Document

Rein Vihalemm: 'The Cognitive Move from Being (Immediate Phaenomena) to Essence in the History of the Study of Chemical Affinity'[1]

Translated by Ave Mets

V. I. Lenin, revising Hegel's *Science of Logic* along materialist lines, underscored that categories are essentially stages in the evolution of cognition. Such most general levels are Being (immediate phaenomena) and essence, whereby cognition moves from less deep essence (first order) to even deeper essence (second order, etc.). Lenin wrote:

> The concept (cognition) reveals the essence […] in Being (in immediate phenomena)—such is actually the *general course* of all human cognition (of all science) in general. […] **Insofar** Hegel's dialectic is a generalisation of the history of thought. To trace this more concretely and in greater detail in the *history of separate sciences* seems an extraordinarily rewarding task. (Lenin, 2008 [1976], p. 316)

This article explores the transition of cognition from immediate phaenomena (Being) to essence on the example of the history of the study of chemical affinity. (The history of the cognition of chemical affinity is, properly speaking, the history of the cognition of chemism, the chemical form of motion in general.) With regard to this, attention will be paid on the sensuous-practical, rational (but short of experiments and theory), empirical (experimental), and theoretical levels of cognition (see Vihalemm, 2022).

* *

*

---

[1] Original: Vihalemm, R. (1968), 'Dvizhenie poznaniia ot bytiia (neposredstvennykh iavlenii) k suschnosti v istorii ucheniia o khmicheskom srodstve,' *Tartu Riikliku Ülikooli toimetised / Uchenye zapiski Tartuskogo Gosudarstvennogo Universiteta. Trudy po filosofii.* XI, vihik / vypusk 212, str. 77–92.
Editorial note: Due to the political circumstances of the Soviet Union, authors were obliged to refer to Marxist classics in their writings. Those references are retained in this translation for historical accuracy.
Square brackets indicate the translator's additions and corrections to the text.

The initial stage of the cognition of chemical affinity. The term 'affinity' (*affinitas*) was first used in chemistry in the 13th century by Albertus Magnus. He wrote: "Sulfur blackens silver and in general burns the metals because of its affinity for these materials" (Albertus Magnus, 1569 in Walden, 1954, p. 30). Here 'affinity' expresses "something similar to an ordinary kin relationship between bodies", and "the Hippocratic hypothesis—*simile venit ad simile*—stood for a law of nature" (Potylitsyn, 1881, p. 1).

Apparently, the logic of reasoning was as follows. Real sulphur is a nearly pure "flammability" which consists of the "principle" sulphur (on the initial level of cognition, properties were regarded as some kind of "substances" or "principles"). And since metals also burn, therefore they too must contain the principle of flammability. Thus the upshot was that metals were similar, akin by nature to sulphur. And this counted as an explanation to why sulphur reacts with metals. It is difficult to explain why kinship counted as the cause for combining of bodies. Here, apparently, anthropomorphism of thinking plays an important role, as many works suggest. But we also deal here with what Hegel called "the formal method of explanation from tautological grounds" because here is expressed "in the form of reflection-into-self, of essentiality, the same content that is already present in the form of an immediate being […]" (Hegel, 1969, §999). Bodies have identical properties (they burn, combine with each other, etc.) because they contain identical "principles," and they contain identical "principles" because they have identical properties. Bodies combine because they have affinity for each other,—affinity, they have because they are akin,—akin they are because they contain identical "principles," etc.

On the perceptual-practical level of cognition, the property—disposition for interaction, transformation—is abstracted from observable chemical processes. This circumstance allowed operating with the term "affinity" to cover up the actual tautology—"substances react with each other because they react"—and, on a purely formal-logical plain, arrive at a non-tautological claim—"substances react with each other because they have affinity to each other." The term "affinity" designates a real, observable (though hitherto in no way explained) phaenomenon in chemistry. Whereby this phaenomenon appeared expressible on a rational level, attempts were made to logically substantiate the facts uncovered in chemical practice (sensuous-practical knowledge), regarding chemical affinity, and various natural philosophical aenigmata concerning its essence emerged. One can say that the "*being*" of chemical affinity was recognized. "Being," though, infamously, is a category that is the most devoid of content. All *cognitive* content of chemical affinity, all *knowledge*, remained merely *sensory-practical*.

Geber's [Abu-Musa-Jâbir-ibn-Hayyân] works from the [8th] century are of great importance from the perspective of the study of chemical affinity (Walden, 1954). Geber talked not merely about affinity, but compared metals (those known to him) based on their juxtaposition with some chemical agents, and arranged the first "affinity series." Thus, it became possible to speak about varying degrees of affinity of different substances relative to one another (this marks the beginning of the quantitative aspect, but in a qualitative form, as it were, since the affinity between each pair of substances remains constant and "changes" only in relation to other substances).

For a long period after that, there was extensive evolution of the study of chemical affinity: an increasingly larger number of substances and phaenomena were discovered, whereas nothing qualitatively changed in the study (it remained a formal way of explanation on tautological grounds). Only new facts and conceptions or "theories" emerged which helped to express this study on a rational level, and while many works did not even attempt to explain affinity, many new phaenomena were "explained" by affinity (or "sympathy" or "love"). As manifestations of chemical affinity (also the term "elective affinity" came to be applied), different behaviours of different substances toward each other were indicated (some substances react better with each other, others more poorly, still others not at all; some substances displace others in compounds in a certain order—the "affinity series," etc.). M. A. Blokh correctly noted that "in the course of the entire evolution of chemistry one can hardly point to a single success in whichever field of natural science that would not have affected the definition of the concept of affinity in chemistry." (Blokh, 1923, p. 117)

In the 16th–17th centuries, the atomistic ideas of ancient philosophers were famously revived (on new grounds). On the basis of the revived corpuscular theory and mechanics, which was the most developed discipline of the time, also chemistry underwent attempts of rational underpinning. Mechanical analogies and qualitative model conceptions about chemical phaenomena emerged, among them chemical affinity ([Joachim] Jungius, Boyle, [John] Mayow, Newton, Lomonosov, [George-Louis Leclerc, Comte de] Buffon, and others). Extrapolation of the only (at that time) strictly logically connected knowledge to chemical phaenomena was essential and undoubtedly constituted an indispensable prerequisite for uncovering the specificity of chemistry and establishing strictly logically connected chemical knowledge. However, corpuscular and mechanical conceptions were very abstract for the chemistry of that time. In the beginning, it was practically imperative to thoroughly study the qualitative aspect of

chemistry. Thus emerged the qualitative "theory of phlogiston," which allowed chemists to investigate the real chemical relations between substances.

It must be noted that many seventeenth- and eighteenth-century scientists ([Nicolas] Lémery, [Antoine] Fizes, [Antoine Grimoald] Monnet, and others) pointed out that the study of affinity has a merely formal character, that affinity does not explain anything. Monnet, for instance, wrote: "the whole theory of affinity was a chimera which could give nothing useful […]" (Partington, 1962, p. 102). This assessment is, of course, not fair, for, as we have already shown, even if affinity did not explain anything, nonetheless this term and various aenigmata about the essence of affinity helped to rationally express and classify specific, objective phaenomena in chemistry, and to discern chemical phaenomena in general from mechanical and other phaenomena. At the same time, chemical affinity too obtained a steady qualitative definition, and the specificity of this phaenomenon (and of chemistry in general) became clear.

The beginnings of experimental inquiry into chemical affinity. In 1718, É. F. [Étienne François] Geoffroy presented to the French Academy of Sciences his table of affinities, where in the upper horizontal line were signs of various substances and under each sign, in vertical columns, were signs of substances which chemically acted upon the given substance. Those were in such a sequence that the upper one substitutes the lower one in a compound with the substance indicated in the upper horizontal line.

Needless to say, the table of É. F. Geoffroy, where substances were arranged, once and for all, in an established order, was very primitive: the conditions of reactions (concentration, temperature, environment, etc.) were not taken into account, all comparable and non-comparable reactions were gathered in one table. Nevertheless, it was an indispensable stage in the cognition of chemical phaenomena in general, and of chemical affinity specifically. According to our reckoning, A. Potylitsyn was right when he wrote:

> Geoffroy's merit lies in that he, among the first, recognised affinity not as a metaphysical (in the sense of natural philosophy—R. V.) essence, but as a physical force, whose magnitude can be measured and expressed in numbers, whatever its essence. Thenceforth the study of chemical affinity steps *on a path of experiment, which therefore ceases to be haphazard* (our emphasis—R. V.) and is guided by a scientific hypothesis. (Potylitsyn, 1880, p. 7)

Geoffroy regarded the phaenomenon of chemical affinity as a manifestation of the regular relations of substances. He no longer restricted himself, as his predecessors, to ascertaining that the cause of substances combining is their property—affinity to each other (according to such a statement, speaking in the style of Hegel, affinity is seen merely as something internal, and consequently as something inherent). He did not speculate about the essence of affinity either, but posed the question differently: he indicated that nature contains experimentally determinable, constant relations between substances, in agreement with which chemical reactions proceed.

That is the beginning of a new period in the history of the study of chemical affinity, namely, its *experimental* inquiry; the *empirical object* of inquiry is clarified. Here a remark by Lenin is in place:

> as long as people did not know how to set about studying the facts, they always invented a priori general theories, which were always sterile. The metaphysician-chemist (in the sense of natural philosopher—R. V.), still unable to make a factual investigation of chemical processes, concocts a theory about chemical affinity as a force. […] Here, it is the method itself that is absurd. […] here, progress must consist precisely in abandoning general theories and philosophical discourses […], and in being able to put the study of the facts […] on a scientific footing. (Lenin, 2001 [1894], Part I)

For some time, the main activity was simply complementing and compiling tables of affinity. The most famous of them is [Torbern Olaf] Bergman's table (1775). (In the question concerning the nature of chemical phaenomena, Bergman's views resembled those of the French scientist Buffon.) According to Bergman, the force of elective affinity is always a determinate and constant property of each substance, which uniquely determines the progress of a reaction.

Bergman's position is the same explanation from tautological grounds: the "theory of affinity" merely states what is observable in chemical practice. There were tables (series) of affinity, compiled from qualitative experimental outcomes, but there were not yet sufficiently recorded experimental data (especially quantitative data) on the effects of various conditions on the course of reactions, on the existence of reversible chemical transformations. Thus, naturally, the only possible "explanation" was the proposition that the tables of affinity are constructed on the grounds of constant force of affinity of each substance with respect to other substances. Bergman attempted to express the force of affinity also in numbers. He juxtaposed a qualitative affinity series with a quantitative

series of saturation of a certain weight of alkali or acid. (Such experiments were also carried out by other scientists.)

Soon after (in 1801–1803), consistently with the law of duality of being and cognition of its opposite moments, Berthollet revealed his views that opposed Bergman's. In chemical practice, one was increasingly confronted with metathetical [i.e., exchange] reactions, and this is where Bergman's study appeared insufficient. As a result of his inquiry of metathetical reactions, Berthollet came to the conclusion that

> elective affinity […] does not work as a determinate force, by which one body separates completely another from a combination; but […] in all compositions and decompositions produced by elective affinity, a partition of the base, or subject of the combination, between the two bodies whose actions are opposed, takes place; and the proportions of this partition are determined, not solely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies; so that an excess of quantity of the body whose affinity is the weaker, compensates for the weakness of affinity. (Berthollet, 1804, pp. 4–5)

The chemical action is determined, according to Berthollet, by the product of a substance's affinity and its weight quantity (he called this relation 'mass'[2]).

Berthollet's views corresponded to the new qualitative empirical data (the necessary quantitative data for a quantitative research did not yet exist) of the chemical process. Just like Bergman, Berthollet also attempted, without intermediary nexuses or quantitative data, to directly explain macro-phaenomena by micro-phaenomena, whereby they interpreted the latter speculatively as mere mechanical interactions of bodies, reduced to microscopic particles. Neither Bergman nor Berthollet had any experimental micro-quantities yet. The role of Bergman and Berthollet in the development of the study of chemical affinity consists in expressing qualitative experimental data on chemical affinity with the help of mechanical conceptions in a rational, logical form. No *theoretical* explanation of chemical affinity could be found at that time: to this end, quantitative study of the issue was indispensable, first of all, for clarifying how to measure the reacting chemical substances and finding *chemical* units, instead of the simple mass units that are abstract in chemistry.

---

[2]   Translator's note: On the basis of Berthollet's 'mass', the terms 'chemical mass' or 'chemical moment' were later proposed (Berthollet, 1896, p. 107, endnote 2); in Vihalemm's text, the term 'chemical mass' ('*khimicheskaia massa*') is used.

The development of Berthollet's ideas became possible only in the second half of the 19th century.

Differentiation of the problem of chemical affinity. Chemical units were established with the emergence of theoretically substantiated stoichiometric equations at the beginning of the 19th century, i.e. with the rise of chemical atomism (Avogadro, 1811; Ampère, 1814).[3] For the first time in the history of chemistry, the problem of the constituents and structure of substances consistently shifted to the foreground. The problem of chemical affinity was differentiated: firstly, the manifestation of chemical affinity among substances in a chemical process; secondly, the manifestation of chemical affinity in the composition and structure of substances, the affinity between atoms in a molecule.[4]

On the basis of facts about chemistry and electricity, Davy (1807) and Berzelius (1812 [1825/1808], 1818–1820 [1819; 1820]) proposed the idea that the affinity between atoms is of electrical nature. Qualitative conceptions of the functioning of electrical forces in the combination of atoms were proposed. Berzelius' ideas were later confirmed (on a new basis), as it were, in the study about ions in Arrhenius' theory of electrolytic dissociation (1885–1887 [1884, 1887]). Soon after the discovery of the electron, the study of the affinity of atoms with the electron was conceived (Abegg & Bodländer, 1899), as well as a multitude of qualitative (before the application of quantum mechanics) conceptions of the electronic structure of molecules.

From the 1830s to 1860s, organic chemistry evolved especially intensively. Questions about the nature of chemical affinity were pushed aside, but its qualitative characteristics were concretised: the study of valency, or "atomicity," was initiated, talk about units of the strength of affinity gained ground (Frankland, Cooper, Kekulé, in the late 1850s) and the theory of chemical structure emerged (the foundations were laid by Butlerov in [1861], and Le Bel and van't Hoff expanded the theory with stereo-chemical conceptions in 1871). As in inorganic chemistry, there were so-called molecular (complex) compounds, which could not be explained by the classical theory of chemical structure, yet the study of complex compounds was initiated (Werner, 1893), linked to the conceptions of primary ("ordinary") and secondary valencies.

---

[3]   A clear definition of the concepts of atom, molecule, and equivalent, became possible only after the Karlsruhe Congress, an international meeting of chemists (1860), to a great extent on the basis of Cannizzaro's (1910 [1858]) work.

[4]   D. P. Konovalov focused on this bifurcation in his speech (Konovalov, 1898, p. 227).

This "organic" stage of the history of chemistry was significant in yet another respect. It is namely organic reactions that progress slowly (in contrast to inorganic reactions) and incompletely. This factor provided the opportunity to scrutinise the indispensable conditions for solving the problem of affinity between substances: speed, circumstances of the progress, and equilibrium of the chemical reaction.

Let us attempt to explain the differentiation of the problem of chemical affinity from the logical-epistemic aspect. Already Engels pointed out: "One had first to know what a particular thing was before one could observe the changes it was undergoing." (Engels, 1994 [1886], Part IV) B. M. Kedrov shows that by learning about substances, i.e. by figuring out "what a given subject is," the following problems successively arise: properties, properties–composition, composition–structure, structure–properties. Thereby it appears that the new cycle (learning about a new type of substance) begins before the previous one "closes" (Kedrov, 1960; 1965). These general regularities of cognition of substances must be also kept in mind when analysing the history of the study of chemical affinity.

Properties, as we know, manifest themselves in relations. The property of chemical affinity manifested itself in the relations between substances in chemical processes. After the composition of chemical substances was determined, their properties, including chemical affinity, started to correlate to their qualitative and quantitative composition; and regularities of the composition, and thereafter of properties, came to be explained by the structures of compounds. Besides the relations of substances in chemical processes, from where the knowledge about the chemical properties of bodies was sourced, including the conceptions of chemical affinity, there appeared relations between constituent parts (atoms) of chemical compounds, and thus also the properties which now pertain to those parts (atoms). Such is the emergence of a new cycle in the knowledge of substances (the knowledge of atoms occurs), arising again from the knowledge of properties (of properties of atoms) after determining the composition in the previous cycle. The property of substances uncovered in chemical processes— their affinity to each other—is transferred to the elementary parts of chemical substances, thereby acquiring an explanation. From the given reactions between simple substances, and from the composition and structure of substances, emerges knowledge about the affinity of chemical elements, or atoms, to each other. With the intrusion into the composition of atoms, after the discovery of the electron, another "transfer" of properties takes place: it is considered between the atom or its distinct group, and the electron (Abegg & Bodländer, 1899).

Such a "transfer" of the chemical affinity, that is, of a specifically chemical property, from substances to atoms (and thereafter to the level of atomic structure) was of substantial significance because instead of a summarised, qualitative approach, a different approach became possible. The measure of a chemical substance, and the sphere of elementary interactions in the transformation of substances, were specified. The truth is that the chemical transformation of substances, the actual chemical process, is a unity of mechanical, physical, and the so-called elementary-chemical processes. Therefore, by applying model conceptions, it was necessary to inquire into the manifestation of already known mechanical and physical laws and principles in the chemical process, in order to uncover new laws—(quantitative) laws of chemical transformation. In the chemical process, two levels and two stages ("intermediary nexuses") were discerned: (1) the molecular level—the motion of molecules (the initial ones and those arising as a result of the reaction) and the change of their quantity (as a result of the transformation of one type of molecules into other ones), that is, no elementary transformation is observed (immediately)—transformation of molecules; and (2) the atomic level—the interactions and interrelations between atoms by dissociation of some and building of other molecules, that is, the elementary chemical transformation itself.

In the second half of the 19th century, with the emergence of physical chemistry, uncovering of the nature of chemical affinity at the molecular level became possible (the corresponding "subjects"—the reacting substance and the molecule—had been sufficiently studied, it was possible to "engage in those changes that happened to them"). This essence of chemical affinity on the atomic level could be discussed only after the birth of quantum chemistry in the second quarter of the 20th century, when the character of the motion of electrons during the composition of atoms was discovered (for this, it was necessary to know what is this "given subject"–atom; in learning about the atom "the circle had to be closed": properties, properties–composition, composition–structure, structure–properties).

The molecular-kinetic essence of chemical affinity

The first quantitative study on affinity was carried out by C. Guldberg and P. Waage (1864) (Kipnis, 1963, pp. 329–369). Their collaboration in 1864 (Guldberg & Waage, 1899) was purely empirical. What is important is that Guldberg and Waage introduced in chemistry an experimental quantity—the concentration of substance—replacing the absolute mass of substance and Berthollet's unspecific force of bonding (which made it impossible to determine the equilibrium experimentally). Using empirical coefficients and indicators of grades by concentration, Guldberg and Waage determined the mathematical dependence between the concentrations of initial and final substances at chemical equilibrium (they construed equilibrium as an equilibrium of reverse forces of reactants and products of the reaction).

The transition to the essence occurs at the theoretical stage of cognition. Theoretical thinking is dialectical, "presupposes investigation of the nature of concepts themselves" (Engels, 2006 [1986], p. 223). In the next work, Guldberg and Waage (1867) already made an attempt at an analysis of the discovered empirical dependency (the law of mass action) and the corresponding concepts. By substantiating the effect of concentration (the authors use the term 'active mass') in the chemical process, Guldberg and Waage articulate the interrelationship of mechanical and specifically chemical forces:

> Chemical attractive forces only manifest themselves on very small distances. When the distance expands, their effect dwindles. A certain sphere defined by a radius equal to the distance beyond which their action is insensible, is called *sphere of attraction* or *sphere of action*. The absolute magnitude of this sphere cannot be determined: fortunately it suffices to know its relative magnitude, and we can choose an arbitrary volume, for instance a cubic centimetre. The amount of substance contained in 1 cm^3 of the total volume, will be called the *active mass* of the body. (Guldberg & Waage, 1899, p. 16; 1867, p. 4)

In 1879, Guldberg's and Waage's 'On chemical affinity' appears, already propounding a theoretical construal of chemical affinity and clarifying its molecular-kinetic essence on the basis of molecular-kinetic conceptions of chemical equilibrium (developed since the 1850s by [Alexander William] Williamson, [Rudolf] Clausius, [Leopold] Pfaundler [von Hadermur] and others; the concept of reaction rate was introduced in chemistry by [Ludwig]

Wilhelmy in [1850]). Guldberg and Waage analyse the nature of the concepts applied in the study of chemical affinity. They write that, in considering the equilibrium between the initial substances A and B, and the products A^1 and B^1, it is not sufficient to assume the forces of attraction between substances and their constituent parts.

> The equilibrium state which eventuates from such processes, is a state of moving equilibrium, since two opposite chemical reactions progress at once, as long as not only A^1 and B^1 are composed, but also a restitution of A and B is in progress. If in a time unit equal amounts of each are composed, we have equilibrium. (Guldberg & Waage, 1899, pp. 131–132)

According to this new view, reaction rate depends on the frequency of collisions between the molecules of the reactants, which is proportional to the amount of those molecules in a unit of volume. In this manner, the "force" of the initial substances, for instance, appears as the rate of direct reactions (the "force" of products appears as the rate of the reverse reaction). Empirical constants obtain a precise physical interpretation.

Theoretical knowledge of some sort of phaenomenon, the discovery of its essence, lies in achieving a unity of opposites by way of analysing the nature of the concepts themselves. The phaenomenon appears to be logically expressed, defined through "its other," it is corroborated by its own negation. Chemical affinity, the tendency of substances towards mutual chemical interaction, is defined through chemical stability, the equilibrium state of substances. Thereby specifically chemical is explained by non-chemical as "its other."

The transition to the essence occurs through the recognition of the unity of qualitative and quantitative changes, that is, measures. Until quantitative inquiry, affinity seemed to be a genuinely constant property between each pair of substances (and also construed merely qualitatively). As to the variability of affinity, its specific level, including the absence of affinity, could only be considered in relation to various substances (the presence of affinity, its specific level, and absence were not inherently connected). Gradually, the dependence of affinity between the same pairs of substances on different conditions was uncovered. Guldberg and Waage showed that the quantitative aspect of chemical affinity manifests itself in a change in the ratio of the concentrations of initial and produced substances, that is, in the amount of those substances (their particles, molecules) in a unit volume. The measure of this change is equilibrium, the equality of the rates of forward and reverse reactions, which is expressed by

the equilibrium constant ($K = \frac{C_Q^q \, C_R^r}{C_L^l \, C_M^m} = \frac{k_1}{k_2}$, where C_Q, C_R are concentrations of reaction products Q, R; C_L, C_M are concentrations of reactants L, M; q, r, l, m are corresponding stoichiometric constants, that is, numbers corresponding to reacting molecules; k_1, k_2 are, correspondingly, constants of the rates of forward and reverse reactions). Here the presence of affinity is already inherently linked to its opposite side—the absence of affinity (the equilibrium state) between the same set of substances. Chemical affinity manifests through the molecularly-kinetically construed equilibrium.

This is what could be called the molecular-kinetic (or mechanical) essence of chemical affinity, which, in this case, is the essence of the first order. This essence comprises only some aspects, links, and relations of the chemical transformation of substances, but it remains an integral construal of chemical affinity nonetheless. In the next stage, the interconnection between chemical transformation and other forms of motion are revealed, especially heat motion.

The thermodynamic essence of chemical affinity. Already the chemists-phlogistonists knew that chemical processes are accompanied by heat effects. In the mid-nineteenth century, facts about thermal decomposition surfaced ([William Robert] Grove, 1842 [Grove, 1846]). Sainte-Claire Deville suggested (in 1859) that dissociation brought about an equilibrium between the repulsive force of heat and affinity.

In the 1830s and 1840s, [Germain Henri] Hess developed the idea that the magnitude of affinity is measured by the heat effect of the reaction. [Hans Peter Jørgen Julius] Thomsen linked Hess' discoveries in thermodynamics to the law of conservation of energy (1853–1854). He suggested that the amount of heat emitted by the bonding of substances corresponds to the affinity of those substances, and reactions proceed in the direction of higher affinity. In the years 1867–1873, [Marcellin] Berthelot proposed the so-called principle of maximum work: "Any chemical transformation occurring without confounding energies, tends to the formation of the body or system of bodies which emits the greatest amount of heat." (Kipnis, 1961, p. 58) To reconcile his principle with the numerous facts about reactions proceeding towards the absorption of heat, Berthelot admitted that in those cases, purely chemical processes were connected with various confounding phaenomena, with the external energy. It was, however, difficult to define a "purely chemical process" unambiguously.

The transition to the essence of the second order of chemical affinity proceeds

through the law of conservation and transformation of energy (measures of motion), via developing this law by establishing measures for the transformation of chemical form of motion to other forms of motion.

Thomsen and Berthelot, who accepted the law of the conservation and transformation of energy, and reasoned that the chemical affinity of given substances to one another can be quantitatively characterised by measuring the energy of their interaction through the heat effect of the reaction, were not involved in the study of the nature of the corresponding concepts, and regarded their studies primarily as a generalisation of empirical material. They did not distinguish between heat in the thermodynamic sense (occurring only in the process of transfer) and thermal energy (the energy of heat motion, the chaotic movement of particles), but rather identified the heat of chemical reaction with its work, with the work of chemical affinity. Thomsen and Berthelot remained on the empirical level of cognition, on the level of Being. And they took the manifest—the automatic progress of a reaction towards greater emission of heat, observed in many cases—as the essential, the particular as the general. Berthelot's principle of maximum work, for instance, could not convincingly explain the existence of reversible reactions.

Regarding those reactions, Berthelot wrote (1879, referred to in Solovev, 1964, pp. 150–151): "In reversible systems, equilibrium is established due to opposing actions: on one hand, chemical energy, on the other hand, external energy, especially thermal." But Berthelot, first, was not consistent in discerning chemical and thermal energies, and, second, discerned them metaphysically, because the chemical transformations of substances also comprise heat motion of particles. Criticising Berthelot, [Lothar] Meyer correctly wrote (in 1884):

> If one should style as external energy the heat contained in the interacting substances, in the form of molecular motion, then most probably there is not any chemical change completed without the aid of external energy, at any rate, such could only be observed at absolute zero, viz. at –273° C. (Lothar Meyer, 1888, pp. 433–434)

Thermal energy, being a qualitative quantity, a measure of *thermal* motion, can be equated with chemical energy only if the transformation of a "purely" chemical form of motion (without thermal motion) into a thermal one (the qualitative aspect of chemical energy) is considered, and the work of this transformation (quantitative aspect of chemical energy), that is, the work of the forces of chemical affinity, is taken into account.

Potylitsyn established the boundaries of Berthelot's principle in a qualitative form, and proposed the idea of dependence of the direction of reaction on temperature already in 1881 (Potylitsyn, 1881, pp. 442–443). The problem was quantitatively solved on the basis of thermodynamics by van't Hoff (1884–1886) (a fundamental solution was already contained in the works of thermodynamics of Gibbs and Helmholtz, and the first steps were made by [August Friedrich] Horstmann).

Van't Hoff demonstrated that a chemical reaction can be carried out as a thermodynamic quasi-static process. To this end, he applied the following thought experiment (called 'Van't Hoff's Equilibrium Box'): in a system of chemical equilibrium (in a big box), reactants are introduced through semipermeable membranes reversibly and isothermally by means of a cylinder and a valve (to simplify the calculating of the thermodynamic work). At the same time, equal amounts of the product of this reaction are withdrawn. In another box (which contains the same equilibrium system at different equilibrium concentrations), a reverse process is carried out in the same manner. The result is a chemical reaction in the form of a reversible cyclic thermodynamic process, the unity of opposites is achieved: the process and its outcome, the introduction of substances into a reaction and their equilibrium state, whereby the chemical transformation is linked with the thermodynamic work. By aid of this "box of equilibrium" and the equation of ideal gas (which means that the outcome is only valid in the domain of rarefied gases and dilute solutions), van't Hoff calculated the work of reaction and derived the equation of the laws of mass action. (In this manner, through the knowledge of the essence of the second order, also the essence of the first order is comprehended on a new basis.)

Van't Hoff arrived at yet another fundamental equation of chemical thermodynamics—the equation of reaction isochores, expressing the dependence between equilibrium yielded by heat and temperature (d [log] $K / dT = q / 2T^2$, where K is the equilibrium constant, T the absolute temperature, q the quantity of heat released when a unit of one system is transformed into another at constant volume). He proposed the principle of mobile equilibrium: "*Every equilibrium between two different conditions (systems) is displaced by lowering the temperature, at constant volume, towards that system, the formation of which evolves heat.*" (van't Hoff, 1896, p. 217) We already noted that the position of Thomsen and Berthelot (chemical transformation proceeds towards greater emission of heat) was empirical, on the level of Being, where the apparent was taken as essential.

> Since *the temperature on the surface of the earth*, at which the majority of observations is made, is *relatively low*, about 273° above absolute zero, it is *a priori* to be expected that under ordinary conditions the majority of chemical equilibria have been displaced towards those systems which are formed with evolution of heat. (van't Hoff, 1896, p. 223; italics by R. V.)

And further:

> The application of the principle shows, also, that at very high temperatures, equilibrium will exist in the majority of cases when the system which is produced with absorption of heat predominates, and therefore that most changes which occur at high temperature will absorb heat; we might in this case, following the example of *Berthelot*, speak of a *principle of minimum work*. (van't Hoff, 1896, p. 225)

Linking work (from the equation of isotherms) and heat (from the equation of isochores) of a reaction, van't Hoff obtains a general expression for the measure of affinity (maximum work of a reaction):

> the work of affinity (A) equals the heat evolved by the transformation (q), divided by the absolute temperature of the point of transition (P) (the point at which the equilibrium constant is K = 1—R. V.) and multiplied by the difference of the latter and the given temperature (T): $A = q\,(P - T)/P$. ([paraphrased from] van't Hoff, 1896, p. 240[5])

This equation shows that Berthelot's principle holds only at T = 0. At higher temperatures, the work of affinity merely remains a part of the emitted heat at the point of transition A = 0, but after that, the reaction direction changes.

Thus here, too, as in the cognition of the essence of first order, affinity is articulated via its opposite ("its other")—via the absence of affinity (equilibrium state). However, chemical equilibrium is now discussed more concretely: it is recognised that a chemical process also contains heat motion, and, in general, that chemical phaenomena are not isolated from other phaenomena and interactions (this is achieved by the concept of the measure of chemical processes—the work of affinity). This is the essence of the second order of chemical affinity, which can also be called the thermodynamic essence.

---

[5] Translator's note: the equation in the original is: $A = q\,(P - T)/P$, that is, the work, expressed in calories, which the affinity in a chemical reaction can perform as the reaction takes place at a given temperature, is equal to the quantity of heat released by the reaction, divided by the absolute temperature of the transition point, and multiplied by the difference between the temperature of the transition point and the temperature at which the reaction takes place.

On the quantum-chemical essence of chemical affinity. An analysis of the history of knowledge on chemical bonds requires a separate essay. Therefore, we will restrict our discussion to the most general observations.

As already shown, the logic of cognition is such that, until the recognition of the essence of chemical affinity on the atomic level (chemical bond), it was necessary to uncover the composition and structure of atoms, and to formulate a theory of atomic structure. This was done on the basis of quantum mechanics. To this end, it was necessary to clarify, to define the chemical bond on the level of Being, to investigate it as a fact (whose nature is unknown), and to know how to find the bonding energy (from thermochemical data).

In 1927, [Walter Heinrich] Heitler and [Fritz Wolfgang] London applied quantum mechanics to explain the structure of hydrogen molecule and (in principle) uncovered the nature of covalent bond. Thereby they laid the foundations of quantum chemistry. Subsequently, other scientists developed various methods (based on different thought models) to theoretically scrutinise the chemical bond (see Bykov, 1963). Currently, the method of molecular orbits is considered the principal and most promising one.

The quantum mechanical inquiry of molecules has shown that the "forces of chemical affinity" that ensure the chemical bond have an electrical (or, more precisely, electromagnetic) nature. Chemical forces, were ascribed, as already noted, an electrical (and later, more concretely, electronic) nature soon after the discovery of the connection between chemical and electrical phaenomena. But those were merely qualitative model conceptions, established without any knowledge of many intermediate nexuses. Therefore, they did not enable creating quantitative definitions of chemical forces, and also contradicted many known facts. The problem is that the interatomic electrical attraction and repulsion only come to light once the nature of the wave functions of electrons in a molecule obtains a quantum-mechanical definition. With the help of quantum mechanics, all types of chemical bond, and the structure of all "enigmatic" (including complex) compounds, are explained from a single standpoint.

Currently, scientists attempt to theoretically connect the micro- and macro-levels of the transformation of substances, and take into account more and more interactions in the real chemical process.

***

To summarise, we have made an attempt to corroborate and concretise the general progress of cognition from the level of Being, from recording and describing phaenomena (qualitatively and quantitatively), to the level of essence, to explaining phaenomena (phaenomena are recognised as manifestations of essence) on the example of the history of the study of chemical affinity. The level of Being has sensuous-practical, rational, and empirical stages. Essence, however, is reached at the theoretical level of cognition, where the unity and interpenetration of the opposites emerges through conceptual analysis. At both levels, analogies and model conceptions are used profusely (on the level of Being, they are qualitative in nature).

Submitted for review on 28 November 1966.

References

Abegg, R. & Bodländer, G. (1899), 'Die Elektroaffinität, ein neues Prinzip der chemischen Systematik,' *Zeitschrift für anorganische Chemie*, vol. 20, no. 5, pp. 453–499. https://doi.org/10.1002/zaac.620200505

Albertus Magnus (1569), *De mineralibus et rebus metallicis libri quinque*, Coloniæ: Apud Ioannem Birckmannum & Theodorum Baumium.

Ampère, A.-M. (1814), 'Lettre de M. Ampère à M. le comte Berthollet, sur la détermination des proportions dans lesquelles les corps se combinent d'après le nombre des molécules dont leurs particules intégrantes sont composées,' *Annales de chimie ou recueil de mémoires concernant la chimie et les arts qui en dépendent, et spécialement la pharmacie*, vol. 90, pp. 43–86.

Arrhenius, S. (1884), *Recherches sur la conductibilité galvanique des électrolytes. Première partie: La conductibilité des solutions aqueuses extrêmement diluées déterminée au moyen du dépolarisateur* (mémoire), Stockholm: Kongliga Boktryckeriet.

Arrhenius, S. (1887), 'Über die Dissociation der in Wasser gelösten Stoffe,' *Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre*, vol. 1, pp. 631–648. https://doi.org/10.1515/zpch-1887-0164

Avogadro, A. (1811), 'Éssai d'une manière de déterminer les masses relatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans ces combinaisons,' *Journal de physique, de chimie, d'histoire naturelle et des arts par J.-C. Delamétherie*, vol. LXXIII, pp. 58–76.

Berthelot, M. (1879), *Éssai de mécanique chimique fondée sur la thermochimie*, vol. II, Paris: Dunod.

Berthollet, C. L. (1804), *Researches into the Laws of Chemical Affinity*, transl. from French by M. Farrell, Edinburgh: Bell and Bradfute; Dublin: Gilbert and Hodges.

Berthollet, C. L. (1896), *Untersuchungen über die Gesetze der Verwandtschaft*, Ostwalds Klassiker der exakten Wissenschaften, Nr. 74, Leipzig: Verlag von Wilhelm Engelmann.

Berzelius, J. J. (1825 [1808]), *Lehrbuch der Chemie, Band II*, transl. by F. Wöhler, Dresden: Arnoldsche Buchhandlung.

Berzelius, J. J. (1819), *Éssai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité*, Paris: Méquignon-Marvis, Libraire pour la partie de médecine.

Berzelius, J. J. (1820), *Versuch über die Theorie der chemischen Proportionen und über die chemischen Wirkungen der Electricität*, transl. by K. A. Blöde, Dresden: Arnoldischen Buchhandlung.

Blokh, M. A. (1923), *Zhisn' i tvorchestvo Vant Goffa* [Life and work of Van't-Hoff], Petrograd: Nauchnoe Khimichesko-Tekhnicheskoe Izdatel'stvo.

Butlerov, M. A. (1861), 'Formation synthétique d'une substance sucrée,' *Comptes rendus hebdomadaires des séances de l'Académie des Sciences*, vol. LIII, no. 4, pp. 145–147.

Bykov, G. V. (1963), *Istoriia elektronnykh teorii organicheskoi khimii* [History of electronic theories of organic chemistry], Moscow: Izdatel'stva Akademii Nauk SSSR.

Cannizzaro, S. (1910[1858]), *Sketch of a Course of Chemical Philosophy*, Edinburgh: The Alembic club.

Davy, H. (1807), 'The Bakerian Lecture, on some chemical Agencies of Electricity,' *Philosophical Transactions, of the Royal Society of London*, Part I, pp. 1–56. https://doi.org/10.1098/rstl.1807.0001

Engels, F. (1994 [1886]), *Ludwig Feuerbach and the End of Classical German Philosophy*, Stuttgart: Verlag von J. H. W. Dietz / Marx Engels Internet Archive. Retrieved from https://www.marxists.org/archive/marx/works/1886/ludwig-feuerbach/index.htm [accessed 30 Aug 2022]

Engels, F. (2006 [1986]), *Dialectics of Nature*, transl. by C. Dutt, Moscow: Progress Publishers / Marx Engels Internet Archive. Retrieved from https://www.marxists.org/archive/marx/works/1883/don/index.htm [accessed 30 Aug 2022]

Grove, W. R. (1846), *On the Correlation of Physical Forces, Being the Substance of a Course of Lectures Delivered in the London Institution in the Year 1843*, London: London Institution.

Guldberg, C. M. & Waage, P. (1867), *Études sur les affinités chimiques*, Christiania: Imprimerie de Brogger & Christie.

Guldberg, C. M. & Waage, P. (1899), *Untersuchungen über die chemischen Affinitäten. Abhandlungen aus den Jahren 1864, 1867, 1879*, transl. by R. Abegg, Ostwalds Klassiker, 104, Leipzig: Wilhelm Engelmann.

Hegel, G. W. F. (1969), *The Science of Logic*, transl. by A. V. Miller, London: George Allen & Unwin / Marx Engels Internet Archive. Retrieved from https://www.marxists.org/reference/archive/hegel/works/hl/hlconten.htm [accessed 30 Aug 2022]

Kedrov, B. M. (1960), 'Die dialektische Logik und die Naturwissenschaft,' in G. Harig & J. Schleifstein (eds.) *Naturwissenschaft und Philosophie*, Berlin: Akademie-Verlag, pp. 369–388. https://doi.org/10.1524/dzph.1960.8.3.299

Kedrov, B. M. (1965), 'Obshchii khod poznaniia veshchestva' [The general progress of knowledge of substances], *Voprosy filosofii*, no. 4, pp. 92–103.

Kedrov, B. M., ed. (1965), *Protivorechiia v razvitii estestvoznaniia* [Contradictions in the evolution of natural science], Moscow: Nauka.

Kipnis, A. Ia. (1961), 'Ocherk istorii vozniknoveniia khimicheskoi termodinamiki' [Essay on the history of the emergence of chemical thermodynamics], in *Trudy Instituta istorii estestvoznaniia i tekhniki*, tom 35: *Istoriia khimicheskikh nauk* [History of chemical sciences], Moscow: Izdatel'stvo Akademii Nauk SSSR, pp. 39–107.

Kipnis, A. Ia. (1963), 'Gul'dberg i ego vklad v razvitie fizicheskoi khimii' [Guldberg and his contribution to physical chemistry], in Iu. I. Solovev (ed.) *Ocherki po istorii khimii* [Essays on the history of chemistry], Moscow: Izdatel'stvo Akademii Nauk, pp. 329–369.

Konovalov, D. P. (1898), 'O khimicheskom srodstve' [On chemical affinity], *Zhurnal Russkago fiziko-khimicheskago obshchestva*, vol. XXX, no. 7, (chemical part), dep. II, pp. 225–232.

Lenin, V. I. (2001 [1894]), *What the "Friends of the People" Are and How They Fight the Social-Democrats. Lenin's Collected Works, Vol. 1*, Moscow: Progress Publishers, pp. 129–332. / Lenin Internet Archive. Retrieved from https://www.marxists.org/archive/lenin/works/1894/friends/index.htm [accessed 30 Aug 2022]

Lenin, V. I. (2008 [1976]), *Plan of Hegel's Dialectics (Logic)*, transl. by C. Dutt, *Lenin's Collected Works, Vol. 38*, Moscow: Progress Publishers, pp. 315–318. Digital Reprints / Marx Engels Internet Archive. Retrieved from https://www.marxists.org/archive/lenin/works/1915/misc/x01.htm [accessed 30 Aug 2022]

Lothar Meyer, J. (1888), *Modern Theories of Chemistry*, transl. by P. P. Bedson & W. C. Williams, London: Longmans, Green & Co.

Partington, J. R. (1962), *A History of Chemistry*, vol. III, London: McMillan & Co. https://doi.org/10.1007/978-1-349-00309-9

Potylitsyn, A. (1880), *O sposobakh izmereniia khimicheskago srodstva* [On methods of measuring chemical affinity], Dissertation, St. Petersburg: Tipografiia V. F. Demakova.

Potylitsyn, A. (1881), 'O zakonakh dvoinykh razlozhenii. Stat'ia tret'ia' [On the laws of dual dissolution. Third article], *Zhurnal Russkago fiziko-khimicheskago obshchestva*, vol. XIII, no. 4, pp. 289–298.

Solovev, Iu. I. (1964), *Ocherki po istorii fizicheskoi khimii* [Essays on the history of physical chemistry], Moscow: Nauka.

Van't Hoff, J. H. (1896), *Studies in Chemical Dynamics*, Amsterdam: Frederik Muller & Co; London: Williams & Norgate.

Van't Hoff, J. H. (1902), *Die Gesetze des Chemischen Gleichgewichtes für den verdünnten, gasförmigen oder gelösten Zustand*, Leipzig: Wilhelm Engelmann.

Vihalemm, R. (2022), 'On stages of cognition,' transl. by A. Lazutkina, *Acta Baltica Historiae et Philosophiae Scientiarum*, vol. 10, no. 1, pp. 138–155. https://doi.org/10.11590/abhps.2022.1.08

Walden, P. (1954), 'The beginnings of the doctrine of chemical affinity,' *Journal of Chemical Education*, vol. 31, no. 1, pp. 27–33. https://doi.org/10.1021/ed031p27

Werner, A. (1893), 'Beitrag zur Konstitution anorganischer Verbindungen,' *Zeitschrift für Anorganische Chemie, Dritter Band*, pp. 267–330.
https://doi.org/10.1002/zaac.18930030136

Wilhelmy, L. (1850), 'Ueber das Gesetz, nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet,' *Annalen der Physik und Chemie*, vol. LXXXI, pp. 413–427; 499–526. https://doi.org/10.1002/andp.18501571203