Operationalism and Realism in 19th-century Atomic Chemistry[1]

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In this paper I offer a new philosophical interpretation of the development of atomic chemistry in the 19th century. I argue that the success in this field owed much to a kind of *operationalism* at work.[2] Such operationalism was a key component of an epistemic attitude which I call *active realism*, though it is not so consonant with realism as conceived in standard philosophical discourse. We lose crucial aspects of this history when we approach it through a preoccupation with the question of whether atoms really exist (or, whether the term "atom" really refers), or with the question of whether statements we make about the unobservable atoms and molecules (such as Avogadro's hypotheses) are "really true".

As Alan Rocke has argued extensively,[3] the development of atomic chemistry in the 19th century was unhampered by the persisting doubts about the real existence of physical atoms. Rather, chemists starting with John Dalton devised various ways of operationalizing the chemical concept of the atom, by incorporating it into clear and stable epistemic activities. William Hyde Wollaston's method was to assign weights to atoms on the basis of the gross combining weights of chemical substances; his table of "chemical equivalents" came to be in widespread use. Another very popular method of operationalizing the atom was through electrolysis: it was normally taken that the decomposition of a substance by the application of electricity was the break-up of each of its molecules into components of opposite electric charges, which reliably came out at electrodes supplying electricities opposite to themselves. Humphry Davy isolated the alkali metals in this way, and Jöns Jakob Berzelius built his dualistic system of chemistry on the basis of the electrochemical operationalization of atoms.

The mid-century success of atomic chemistry was based on operational methods of *atom-counting*. Most importantly, starting with Joseph-Louis Gay-Lussac's observations on the simple volume-ratios in which gases reacted chemical with each other, chemists established the practice of counting the relative number of atoms and molecules by measuring how much volumes were occupied by gaseous ingredients and products of reactions. Another method was to use "atomic heat", namely the amount of heat required to raise the temperature of a substance by one degree, per atom, which was taken to be constant. Using such atom-counting methods, chemists could track the arrangements and re-arrangements of atoms in some key chemical reactions quite confidently. That allowed a stable determination

[1] This is as yet unpublished work, forthcoming as part of my book *Is Water H_2O? Evidence, Realism and Pluralism* (Springer, 2012).

[2] This view is consonant with Alan Chalmers's in *The Chemist's Atom and the Philosopher's Stone* (Springer, 2010).

[3] See e.g. *Chemical Atomism in the Nineteenth Century* (Ohio State, 1984), and *Image and Reality* (Chicago, 2010).

of some key atomic weights, which allowed further atom-counting, and then further atomic-weight determinations.

However, this was not a smooth success story. As manifested in the fact that at least 4 different sets of atomic weights were in widespread use until the 1860s, different operationalizations of the atom often diverged from each other. This brings us to a fundamental dilemma faced by Percy Bridgman: when there are multiple methods purporting to measure the same quantity (e.g. using meter-sticks, reflection of light, or astrophysical theories to measure distance), does each method really define a separate concept as his operationalist philosophy dictated, or are we somehow justified in regarding the different methods as different ways of getting at the same thing? Ultimately Bridgman left this issue unresolved. Interestingly, the same philosophical indecision was at the heart of the successful development of 19th-century atomic chemistry.

For many decades chemists could not be sure if different operationalizations of the atom really got at the same thing, and they let that situation be. Different systems of atomic chemistry developed simultaneously, based on different operationalizations. Most chemists agreed that there was something real to the concept of the chemical atom, but there was no precise agreed concept of it. Charles Gerhardt, one of the pioneers of the reform of atomic weights and molecular formulas that eventually bore fruit by the 1850s, was explicit about the utility of multiple operationalizations: "one and the same body can be represented by two or more rational formulas; if one "freezes a compound into a single formula, one often conceals from oneself chemical relationships that another formula would immediately make evident."[4] If there is plurality in the operationalization of what is widely presumed to be one concept, the assumptions underlying each operationalization function as tautologies. For example, it is a mistake to think that the "EVEN" (equal volume—equal number) assumption grounding volumetric atom-counting was a hypothesis liable to falsification. Rather, it was untestable, until it was agreed that other methods of atom-counting measured exactly the same thing and could be used to check the results of volumetric atom-counting. In the absence of unification, each operationalization provides an independent window on reality.

This is the aspect of the story that most strikingly conforms to my doctrine of "active (scientific) realism", which maintains that science should strive to maximize our learning from reality, understanding "reality" as whatever it is that is not subject to one's own will, capable of offering resistance to one's expectations and plans. Many venerable old philosophies of science, ranging from Peirce's pragmatism to Popper's falsificationism, can be regarded as different manifestations of active realism. The maximal operationalization of concepts is a key active-realist imperative, as there will be no learning from reality without operationalized concepts. The success of atomic chemistry in its first half-century owed much to an active-realist multiplication of methods of operationalizing the atom, without insisting on a premature unity between them. Each operationalization delivered a rich harvest of

[4] Quoted by Rocke (2010), p. 13.

results, from which chemists eventually learned enough to be able to attempt a unification of the different operationalizations. One outcome of this unification, consolidated in the 1860s, was a reasonable consensus on all atomic weights and most molecular formulas for the myriad of known substances, on the basis of which much further developments were made. However, two qualifications are needed to this story of unification. First, unification was difficult and creative work, most likely involving the warping of each operationalization being brought together, not just a discernment of some magical pre-existing harmony. Second, not all aspects of early atomic chemistry could be fitted into the unification into structural theory, and had to be put aside (e.g., electrical and thermal aspects into the new sub-fields of physical chemistry and chemical thermodynamics); thus a pluralistic situation continued, on a larger scale.