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The Operational Definition of the Elements: A Philosophical Reappraisal

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In memory of Rom (Horace Romano) Harré (1927–2019)

1. Introduction

The definition of elements to be reappraised from a philosophical point of view in this chapter is well known among chemists and historians of chemistry. It plainly says:

> An element is any substance that we, at the current state of our art, cannot decompose further by chemical analysis.

Lavoisier was perhaps the most forceful advocator of that definition.[1] However, from an epistemological point of view, it does not matter who first formulated the definition, for what reasons, in what context, and if such formulations were consistent with other views by the respective author. It is sufficient to acknowledge that the definition was accepted by the vast majority of chemists around 1800, but even the exact date is largely unimportant.

The reason for the neglect of such details is not motivated by disinterest in the history of chemistry, but justified by the epistemological status of definitions. A definition is not to be confounded with a discovery, a hypothesis, or a theory, achievements for which we can frequently give credit to an individual. In contrast, a definition defines the meaning of a term, here “element,” which serves communicational purposes. Individuals can suggest a new definition and provide arguments pro and con its adoption, but only a community can agree upon a definition by convention.

Almost all commentators of the “chemical revolution” have discussed the definition, whether it should be considered part of that “revolution,” and if Lavoisier consistently applied it in his own works, which does not concern us here. They have used various terms, such as “empirical definition,” “analytical definition,” or “operational criterion,” but only a few have called it an “operational definition,” which it actually is from an epistemological point of view.

An operational definition defines a general term, here “being elemental,” by reference to one or more operations. For instance, modern physicists define “time” by reference to measurement operations involving a clock. Empirically working psychologists and social scientists work hard to operationalize their concepts by reference to measurements. Operationalism, that is, the view that all basic concepts of science should ideally be operationally defined, was first elaborated by Physics Nobel Laureate Percy Bridgman (1927). Although it received

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[1] “*Nous nous contenterons de regarder ici comme simples toutes les substances que nous ne pouvont décomposer; tout ce que obtener en dernier résultat par l’analyse chimique. Sans doute un jour ces substances, qui sont simple pour nous, seront décomposées à leur tour...mais notre imagination n’a pas dût devancer les faits, & nous n’avons pas dû en dire plus que la nature ne nous enapprend*” (Lavoisier 1787, 17-18, quoted from the original).

harsh criticism by logical positivists who mistook it as a general semantic theory, it arguably plays an important methodological role in most empirical sciences.

The operational definition of elements, as formulated above, is special in two regards. First, it defines a kind of material entities, elements, in such a way that they can be produced in the laboratory by following the definition: if you take any substance and apply all available methods of chemical analysis, you end up with elements per definition. That is because the definition refers to experimental operations of chemical analysis rather than to measurement operations. (The definition also implicitly refers to measurements of equivalent masses that allow one to decide on empirical grounds if a chemical reaction is actually a decomposition or a synthesis.) Second, the definition refers to the current state of the art, which may change over time, such that what was once considered an element is no longer an element, but not the other way round. The meaning of "element" is thereby bound to the limits of human capacities, acknowledging that this is not something given but changing in an unpredictable manner. All assignments of the elemental status are thus provisional and contingent on the current laboratory practice.

If one considers that in the entire history of natural philosophy before, elements had been the central theoretical entities for explanations, not only in chemistry but also in medicine, mineralogy, and most of the sciences, the adoption of the operational definition with all its oddities and contingencies appears almost crazy. And yet, all of modern science has been built on the operationally defined elements, both experimentally and theoretically, and quite successfully so.

In the following,[2] I first point out the radical disruption that the adoption of the operational definition implied for chemistry and natural philosophy. Against the background of the traditional role of elements in natural philosophy (Section 2.1), the main disruption consisted in giving up explanation, the primary goal of natural philosophy, because the new elements had to be discovered first of all (Section 2.2). Then I compare the operational turn in chemistry with several well-discussed "revolutions," including the Kantian, relativistic, and quantum revolutions in physics, which similarly modified our understanding of fundamental concepts of natural philosophy, such as time, space, and causation (Section 2.3). Section 2.4 offers some explanation of why most historians of science have neglected the radical disruption and its significance for science.

Complementary to Section 2, the subsequent section emphasizes continuities of the concept of elements across the operational turn, by using a threefold epistemological framework (Section 3.1) that the eminent philosopher of science Rom Harré developed in 1986. If one considers all three roles or functions that elements have played with varying emphasis throughout history – explanation, classification, experimental accessability – the operational turn perfectly meets the needs of experimental access (Section 3.2) and classification (Section 3.3) at the temporary expense of explanation. With the exception of that temporary period, conceptual tensions arising from reconciling all three functions in one concept have always been obvious and caused numerous debates (Section 3.4), which I illustrate by medieval debates on elements in compounds and by IUPAC's current definition of chemical elements.

In conclusion I discuss the legacy of the operational definition and the importance of philosophy for both chemistry and the history of chemistry.

2. Discontinuity

2.1 Principles of Nature

The notion that the material variety and dynamics of our world are somehow based on fundamental principles has been central to all natural philosophy, from early ancient Greek, Chi-

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[2] Much of this chapter draws on Schummer 1996

nese, and Indian philosophy to modern science. To be sure the particular ideas have greatly varied, for instance, whether these principles have material, nonmaterial, or processual qualities; whether there is only one principle (*e.g.*, Thales), or infinitely many (Anaxagoras), or an ordered set of a few principles (Plato, Aristotle); and whether they were called *stoicheia* (Greek), *elementa* (Latin), *xing* (Chinese, Taoism), *mahābhūta* (Sanskrit and Pāli, Buddhism), or elementary particles (modern physics). Regardless of their differences, all natural philosophies have shared the combined ontological and epistemological assumptions that the world is based on stable or recurrent principles and can be best understood (explained, predicted, controlled) by referring to such principles. These assumptions have distinguished natural philosophy from all other approaches to understanding the world, including theistic religion, craft, and mere description, be it qualitatively as in natural history or quantitatively as in applied mathematics. And they became a model for other scientific approaches, including geometrics, for which Euclid first introduced his definitions and axioms as “elements.”

How did natural philosophers arrive at their principles? Those who favored material principles mostly developed the characteristic properties of their principles by analogy from material experience and supported them by explanations. The analogy reasoning is already obvious on the surface level of their terminology. Although they usually emphasized that the principles should not be confounded with ordinary materials, they used terms such as “fire,” “air,” “water,” “earth,” “metal,” “wood,” “sulphur,” and “mercury.” The more sophisticated approaches, such as by Aristotle and the Buddhist mahābhūta doctrine, developed their principles from a systematics of material properties. For instance, Aristotle (*De gen. et cor*., II. 2-3) selected two pairs of opposite properties, cold-warm and liquid-solid, such that all properties are tangible and the first pair has active effects on other materials (expanding or shrinking them) and the second one passive properties (being more or less ductile). With that he could redefine the four classical elements (called fire, air, water, earth) by the four possible binary combinations of active and passive properties, which allowed him and his followers to make explanations of what we would today largely call thermodynamic, mechanical, and chemical properties and interactions.

The principles or elements of nature were not only used in armchair philosophy and supported by a few explanations of everyday life phenomena. Aristotle, for instance, widely used them for explanations, from the structure and dynamics of the cosmos, to the physiology of biological organisms, to processes of chemical crafts. However, their most important, and most popular, use was probably in medicine, both in China and the West. For instance, already Hippocrates employed, perhaps co-created, the classical four elements doctrine in his physiology, which Galen would develop into his theory of the four humors, that is, four fundamental fluids of the body, corresponding to the four elements. Assuming that the four humors are in a certain balance in a healthy body, he explained many diseases (as well as a variety of human temperaments) by their imbalance, to be cured by medicines that could restore the balance. The humoral theory was the most important theoretical basis in Greek, Roman, Islamic, and European medicine at least until the end of the eighteenth century.

Also most alchemists and chemists accepted the classical four elements as their basic principles up to the late eighteenth century. However, they supplemented them by higher-level principles, such as “sulphur,” “mercury,” and phlogiston, to explain chemical phenomena, including combustion and calcination, which all showed radical changes of properties. As “property-conferring principles” they were supposed to survive all chemical transformation, but would change their appearance from being latent in some combinations to openly displaying their properties in others. Apart from occasional references to divine help and astrological influence, which was favored by theological authorities such as Thomas Aquinas, the general explanatory approach of material properties did not change much since antiquity. The properties of materials were explained by the principles that they were supposed to be composed of and had inherited from other materials by earlier chemical transformations. When the simple combination of the properties of the principles did not suffice, the usual assumption, in accordance with Aristotle, was that the principles combined to form new substantial forms. As the number of known chemical transformation increased, references to new substantial forms grew, which in modern terms correspond to *ad hoc* hypotheses to save an explanatory approach.

2.2 Epistemological Disruption

Historians of chemistry usually call the principles of premodern chemistry "metaphysical principles," but it is not so clear what that means, particularly if one considers Aristotle's inference of his elements from tangible properties. If postulating a theoretical entity for explanatory purposes were metaphysics, then all of classical natural philosophy and most of today's theoretical sciences would be branches of metaphysics. It is more likely that historians just adopted the term "metaphysical" from contemporary chemists who favored an operational approach in chemistry. And that was probably the most radical departure from the received understanding of science ever since. It not only broke up with metaphysics, it also gave up, at least temporarily, the idea that the main goal of science (natural philosophy) is explanation.

Remember that elements had before been conceptually developed for explaining material properties and transformations, not only in chemistry but also in biology, medicine, meteorology, and many other fields of science. If you now define elements as those substances that resist any kind of separation according to the contemporary state of the art, you are not replacing one set of principles with another one. Instead you abolish the explanatory basis of all these sciences. At the beginning you do not even know what the new elements might look like, because the definition gives no hint at all. Once you have found a substance that resists any separation effort, you first need to study its properties. How can you make use of these empirical properties for developing explanatory approaches? You can never be sure whether that substance remains an element or not, because further improvement of separation techniques might take it apart. And would not a scientific approach require that the complete set of elements, that is, all explanatory factors, are known before you should dare any serious explanation?

The overall discovery of the new elements was a very slow process that included numerous research programs (Schummer 1997). After an early period of many discoveries their number has almost linearly grown since about 1808 (1800, 27; 1808, 39; 1850, 55; 1900, 81; 1950, 98; 2000, 114). Of course later discoveries brought about only rare and even artificially made elements. However, in the early nineteenth century the most widely spread elements, including the alkali metals, alkaline earth metals, and halogens (except chlorine), were unknown. What kind of chemistry is possible on such a limited elemental basis? Chemists focused on discoveries, both of new elements and their combinations, and postponed explanation.

What appears like a crazy move has a deeper reason in philosophical ontology. Indeed, it redefines the ontological concept of "substance," that which persists through all possible changes, on experimental grounds. If by definition the elements cannot be destroyed by any chemical means, then they necessarily persist in all our chemical transformations.

2.3 Similarities and Differences to Scientific "Revolutions"

Was there any other event in the modern history of science comparable to the epistemological disruption in chemistry? If we believe our historians and philosophers of science, all the big discontinuities or "revolutions" have been theory changes, one theory replacing another one. In endless debates since the 1960s they have discussed if in all these cases the explanatory potential of the competing theories can either be compared or not, which implies that no single discontinuity consisted in temporarily giving up explanations at all. Moreover, all big revolutions concerned only very specific fields of science, with little to no immediate impact on others, such as astronomy (Copernican revolution), mechanics (relativistic, quantum mechanics), biology (Darwinian evolution), geology (tectonics), and so on. In contrast, the epistemological disruption in chemistry strongly influenced most other sciences who relied on the age-old concept of elements.

At the risk of provoking harsh criticism from philosophers, I would like to point out some epistemological similarities to the relativistic, quantum, and Kantian revolutions, all being favorite topics in philosophy. The core of the operational definition consists in relating elements to human capacities, here to the experimental capacities of taking chemical substances apart. In all the other three examples we can identify the same move (although there exist alternative interpretations that try to avoid that).

Both the special and general relativity theories can be derived from classical mechanics, and in fact have frequently been described and taught so in the tradition of Ernst Mach, if one requires that all properties in mechanics are strictly related to human measurement capacities, rather than being conceived of from a God-eye's view. The measurement of time and length of some object moving at a distance is bound by the signal speed of light, which was empirically found to be constant. If you include that so-called relativistic factor into the formalism of classical mechanics for different observers, thereby forgoing a God-eye's view, you end up with special relativity theory. Similarly, there exists no physical measurement apparatus that can distinguish between gravitational force and acceleration (or between gravitational mass and inert mass). Once you replace gravitational force with acceleration in the formalism of classical mechanics, you end up with general relativity theory.

According to the most influential Copenhagen interpretation of quantum mechanics, particularly in Heisenberg's version, quantum mechanics followed a similar move, best expressed in Heisenberg's uncertainty principle. It claims that for certain pairs of physical properties, such as location and momentum or time and energy of a particle, there is a limit of precision at which they both can be known simultaneously. Whereas others have later taken that principle as an axiom that requires no interpretation, Heisenberg himself considered the limit being posed by any possibly accurate measurement that would necessarily interact with the particle. In that tradition, physics is no longer striving for a God-eye's view but for a generalized human view that needs to take into account the limits of human capacities.

In a certain sense physicists followed the third and much earlier example of Kant, who had developed his "Copernican Revolution" in epistemology around the time of the "chemical revolution" in his *Critique of Pure Reason* (1781). Kant argued that true scientific knowledge ("synthetic statements *a priori*") cannot be derived from mere sense perception nor from metaphysical assumptions about the world as such, but only from understanding the fundamental capacities of the human mind. For instance, space, time, and causality are not something given or to be inferred from perceptions. Instead the human mind necessarily constructs our sensible world such that it has a certain spatial, temporal, and causal order. By investigating the perceptual and intellectual capacities in detail, Kant hoped to proof the a priori truth of Euclidean geometry and Newtonian mechanics, which turned out to be wrong, however, by Riemannian geometry and relativistic mechanics.

All four examples have in common that they redefine central concepts of natural philosophy by relating them to human capacities and their limits: experimental measurement in physics, cognitive capacities in epistemology, and experimental separation in chemistry. Yet, while the first three cases are widely considered landmark revolutions in the history of science and philosophy, the chemical turn to operationally defined elements has never been recognized as an epistemological revolution despite the fact that all of modern chemistry, and almost all the sciences, nowadays refer to the chemical elements that have first been identified by the operational definition.

Furthermore, the historical move from a God-eye's view to one that is specified by human conditions is not restricted to science. Since Renaissance humanism that has been a central feature of modernity in most branches of Western culture, including art (*e.g.*, central perspective, aesthetics modeled after the human body), ethics (justification of moral rules by rational principles instead of divine order), law (natural law based on human nature), and politics (legitimation of power by democratic procedures instead of divine order). It would be more appropriate to understand the chemists' operational turn of the elements of nature in this broader cultural context rather than discussing it as an appendix of some contemporary theory change.

2.4 Why Was the Disruption Neglected?

To be sure, historians and philosophers of chemistry have all been aware of and mentioned the change from "metaphysical principles" to operationally defined elements. However, they usually did so as if just one set of elements was replaced by another one, and they did hardly acknowledge the radical epistemological disruption in natural philosophy. There are several reasons for the neglect that are all related to the so-called "chemical revolution" and Lavoisier's role therein.

Lavoisier has rightly been considered the most influential proponent of the operational definition of elements during his time. However, he did not consistently apply it in his own scheme. Instead he included, for instance, imponderables such as light and heat (*calorique*) that would not meet the operational definition, suggesting that the definition was not of central importance to him. For instance, the decomposition of light by diffraction in prisms was well known and accepted since the seventeenth century through works by Francesco Grimaldi. The more Lavoisier was seen as the hero of the New Chemistry, the more one could copy his mixed attitude toward the operational definition.

Second, historians of chemistry have dealt with the operational definition mostly by answering who-did-what-first questions. For instance, some argued that not Lavoisier but Boyle would have first formulated the definition, while others rightly pointed out that Boyle had rejected elements and chemical principles altogether in his *Skeptical Chymist* (Davis 1931). Some tried to give Joachim Jungius the credit, although his complex ontology was entrenched in medieval scholastics and had little connection to experimental practice (Meinel 1982). Others have argued that the operational definition was already used in mid-eighteenth-century mineral chemistry for pragmatic reasons, particularly by Torbern Bergman (Oldroyd 1975). All these historiographical debates on whom should credit be given have moved epistemological questions to the background.

Third, Lavoisier's own engineering of a "chemical revolution" was tailored against the received phlogiston theory to promote his own oxygen theory. Oxygen, which literally means "acid generator," actually met the operational definition and at the same time took a unique explanatory role in his acid theory, according to which all acids contain the acidic principle oxygen. It thus appeared that the new elements could immediately replace the old principles in chemical explanations. However, Lavoisier's acid theory was very soon given up because of massive counter-evidence: many basic substances such as potash were found to be composed of oxygen, and acids such as muriatic acid (HCl) contained no oxygen. The short life of the acid theory thus covered the fact that the new elements could at first not serve in explanations.

Fourth, from the 1960s onward, the "chemical revolution" was usually framed in terms of a change of competing theories that are structurally similar, such as classical and relativistic mechanics. For instance, while the phlogiston theory described combustion as the release of phlogiston from the burning substance into the air, the oxygen theory described it as a reaction of that substance with oxygen from the air. However, that framework made people ignore that the two "theories" are of entirely different epistemological kinds. It is one thing to describe a chemical transformation in terms of the exchange of one or the other element, and quite another thing to provide an explanation for why the transformation occurs at all. While the phlogiston theory explained the combustibility of all substances by their containment of phlogiston, the oxygen theory had no explanation to offer for combustibility or any other kind of chemical property for more than a century, before explanatory theories emerged in terms of chemical bonding energies. Thus, a misleading philosophical framework, taken from debates in the philosophy of physics, hided the radical epistemological disruption.

Fifth, Lavoisier was quick to incorporate the newly recognized elements into a chemical classification and nomenclature of hitherto unseen systematics, such that the identity of compounds was now based on their new elemental composition, which became extremely successful. While that has been recognized comparatively recently as being part of the "chemical revolution" (Siegfried and Dobbs 1986), it shifted the attention even more away from explanation. As will be shown below (Section 3.1), classification and explanations are distinctly different epistemological functions of elements.

Sixth, two decades after the "chemical revolution," Dalton's atomism offered a new theoretical approach in which atoms corresponded to the elements. That suggested that the new elements could almost immediately take on the role of explanatory entities. However, Dalton's original atomism, while explaining or reformulating the laws of definite and multiple proportions, did not explain chemical properties of compounds. It took many decades before the approach gained any explanatory potential worth mentioning, such that most chemists considered it just a formalism to describe relative equivalent masses of the respected elements. Many twentieth-century historians and philosophers of science, who were enthusiastic about the much later success of atomism in structural chemistry, have overlooked that long period. And they equally tend to overlook that all of modern chemistry, and most of modern science, is based on the turn from the received principles to operationally defined elements.

Overall, the historiographical focus on the "chemical revolution" and its various interpretations have made historians and philosophers of chemistry neglect the epistemological disruption caused by the adoption of the operational definition of elements that occurred at about the same time. There is no hero in adopting a definition. The international chemical community did it sometime around 1800. But the exact dates and individuals do not matter for its epistemological understanding and appreciation.

3. Continuity

3.1 An Epistemological Framework for Understanding the Elements

A more general reason for the little appreciation is the lack of an epistemological framework that allows one to understand what epistemological roles elements have played in the history of science. A framework is not to be confused with a theory; it does not depict anything. It is a conceptual tool or scheme that can be applied to any historical period in order to grasp its epistemological particularities and to identify continuities and discontinuities.

The framework I am suggesting is borrowed from Rom Harré's pioneering work *Varieties of Realism* (Harré 1986). Although he himself developed it for understanding particle physics, despite his earlier background in chemical engineering before he became one of the most influential philosophers of science, his ideas can easily be generalized and applied to the entire history of elements (Schummer 1996, chapter 4).

In his book Harré presented three versions of realism: (1) for ordinary world experience, (2) for theoretical entities, and (3) for abstract mathematical structures. The second one, called "reference realism," transformed the contemporary language-focused debate (when do theoretical terms in science refer to real entities?) into a question of scientific practice: when is it reasonable to believe that a theoretical entity exists such that we should actually start a research program to experimentally identify it? To answer that question, Harré developed a sophisticated scheme that allows assessing the overall scientific context. What matters in the present context is that he distinguished between three different epistemological roles or functions of theoretical entities, all of which should ideally be considered at the same time.

The received philosophy of science has usually considered only the first role of theoretical entities, their explanatory potential within a certain theory. Many even went as far as to define theoretical entities just by that, such that two theories that happen to use the same theoretical term, say “electron,” refer to different entities. However, Harré added a second function, their ontological role in a classification system. While classification came to the awareness of most philosophers of science only through particle physics, it has always played a pivotal role in most sciences other than mechanics, including chemistry, biology, mineralogy, and so forth. Scientific classifications frequently employ theoretical entities, the most prominent historical case being the classical elements or principles that allowed ordering the realm of substances by their supposed composition of the elements. The third role, which is a central requirement of Harré’s “reference realism,” is that the theoretical entities are conceptualized such that they potentially belong to the observational world. Even if we do not yet exactly know how to do it, there should be a possible way to get direct experimental access to these entities.

If we apply this threefold framework to the entire history of chemistry and alchemy, it turns out that there have always been tensions between the three roles, up to the present day. Many theoretical conceptions of the elements or principles have focused on explanation, at the expense of classification and direct access. Others have highlighted classification, neglecting explanations and experimental access. And there were, even long before the operational definition, approaches that emphasized experimental access.

Rather than analyzing the entire history of elements here, I will use the framework to point out three aspects: (1) the continuity of the third role, (2) the importance of the operational definition for classification, and (3) conceptual tensions arising from difficulties in reconciling all three roles.

3.2 Experimental Access

The threefold framework allows us to recognize the operational definition of elements as an extreme concept that takes the third role, experimental access, as the defining characteristics of elements. However, other historical conceptions of elements have taken that role also into account, even though they put more emphasis on the other roles, such that the framework helps us to see more continuity in the history (Schummer 1996, 101-165). Let us take a brief look at four examples.

In Aristotle’s scheme the four elements are considered real material substances (composed of matter and form, in his ontology) with tangible properties. They therefore seem to perfectly meet Harré’s third criterion for theoretical entities, direct accessibility, even if one does not yet know exactly how to do that. But Aristotle himself was skeptical for reasons consistent with his own account. The elements can not only move around, mix with one another, and build compounds, they can also convert into one another. Any attempt to isolate them by experimental methods would have to apply material means - for instance, fire in distillation - which would result in transformation rather than in isolation.

The experimental tradition of alchemy and chemistry was more optimistic than Aristotle was. For instance, Christian Gottlob Gmelin, who based his 1780 chemistry textbook on the Aristotelian elements, provided even a version of the operational definition (Gmelin 1780, 36):

> Simple bodies in the chemical sense are those which can be no further decomposed into unlike particles by chemical artifices, they are called by another name “elements.”

The second example, classical atomism, literally includes an operational definition in its name. An atom (from Greek *átomos*: the indivisible, uncuttable) is a material body that cannot further be divided. In the Christian tradition, that limit of division usually marked the distinction between human and divine capacities of division. For mechanically minded philosophers, it was the limit of cutting a piece of matter by an imagined small knife. Whatever the specific account, classical atoms were conceived as material entities by a hypothetical operational criterion, even though direct access was considered to be restricted by their supposed smallness. However, by making the operational criterion hypothetical beyond human reach, atomism did not encourage experimental approaches of isolating individual atoms.

My third example is the sulphur-mercury theory from Arab and Latin medieval alchemy. Both “sulphur” and “mercury” were usually considered higher-level principles composed of the classical four elements, and in turn were the essential components of many materials. Particularly detailed were views about metals whose characteristic properties alchemists explained by their different proportions of the two principles. Rather than being “metaphysical principles,” or identical with the common substances of the same name, “sulphur” and “mercury” were thought to be material substances that can be isolated by experimental methods (Newman 2014). Unlike the Aristotelian elements and the atoms, these chemical principles encouraged developing for the first time in history sophisticated experimental laboratory techniques for taking substances apart and combining them anew (solve et coagula, as it was called in Latin), which became the model of the modern chemical laboratory for analysis and synthesis, and, for that matter, of laboratory science in general. Thus, the notion that “sulphur” and “mercury” are potentially real and pure substances, from which one could even produce highly valued substances such as gold, enabled the development of the idea of laboratory science in the sense of performing controlled, reproducible, and theoretically guided operations.

Fourth, many later commentators have ridiculed phlogiston as a fancy detour of science that postulated an imagined chemical principle for explanatory reasons only without any experimental foundation (Harré’s first criterion), echoing Lavoisier’s own rhetoric. However, eighteenth-century “phlogistonists,” that is, almost all chemists by then, had long given up speculative natural philosophy, as the philosopher of chemistry Elisabeth Ströker (1982) convincingly argued on the basis of the original, mostly Latin, texts. Already Johann J. Becher, on whose theory of various “earths” Georg Ernst Stahl developed the generalized phlogiston theory, tried to base his principles on experimental grounds. Before the so-called “chemical revolution” chemists identified phlogiston, which by then had gained tremendous explanatory success for such diverse fields as combustion, calcination, breathing, and meteorological cycles, with experimentally identifiable substances, including what we would today call hydrogen, carbon, and energy. One could even argue, as Chang (2012) has done, that the phlogiston theory pre-formulated modern redox theory, making phlogiston a predecessor of today’s electrons. Whatever the interpretation and its specific role in explanations, phlogiston was from its very beginning thought to be a chemical substance that could possibly be isolated and analyzed in pure form in the laboratory.

In all four examples, experimental accessiblity is an operational criterion of elements, at least on hypothetical grounds, that illustrates the continuity of Harré’s third role in the history of chemistry.

3.3 Classification

The simplest form of a systematical classification takes two independent properties and their opposites (A, non-A, B, non-B) and combines them in a table of four classes (A and B, A and non-B, B and non-A, non-B and non-A). In some sense, Aristotle’s scheme of fundamental properties (solid, fluid, cold, warm) corresponds to that account. However, the central idea of natural philosophy has always been the classification of matter not by properties but by elemental compositions, such that Aristotle defined the elements by primary matter bearing each a binary combination of fundamental properties. Indeed, the notion of elemental entities is logically tied to a classificatory approach based on elemental composition, that is, every account of elements implies a classification based on composition, ideally in quantitative terms.

The main historical problem of classifying matter in terms of elemental composition was insufficient knowledge about composition. The composition could not simply be inferred from observational properties. As long as elements were theoretical entities postulated for explanatory purposes, the only way of inference was from successful explanations, such that classification and explanation were epistemologically tied together, despite being epistemologically different functions. For instance, determining whether a substance contained phlogiston or not could only be assessed from the explanation of certain chemical properties, such as combustibility, which the phlogiston theory explained. On the other hand, an ever-increasing repertoire of experimental techniques of analysis, such as various forms of distillation, allowed taking substances apart and provided direct access to components. Much of the history of alchemy and early chemistry is about reconciling the explanatory and experimental approaches to elemental composition, without success.

Against that background we can appreciate the operational definition of elements as a move that perfectly combines classification and experimental access, at the expense of explanation. If elements are those substances that by definition resist any separation technique, then the experimental separation of any substance ultimately provides its elemental composition by experimental access to the elements. Moreover, if the analysis is performed quantitatively in terms of relative elemental masses, every substance can be classified based on the quantitative composition of elements, which previous accounts could only dream of.

The new definition of elements was not the only operational solution to classificatory problems in chemistry (Schummer 1996, 170-181). Instead, the old hierarchy of materials, from elements to compounds, to homogeneous mixtures and heterogeneous mixtures, that Aristotle had already developed on partly observational and partly theoretical grounds, could be redefined by reference to experimental techniques. Mechanical separation techniques – such as cutting, grinding, and sorting – decided if the material was a heterogeneous mixture or not; thermodynamic separation techniques (distillation, crystallization) decided if it was a homogenous mixture or not; and chemical analysis decided if it was a compound or an element. Of course, the operational definitions did not always provide simple and decisive results, as with azeotrope mixtures and many presumed elements that turned out to be compounds by more sophisticated chemical techniques. However, those substances could not undermine the classificatory approach because they thereby just moved one step up the hierarchy.

It should be noted that the operational definitions of elements and compounds worked safely only on the basis of a reliable and uniform system of relative equivalent masses, which was developed only during the nineteenth century by tremendous collective efforts of the chemical community. Whether a chemical transformation was actually an analysis rather than a synthesis did not depend on the absolute masses of educts and products, but on their relative equivalent masses, the determination of which employed a large set of mutually correcting experimental techniques (Schummer 1996, 185-203), including volumetric and gravimetric measurements of combining volumes and masses in chemical reactions; thermodynamic measurements such as the decrease of melting points, the increase of boiling points, osmotic pressure, specific heat capacities; and analogy reasoning such as by isomorphism of crystals and chemical similarities of elements that eventually led to the periodic system.

Against that background it would be misleading to use the terms “empiricism” or “positivism” for describing the chemical approach to classification. The most appropriate term would be “experimentalism.”

3.4 Tensions: Debates on Elements in Compounds

One major strength of Harré's threefold framework is that it allows us to identify and understand tensions within the concept of elements throughout history. Such tensions occur when the three roles or functions cannot smoothly be integrated into one concept. The notion of elements then tends to disintegrate into two or three concepts.

In one of the rare philosophical papers by a twentieth-century chemist, Fritz Paneth (1931) argued that modern chemistry has actually two concepts of elements, which he called *einfacher Stoffe* (simple substances) and *Grundstoff* (basic substances). The first concept refers to material bodies that meet the operational definition; the second one is used when we think of a compound being composed of elements to explain the compound's properties from the elements. Obviously the split results from obstacles to reconciling the two roles, experimental access and explanation. Note that classification can be achieved by both concepts: operationally by chemical analysis and synthesis, and representationally by referring to the constituents of a compound.

Paneth was not the first to notice the double meaning. As Scerri (2007, 117) and Hooykaas (1947) have pointed out, already Mendeleev observed the inconsistency and distinguished between simple substances and abstract elements. To some extent, also Lavoisier's terminological vacillation in his *Traité élémentaire de chimie* (1789) between "*principes*" and "*substances simples*" for his elements expresses the double meaning, because of his efforts to take some elements, particularly oxygen, as explanatory principles. In the period between Lavoisier and Mendeleev, who tried to reintroduce an explanatory account with his periodic system, the double meaning was largely absent, because explanatory ambitions were temporarily given up for the elements that still had to be discovered. However, in the past six or seven centuries that was rather an exception.

The main tension became visible in endless debates about whether elements are constituents in compounds, and, if so, how one could explain that most compounds radically differ in their properties from the elements they were presumably built of and classified by. The issue has been a major explanatory challenge to chemistry and its precursors. Much of the debate during the ancient, early modern, and modern periods has been documented (*e.g.*, Duhem 2002; Hoykaas 1947), such that I confine myself to a few remarks on the medieval period that is lesser known and then look at IUPAC's solution.

Aristotle himself argued that in true compounds, elements are only in the state of potentiality (*De gen. et cor*., I. 10). The two leading Islamic commentators, Avicenna and Averroes, developed – each with a sophisticated metaphysical apparatus – opposite views (for detailed references and discussion, see Lasswitz 1890, 239-254; and Maier 1943, chapter 1). In much simplified terms, Avicenna held that the elements as such are preserved in compounds and that only their properties combine into new substantial forms, whereas Averroes thought that the elements lose their identity in compounds (unlike in mixtures) to build new substantial forms. Almost all prominent Latin philosophers who dealt with natural philosophy debated the issue and sided either with Averroes or Avicenna or developed a middle way, including Albert the Great, Thomas Aquinas, Roger Bacon, Duns Scotus, and William of Ockham. They all engaged in what came to be a central issue of chemistry, although none of them could convincingly solve it.

Starting with Lasswitz (1890) modern commentators have frequently argued that the issue was eventually solved by modern atomism. However IUPAC still upholds a double definition of "chemical element" based on atomism in its Gold Book:[3]

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[3] IUPAC, *Compendium of Chemical Terminology*, 2nd ed., comp. A. D. McNaught and A. Wilkinson (Oxford: Blackwell Scientific Publications, 1997), s.v. "chemical element," https://goldbook.iupac.org/html/C/C01022.html.

> (1) A species of atoms; all atoms with the same number of protons in the atomic nucleus.
>
> (2) A pure chemical substance composed of atoms with the same number of protons in the atomic nucleus.

While definition 2 highlights the role of experimental access by purification resulting in a collection of atoms, definition 1 defines elements not by a collection but by a species of atoms that might serve in explanations and classificatory representations such as structural formulas. The phrase “all atoms with the same number of protons in the atomic nucleus” suggests that the number of neutrons is an accidental property of elements, such that isotopes belong to the same atomic species and element in both definitions. But what about electrons? IUPAC defines “atom” as the

> smallest particle still characterizing a chemical element. It consists of a nucleus of a positive charge (Z is the proton number and e the elementary charge) carrying almost all its mass (more than 99.9%) and Z electrons determining its size.[4]

Hence, the number of electrons, Z, is an essential property of the atom and the element, such that an ion is, according to IUPAC’s definition, not an element. It follows that elements do not exist in ionic crystals because the electrons can no longer be assigned to the nuclei as in elements, and similar reasoning can be developed for covalent and metallic bonds, or any other theory of chemical bonding. Since compounds are not composed of elements, they cannot be classified according to elemental constituents. Obviously IUPAC, I assume unknowingly and unwillingly, sides with Averroes, despite the double definition.

If, on the other hand, and contrary to IUPAC, one considers the number of electrons, like the number of neutrons, an accidental property of atoms, then one could define atoms and, thereby, chemical elements as proton aggregates, regardless of neutrons, electrons, energy and spin state exchange with the surroundings, and so on. Atoms/ elements in that sense can without contradiction be said to exist in compounds, and their specific configuration may be used for classificatory purposes. That corresponds to Avicenna’s view. However, all modern chemical explanations refer to the electrons of atoms, which would, strictly speaking, be ruled out. One could try a middle way, as did Albert and Thomas, for instance, by distinguishing between core electrons and outer shell electrons, but that only blurs the issue rather than solves the tension convincingly.

In sum, from the Middle Ages to today’s chemistry, all three roles or functions of elements could not be reconciled in one consistent approach. The operational definition took experimental access as the defining feature of elements and achieved classification by experimental analysis, but at the price of giving up explanations. Once the explanatory role of elements was revived, conceptual tensions arose anew, of which IUPAC’s definitions are a telling example.

4. Conclusion

4.1 The Legacy of the Operational Definition

Definitions cannot be true or false, they are the undisputed conventional parts of science, that is, the scientific community decides whether they accept it or not. Once accepted the community can at any time change their minds and drop the definition; or the community splits such

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[4] IUPAC, *Compendium of Chemical Terminology*, 2nd ed., comp. A. D. McNaught and A. Wilkinson (Oxford: Blackwell Scientific Publications, 1997), s.v. “atom,” https://goldbook.iupac.org/html/A/A00493.html.

that one group accepts it and the other one drops it. In general, definitions specify the meaning of terms which enables more precise communication and avoids misunderstandings. Operational definitions, for example, the definition of “time” by clock measurement, do not essentially differ in that regard, but they relate concepts to established and shared laboratory practices and try to cut off theoretical and metaphysical connotations as far as possible, which makes the definition acceptable across metaphysical views and theory changes.

However, the operational definition of elements is very special in two regards. First it defines not some property but elements, that is, the fundamental entities that all explanatory and classificatory approach in natural philosophy is supposed to refer to. Thus, any definition of elements shapes the entire conceptual and theoretical apparatus. Second, the operational definition of elements does not only define a term, it provides laboratory rules for literally producing those entities to which the term “element” refers. All of modern chemistry, both experimental and theoretical, has been built on studying those entities, their properties and compounds, their systematization and theoretical conceptions from Daltonian atomism to quantum chemistry. Moreover, almost all sciences – including physics, medicine, biology, and mineralogy – have adopted these chemical elements in their experimental and theoretical frameworks as the unquestionable material basis or starting point. When nuclear physics began to study subatomic particles, they did so not on the basis of Aristotelian elements but on the basis of the operationally defined and produced chemical elements; that is, without the operational definition today’s nuclear and particle physics would not exist.

Theoretical scientists might be inclined to take atoms in their models as given entities, but the properties of the atoms that they take for granted came to be known only by studying those pieces of matter that met the operational definition. Thus the operational definition of elements became materialized in science in a unique way, both literally by providing a new material basis for science, and conceptually by integrating the new entities in theoretical frameworks.

One could argue that, once the operational definition was materialized, it could have been abandoned, like a tool that was temporarily useful to redirect science into a new direction. However, the operational definition was challenged several times, particularly through the discovery of electrons and isotopes (Kragh 2000). That caused debates on whether the electron is an element and whether isotopes are different elements or not, because their experimental isolation and separation actually met the operation definition, unless the techniques of separation would be better specified. In these debates, chemists had to rethink the definition and employ the usual criteria for accepting a definition, including its usefulness. In both cases their negative decisions reflect the contemporary chemical perspective of usefulness: electrons could not be isolated and experimentally employed in the same way as the other elements; isotopes do hardly differ in their chemical properties from one another such as the other elements. They could have decided, and perhaps will do so in the future, otherwise. The examples illustrate that definitional problems can come up anew at any time, such that it is better to be aware of the conceptual basis on which chemistry historically rests.

4.2 The Usefulness of Philosophy for Understanding Science

Epistemological reasoning might not be the main strength of scientists and historians of science, but some acquaintance with epistemology is certainly an advantage in both fields. The history of elements provides ample evidence.

To be sure, some time ago historians of science made frequent use of the methodological theories by Popper, Kuhn, Lakatos, and others in case studies that were meant to support or criticize ideas about scientific progress. However, using the historiography of science in support of a philosophical theory and using an epistemological framework for analyzing a historical period of science are two different things. The former takes epistemology as a theory that claims truth; the latter employs epistemological concepts as tools for better understanding the epistemic practices of science. Only the latter approach, philosophy as a toolbox or skills, serves historiography.

That was illustrated in Section 3 by using Harré's threefold framework. By considering all three functions of elements – explanation, classification, and experimental access – we can analyze both the continuities and discontinuities in the entire history of elements. The turn to the operational definition of elements then appears as a radical disruption, by temporarily giving up explanation in favor of perfectly meeting experimental access and classification. That was arguably the most radical and most influential disruption in science ever since, because it broke up with the entire tradition of natural philosophy and reoriented not only chemistry but most of the sciences toward a new material basis on which all subsequent ideas of science have built. One may call it a "revolution," but that term has long been watered down by numerous case studies on marginal events in science. Its scientific impact dwarfs all the other so-called revolutions, such as the Kantian, relativistic, and quantum revolutions, which have been vividly debated in philosophy despite their limited impact on specific fields.

Although the operational turn follows a similar epistemological pattern as these local revolutions, the history and philosophy of science has hardly acknowledged its scientific importance and epistemological significance. Whereas philosophers of science have focused on physics and neglected chemistry, historians of chemistry would rather debate the so-called "chemical revolution" and Lavoisier's role therein. The person-centered historiographical approach tends to overlook the broader epistemological dimension of the operational turn in chemistry, that it redefined central concepts of natural philosophy by relating them to human capacities and their limits, and its place in the wider cultural history of modernity.

Moreover, Harré's framework allows us to identify and understand conceptual tensions and debates that arose from insufficient integration of all three roles into one account, from the Middle Ages up to the present day. Of course one needs detailed knowledge of scholastic metaphysics to understand the medieval debates. But only little training in logic is required to understand that current chemistry seems to favor the view of Averroes. I assume that most chemists agree to IUPAC's definitions of "chemical element" and "atom" cited above. However, they would probably disagree about the claim that elements are not constituents of compounds, although that exactly follows from these definitions. As conceptual tensions have reached a historical maximum, philosophy can help build a more consistent basis of chemistry.

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