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Rein Vihalemm: 'On the Transition to Quantitative Inquiry in Chemistry'[1]

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In the works on the history of chemistry, categories are often applied uncritically, with a disregard for philosophical studies. As a result, many logical transitions in the motion of cognition in the field of chemistry have remained unnoticed. In this paper, I observe the logical aspect of the development of certain concepts in the history of chemistry from the perspective of the transition from qualitative to quantitative inquiry.

As is known, the first integral conception in chemistry was the so-called phlogiston theory. While the phlogiston theory explained chemical transformations from the qualitative aspect, primarily the observable opposite processes of oxidation and reduction, then in the next stage chemists focused their full attention on the measurement of the weight and volume of chemical substances. This allowed to overturn the relations found by chemists-phlogistonists. At the same time, this quantitative approach was *for chemistry* a further *qualitative* determination of substances. It is important to note that the recognition of gases as qualitatively different kinds of substance, and separation of their mixtures, would have been impossible without measuring their weight and volume, since many gases have no immediately perceivable qualitative differences, and were simply regarded as "air". Also, it was only due to the quantitative criteria that Lavoisier could determine real chemical elements, which became an essential pre-requisite for the founding of chemical atomism.

At the beginning of the 19th century, the question of the *process* of transformation of substances arose in chemistry. Berthollet uncovered that not the entire initial substance would turn into another substance—that the reaction does not go to completion. Thus, he encountered problems with the quantitative characteristics of substances. It became clear that the reactivity of *substances* depends, firstly,

[1] Original: Vihalemm, R. A. (1971), '*O perekhode k kolichestvennomu issledovaniiu v khimii*,' Tartu Riikliku Ülikooli toimetised / Uchenye zapiski Tartuskogo Gosudarstvennogo Universiteta. Trudy po filosofii XV, vihik / vypusk 273, str 12–17.

on the quality, i.e. the reactive capacity of the substance, and, secondly, on the amount of that substance.

In other words, Berthollet showed that a chemical reaction must be characterised both from a qualitative aspect (*which substances* react) as well as from a quantitative one, and that, aside from the question of whether the given substances react or not and how they react in comparison to other substances, there is the question of substantial importance of *how much* of the substance reacts. But is it fair to say that Berthollet carried out a *quantitative* inquiry of chemistry?

The thing is that Berthollet had no *units* of measurement for the amounts of chemical substances. He employed the general mechanical units of weight, which, however, are too abstract for chemistry. In fact, Berthollet made a logical error because, on the one hand, he talked about *different* chemical substances, but on the other hand, he considered those substances simply as masses, even though he also talked about the *quantity of active substances*. After all, a quantitative expression of active substances presupposes a uniformity of its properties (in a certain respect). Berthollet, however, did not indicate the cause for this similarity of reacting substances, which allows the discussion of the quantity of those substances in the first place. Berthollet proceeded from the preconception that the atoms of all substances are of the same weight: only in such a case it is possible to say that the weight of a substance expresses the quantity of the given substance; or rather, only then it is possible to compare the quantities of substances (the amount of units of individual substances) by comparing their weights.

Empirically, Berthollet proceeded from chemistry and uncritically incorporated physical-mechanical knowledge. He did not turn to quantity, since he did not propose units of chemistry, neither did he achieve the maximal qualitative distinction of chemical substances from other determinations of substances, but also from each other. The logical implication here is that, according to Berthollet's view, any macro-substance must be considered as an individual chemical substance, since the composition of a chemical compound, according to Berthollet, is non-constant, and substance consists directly of chemically combined abstract atoms, that is, it is a chemical compound. Thereby it was accepted as an empirical fact that a certain substance, in different macroscopic amounts, remains the same substance. Thus, it was necessary to admit that atoms as if had no qualities; or, at least, that the chemical quality of a substance must not depend on the quantity of combined atoms. In other words, from a logical point of view it remained completely unintelligible where the chemical quality comes from (for Berthollet it was just "given"), and how chemical transformations of substances (changes in their qualities) occur.

Here we must keep in mind the following. In the cognition of nature (in mechanics and physics), the conception of substance was acquired which specified as mass that which has weight (it is true that also "imponderable substance" was discussed, but we only have in mind "ponderable substance"), and which all bodies are composed of. Such a conception of substance emerged as a result of its ultimate distinction from other forms of being.[2] This—absolute determination of substance, i.e. substance as such, substance in general—is one (in the determination no different substances exist, there is just *one* single substance).[3]

The quantitative expression of substances in units, which is indifferent towards the qualities of bodies, is based on this kind of determination of substance. However, in the framework of chemistry, which emerged, so to say, not against the "background" of nature in general but only as a result of the inquiry into the transformation of substances, the task involved the differentiation of concrete substances, that is, determination of the being of substance concluded not in distinguishing substance from other forms of being, but in the differentiation of the being of one chemical substance or another, in the determination of individual chemical substance. The ultimate qualitative determination of the being of a chemical substance ([Hegel's] the One), through which the transition to quantity occurs, is the determination of the individual substance as such. (According to the quantitative view, all chemical substances are determined on the basis of them being all merely some aggregates of an individual chemical substance as such.) From the perspective of physico-mechanical sciences, this means the need to analyse the determination of the amounts of substances, to find a qualitative quantity—a measure of substance—for the case of such a body, such a being of substance as an individual chemical substance. This leads us to the conclusion that a determination of an individual chemical substance becomes possible when the concretisation of substance as such, according to physico-mechanical sciences, is successful. Thus, Dalton proceeded by showing that substance (as such) exists in the form of atoms, with definite weight, the

2 Translator's note: Vihalemm seems to use the parlance and ideas of Hegel in *Science of Logic* (see fn 3) ('being', '(qualitative/quantitative) determination', etc.).

3 This corresponds to the Hegelian position that logical transition to quantity occurs through the ultimate qualitative determination of being, through an individual, which is already a quantitative determination—the One, becoming the unit for many (see Hegel, 2002, pp. 157–164).

bonding or dissociation of which leads to the formation or decomposition of a chemical substance (as such). Dalton (relying on atomism) theoretically substantiated the stoichiometric laws in chemistry (1803). Further establishment of the chemical units of substances was realised on the basis of molecular study (Avogadro, 1811; Ampère, 1814; Cannizzaro, 1858).

The chemical units of substances were thus established by physical methods, by ascent from the abstract (and more general and simple) towards the concrete (and complicated). Those units were: (1) atoms—bodies with *definite* weight (*definite* quantities of substance as such); and (2) molecules—*definite* multiples of those bodies—new bodies with definite weight. Strict distinguishing of mechanical (transposition of substance as a result of transposition of self-identical units, self-identical substance), physical (mechanics of molecules, or change of substance as a result of transposition of self-identical molecules), and chemical (physics of atoms, or change of substance as a result of change of molecules ensuing transposition of atoms) change of substance now became possible. This served as a prerequisite for a quantitative study and continuous uncovering of the essence of chemical affinity between substances. The first quantitative research into chemical balance was the work by Guldberg and Waage (1864), in which the concept of concentration of substances was introduced in chemistry to replace the absolute mass of substance.

Some authors believe that stoichiometric laws quantitatively expressed *chemical affinity*.[4] This is a misunderstanding. Establishing definite weight proportions in which elements unite, and the equivalent weights, the discovery of stoichiometric laws is not yet a quantitative expression of *chemical affinity*, but rather merely a concretisation of its qualitative determination: discrete coupling and saturation of affinity of elements. For it is only possible to talk about quantitative expression of chemical affinity after *units of affinity* have been found. To do that, it was necessary, first of all, to find the ultimate qualitative determination of the being of chemical affinity. By then, only chemical units of *substances* had been found. Thanks to Dalton's atomism, construing the chemical interaction of substances as the bonding and dissociation of atoms became possible.

[4] Bykov, for example, notes: "Chemical affinity found its quantitative expression in stoichiometric laws. In accordance with the high development of the mechanics of the essence of chemical affinity, mechanical construing was yielded." (Bykov, 1959, p. 85) Menshutkin writes the following: "Relations of weight, or component weights and equivalents, were experimentally found for all elements, and in the course of new discoveries were determined also for those. The chemical affinity of elements to each other was thereby studied quantitatively and expressed in numbers." (Menshutkin, 1937, pp. 150–151)

Only in the 1850s, with the emergence of the study of valency (atomicity), the discussion of some kinds of units of chemical affinity became justified (Frankland, Kekulé, Couper, thereafter, at the beginning of 1860s, Butlerov and others).

Butlerov leaves aside the concept of physical atoms, and by that also the mechanistic-geometrical conception of corpuscles. He does not seek to attribute chemical properties to such corpuscles, but (relying on the essence of the chemical force of affinity) defines the concept of *chemical* atom and *chemical* structure.

> The concept of chemical atoms is more abstract than that of physical atoms. In discussing chemical atoms, one had to make abstractions on the size, shape, distribution of atoms in space, and consequently, it so seemed, the question of spatial ("mechanical") structure of molecule was ruled out. Meanwhile, there was a stable tradition in chemistry to link chemical properties of molecules with their spatial structure. Butlerov breaks from this tradition. (Bykov, 1960, p. 85)

Iu. A. Zhdanov shows that Butlerov formulated an archetypical abstraction of organic chemistry. The reason for his success was seeing the missing stratum of this abstraction in phaenomena of isomerism that had eluded his predecessors (Zhdanov, 1960, pp. 15–16; 1963, pp. 15–18). Butlerov himself noted in 1885: "Isomers were not studied, not known—it was possible to go on without 'structure', but these days are long gone…" (Butlerov, 1885a, p. 434)

Butlerov also developed further the determinations of chemical affinity (as such) between atoms, units of affinity and quantity of affinity (as a multiple of those units, which is the definition of extensive property) proposed by Kekulé and Couper, but also the vigour or energy of affinity (the definition of intensive property) (Butlerov, 1885b, pp. 71–72).

That certain units of affinity must have been available can be illustrated with an analysis of the allegation that Berzelius, back in the day, made against Avogadro's hypothesis. Berzelius wrote:

> Those scientists who prefer to represent atoms in the form of groups have come up with an easy explanation, accepting that, in compounds, the atoms of molecules of a simple body interchange with the atoms of molecules of other simple bodies, so that in the resulting aeriform compound, the number of molecules remains the same for a given volume. Dumas attributed so great importance to such a division that he even suggested to accept that atoms themselves divide by entering a compound. Yet, this hypothesis, which

> contradicts the theory which it is founded upon, can be entirely eliminated by acknowledging the existence of the groups of atoms. However, this latter suggestion, even though it provides the simplest explanation in the case a compound consists of an equal number of atoms of each element, leads to entirely incorrect relations when the relations between the numbers of atoms are different, for instance, when a group of atoms must, by way of interchange, lose more atoms than it gains by substitution, i.e. when one atom of one element combines with 2 or 3 atoms of another, or when two atoms of one element enter into a union with 3 or 5 atoms of another. Consequently, the theory about simple atoms appears more preferable to the theory about "groups of atoms". (Berzelius, 1845, pp. 64–65 quoted in Feierstein, 1961, p. 106)

Obviously Berzelius, considering the molecule from a mechanical-geometrical perspective and not having any idea of the valency of atoms, could not conceive how dissimilar amounts of atoms can replace each other. As a result, in this case, Berzelius in fact took atom (the unit of chemical substance) for the unit of chemical affinity (analogously to Berthollet who took the unit of the mass of substances for the unit of chemical substances). Therefore, when those units coincide (this occurs in the case mentioned by Berzelius, "when a compound consists of an equal number of each element"), i.e. when only univalent (monatomic) elements combine (say, when the reaction $H_2 + Cl_2 \rightarrow 2HCl$ takes place), then Berzelius agrees that the hypothesis of Avogadro "offers the simplest explanation" (the analogy with Berthollet is that if all atoms had the same weight, and molecules did not exist at all, then Berthollet indeed would have measured the relative quantities of chemical substances).

Thus the analysis expounded above shows that when considering the evolution of the quantitative approach to chemical phaenomena, it is imperative to clearly establish whether we are dealing with a *chemical* quantitative inquiry, and whether *chemical units* have been established to measure one chemical phaenomenon or another.

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