>14</sup> by many experiments as 1.5196 and 1.1036, respectively, Gay-Lussac saw that the density of carbonic oxide gas *had to* be .9678. The elimination of weight-noise—

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<sup>13</sup> “Reducing these proportions to volumes we find—

|               | Nitrogen | Oxygen |
|---------------|----------|--------|
| Nitrous oxide | 100      | 49.5   |
| Nitrous gas   | 100      | 108.9  |
| Nitric acid   | 100      | 204.7  |

The first and the last of these proportions differ only slightly from 100 to 50, and 100 to 200; it is only the second which diverges somewhat from 100 to 100.”

<sup>14</sup> CB 41, n. 17.

each experiment involving a particular kind of chemical reaction yields slightly different weight relations—allowed Gay-Lussac to hear the ideal-exact sound of the volume, by which he could correct, in the second decimal place, the previous value, which depended on weight-experiments.

In his experiments Lavoisier was measuring magnitudes, as dealt with by Euclid in Book V of *The Elements*. Now Gay-Lussac is counting numbers, which Euclid treated in Book VII. Gay-Lussac has, thus, opened the realm of chemistry to include the discrete as well as the continuous. This new seeing of units and numbers of units in chemistry may be what the students glimpsed when they said that Gay-Lussac had introduced mathematics into chemistry.

### **LAVOISIER AND THE ROLE OF IMAGINATION (1789)**

We return to Lavoisier in order to consider the role of imagination in chemistry. In accord with his aim to rely on what we observe and conclude when we perform experiments involving weighing, Lavoisier wanted to avoid being led astray by the imagination. With respect to the things we want to come to know, he presents “imagining them” as an *alternative* to his program of “observing them” (0.41). Moreover, Lavoisier specifically warns us of the dangers of the imagination, “which constantly tends to carry us beyond the true ... [and] invite[s] us to draw consequences which by no means derive immediately from the facts” (0.8). Especially “in the case of things that can be neither seen nor felt, it is of the utmost importance to guard against the deviations of the imagination, which always tends to soar beyond the true and which has considerable difficulty in confining itself within the narrow circle that the facts draw around it” (1.10). Thus, what we imagine, in that it leads to consequences not immediately derivable from the facts, stands squarely opposed to ideas, which do so derive by insight.

For instance, while Lavoisier spoke of particles, he did not go on to imagine what they might be like in detail. “Lavoisier’s ‘particles’ are simply small portions of a substance, not necessarily either the

smallest possible portions or even of uniform size.”<sup>15</sup> He drew no consequences from any suppositions about the nature of the assumed particulate nature of matter.

Nevertheless, under certain conditions, he does draw tentative consequences, in an interesting way, from imagining the *behavior* of particles, namely, their separation by warmth (1.1):

It is understandable that since they are ... continually invited (*sollicitées*) by warmth (*chaleur*) to separate from one another, the particles of bodies would have no connection among themselves and that there would be no solid body if they were not held back by another force that would tend to bring them together and, as it were, to link them to one another...

And so the particles of bodies can be *considered as* obeying two forces, one repulsive and one attractive, between which they are in equilibrium (1.3 & .4; italics added).

This imagined picture—which involves considering-as—does not seem to acquire the status of a consequence that Lavoisier would or could legitimately draw. On the one hand, he imagines “a real, material substance, an exceedingly subtle fluid that insinuates itself throughout the particles of bodies and separates them.” Yet the grounds for speaking of it are that the phenomena of bodies’ changing state as they are warmed up or cooled down are “difficult to understand ... without admitting that they are the effects” of such an imagined substance. So, that substance would appear to be a supposition of a different kind than his sup-position of the principle mentioned above as a foundation for the chemist to stand on. He states: “Even supposing that the existence of this fluid were an hypothesis, we shall see in what follows that it explains the phenomena of Nature quite felicitously” (1.7). “Explaining” must be distinguished from concluding or drawing a consequence. The hypothesis of a subtle fluid would help us to *imagine* a picture of what might be going on “*beneath*” or “*inside*” those things we can actually see and measure in the lab.

“Since the sensation that we call warmth is the effect of the accumulation of” this imagined substance, “whatever it may be,” Lavoisier names it, as being the cause of warmth (Lat. *calor*), “caloric.” Yet in the same paragraph, he assures us that

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<sup>15</sup> Lavoisier, *Op. cit.*, p. 13, note to 1.1.

rigorously speaking we are not even obliged to suppose that caloric is real matter; it suffices ... that it be a repulsive cause of any sort that separates the particles of matter, and so we may view its effects in an abstract and mathematical way (1.8).

Lavoisier seems to be inviting us to fantasize anything whatsoever as long as it helps us to imagine what could be happening when bodies change state with changing temperature. Ultimately, whatever we imagine will have to agree with any empirically established mathematical functions that express change of matter as a function of temperature, as well as with the ideal gas law, which we have already encountered in Ch. VI of *Measurement and Equilibrium*.<sup>16</sup>

While the above account “determines the idea that we ought to attach to the word ‘caloric,’” Lavoisier wishes to “give correct ideas of the manner in which caloric acts on bodies” (1.10). In the course of doing that, he reports that caloric “plays in some way the role of solvent” in the case of every gas, in that it “tends to separate” the particles of all bodies, opposing their attraction (1.28 & 1.30).

Since, in dealing with abstract things, we should not over-rely on the help of sensible comparisons, Lavoisier offers *several* ways in which we may form a picture of these opposing tendencies: “we picture (*figure*) to ourselves,” *now* a vessel filled with little lead balls into which a very fine powder ... has been poured,” *now* pieces of different kinds of wood, submerged in water (1.31-.34). This use of the imagination to picture sensible comparisons clearly does not risk carrying us beyond what is true.

These comparisons may call to mind that earlier in the lab Theophrastus, Aristotle, and Harvey analogized the working of plant parts or animal organs to that of products of art. In those cases, though, we could actually look at the part in question and see the similarity in it, somewhat as we can see a particular expression in a face. However, the substance that Lavoisier is looking at in his imagination bears no visible trace of anything expressive of lead balls or pieces of wood. We are imagining them *alongside* or *inside* the phenomena we are looking at in the lab. Putting it that way is suggestive of the

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<sup>16</sup> *Measurement and Equilibrium* (Annapolis: St. John’s College, printed Fall 2020), pp. 128-30.

transparencies that Archimedes and Pascal used to bring about an essential seeing in the lab. In the case of Lavoisier, however, what we fantasize allows us to picture what could be happening below the level of appearances that could account for them.

Lavoisier's final discussion of caloric in Ch. I is based on the twin suppositions of the existence of particles of matter and of particles of caloric. Having stated that caloric is both an elastic fluid and the cause of the elasticity of bodies, Lavoisier poses the Socratic question, "what is elasticity"? It is the property that "the particles of a body have of moving away from one another when they have been forced to draw near," a "tendency ... that manifests itself even at very great distances." That air can be highly compressed presupposes that particles of air are already quite far from each other. But we know from experiments that they tend to move even further away from each other. The only way to explain that effect is by "supposing that the particles make an effort in every direction to separate" (1.44).

There may, in fact, be such a real repulsion between the particles of elastic fluids, since it would be consistent with the phenomena, but Lavoisier thinks that such "a repulsive force ... is difficult to conceive" (1.45). Trying out another supposition leads him, finally, to the thought that

the separation of the particles of bodies by caloric is due to a combination of different attractive forces, and it is the result of these forces that we seek to express ... when we say that caloric communicates a repulsive force to the particles of bodies. (1.46)

At the very least we may say that Lavoisier's imagining of caloric did not lead him to cling to a *fixed* supposition of what is going on "behind" or "inside" the things we can see with our eyes. He is flexible in the ways in which he imagines the supposed action of caloric. He keeps his eye, simultaneously, both on the phenomena and on the supposed separation of gas particles with increasing warmth. He encourages us to play around with different suppositions, without mistaking any of them for "the true" picture.

## ***DALTON'S SUPPOSITION OF ULTIMATE PARTICLES, OR ATOMS, AND MAKING USE OF THEM (1808)***

(NOTE: The terminology used in the discussion of Dalton and his followers will be a translation into a more modern terminology, established by Cannizzaro,<sup>17</sup> in which “*atom*” refers to a single hitherto un-cuttable, or *in-divisible* particle, which may or may not be attached to other particles by attraction. And “*molecule*” refers to a *separate* particle, one not joined to other particles by attraction; it may consist of one atom or of many.)

Dalton's first great insight is that “we have hitherto made no use of” the pre-supposition that each material thing is made up of a great number of atoms. There are two different uses that Dalton has in mind, first, using experiments to make the particle picture more determinate and, second, using the particle picture to propose and correct experiments.

First, chemists have not “inferred” from their experimental determination of the relative weights of the ingredient and resultant substances to “the relative weights of the ultimate particles or atoms of the [different kinds of] bodies” involved (CB 20-21). If they had done so, they could have seen i) *how many* atoms of each kind of elementary substance were in molecules of various compounds, ii) the *relative weights of different elements in those compound molecules*, and iii) the *relative molecular weights* of the various compounds (CB 21).

The second use that chemists have not made of atoms is dependent on the first. For since the chemists had no accurate, determinate atomic-molecular picture, they had no way of *using* particles “to assist and to guide future investigations, and to correct their results” (CB 21). His claim is analogous to saying that until he *worked out* the mathematics of the motions of heavenly bodies, Ptolemy could not predict the date of a solar eclipse.

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<sup>17</sup> “The conception of [Avogadro and Ampère] contains nothing contradictory to known facts, provided that we distinguish, as they did, molecules from atoms; provided that we do not confuse the criteria by which the number and the weight of the former are compared, with the criteria which serve to deduce the weight of the latter; provided that, finally, we have not fixed in our minds the prejudice that whilst the molecules of compound substances may consist of different numbers of atoms, the molecules of the various simple substances must all contain either one atom, or at least an equal number of atoms” (CB 53).

Dalton's second great insight was that it was *impossible* to make any use of the presupposition of atoms as long as chemists were thinking of molecules of, say, water, as being of diverse weights. Just as Lavoisier could not make any real use of experiments, unless he sup-posed that there is an equal quantity of matter before and after each experiment, so, too, experiments won't be able to show anything about the relative atomic makeup of substances' molecules, unless we sup-pose<sup>18</sup> that

the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, &c. In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen, &c.... (CB 21).

We might say that Dalton has introduced into the world of *presupposed*, imaginary atoms the supposition of *ideally exact* atoms. So, all ingredient and resultant substances will now be seen, at the same time, in a double vision--both as weights, continuous magnitudes, in the lab and as atom-units of different kinds, discrete multitudes, in the particle world. In this respect his seeing is like that of Euclid and of Archimedes' first treatise. The difference, though, lies in that things—in particular, things in the material world—are thought of as “reaching for” and “falling short of” (*Phdo* 75ab) the exact limit-formations of Euclid and Archimedes, whereas Dalton thinks of atoms as (tiny, invisible) things that make up the actual material world. Thus, Dalton is not led to think of his homogeneous particles by what he sees in the lab, in the way that Cebes might be led to think of Simmias by a picture of him or by a face glimpsed in a crowd. Dalton isn't viewing the substance in the lab as an *image* (*εἰκών*) of a number of atom-units. He might, while looking at the particular substance, be supposing a huge number of identical molecule-units. But the substance could not be said to image them. Moreover, at least so far, the number of identical molecule-units would also be quite indeterminate.

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<sup>18</sup> Dalton's word is “conclude.” The grounds for his conclusion are that “from what is known, we have no reason to apprehend a diversity in these particulars” and that “it is scarcely possible to conceive how the aggregates of dissimilar particles should be so uniformly the same.” For it is not conceivable to Dalton that, due to the great number of atoms in any body weighable in the lab, it could be impossible for chemists to distinguish between the sameness of all atoms of each element and a distribution of the specific gravity of each element that is represented graphically in the shape of a bell-curve.

How well does Dalton execute his program and use his supposition of homogeneity? He shows how chemists could go about determining the atomic makeup of molecules and relative atomic weights of elementary substances and relative molecular weights of compound substances. First, in order to guide chemists in deducing such “conclusions” from experimental “facts already well ascertained,” he proposes “general rules” like the following:

- 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.
- 2d. When two combinations are observed, they must be presumed to be a binary and a ternary. (CB 22)

The first two pairs of conclusions that he goes on to mention are “1st. That water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1 : 7, nearly” and “2d. That ammonia is a binary compound of hydrogen and [nitrogen], and the relative weights of the two [elementary] atoms are as 1 : 5, nearly...” (CB 22). He accompanies his statement of the conclusions with “arbitrary ... signs chosen to represent” the atoms and their composites, as shown in Figures 1a & b PLATE IV (CB 24-25).

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

| Fig. |                                   | Fig. |                       |
|------|-----------------------------------|------|-----------------------|
| 1    | <b>Hydrog., its rel. weight 1</b> | 11   | <b>Strontites, 46</b> |
| 2    | <b>Azote, 5</b>                   | 12   | <b>Barytes, 68</b>    |
| 3    | <b>Carbone or charcoal, 5</b>     | 13   | <b>Iron, 38</b>       |
| 4    | <b>Oxygen, 7</b>                  | 14   | <b>Zinc, 56</b>       |
| 5    | <b>Phosphorus, 9</b>              | 15   | <b>Copper, 56</b>     |
| 6    | <b>Sulphur, 13</b>                | 16   | <b>Lead, 95</b>       |
| 7    | <b>Magnesia, 20</b>               | 17   | <b>Silver, 100</b>    |
| 8    | <b>Lime, 23</b>                   | 18   | <b>Platina, 100</b>   |
| 9    | <b>Soda, 28</b>                   | 19   | <b>Gold, 140</b>      |
| 10   | <b>Potash, 42</b>                 | 20   | <b>Mercury, 67</b>    |

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat, its relative weight = ..... 8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen = 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen = 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen = 6
25. An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen = 12

Figure 1a

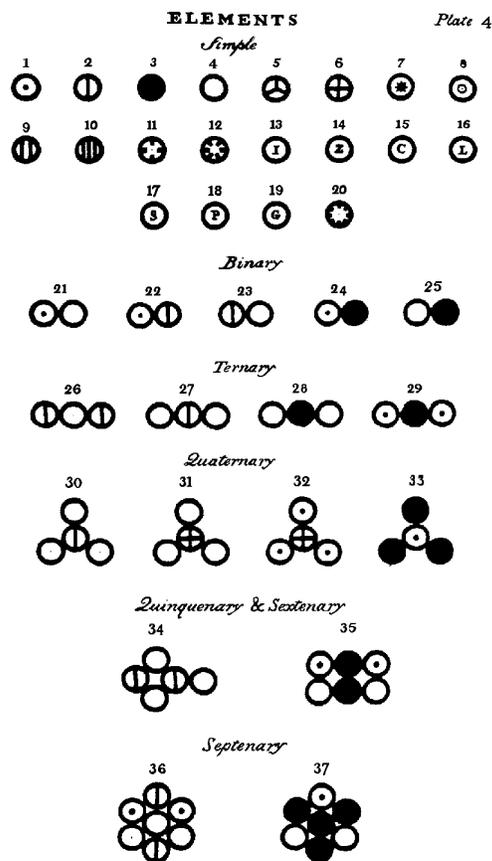


Figure 1b

Hence—*given* Lavoisier’s principle and the results of his and other chemists’ composition and decomposition experiments, in which the weights of the bodies involved were ascertained—*if we presuppose* atoms and *suppose* them to be homogeneous in Dalton’s sense and *apply* his heuristic general rules, *then* both the relative weights of many atoms and the numbers of them in the molecules of various compound bodies do follow as “conclusions.” In this way Dalton’s vision resembles that of Ptolemy.<sup>19</sup>

The manual directs our attention to a conclusion that follows *directly* from Dalton’s supposition, without any need to apply his “general rules” to *particular* experiments. There was a debate, 15 years

<sup>19</sup> This is true, provided Ptolemy’s mathematical apparatus be interpreted simultaneously as showing that for which the motions of the heavenly bodies reach while falling short of it and that which enables the astronomer to say in advance where a given body will be in the sky on a given date. But there is a difference between the two visions, unless Ptolemy be interpreted as considering his cycles and epicycles to be invisible material bodies.

after Lavoisier's *Treatise*, between the chemists Berthollet and Proust as to whether or not substances react and combine in *definite* and *fixed* weight ratios. For example, if 2 gm of substance A reacts with 16 gm of substance B, then 2½ gm of A will react with 20 gm of B, and so on, so that the ratio of the weight of A to the weight of B is 1 : 8 in every case (CB 33). Lavoisier had pre-supposed that this was so, but Berthollet claimed to have demonstrated experimentally that compositions of two substances occur "in all ratios, up to [an] extreme value which ... varies with the temperature." Proust, though, claimed to have found "fixed ratios" in his experiments (CB 104).<sup>20</sup>

*On the basis of Dalton's supposition, Proust must be correct.* For if every molecule of water is made of the *same* number of *homogeneous* oxygen atoms and of the *same* number of *homogeneous* hydrogen atoms, then in a given amount of water, say, one million molecules, the weight ratio of oxygen to hydrogen *must* be the ratio –

$$\frac{(\text{atomic weight of oxygen})(\text{number of oxygen atoms per water molecule})(1,000,000)}{(\text{atomic weight of hydrogen})(\text{number of hydrogen atoms per water molecule})(1,000,000)}.$$

Whether or not Dalton's "general rules" are "adopted as guides," the ratios always have to be the same, on the basis of his supposition. So, in imitation of Gay-Lussac's correction of Cruikshank's experimental determination of the density of carbonic oxide gas (CB 41), Dalton could *correct* Berthollet's empirical claim. This might be like telling an astronomer, who reported having seen an eclipse of the moon between 10:05 PM and 2:44 AM on a given night, that she must have fallen asleep for an hour and ten minutes, because it had actually begun earlier, according to our mathematical calculations.

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<sup>20</sup> The manual adds a second necessary conclusion that follows directly from Dalton's supposition of homogeneity, without reference to his general rules, namely, the Law of Multiple Combining Proportions: "From Dalton's doctrine of atoms it follows that whenever two elements unite in more than one [ratio] there will be small whole number ratios among the [weights] of the first element that combine with a fixed [weight] of the second—whole number ratios because the various [weights] of the first element that combine with a fixed [weight] of the second must always represent whole numbers of atoms; and small because according to Dalton the most prevalent combinations may be presumed to be those between the least numbers of atoms" (CB 30).

### **AVOGADRO'S "ONLY ADMISSIBLE" HYPOTHESIS ABOUT SIMPLE GASES (1811)**

Avogadro saw that in order to use particles, as Dalton wished to do, chemists needed to eliminate Dalton's guesswork, that is, his arbitrary, general rules, as heuristic "guides" (CB 22) to determine the relative number of particles in compounds (CB 46). Avogadro's key insight is that it is necessary to provide "Dalton's system ... with a new means of precision through" connecting it with Gay-Lussac's discovery of small whole-number ratios of ideal-exact unit-volumes of gases (CB49). Then, still looking through the Daltonian lens, Avogadro will be able to see the particles more clearly.

To review where we are at this point: we are supposing that all atoms of any *given* element are identical, that all molecules of any *given* compound are identical, and that at STP all boxes of any *given* gas contain the same number of molecules. The density of most gases have been determined by experiment, as described above. Finally, as Gay-Lussac had shown, gases combine in very simple whole-number ratios by volume.<sup>21</sup>

Avogadro, with all of that in mind, realizes that "viewing" Daltonian particles "through" Gay-Lussacian boxes gives him a way to bring the Daltonian picture into better focus. It makes particles, as it were, into learnables (*μαθήματα*), about which one can learn, apart from doing experiments. He sees an apparent necessity in the relationship between "the relative number of particles which combine and ... the number of composite particles which result," on the one hand, and, on the other, "the ratios of the quantities of substances in compounds."<sup>22</sup> Avogadro believes that introducing a mathematics of numbers of particles and boxes will enable him "to confirm or rectify" Dalton's results (CB46).

This insight immediately leads him to another: "It *must then* be admitted (*Il faut donc admettre*) that very simple ratios [or relations] *also* exist between the volumes of gaseous substances and the

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<sup>21</sup> "The combinations of gases always form in very simple ratios (*rappports*) by volume, and that when the result of the combination is a gas, its volume is also in a very simple ratio with that of [each of] its components" (CB 43).

<sup>22</sup> "The ratios of the quantities of substances in compounds would *appear to be able to depend only* on the relative number of particles which combine, and on the number of composite particles which result" (CB 43; italics added). Avogadro's word "quantities" may cover both weights and volumes. If quantities—weights or volumes—of two gases combine to form a third, the ratios of the first to the second to the resultant "would seem to be able to depend only on the relative number of particles" in the first, the second, and the resultant volumes, respectively.

numbers of simple or compound particles which form them” (CB 43; italics added). Getting mileage out of the simplicity of the relationship between lab experiments involving boxes of gases and pictures of the numbers of atoms or molecules composing gases would be easiest if it turned out that, for *all* gases at STP, the number of particles per box were identically the same. For then the weight ratio of two boxes, or equivalently, the densities of two gases, would at once also show the relative weights of the two gases in the compound molecule. In a way, the boxes would be acting like magnifying glasses, or lenses.

In order to see that, consider Figure 2. Suppose that it turned out that for every gas there were

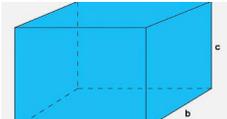
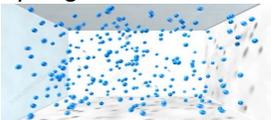
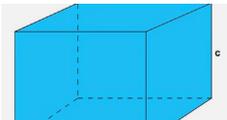
| DALTON's <i>supposed</i> molecules   | AVOGADRO's lens to 'see' weight of Dalton molecules in Gay-Lussac boxes  | GAY-LUSSAC's <i>unit boxes</i> of gases weighed in the lab  |
|--|--|---|
| 1 imagined molecule of oxygen<br>     | 1 box of 100 imagined molecules of oxygen<br>    | 1 actual box of oxygen<br>  |
| 1 imagined molecule of hydrogen<br> | 1 box of 100 imagined molecules of hydrogen<br> | 1 actual box of oxygen<br> |
| $\frac{\text{Weight of 1 oxygen molecule}}{\text{Weight of 1 hydrogen molecule}} =$                                    | $\frac{1/100 \text{ of weight of 100 oxygen molecules}}{1/100 \text{ of weight of 100 hydrogen molecules}} =$                      | $\frac{\text{Weight of 1 box of oxygen}}{\text{Weight of 1 box of hydrogen}}$                                   |

Figure 2

exactly 100 molecules of it in one Gay-Lussac box. Then the experimentally determined weight ratio of a box of oxygen to a box of hydrogen (see left column) would have to be the same as the supposed weight ratio of one oxygen molecule to one hydrogen molecule (see right column), because the lens shows that the former ratio is the same as the ratio of the weight of 100 oxygen molecules to 100 hydrogen molecules.

But could Avogadro *learn* the relative numbers of particles per box of two different ingredient gases that result in a compound gas? He claims that the hypothesis just stated in the previous paragraph, “which presents itself first in this connection,” is not only the first to present itself and the simplest but also “the hypothesis ... which even appears to be the only admissible one” (CB 43).

How could he have learned that no other hypothesis could be admitted? Avogadro devotes most of the rest of the first paragraph to hypotheses about the possible distances of gas particles from each other.<sup>23</sup> But he summarizes these speculations by stating that “in our present ignorance of the manner in which this attraction of the particles ... is exerted, there is nothing to decide us *a priori*” for or against any one of these hypotheses.

However, he concludes that “the hypothesis we have just proposed relies on that simplicity of ratio between the volumes of gases in the combinations, which *would appear to be unable to be explained otherwise*” (CB 44; italics added). In other words, the *necessity* of the simple relationship between experimental boxes and numbers of particles—itsself, the necessary result of bringing Gay-Lussac and Dalton together—forces him to reject any hypothesis other than the simplest one.<sup>24</sup>

Dalton’s first “object” had been to make “use of” the presupposition of particles, in order to determine the relative weights of particles and the composition of composite particles (CB 20-21). Avogadro can claim that relying on his new lens, or hypothesis, he was able to “see,” in all volume experiments involving gases, the relative numbers of ingredient and resultant molecules involved, and so, also, their molecular weights. In this way his first hypothesis makes the supposed, invisible realm distinctly and determinately visible.

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<sup>23</sup> If you think of gas molecules as floating freely, unattracted by each other, then there is no reason to think that two boxes of different gases would contain different numbers of particles.

<sup>24</sup> In order to see that Avogadro’s hypothesis is the only way to arrive at this simplicity, one would have to work through all the known experimental results involving gases, while trying out different numbers of molecules per box. For each trial the supposed molecular composition of each gas would have to remain the same in all reactions. In doing this Avogadro seems to have seen that the simple relations follow only from one hypothesis about the relation between number of molecules per box, namely, that a box of any gas contains the same number of molecules.

### **CANNIZZARO'S DETERMINATION OF A TABLE OF MOLECULAR AND ATOMIC WEIGHTS (1858)**

Avogadro's hypothesis lets us "see" the relative molecular weights of gases, "even before their composition is known," since the molecular weights *have* to be proportional to the experimentally determined densities of the gases, as we've just seen. Cannizzaro's first insight is that instead of focusing on particular reactions and particular compounds "it is useful" (*giova*) to *view all* the elementary and compound gases *together* and, in particular, "to refer" the molecular weights (or, densities) of all gases to that of the lightest gas (CB 56), namely, hydrogen.

He sets up a ratio scale of relative molecular weights. Since it is a scale of relative, not actual, weights, the weight-number to assign to the smallest molecule is completely arbitrary. With later considerations in mind, he assigns to hydrogen the weight-number 2 on the scale, rather, than 1. All other molecular weights will be determined by their ratios to that of hydrogen = 2. Then looking at unit volumes through Avogadro's lens, Cannizzaro can make a table of the molecular weights of all gases, relative to this unit.

For instance, in order to determine the relative molecular weight of any gas, all he has to do is look up the density—that is, the weight per box—at the same temperature and pressure, of hydrogen and of the gas in question. Since

$(\text{molecular weight of gas } x) / (\text{molecular weight of hydrogen, viz., } 2) = (\text{density of gas } x) / (\text{density of hydrogen}),$   
he has only to multiply the density of gas *x* by the density of hydrogen gas and then to multiply that by 2. And he has determined the molecular weight of the gas.

Cannizzaro list the molecular weights of some gases in the right-hand column of Figure 3 (CB 56).

| Names of Substances  | weights of the molecules referred to the weight of a whole molecule of Hydrogen taken as unity. | weights of the molecules referred to the weight of half a molecule of Hydrogen taken as unity. |
|----------------------|---|--|
| Hydrogen             | 1   | 2  |
| Oxygen, ordinary     | 16  | 32   |
| Oxygen, electrised   | 64  | 128  |
| Sulphur below 1000°  | 96  | 192  |
| Sulphur* above 1000° | 32  | 64   |
| Chlorine             | 35.5  | 71   |
| Bromine              | 80  | 160  |
| Arsenic              | 150   | 300  |
| Mercury              | 100   | 200  |
| Water                | 9   | 18   |
| Hydrochloric Acid    | 18.25   | 36.50†   |
| Acetic Acid          | 30  | 60   |

Figure 3

Cannizzaro's second insight is that we must clearly distinguish between the criteria used just now to arrive at the weights of all the gas *molecules* from those that yield the weights of the *atoms* and the numbers of them in the molecules (CB 53). Avogadro—in the course of using his “lens” for looking through equal boxes, at same temperature and pressure, in order to see molecular weights—had been forced, in considering the composition of water, to recognize that a molecule of elementary oxygen contains *two* oxygen atoms.

To see this let's suppose, again, that there are 100 molecules of any gas in one box. In the composition experiment, one box of oxygen combined with two boxes of hydrogen to form *two* boxes, that is, 200 molecules, of water. If the oxygen molecule consisted of only one oxygen atom, there'd be only 100 oxygen atoms available for forming 200 water molecules—not enough!

So, Avogadro “supposes” that the molecules “of any simple gas whatever,” like oxygen, are “not formed of one single” atom, “but result from a certain number of these molecule joined together in a single one” (CB 45). He also supposed that for instance, if oxygen and hydrogen molecules were, respectively,  $O_2$  and  $H_2$ , then one atom from each box of oxygen and of hydrogen would have to join to compose one compound molecule; so, there would be 200 water molecules of the composition  $H_2O$ , since there are two boxes (200 molecules, or 400 atoms) of hydrogen and only one box (100 molecules, or 200 atoms) of oxygen.

But if oxygen and hydrogen molecules were, respectively,  $O_4$  and  $H_2$ , then *two* atoms of oxygen would have to join with one hydrogen atom from *each* box of hydrogen to compose one compound water molecule. So, there would be 200 water molecules of  $H_2O_2$ . In either case the number of water molecules “becomes ... exactly what is necessary to satisfy the volume of the resulting gas” (CB 45),<sup>25</sup> that is, *two* boxes of water. Perhaps it is the principle of simplicity, reminiscent of Dalton, that decides him in favor of  $H_2O$ .

In order to determine molecular formulas in a more systematic and reliable way, Cannizzaro considers in one view all of the elements that can be produced in gaseous form. In agreement with the argument of Proust and the conclusion from Dalton’s supposition, he begins with *fixed, determinate, experimental ratios* between the weights of the two component substances in a given compound.

Then the weight of the molecule is divided into parts proportional to the numbers expressing the [experimentally determined] relative weights of the components, and so we have the [weights] of [the components] contained in the molecule of the compound, referred to the same unit as that to which we refer the weights of all the molecules [namely, hydrogen = 2] (CB 57).

This method allows him to construct the following table, shown in Figure 4 (CB 58):

| Name of Substance         | [molecular wt (H's = 2)] | [weights of the molecule's components] |
|---------------------------|--------------------------|--|
| Hydrogen                  | 2                        | 2 Hydrogen                             |
| Oxygen, ordinary          | 32                       | 32 Oxygen                              |
| Oxygen, electrised        | 128                      | 128 "                                  |
| Sulphur below 1000°       | 192                      | 192 Sulphur                            |
| Sulphur above 1000° (?)   | 64                       | 64 "                                   |
| Phosphorus                | 124                      | 124 Phosphorus                         |
| Chlorine                  | 71                       | 71 Chlorine                            |
| Bromine                   | 160                      | 160 Bromine                            |
| Iodine                    | 254                      | 254 Iodine                             |
| Nitrogen                  | 28                       | 28 Nitrogen                            |
| Arsenic                   | 300                      | 300 Arsenic                            |
| Mercury                   | 200                      | 200 Mercury                            |
| Hydrochloric Acid         | 36.5                     | 35.5 Chlorine 1 Hydrogen               |
| Hydrobromic Acid          | 81                       | 80 Bromine 1 "                         |
| Hydriodic Acid            | 128                      | 127 Iodine 1 "                         |
| Water                     | 18                       | 16 Oxygen 2 "                          |
| Ammonia                   | 17                       | 14 Nitrogen 3 "                        |
| <b>Arseniuretted Hyd.</b> | 78                       | 75 Arsenic 3 "                         |
| Phosphuretted Hyd.        | 34                       | 31 Phosphorus 3 "                      |

<sup>25</sup> “When particles of another substance unite with the former to form a compound particle, the whole [compound] particle which should result is divided into two or several parts (or separate particles) [each] composed of half, quarter, etc., the number of elementary particles going to form the constituent particle of the first substance, combined with half, quarter, etc., of the number of constituent particles of the second substance, which should combine with the whole particle (or, what comes to the same thing, [combined] with a number equal to this [last number] of half-particles, quarter-particles, etc., of the second substance); so that the number of separate particles of the compound becomes double, quadruple, etc., what it would have been if there had been no dividing, and exactly what is necessary to satisfy the volume of the resulting gas” (CB 45).

|                             |       |       |          |               |
|-----------------------------|-------|-------|----------|---------------|
| Calomel                     | 235.5 | 35.5  | Chlorine | 200 Mercury   |
| Corrosive Sublimate         | 271   | 71    | "        | 200 "         |
| Arsenic Trichloride         | 181.5 | 106.5 | "        | 75 Arsenic    |
| Protochloride of Phosphorus | 138.5 | 106.5 | "        | 32 Phosphorus |
| Perchloride of Iron         | 325   | 213   | "        | 112 Iron      |
| Protoxide of Nitrogen       | 44    | 16    | Oxygen   | 28 Nitrogen   |
| Binoxide of Nitrogen        | 30    | 16    | "        | 14 "          |

Figure 4

In order to understand Cannizzaro's procedure, let's suppose that the relative weight ratio for producing 100g of arseniuretted hydrogen has been found by experiment to be -

$$\text{weight of arsenic} : \text{weight of hydrogen} :: 96.15\text{g} : 3.85\text{g}.$$

Cannizzaro would divide the relative molecular weight, 78, of arseniuretted hydrogen into two numbers,  $a$ , representing how much of the 78 is due to arsenic, and  $h$ , representing how much of the 78 is due to hydrogen. So,

$$78 = a + h.$$

But also, since the 78 is to be divided in the same proportion as the 100, he knows that

$$96.15\text{g} : 3.85\text{g} :: a : h.$$

Solving these two simultaneously<sup>26</sup> tells him that the breakdown of the molecular weight of arseniuretted hydrogen into the weights of its component elements *has* to be 75 parts from arsenic atoms and 3 from hydrogen atoms.

At this very moment Cannizzaro says the following to his students (CB 59):

'Compare ... the various quantities of the same element contained in the molecule of the free substance and in those of all its different compounds, and you will not be able to escape the following law: *The various quantities of the same element contained in different molecules are all integral multiples of one and the same quantity, which, always being integral, ought rightly be called [the atomic weights relative to that of hydrogen as 1]* (CB 59, underlining added).<sup>27</sup>

For instance, if we look for chlorine in the right column of Figure 4, we see that the number it has been found to have is 35.5 or twice that, or triple that. So, 35.5 must be chlorine's relative atomic weight; and its molecule must be diatomic; and, for instance, there must be three chlorine atoms in

<sup>26</sup> If  $a + h = 78$  and  $a/h = 96.15/3.85 = 25$ , then  $(78 - h)/h = 25$ . So,  $78 - h = 25h$ , and  $78 = 26h$ . Or  $h = 3$  and  $a = 75$ .

<sup>27</sup> His actual words are: "*ought rightly be called atom.*"

protochloride of phosphorus (molecular weight = 138.5). A similar search for phosphorus tells us that its relative atomic weight must be 32 and that there must be one phosphorus atom in a molecule of protochloride of phosphorus. It is easy to see that we can now “express all chemical reactions by means of the same numerical values [that is, these relative atomic weights] and integral coefficients” of them (CB 60). That is, we can write reliable, accurate chemical formulas for such compounds. For the present example of protochloride of phosphorus, the chemical formula must be  $\text{PCl}_3$ .<sup>28</sup>

### ***MENDELEEV'S CONSTRUCTION OF THE PERIODIC TABLE (1870-71)***

Mendeleev points to his fundamental insight right at the beginning of the excerpt in the manual. In order to make the “inadequacy” of current atomic doctrine in chemistry “disappear,” he will “put at the foundation of the study of the main [physico-chemical] properties of the elements their [relative] atomic weights,” which Cannizzaro had worked out, less than 10 years before Mendeleev set to work. Mendeleev’s bringing two previously separate realms into relationship may remind us of Avogadro’s advancing to a new insight by bringing into relationship Gay-Lussac’s perception of small whole numbers of boxes of gases and Dalton’s supposed ideal-exact atoms. Mendeleev indicates several steps by which he came to his insight.

Chemists had long recognized certain “natural groups” of elements based on their physico-chemical properties. For instance, lithium, sodium, potassium, rubidium, and cesium had been referred to as *alkali metals*; they are good conductors of heat and electricity, are highly malleable and ductile, have very low boiling and melting points and shiny surfaces, and are distinguished from other metals by their lower densities and softness. Beryllium, magnesium, calcium, strontium, and barium were known as *alkaline earths*; they are solid, hard, dense, and usually shiny, are less reactive than metals, are often insoluble in water, and are found in the earth crust. Fluorine, chlorine, bromine, and iodine are non-

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<sup>28</sup> It is, of course, clear to Cannizzaro that the numbers may have to change as future empirical discoveries are made.

metallic, have relatively low melting and boiling points and generate salts (ἄλας) when they react chemically with metals; they had been grouped together as *halogens*. Other natural groupings were “*analogues to sulfur*,” including oxygen, selenium, and tellurium; as well as *analogues to nitrogen*, including phosphorous, arsenic, antimony, and bismuth (CB 81).

Initially the elements were put in groups due to their similarities with respect to these properties. Then some chemists noticed among pairs or triples of elements of high atomic weight, *analogues* to pairs or triples of elements of much lower atomic weights. This noticing of analogues “gave the first impetus to compare the different properties of the elements with their atomic weights” (CB 81).

For example, the physico-chemical properties of cesium ( $w^{29} = 133$ ) and barium ( $w = 137$ ) were analogous to those of potassium ( $w = 39$ ) and calcium ( $w = 40$ ). With respect to such properties, they are proportional, in the sense that

$$\text{K} : \text{Cs (among alkali metals)} :: \text{Ca} : \text{Ba (among alkaline earths)}.$$

In other words, within the natural group of alkali metals, the ways in which K differs from Cs, in its physico-chemical properties, is analogous to the ways in which Ca differs from Ba, in those properties, within the group of alkaline earths.

Such analogies led to the insight that the way a given physico-chemical property alters, as we consider, one after the other, the elements of increasing atomic weight within one natural group, may often occur in parallel with corresponding changes in other natural groups. That insight, in turn, led to “thinking of classifying all the elements according to their atomic weights,” as determined by Cannizzaro, in order to see what might be revealed. Mendeleev reports that when we do this “we find an astonishing simplicity of relationship” (CB 82).

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<sup>29</sup> The letter “w” will stand for relative atomic weight, according to Mendeleev’s figures.

His illustration of that simplicity is the arrangement, shown in Figure 5, in two horizontal rows of all the elements of relative atomic weight between 7 and 36, “in arithmetical order according to their atomic weights.” He looks in two different ways at these rows.

Li=7    Be=9.4    B=11    C=12    N=14    O=16    F=19.  
 Na=23    Mg=24    Al=27.3    Si=28    P=31    S=32    Cl=35.5.

Figure 5

First, when he *looks at a row by itself* and attends, one by one, to the different physical and chemical properties, he notices “that the character of the elements changes *regularly and gradually* with increasing magnitude of the atomic weights” (CB 82; italics added). For instance, the characteristics—whether qualitative or quantitative—of the elements in the row change from left to right in the following ways:

- i) from being basic to being acidic;
- ii) from metals, through semi-metals, to non-metals;
- iii) from being good conductors of heat and electricity to being insulators;
- iv) from being lustrous and shiny to being dull;
- v) from a boiling point of 1330°C rising in the middle and then falling to -188°C;
- vi) again rising, from a melting point of -180°C, to a maximum and then falling to -187°C;
- vii) density, too, rises to a high point and then falls, as shown in Figure 9;
- viii) a graph of the relative atomic volumes [that is, the relative atomic weight (weight per atom) divided by its density (weight per unit volume) = relative volume per atom] would be U-shaped
- ix) and, finally, a graph of the volatility would also be U-shaped (CB 83-84). (See Figure 6 for viii and ix.)

|               | Na   | Mg   | Al   | Si   | P    | S    | Cl   |
|---------------|------|------|------|------|------|------|------|
| vii) Density: | 0.97 | 1.75 | 2.67 | 2.49 | 1.84 | 2.06 | 1.33 |
| viii) At Vol: | 24   | 14   | 10   | 11   | 16   | 16   | 27   |

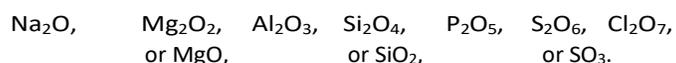
Figure 6

Second, when we *compare the patterns of change*, from left to right, along the top row with

those along the bottom row, we find that “the character of the elements changes ... in the same way in both series, so that the corresponding members of them are analogues.” In this example, the patterns of change are the same for all nine characteristics listed above. Thus, lithium and sodium, the respective members of each series that are highest in basic character, metallic character, luster, and conductivity are the leftmost ones, are also at the beginning of rising curves of the graphs of melting and boiling points and density, and so on (CB 82).

Finally, Mendeleev stresses the importance of the *forms* of the compounds that are formed—in order along each of the two rows—with *oxygen* and with *hydrogen*. The forms of these compounds present regularities that are familiar to chemists from their experimental work. As we look from the beginning of either row, “the corresponding elements in the two series have the same kind of compounds” with oxygen: That is, two atoms of the given element combine with the following numbers of oxygen atoms—1, 2, 3, ... respectively, a uniformly increasing sequence of whole numbers, as the atomic weight of the element increases. For instance:

The seven elements of the second series give the following higher oxides capable of forming salts:—



Thus, the seven members of the above [second] series correspond in the same sequence to the seven generally known forms of oxidation (CB 83).

Moreover, beginning with the righthand member in either row and moving left, a similar pairing of compounds with hydrogen occurs—hydrofluoric acid (HF) and hydrochloric acid (HCl) are 1 : 1; water (H<sub>2</sub>O) and hydrogen sulfide (H<sub>2</sub>S) are 2 : 1, and so on, up to 4 : 1..

Mendeleev states: “This regularity *proves* that the above comparison of elements presents natural series in which it is *impossible* (*нельзя*) to assume any intermediate members” (CB 82-83; italics added). The arranging of the elements in the order of increasing relative atomic weight has led Mendeleev to see a new necessity, or rather impossibility, such as we might find in mathematics.

He goes on to present such pairings for *all* the elements. That he can do so “indicates a close

dependence of the properties of the elements on their atomic weights.” As we have seen from his example and as he goes on to show, all the individual relationships of the dependence of physico-chemical properties on atomic weight are “*periodic*.” “First, the properties of elements change with increasing atomic weight; then, they repeat themselves in a new series of elements, *a new period*, with the same regularity as” in the series we just went through in detail (CB 84). Mendeleev is using “period,” in the sense familiar to us from Ptolemy. Just as a heavenly body has different positions over time and *returns* to its starting point, after completing one period, and then *begins a repetition*, a new period, so a given physico-chemical property has different values as we consider, in turn, elements of increasing atomic weight along one row, and *returns* to a value near its starting value, after completing one period, and then *begins a repetition*, a new period, at the first element of the next row.

Once Mendeleev had thought to arrange all the elements in the order determined by their atomic weights, these repetitive patterns suddenly became visible to him, as a picture of wave-like motions. His experience might be analogous to suddenly seeing something appear in Figure 7.



Figure 7

Mendeleev next goes on to show how he found the *complete* periodic dependence of the physico-chemical properties on the relative atomic weights (CB 85ff). He lined the elements up in rows, like the ones we've considered. Table II, in Figure 8, shows all the elements in eight columns—

ТАБЛИЦА II.

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| Ряды | Группа I<br>—<br>R <sub>2</sub> O | Группа II<br>—<br>RO | Группа III<br>—<br>R <sub>2</sub> O <sub>3</sub> | Группа IV<br>RH <sub>4</sub><br>RO <sub>2</sub> | Группа V<br>RH <sub>5</sub><br>R <sub>2</sub> O <sub>5</sub> | Группа VI<br>RH <sub>2</sub><br>RO <sub>3</sub> | Группа VII<br>RH<br>R <sub>2</sub> O <sub>7</sub> | Группа VIII<br>—<br>RO <sub>4</sub>       |
|------|-----------------------------------|----------------------|--|---|--|---|---|---|
| 1    | H = 1                             |                      |  |   |  |   |   |   |
| 2    | Li = 7                            | Be = 9,4             | B = 11   | C = 12  | N = 14   | O = 16  | F = 19  |   |
| 3    | Na = 23                           | Mg = 24              | Al = 27,3  | Si = 28   | P = 31   | S = 32  | Cl = 35,5   |   |
| 4    | K = 39                            | Ca = 40              | — = 44   | Ti = 48   | V = 51   | Cr = 52   | Mn = 55   | Fe = 56, Co = 59,<br>Ni = 59, Cu = 63     |
| 5    | (Cu = 63)                         | Zn = 65              | — = 68   | — = 72  | As = 75  | Se = 78   | Br = 80   |   |
| 6    | Rb = 85                           | Sr = 87              | ?Yt = 88   | Zr = 90   | Nb = 94  | Mo = 96   | — = 100   | Ru = 104, Rh = 104,<br>Pd = 106, Ag = 108 |
| 7    | (Ag = 108)                        | Cd = 112             | In = 113   | Sn = 118  | Sb = 122   | Te = 125  | I = 127   |   |
| 8    | Cs = 133                          | Ba = 137             | ?Di = 138  | ?Ce = 140                                       | —  | —   | —   | — — — —                                   |
| 9    | (—)                               | —                    | —  | —   | —  | —   | —   | —   |
| 10   | —                                 | —                    | ?Er = 178  | ?La = 180                                       | Ta = 182   | W = 184   | —   | Os = 195, Ir = 197,<br>Pt = 198, Au = 199 |
| 11   | (Au = 199)                        | Hg = 200             | Tl = 204   | Pb = 207  | Bi = 208   | —   | —   | —   |
| 12   | —                                 | —                    | —  | Th = 231  | —  | U = 240   | —   | — — — —                                   |

Figure 8

the eight natural groups—and twelve rows. Rows 2, and 3 are the two complete series we've already considered. However, the remaining elements revealed their periodicity only when Mendeleev lined them up below one another in longer rows, in the following way:

- Row 4 (group I-VII) + Group VIII + Row 5  
above**
- Row 6 (group I-VII) + Group VIII + Row 7  
above**
- Row 8 (group I-VII) + Group VIII + Row 9  
above**
- Row 10 (group I-VII) + Group VIII + Row 11**

Thus, one circuit begins with K and Ca's properties and ends only with those of Se and Br; a new circuit begins with Rb and Sr's properties and ends with those of Te and I. And so on.

Mendeleev concludes by returning to what Dalton saw as the second use that chemists had not made of particles—using them “to assist and to guide future investigations, and to correct their results” (CB 21). Perhaps Mendeleev thought that by his time it was not particles, but *relative atomic weights* that still had not been made use of. He says that in order for a law, like his periodic law, to acquire scientific importance its logical consequences have to be useful, in the sense that they “explain the as yet unexplained, give indications of hitherto unknown phenomena, and [allow] one to make predictions that are accessible to experimental verification” (CB 89).

He does all that in the rest of his article. For instance, the element *indium* had been discovered in 1867 and assigned the relative atomic weight of 75.6. Mendeleev saw that there was no open slot in the periodic table for an element of relative atomic weight 75.6. But by comparing its compounds with those of other elements, Mendeleev saw that indium would *have to* be placed in an open slot in in Group III, row 7, with atomic weight about 113 (CB 91-92).

Moreover, Mendeleev investigated the empty slot in Group IV, row 5. He saw that there *had to* exist an element of relative atomic weight “about 72” in that slot. Based on the known physico-chemical properties of the elements in the slots around the empty one, he predicted the properties that the yet-to-be-discovered element would *have to* possess. About 15 years later the element germanium (Ge), of relative atomic weight about 72.5 and possessing those properties, was discovered (CB 93-95). Perhaps chemists experienced this discovery as somewhat like reading a novel, coming away with a very precise sense of the main character, and then meeting someone at a party who strikes us as perfectly fitting the fictional portrait. It might seem as if we knew him “from before.” Would Socrates say that we are “recollecting,” but in some to-be-determined different sense (Ph 72e-73cd)?

What do we make of Dalton’s seeing *supposed* particles—not actual chalk marks on the blackboard or lines drawn on paper—as ideal-exact limit-entities, in the realm of *μαθήματα*, of objects of study leading to insightful learning? Do they eventually lead to acts of insight into the actual material

world, in the way that Archimedes' learn-ables about weight or Ptolemy's about motion do? How does the way in which they allow us to see more in the world compare with the way Archimedes' transparencies refine our vision?

Do Mendeleev's successes in making use of the supposed particles and of their relative atomic weights *show* that atoms and molecules are not merely supposed but also actually existing entities in the material world?