

AVOGADRO'S HYPOTHESIS AND THE DUHEMIAN PITFALL

Amedeo Avogadro published his famous gas hypothesis in 1811¹, but about 50 years passed before the hypothesis became widely accepted by chemists. Many reasons have been given for the delayed acceptance of Avogadro's hypothesis (see, in particular, Nash² and Knight³). This article is a review of certain chemists' roles in the history of the delayed acceptance of this hypothesis. These chemists' experiences are interesting case histories of what is called the "Duhemian Pitfall," which can be an important cause of error in hypothesis testing.

In contrast, we will see that physicists, when they began to develop the kinetic theory of gases, were less likely to become ensnared in this pitfall, and more readily inclined to accept Avogadro's hypothesis.

These case histories are interesting in themselves, and they are also of interest because they show some important problems, and possible blind alleys, of hypothesis testing. Thus, they demonstrate some significant features of the growth and structure of scientific theories.

The Duhemian Pitfall

Pierre Duhem was not only a distinguished physicist and historian of science, but also a very original thinker in the philosophy of science, where he is best known for describing problems of hypothesis testing. Duhem maintained that, in the physical sciences, an experiment never tests a single hypothesis, but rather a conjunction of several hypotheses. Thus, if the experimental result is contrary to a prediction correctly deduced from the hypotheses, it can be difficult to decide which hypotheses are in error⁴. Actually, Duhem exaggerates the difficulty of testing a single hypothesis, but he did have an important insight. It is appropriate to name after him the following pitfall of hypothesis testing.

Suppose that a scientist is interested in testing a hypothesis, H , and suppose that he has deduced an observational prediction from H in conjunction with certain other hypotheses, which will be called the "auxiliary hypotheses." Assume further that he believes all the auxiliary hypotheses are true. If H is in fact true, and one or more auxiliary hypotheses are false, then he may obtain a negative observational result and conclude (mistakenly) that H has been falsified by the experiment. *The Duhemian Pitfall is the possibility of making this kind of mistake.*

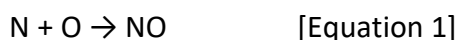
In the following, the Avogadro hypothesis and certain auxiliary hypotheses that are accepted today are taken to be true. The case histories described will then illustrate the Duhemian Pitfall. It should be understood that the distinction between H and the auxiliary hypotheses is conventional, based on the fact that H is the hypothesis originally in question to be tested. In some cases, the auxiliary hypotheses are (or ought to be) as questioned as H . It should also be understood that a test need not involve a new experiment or observation; a test can simply involve comparing the observational prediction with previously acquired data.

Chemists' Reception of Avogadro's Hypothesis

Avogadro hypothesized that equal volumes of all gases (at the same temperature and pressure) contain equal numbers of molecules. He formulated this hypothesis (henceforth to be denoted by "A") primarily to explain Gay-Lussac's Law of Combining Volumes.

One can explain the volume ratios of reacting gases if one assumes A plus suitable auxiliary hypotheses. For instance, Avogadro made the very bold assumption that the molecules of many elemental gases are polyatomic. However, it is also the case that almost any observational test of A that could be performed in the early 1800s involved assuming certain auxiliary hypotheses along with A. Thus, by assuming incorrect auxiliary hypotheses, it was very easy for chemists to become trapped by the Duhemian Pitfall and conclude that A was false.

One chemist who became trapped was John Dalton. As early as 1807, Dalton independently considered A and then rejected it⁵. One of his arguments against it was based on the reaction between nitrogen and oxygen to form nitric oxide. He thought that the reaction was:



But A plus Equation 1 imply that one volume of nitrogen should react with one volume of oxygen to form one volume of nitric oxide. However, Dalton knew the experimental volume ratios are not those implied by A plus Equation 1. Thus, he concluded that A was incorrect, whereas in fact his auxiliary hypothesis, Equation 1, is incorrect. In addition, Dalton had other, more complex reasons for rejecting A. Some of these are discussed by Nash⁶.

Another chemist who rejected A was J. J. Berzelius. He did believe that equal volumes of gaseous elements contain equal numbers of atoms, but he did not believe that elemental gases could be composed of polyatomic molecules⁷. This disbelief was apparently based on his dualistic theory, which he developed to explain chemical composition.

Berzelius maintained that atoms have electrical charges and that molecules are held together by electrical attraction between opposite charges. For instance, oxygen atoms were assumed to have a strong negative charge. But if this is the case, then it is hard to see how there could be a stable O₂ molecule. Berzelius therefore rejected Avogadro's auxiliary hypotheses, which assert the existence of polyatomic molecules of gaseous elements. Thus, because of his dualistic theory, he rejected the correct form of A and assumed an incorrect hypothesis in its place.

Since Berzelius was influential and the dualistic theory was rather popular for a few decades, this was probably a major reason for the general ineffective use of A for some time. Yet, despite this, there was considerable interest in the hypothesis in some circles. We are not concerned with its detailed history, but we should consider one more rather complicated and dramatic example of the Duhemian Pitfall. This is the case of A. M. Ampère and some of his followers.

Ampère published **A** in 1814⁸ in an article concerned with the geometry of molecules. His geometrical theory was rather complex, and its details need not concern us here. A good recent review of it is given by S. H. Mauskopf⁹.

What is interesting here is Ampère also had difficulties with auxiliary hypotheses. Unlike Dalton and Berzelius, he assumed the existence of polyatomic elemental molecules, but he guessed the wrong formulas for them because of his geometrical theory. For instance, he assumed that oxygen, nitrogen, and hydrogen were tetratomic, and that chlorine was octatomic¹⁰. Despite this, he was able to explain some of Gay-Lussac's results. Thus, although he used incorrect auxiliary hypotheses, Ampère was not completely trapped by the Duhemian Pitfall. However, he inadvertently led other chemists into the trap, most notably J. B. A. Dumas.

Dumas tried to use **A** with vapor density measurements to determine atomic weights, but he encountered problems¹¹. Very briefly, they are as follows: In 1826, Dumas began by stating **A** as applying to the "atoms" of gases. But he believed the "atoms" of all elemental gases were composed of two "half-atoms" that could be separated in reactions. These assumptions led to some satisfactory atomic weights. But also various discrepancies were obtained with elements such as mercury, sulfur, and phosphorus, when his results were compared with results obtained by other methods. It is now accepted that the molecular formulas of the vapors of these elements are Hg, S₆, and P₄. But Dumas would not accept such auxiliary hypotheses. Instead, he rejected **A** and, in the 1830s, came to doubt the entire atomic theory.

It is especially sad that Dumas became a victim of the Pitfall because, in 1833, Ampère's student M. A. A. Gaudin¹² showed how to avoid the snare by hypothesizing different numbers of atoms in different polyatomic elemental molecules. However, Dumas was a distinguished chemist, while Gaudin was little known and his theory was not taken very seriously by most chemists.

It is generally agreed that wide acceptance of **A** by chemists did not occur until the 1860s, after S. Cannizzaro published his extensive use of it in establishing a consistent system of atomic and molecular weights¹³. The existence of the Duhemian Pitfall was one of several important reasons for the slow acceptance of **A**.

Physicists' Reception of Avogadro's Hypothesis

One might expect physicists who were trying to develop a general theory of gases to be less concerned than chemists with detailed chemical data, and hence less concerned with the auxiliary hypotheses surrounding **A**. Therefore, one might conjecture that physicists considering **A** would have been less likely than the chemists to become ensnared by the Duhemian Pitfall. At least in the case of the kinetic theorists, there is some evidence that this conjecture is correct. Let us consider two important cases.

Supposedly, the first kinetic theorist to consider **A** was J. J. Waterston. In 1845, he submitted to the Royal Society a paper on kinetic theory; unfortunately, he never succeeded in getting it published. This paper developed the kinetic theory far beyond previous work, and it presented results that later had to be independently discovered by others. In his article, Waterston stated several gas laws, including **A**.

He was aware of the Law of Combining Volumes, and he suggested this law is true because of **A** and the existence of polyatomic elemental molecules. He maintained that such molecules could split into parts in reactions, even though the parts were not known to exist in the free state¹⁴. It seems clear that Waterston was not excessively bothered by the dualistic theory, or by other chemical problems with polyatomic elemental molecules. It is extremely unfortunate that his ideas were not appreciated in his own time.

In contrast to Waterston, R. Clausius was an early kinetic theorist who was influential. His paper, "On the Nature of the Motion Which We Call Heat," was first published in German and then in English in 1857¹⁵. Clausius' principal contributions in this paper are his treatment of molecular energies other than just translational energy, and his treatment of specific heats. But he also mentioned the need to explain the Law of Combining Volumes, and proceeded to argue for **A**. His reasoning is quite interesting.

Let e be the mean translational kinetic energy (Clausius says "*vis viva*," which is just $2e$) of a molecule. Then, he says, for a fixed temperature T , pressure P is proportional to the number n of molecules per unit volume V and to e . In other words,

$$P = K \left(\frac{n}{V} \right) e \quad \text{[Equation 2]}$$

or

$$PV = nKe \quad \text{[Equation 3]}$$

where K is a proportionality constant. Thus, if P and T are fixed, and if **A** is assumed, then all molecules of all gases have the same e , or mean translational kinetic energy.

Clausius first gives the above argument for atomic gases. Then, he discusses its extension to polyatomic gases, and mentions some of the anomalies noticed by chemists, particularly the troubles with the vapor densities of sulfur and phosphorus. But he was not disturbed by such problems, and he concluded:

"I am of opinion, however, that, under the present uncertainty with respect to the inner constitution of several bodies, and particularly of those which possess a complicated chemical composition, too great weight ought not to be laid upon individual anomalies; and I deem it probable, that, by means of the above hypothesis respecting the molecules of simple substances [that they can be polyatomic], all relations of volume in gases may be referred back to the theorem,

that the several molecules of all gases possess equal vis viva in reference to their translatory motion¹⁶.”

It appears, therefore, that Clausius is recommending that the hypothesis of a constant e , at a fixed temperature, be considered even more fundamental than **A**. Of course, if one assumes this hypothesis, then **A** follows from Equation 2. It should also be noted that Clausius' theory of specific heats indicated that there are probably polyatomic elemental molecules. L. K. Nash has previously mentioned this aspect of the kinetic theory¹⁷.

Further development of the kinetic theory followed, but by 1860, Cannizzaro was aware of the work of Clausius, and both chemists and physicists were just about ready to accept Avogadro's hypothesis. Ultimately, the history of science has many illustrations of the Duhemian Pitfall. Moreover, the testing of theories is fraught with many difficulties, of which the Pitfall is only one. But in the case of Avogadro's hypothesis, the Duhemian Pitfall was manifested as a series of stubborn obstacles to the confirmation of the hypothesis.

Source

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