

Dialectics and synergetics in chemistry. Periodic Table and oscillating reactions

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Abstract This work utilizes examples from chemical sciences to present fundamentals of dialectics and synergetics. The laws of dialectics remain appropriate at the level of atoms, at the level of molecules, at the level of the reactions, and at the level of ideas. The law of the unity and conflict of opposites is seen, for instance, in the relationships between the ionization energy and electron affinity of atoms, between the forward and back reactions, as well as in the differentiation and integration between the various areas of chemistry. The law of the passage of quantitative changes into qualitative changes describes the transformation properties of the compounds when the number and arrangement of atoms in the molecule undergoes changes. According to this law, the development is accompanied by breaks and jumps. This paper suggests equations for the description of these relationships. The law of the negation of the negation is manifested in the Periodic Law, in the evolution of ideas about the mutual transformation of chemical elements, in the development the concept of triads of elements, etc. Small changes in the conventional Periodic Table on the basis of previously rejected versions allow reflecting secondary and additional periodicity. Synergetics, similarly to dialectics, is dedicated to the studies of general laws of evolution. Synergetics includes highly advanced and specified ideas of dialectics. The cornerstone of synergetics is the principles of self-organization and nonlinearity. Mathematical development of these concepts was substantially facilitated by considering oscillating chemical reactions as an example. These reactions are quite complex and therefore provide adequate models for self-organization. Oscillations may exist only upon execution of specific thermodynamic, mathematical, and chemical conditions. Mechanisms of several oscillatory reactions (Belousov–Zhabotinskii, Bray–Liebhavsky, oxidative carbonylation of acetylenes) are briefly reviewed. The construction of novel biomimetic or smart materials based on oscillating reactions is described.

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Introduction

After a long hitch at the start, philosophy of chemistry is becoming one of the most rapidly growing fields of philosophy (Stemwedel 2008; Schummer 2006). There are extensive bibliographies on this and related questions (Schummer 1991). Four books may deserve especial mention among the large number of published material:

- Philosophy of Chemistry. Synthesis of a New Discipline. Baird, D., Scerri, E., McIntyre, L. (eds). Springer, Dordrecht (2006). 365 pp. Boston Studies in the Philosophy of Science. Vol. 242.
- Scerri, ER: Collected Papers on Philosophy of Chemistry. Imperial College Press, London (2008). 235 p.
- Handbook of the Philosophy of Science, Vol. 6. Philosophy of Chemistry. Woody A.I., Hendry R.F., Needham P. (eds). Elsevier, Amsterdam, Boston, Heidelberg, London et al. (2012). 362 pp.
- The Philosophy of Chemistry: Practices, Methodologies, and Concepts. Llored, J.-P. (ed.). Cambridge Scholars Publ., Newcastle upon Tyne (2013). 764 pp.

Two scientific journals are specialized in the philosophical aspects of chemistry:

- Foundations of Chemistry, Editor-in-Chief: Eric R. Scerri, published by Springer, Dordrecht, Netherlands.
- HYLE, International Journal for Philosophy of Chemistry, Editor Joachim Schummer, published by HYLE Publications, Berlin, Bundesrepublik Deutschland.

However, in my opinion, not enough attention is being paid to the chemical aspects of relatively old and relatively new areas of scientific knowledge: the dialectics and synergetics.

The primary form of dialectics was created by a Greek philosopher Heraclitus five centuries B.C. The great German philosopher Hegel (1770–1831) developed the fundamental doctrine of the dialectical evolution (Williams 1989; Houlgate and Baur 2011). Engels (1820–1895) transformed idealist dialectics of Hegel into a materialistic¹ knowledge (Bellu 1973; Mackay 1999). Materialistic dialectics was part of Marxist-Leninist philosophy. In this form it was widely used in the Soviet Union and other countries of Eastern European (Communist) bloc in the twentieth century.

Philosophers of the Communist countries undertook an extensive research in dialectics (Spirkin 1990; Marxist-Leninist dialectics 1983; Materialistic Dialectics 1981). However, the Marxist-Leninist philosophy was adopted as the ideology and canonized as the “only true doctrine”; this resulted in its essential dogmatization. Thus, the dialectics became part of the political struggle in the twentieth century, and its development in the West (in the “open society”) actually stopped: the majority of Western philosophers rejected the dialectics due to the fact that it was used as an ideological backbone for support of totalitarian regimes and revolutions (Imyanitov 2009a).

¹ It should be noted that in modern natural sciences drift occurs in the opposite direction towards idealism (Imyanitov 2003b, p. 10). In particular, taking into account the need to consider not only the phenomenon but also the observer.

When dismantling socialism (in the early 90-s of twentieth century), the dialectics was thrown away together with all Marxist-Leninist ideas. As a result, the dialectics was lost both for “open” (“Western”) and for the post-socialist societies. I believe this is detrimental for the modern paradigm and needs to be corrected. This task is made easier by the fact that intuitive, “natural” dialectical thinking is common to many intellectuals. It is formed as a result of comprehension of reality and research.

In this article I try to demonstrate the beauty and the heuristic of dialectics. At the same time, one should not forget that philosophy provides a method of perception that is in no way a substitute for scientific research, experiment. The content of the present work is limited to the laws of dialectics and dialectical concepts of higher and lower.

Synergetics (Haken 2012), as well as the dialectics, describes the development; this raises the question of their mutual relationships. If we consider all formally possible approaches to this issue, they all have already been articulated in the literature²:

- synergetics is an example of the dialectical approach,
- synergetics represents a peculiar form of “natural” dialectics,
- the dialectics has to be based on the fundamental principles of self-organization, which has been developed by synergetics,
- the results of synergetic have confirmed the universality of laws of dialectics and deepened their content,
- dialectics and synergetics are complementary disciplines,
- there is a need for integration dialectics and synergetics,
- the dialectics as a general theory of development is outgrown in synergetics as a universal theory of evolution:

Metaphysics → Dialectics → Synergetics

The last concept can hardly be regarded adequate enough: synergetics is limited by the processes, which are far from equilibrium. Thus, if synergetics falls within the realms of philosophy, dialectics and synergetics relate as a whole and its part. Indeed, the transition of water into steam and ice under thermodynamic equilibrium conditions has been cited repeatedly as an example of dialectics; this transition cannot be considered as a synergetic process (Imyanitov 2009a). Perhaps, synergetics should not be considered as a part of philosophy because it includes too much mathematics and has immediate practical applications.

The most plausible definition of the position of synergetics assumes that it provides specific examples and applications for dialectics, and plays a role of a mediator between universal dialectical laws and specific scientific knowledge (Poddubnyj 1999).

This article attempts to examine the most common dialectical and synergetic aspects of chemistry.

Dialectics

The laws of dialectics and Periodic System

The laws of dialectics are a generalization of the most important connections and relationships in nature and society. They are formulated as follows:

² Relevant references are given in review (Imyanitov 2009a).

1. The law of the unity and conflict of opposites
2. The law of the passage of quantitative changes into qualitative changes, “transformation of quantity into quality”
3. The law of the negation of the negation

Chemistry is an ideal source of vivid patterns of illustrating these laws. This applies in particular to the passage of quantitative changes into qualitative changes (see below).

The law of the unity and conflict of opposites

This law is the central feature of dialectics, the other laws contributing to its development. As an example, the unity and conflict of opposites takes place between the ability of an atom to give and accept an electron. Each chemical element has its ionization energy and electron affinity, which is the most important characteristics of the atom. Thus, there is a *unity* of opposites. Increase of nuclear charge is repeatedly accompanied alternating pre-dominance of one or the other opposites. Thus, there is a *conflict* of opposites.

Manganese, being a typical metal, forms characteristic of the metal's cation Mn^{2+} . However, manganese may also exist in the form of an anion MnO_4^{2-} , which is characteristic for the nonmetals and similar to SO_4^{2-} . Depending on the reagent, sulfur may behave as oxidant (e.g., by reaction with iron) or as a reducing agent (reaction with oxygen). Unity and conflict of attraction and repulsion between atoms (molecules) leads to the formation of intramolecular (intermolecular) bonds. The ratio of these opposites determines the length and strength of the bond (Budrejko 1970, pp. 121–174).

Chemical equilibrium is the result of unity and conflict between the forward and back reactions. These reactions are so tightly linked, that the catalyst of the direct reaction accelerates to the same extent the back reaction. Organic substances also show unity and conflict of opposites when considering their oxidation to carbon dioxide, water and nitrogen by atmosphere oxygen. On the one hand, organic substances are thermodynamically unstable; on the other hand they are kinetically stable. This kinetic stability of organic matter makes possible the existence of Life.

Conflict of opposites is the driving force of evolution of knowledge. Differentiation and integration within chemistry is an example of this. On the one hand, there is an appearance of new fields (radiation, organometallic, bioinorganic, bioorganic, mathematical, “green” chemistry), on the other hand there is a development of general approaches to the understanding and the description of different areas of chemical science. For example, the original characteristics for steric effects in organic chemistry were based on the constants E_s , which were derived from kinetic data, while the coordination chemistry used geometric constants Θ , cone angles.³ Subsequently the cone angles managed to extend to organic chemistry (Imyanitov 1987), and then to other fields of chemistry.

Further development included a system of constants for characterization of the electronic effects, which is applicable to a broad range of areas of chemistry (Imyanitov and Shmelev 1987, Imyanitov 1996).

Conflict between supporters of discreteness (Proust, Dalton) and continuity (Berthollet) of chemical organization of the matter at the beginning of the nineteenth century led to the establishment of the law of equivalents, multiple proportions law, and law of definite proportions (Kuznetsov 1973, pp. 28–50).

³ The apex angle of the cone, encompassing the ligand. Apex of the cone—the central atom nucleus.

See further comments in the reductionism and holism as the unity and conflict of opposites below, in “[Dialectics of higher and lower](#)” section.

It should be noted that the conflicts are less pronounced in chemistry than in living nature and society. Furthermore, it is sometimes not immediately seen in chemistry that the conflict of opposites plays a role of engine of development.

Synergetics made a significant contribution in the development the law of the unity and conflict of opposites (Imyanitov 2009a). This will be exemplified below using chemical oscillators (see “[Dialectics in oscillating reactions](#)” section).

The law of the passage of quantitative changes into qualitative changes

Changing the number of oxygen atoms in the O, O₂ and O₃ results in a dramatic change in the physical properties and reactivity. Again, one can take the various proportions in which oxygen combines with nitrogen or sulphur, each of which produces a substance qualitatively different from any of the others. How different laughing gas (nitrogen monoxide N₂O) is from nitric anhydride (nitrogen pentoxide, N₂O₅)! The first is a gas; the second is a solid crystalline substance at ordinary temperatures. And yet the whole difference in composition is that the second contains five times as much oxygen as the first, and between the two of them are three more oxides of nitrogen (NO, N₂O₃, NO₂), each of which is qualitatively different from the first two and from each other (Engels 1883).

This law is seen even more strikingly in the homologous series of carbon compounds, especially in the hydrocarbons. Under normal conditions, the hydrocarbon H(CH₂)_nH with n = 1 (methane) is a gas, at n = 5 (pentane) is a liquid, and at n = 20 (eicosane) is a solid substance. In the case of alcohol “qualitative difference can be caused by the quantitative addition of C₃H₆ is taught by experience if we consume ethyl alcohol, C₂H₆O, in any drinkable form without addition of other alcohols, and on another occasion take the same ethyl alcohol but with a slight addition of amyl alcohol,⁴ C₅H₁₂O, which forms the main constituent of the notorious fusel oil. One’s head will certainly be aware of it the next morning, much to its detriment; so that one could even say that the intoxication, and subsequent “morning after” feeling, is also quantity transformed into quality, on the one hand of ethyl alcohol and on the other hand of this added C₃H₆” (Engels 1883).

In the homologous series of carbon compounds encounter the second law in yet another form. The lower members permit only of a single mutual arrangement of the atoms. If, however, the number of atoms united into a molecule attains definitely fixed size, the grouping of the atoms in the molecule can take place in more than one way; so that two or more isomeric substances can be formed. Thus, in the paraffin series, for C₄H₁₀ there are two, for C₆H₁₂ there are three; among the higher members the number of possible isomers mounts very rapidly. Hence once again it is the quantitative number of atoms in the molecule that determines the possibility and, in so far as it has been proved, also the actual existence of such qualitatively distinct isomers (Engels 1883). Isomerism is interesting because *quantitatively* identical *in analysis* substances differ from each other *qualitatively*, sometimes belonging even to distinct classes. This is possible because the isomers have a different structure.

The law of the passage of quantitative changes into qualitative changes describes the source of the formation of a new quality, which is a result of the conflict of opposites described in the first law.

⁴ Instead «amyl alcohol, C₅H₁₂O», or rather «isoamyl alcohol, C₅H₁₂O», more precisely, «isoamyl alcohol, (CH₃)₂CHCH₂CH₂OH».

Breaks and jumps If we consider sufficiently representative dependence between quantitative and qualitative changes, there are clearly seen monotonous sections, as well as breaks and jumps. For example, the second period of Mendeleev Table (Table 1) begins with a metal Li, but when moving over the period with increasing nuclear charge (quantitative changes) metallic properties of elements decrease monotonically (qualitative changes). In Ne they are completely absent, but the transition to the next period is a jumping increase of metallic properties in Na.

Jump has a clear physical cause: at the end of the period (in inert gases He–Rn) outer electronic shell is completely filled, and the next electron is forced to enter into a new, more remote, shell. Despite the increase in nuclear charge, the electron from a remote shell is easily split off, and a new element is metal. *This is the way how periodicity arises and the Periodic System is formed.* This regularity is fundamental in its nature: it describes the changes in the vast majority of physical and chemical properties of elements and their compounds, depending on the charge of the nucleus of the atom⁵ (atomic number).

The dependencies describe above are quite complex. However, these relationships can be greatly simplified with consideration of the elements separately in blocks and the introduction of a new characteristic of quantity. Instead of the traditional nuclear charge as the independent variable, the total number of differentiating electrons is considered. These are electrons which determine “membership category” of the element within the block: *s* electrons in the *s* block, *p* electrons into the *p* block, and so on. This allows obtaining simple dependencies and develop equations for describing a number of properties, e.g. ionization energy (Fig. 1), electron affinity and electronegativity of atoms, proton affinity and gas basicity of elements, electronic effect value of coordinating metals, and infrared spectroscopic parameters of the coordinating metals (Imyanitov 1999a, 2003a, 2010, 2011a).

This approach is effective for describing the properties not only of elements, but also of their compounds, e.g. acidic properties of the hydrides and protonated molecules, proton affinity and gas basicity of various compounds, inductive effects of atoms and groups, electronic parameters of neutral ligands in coordination compounds (Imyanitov 1999a, b, 2001a, b). The proton affinity of 20 elements was predicted using the equation constructed with this approach (Imyanitov 2011a). New approach may be extended also to cases where fundamental transformations occur in the composition and reciprocal location of the blocks, and also in the composition and length of the periods of Mendeleev’s Table (Imyanitov 2014).

It is neither the nuclear charge, nor the number of electrons in the outer shell that are important, but the total number of differentiating electrons. This statement is an improvement of the Periodic Law formulation (in respect of the characteristics of the determining properties) in the order: *atomic weight—nuclear charge—overall number of differentiating electrons in the atom.* The refined description may be regarded as a new basis for describing periodicity, a new formulation of the Periodic Law or as a supplement to the classic formulation (Imyanitov 2010, 2011b). More detail can be found in the review on formulations, equations, and graphic representations of the Periodic Law (Imyanitov 2011b).

In the above cases there are periodic functions with breaks and jumps. To explain this, let’s consider again the ionization energy (Fig. 1). Periodicity and breaks are occurring because the ionization energy of the outer shell electron is considered, and the outer shell is changed during the transition to each subsequent period (see above). Thus, the line B–Ne

⁵ Unlike many other evolutionary objects the complication in the Periodic System does not occur in time, but it does with the increasing nuclear charge, the number of electronic shells in the atom, the number of electrons in the shell.

Table 1 Medium-long Periodic Table. Symbols of corresponding elements (e.g., elements of the even periods of *p* block) are shifted in their cells to the right in order to reflect secondary (vertical) periodicity. Secondary periodicity implies that the elements of even periods (of 2nd, 4th, and 6th) and their compounds differ from the elements of the odd periods (3rd and 5th) in the chemical and physical properties (Scerri 2007, pp. 270–272, 324; Imyanitov 2011b, 2015). “Early” and “late” elements are separated by vertical dashed lines in order to reflect additional (supplement) periodicity (Imyanitov 2015). Additional periodicity implies that compound properties of the “late” elements repeat those of the “early” elements: Co–Ti, Ni–V, Zn–Mn; Tb–Ce, Dy–Pr; Yb–Eu (Korableva and Korol’kov 2005, pp. 128–131)

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																			
Period ↓	1																																																				
	2																																																				
1	H																																																				
2	3	4																5	6	7	8	9	10	11	12	13	14	15	16	17	18																						
	Li	Be																B	C	N	O	F	Ne																														
3	11	12																13	14	15	16	17	18																														
	Na	Mg																Al	Si	P	S	Cl	Ar																														
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54																	
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																	
5	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102					
	Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo				
6	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	
	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo
7	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	
	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo	Uuq	Uup	Uuh	Uus	Uuo			

*Lanthanides
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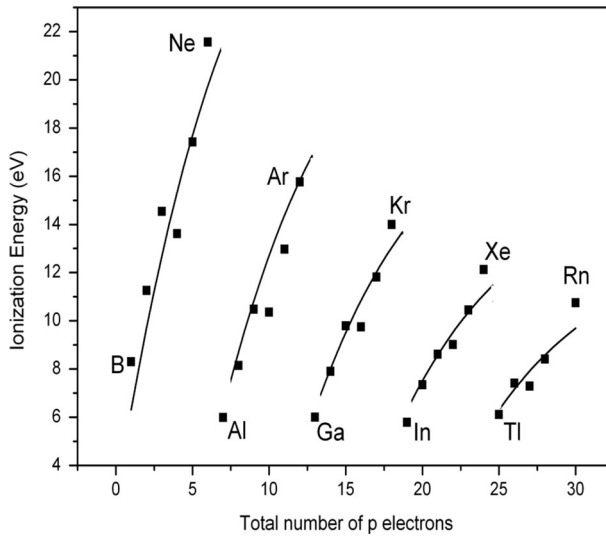


Fig. 1 Ionization energy of the neutral atoms of the p block elements in the ground state versus the total number of p electrons (Imyanitov 2010, 2011b)

on Fig. 1 characterizes the ionization energy for $2p$ electrons, line Al–Ar describes the one for $3p$ electrons, and so on.

However, if one considers only $2p$ electrons in B–Ne, Al–Ar and all other atoms, there will be no reasons for the jumps and recurrences, and the monotonous line will accommodate all the elements. Such dependencies are characteristic for the X-ray spectroscopy. By Moseley law, there is a rectilinear relationship

$$\sqrt{\nu} = K(Z - k) \quad (1)$$

where ν is the X-ray frequency, Z —nucleus charge, K and k —constants.

After the squaring of both equation sides, and taking into account that $E = h\nu$, we obtain

$$E = hK^2(Z - k)^2 \quad (2)$$

where E is the energy of the corresponding electron transition.

Equation (2) represents a quadratic function of Z , and is depicted as a branch of a parabola, i.e. the curve without jumps and periodicity. This dependence is fundamentally different from the one presented in Fig. 1. Such dependence (2) is not typical for chemistry, because chemical phenomena are determined by the outer electronic shells.

The law of the passage of quantitative changes into qualitative changes was advanced by the concepts of synergetics. This applies in particular to the detailed elaboration of the mechanism of jump transitions (Imyanitov 2009a).

The law of the negation of the negation and new Periodic Table

As already mentioned, in the Periodic Table (Table 1) metallic properties are decreasing and nonmetallic features are increasing from Li to Ne. This is the first law of dialectics, the law of the unity and conflict of opposites. The passage of quantitative changes into

qualitative changes takes place upon the transition to the next period, Na–Ar: a typical nonmetal F is followed by an inert Ne, after that by a typical metal Na. This is in accordance with the second law of dialectics. The third law is exemplified by the fact that during the transition from Li to F there is a negation of metallic properties in favor of the nonmetallic ones. The transition from Ne to Na represents the negation of preceding negation: nonmetallic properties are replaced by the metallic ones.

The dialectics states that the negation of the negation does not return the process to its original position, but initiates a development. Indeed, while considering the above example, Na is superior to Li with respect to metallic properties, such as the intensity of the reaction with water and oxygen. In more complex cases, one can clearly notice that the negation of the negation occurs under the scheme.

$$\text{Thesis} \rightarrow \text{Antithesis} \rightarrow \text{Synthesis} \quad (3)$$

In this case, the result of the synthesis involves thesis and antithesis at a higher level of generalization. For instance, the idea of the alchemists of the possibility of mutual transformation of elements (Thesis) was rejected by classical chemistry (Antithesis), but proved to be correct and even trivial for nuclear physics. The concept on the impossibility of mutual transformation of elements by chemical methods⁶ remains nevertheless generally recognized (Synthesis).

The evolution the concept of triad of Döbereiner represents a good illustration of repetition at a higher level as the result of the negation of the negation. In years 1817–1827 he discovered the existence of groups of three elements in which one element is intermediate in terms of chemical reactivity and also in its atomic weight (Scerri 2008, 2011).

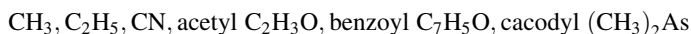
Ca	Sr	Ba
Cl	Br	I
Li	Na	K
S	Se	Te

Following the work of Newlands, Odling, Meyer, and Mendeleev, it was common to consider that the Döbereiners' triad has mainly a historical significance as fragments of vertical columns in the Periodic Table. However, this negation of triads as a result of the following negation changed the situation. It has been further shown that the construction of the triad should involve not the use of atomic weight, but utilize the atomic number instead (Scerri 2008; Bent 2006, pp. 22–23). It was revealed that that approximately 50 % of all vertical triads built on the basis of atomic number, rather than atomic weight, are mathematically exact.

It was suggested to use triadic relationships between atomic numbers for the purpose of secondary classification, namely the placement of elements in groups or columns. In particular, He–Ne–Ar form a triad, while He–Be–Mg do not form one. This is an argument in favor of the classic location of He(s^2) within the group of inert gases, although they have outer shell p^6 (Scerri 2008). Triadic relationships between atomic numbers testifies against positioning of He(s^2) above Be(s^2) in the s^2 elements group, despite the existence of many convincing arguments (Bent 2006). On the other hand, H–F–Br do form a triad, that can be considered as an argument for a long time discussed belonging of H to the halogen group (Scerri 2008).

⁶ That is, by changes in the outer electron shell.

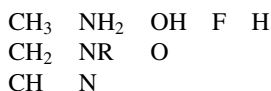
Radical theory⁷ was pioneered by Liebig, Wöhler and Laurent around 1830. In this theory, organic compounds were thought to exist as combinations of radicals that could be exchanged in chemical reactions just as chemical elements could be interchanged in inorganic compounds. Group of atoms in the radical is considered to be constant being a kind of one big atom. As radicals were



benzaldehyde is presented as benzoyl hydride, benzoic acid—as benzoyl hydroxide.

However Dumas' chlorination of acetic acid (“acetyl hydroxide”) to chloroacetic acid showed that acetyl radical does not remain unchanged in the reaction. There were other arguments against this theory. As a result of the negation, statements of this theory are preserved only in the nomenclature of organic compounds.

But after 150 years the theory of radicals revived at a new, higher level as the isolobal principle (isolobal analogy). Hoffmann (1982) described molecular fragments as isolobal “if the number, symmetry properties, approximate energy and shape of the frontier orbitals⁸ and the number of electrons in them are similar—not identical, but similar”. Implicitly, this principle has long been used in organic chemistry. For example, CH_3 and NH_2 are isolobal:



Isolobality of CH_3 , CH_2 , and CH with $\text{Co}(\text{CN})_5^{3-}$, $\text{Pt}(\text{PR}_3)_2$, and $\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ is shown in Fig. 2. The use of isolobal analogy was particularly successful in transition-metal chemistry (Table 2).

Isolobal CH_3 and $\text{Mn}(\text{CO})_5$ are certainly not isostructural nor they are isoelectronic. However, both possess a frontier orbital which looks approximately the same for the two fragments. Therefore, their properties are similar. CH_3 dimerizes to ethane, while $\text{Mn}(\text{CO})_5$ dimerizes to $\text{Mn}_2(\text{CO})_{10}$, can be obtained mixed $(\text{OC})_5\text{MnCH}_3$. Reactions of CH_3 and $\text{Mn}(\text{CO})_5$ as free radicals are analogous as well (Hoffmann 1982).

Isolobal fragments may be used interchangeably in constructing the molecules. Isolobal analogy can predict the bonding and reactivity of a lesser-known species from that of a better-known species (Hoffmann 1982; Stone 1984; Hor and Tan 1989). This analogy shows the deep unity of various fields of chemistry (Fig. 2; Table 2; Hoffmann 1982). So the negation and negation of the negation of the radical theory has led to the evolution of knowledge.

The negation of the negation is also characteristic for the development of the Periodic Table. For example, there was no subdivision of the columns into subgroups in the first versions of the Table. Later, in nineteenth and first half of twentieth century, the “Short-long” version served as conventional form of the Table (Sneed and Maynard 1944; Imyanitov 2011b). In this Table the “a” (“main”) subgroups contained *s* and *p* elements, the “b” (“side”)—*d* elements, which had secondary kinship (Bent 2006, p. 68) with *s* and

⁷ This theory is not related to the modern understanding of free radicals.

⁸ These are the highest-energy occupied molecular orbital (HOMO) and lowest-energy unoccupied orbital (LUMO).

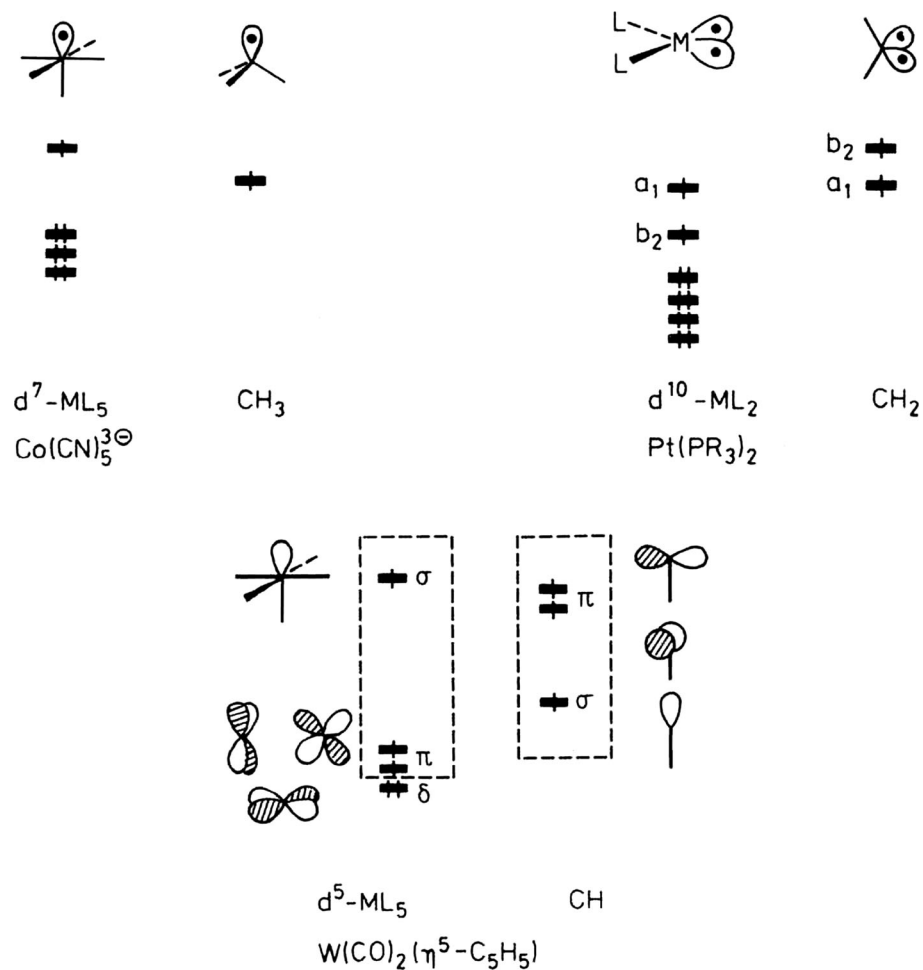


Fig. 2 Isolobal analogies between hydrocarbon and metal–ligand fragments (Stone 1984)

p elements. For example, in the group VII F–Cl–Br–I–At belonged to the “a” subgroup, while Mn–Tc–Re were considered “b” (Mazurs 1974, p. 36).

Later “Short-long” Table was replaced by the Medium-long Periodic Table that was recommended in 1989 as conventional one by the International Union of Pure and Applied Chemistry (IUPAC). In this form of the Periodic Table the subgroups are absent, and *d* elements are divided into separate groups. To improve this Table further, it was suggested (Imyanitov 2015) to move the relevant elements of the right with respect to the other in order to reflect secondary periodicity (Scerri 2007, pp. 270–272, 324; Imyanitov 2011b, 2015) (Table 1). This again leads to the appearance of subgroups (negation of the negation), however they now reflect quite different relationships. These dependencies (secondary periodicity) were not seen in previous versions of the conventional Periodic Tables.

According to Berzelius (1812–1819), there are positive and negative poles in atoms. They enable the formation of a chemical bond. These electrostatic ideas were initially

Table 2 Isolobal relationships (Hoffmann 1982; Stone 1984)

CH_3	CH_2	CH	CH_3^+	CH_2^+	CH^+
$\text{Mn}(\text{CO})_5$	$\text{Fe}(\text{CO})_4$	$\text{Co}(\text{CO})_3$	$\text{Cr}(\text{CO})_5$	$\text{Mn}(\text{CO})_4$	$\text{Fe}(\text{CO})_3$
$\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$	$\text{Rh}(\text{CO})(\eta^5\text{-C}_5\text{Me}_5)$	$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)$	$\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$	$\text{Fe}(\text{CO})(\eta^5\text{-C}_5\text{H}_5)$	$\text{Rh}(\eta^5\text{-C}_5\text{H}_5)$
$\text{Mo}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$	$\text{Re}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$	$\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$	BH_3	BH_2	BH
$\text{Co}(\text{CN})_3^-$	$\text{Cr}(\text{CO})(\text{NO})(\eta^5\text{-C}_5\text{H}_5)$	$[\text{Mn}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]^+$			
$\text{Co}(\text{CO})_4$	$\text{Cr}(\text{CO})_5$	$\text{Re}(\text{CO})_4$			
$\text{PtH}(\text{PPh}_3)_2$	$\text{Pt}(\text{PMe}_3)_2$	$\text{Rh}(\eta^6\text{-C}_6\text{H}_6)$			
$\text{Zn}(\eta^5\text{-C}_5\text{H}_5)$	$\text{Cu}(\eta^5\text{-C}_5\text{Me}_5)$	$\text{Re}(\text{CO})_3\text{Br}_2$			
$\text{Au}(\text{PPh}_3)$	$\text{IrCl}(\text{CO})_2$	$\text{Mn}(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})$			
$\text{Rh}(\text{PPh}_3)_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})$	$\text{Fe}(\text{CO})_2(\eta^5\text{-C}_2\text{B}_9\text{H}_{11})$	$\text{TaCl}(\text{PMe}_3)_2(\eta^5\text{-C}_5\text{H}_5)$			
MnCl_5^{5-}	$\text{TaMe}(\eta^5\text{-C}_5\text{H}_5)_2$				
$\text{Fe}(\text{CO})_4^+$					

rejected (negation) because of the existence of a large number of non-polar compounds (H_2 , N_2 , CH_4). But 70 years later the electrostatic approach was revised by Kossel, who articulated the theory of ionic bonding (the negation of the negation). Intermolecular interactions of polar molecules also occur according to Berzelius.

I hope that this paper will contribute to further implementation of the negation of the negation (3), in which the Thesis is a dogmatic dialectics, Antithesis is a forgotten dialectics, and Synthesis is a new dialectics coupled with synergetics.

The negation of the negation is also discussed in “[Dialectics in oscillating reactions](#)” section.

Spiral as the form to display the negation of the negation Law of the negation of the negation provides theoretical support to the use of spiral for description of repetitions at a higher level. However, many investigators came to spiral-like descriptions of various relationships rather empirically. The first description of the periodicity in chemistry was done Chancourtois; it was made in the form of a *spiral* prior to the development of the *tables* by Newlands, Odling, Meyer and Mendeleev (Mazurs 1974; van Spronsen 1969).

The spiral form of the Periodic Law is proposed as its fundamental representation (Imyanitov 2015). This idea is based on the fact, that the location of the elements in the order of the growing nuclear charge initially may be represented by a straight line. The complexity of the atom structure, in particular, of their electron shells, grows along this line. The transition from simple to complex is advancement (evolution), and it does not follow a straight line, but occurs with periodic repetitions and is usually described by a spiral, where the repeating fragments are located in the same sector. Therefore it is

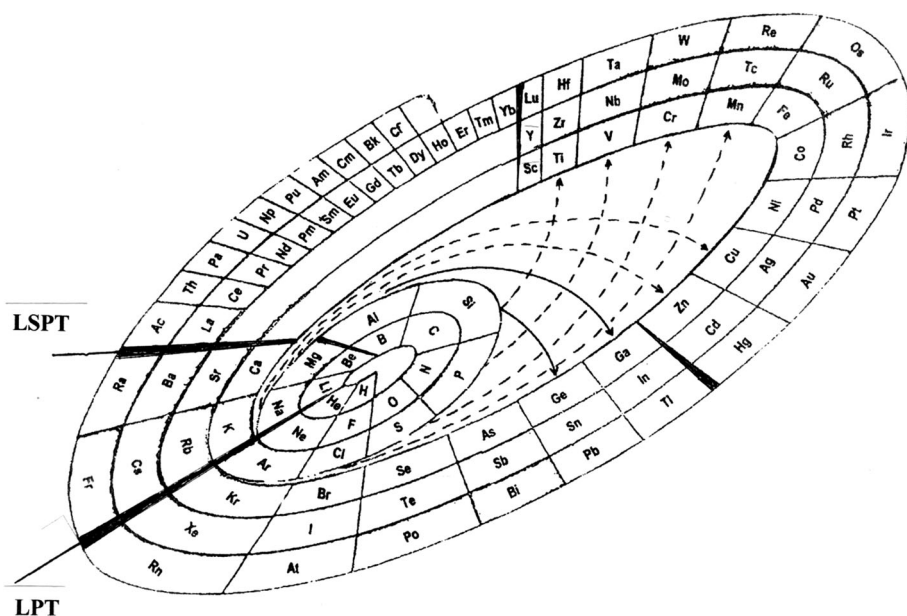


Fig. 3 Longman's spiral (Longman 1951; Stewart 2007; Wang and Schwarz 2009). The original image is supplemented with wedge-shaped lines showing the boundaries between the blocks. Cuts along lines LPT (Long Periodic Table) and LSPT (Left-Step Periodic Table) result in the corresponding versions of the Periodic Tables (Imyanitov 2015)

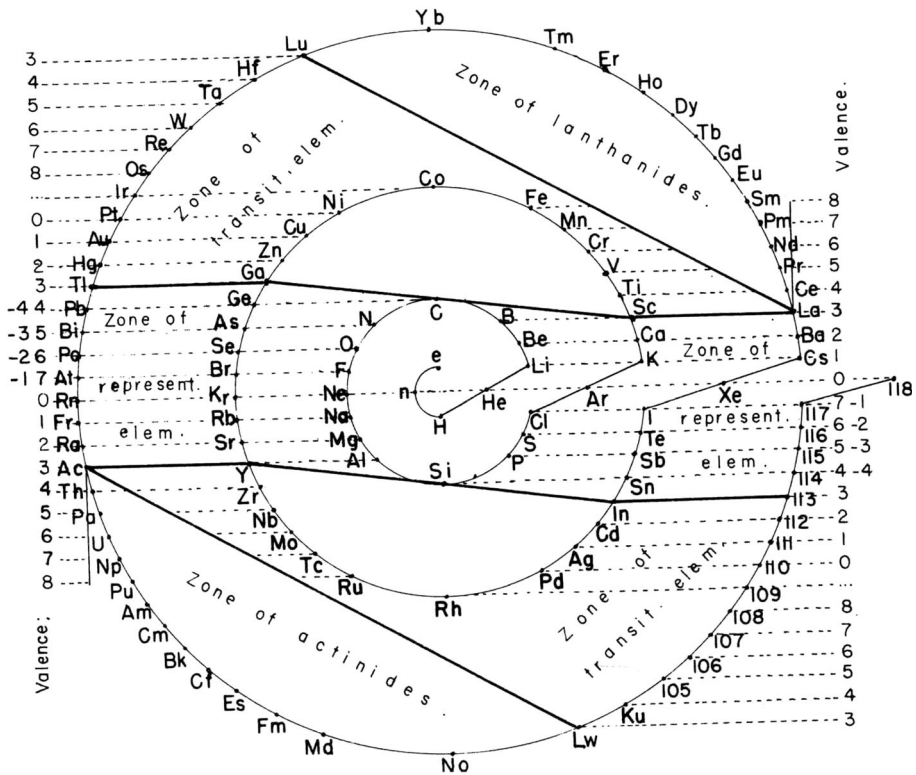


Fig. 4 Planar spiral Rydberg with breaks and jumps (Mazurs 1974, p. 73)

expedient to roll the straight line formed by the elements into a spiral (Imyanitov 2009b, Imyanitov 2015).

Further, if desired, the spiral (fundamental representation) can be simply transformed (by compression, bending, cutting) into many other graphic representations, including tables (Imyanitov 2015). For example, Fig. 3 shows how the cutting of the spiral produces Long Periodic Table⁹ and Left-step Periodic Table.

Today the Chemogenesis web book, The INTERNET Database of Periodic Tables (Spiral & Helical 1951) contains about 100 different versions of the image of Periodic Law in the form of spirals and helixes. Planar, spatial, eccentric, pyramidal and combined modifications of the spiral have been developed (Semishin 1969, p. 71). The principal disadvantage of the vast majority of published spirals and helixes is the lack of breaks and jumps occurring during the passage of quantitative changes into qualitative changes. This contradicts both the second law of dialectics and with the reality (see above).

The mentioned disadvantage can be partly overcome by showing the boundaries between the blocks (Fig. 3). Breaks and jumps occur exactly at the boundaries. The picture is getting more appropriate if the spiral is cut and the next loop is originating further from the center. This approach was used by Rydberg in 1913 (Fig. 4). A similar strategy has

⁹ Relocation of lanthanides and actinides to the bottom of the Long Periodic Table results in appearance of IUPAC-recommended conventional Medium-long Periodic Table.

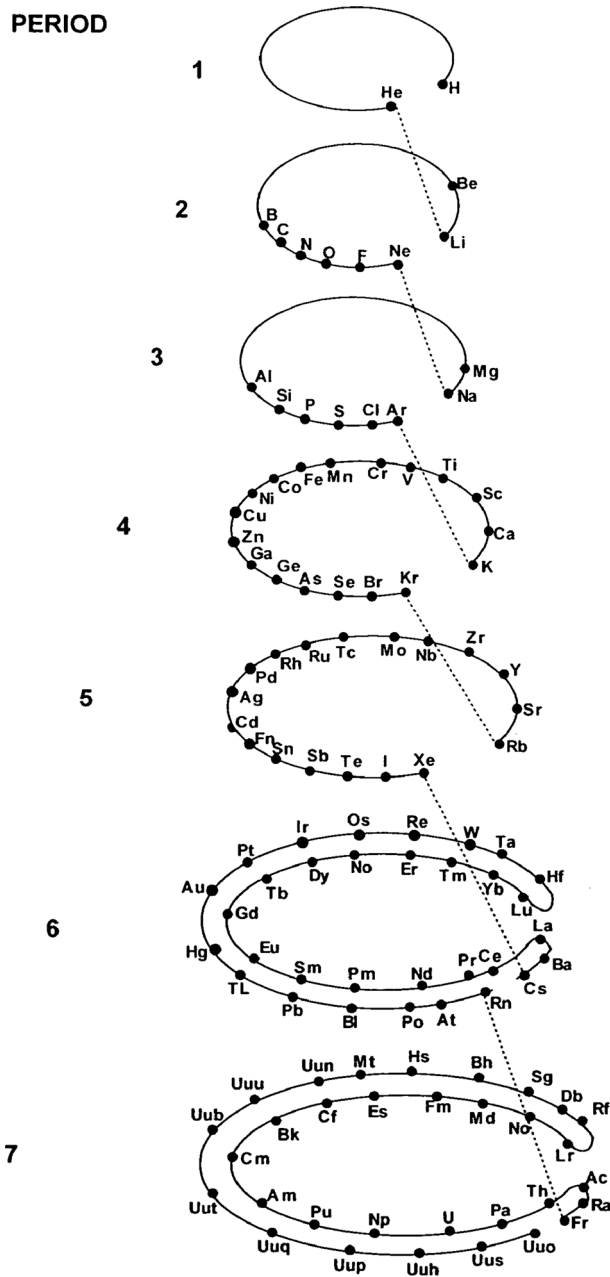


Fig. 5 Spatial spiral (helix) with breaks and jumps (Bernard 2007)

been implemented in the spatial version by moving the next spiral loop down (Bernard 2003, 2007). The elements of each period are placed on separate levels, located one down the other (Fig. 5).

Finishing the review of the dialectics laws it is worth to mention that there appear occasional attempts to formulate new laws. For example, the fourth law of dialects has been recently proposed (Imyanitov 2002):

Development of one property can occur only at the expense of the degradation of another property.

Thus, the development and degradation are interdependent. Indeed, the increase in the number of occupied orbitals in a shell occurs by reducing the number of vacant orbitals. Increasing the polarity of the substances is accompanied by increase of their solubility in water and reduction of their solubility in hexane. Generally, the higher the activity of the catalyst or reactant, the lower is the reaction selectivity. A special case of the fourth law is the conservation laws, for example, the energy conservation law. The new law is complementary to the well-known ones, indicating the source of resources for development.

In general, the laws of dialectics remain true at all levels, including the level of atoms, the level of molecules, the level of the reactions, and the level of ideas.

In this article, the presentation of the dialectics laws is focused on chemistry. The comprehensive description of these laws is reviewed in (Imyanitov 2002, 2009a, b).

Dialectics of higher and lower

The first structural classification of matter and movement was created by Hegel (1812) to differentiate between three levels: mechanics, chemism, and teleology. Engels (1873) identified five levels: mechanical, physical, chemical, biological and social. The issues of interrelations between the higher and the lower underwent significant development in the works of Russian (Soviet) philosophers. Let's consider modern formulations of these relationships (Orlov 1999, pp. 75–78):

- The evolution is the appearance of the higher from the lower (however, not from maximally but optimally developed the lower);
- the higher includes the lower and saves it as its basis, providing the conditions for the maximum development of the lower;
- the included lower obeys the higher;
- the vast majority of the lower is not included in the higher, and creates an environment where the higher exists,
- the newly created higher has a hierarchical structure.

For several centuries, there are disputes about whether it is possible to deduce the higher out of the lower. In the context of this article, the question is articulated as follows: whether physics, as it develops, will be able in the future to explain all chemical relationships? (Kurasvhov 2009, pp. 291–336). In particular, whether it is possible to construct a logically blameless version of the Periodic System only on the basis of quantum mechanics? Reductionists answer positively to both questions.¹⁰ Overview of the opposing opinions regarding the latter question is provided by Scerri (2011, 2007).

Lack of clarity on the latter question makes it impossible to give an answer to the former one. It is also necessary to acknowledge, that the dispute will not be resolved in favour of reductionists, even if *in the future* the physics will explain all aspects of the *modern* chemistry. Upon the development of a given scientific discipline, the objects of its scope

¹⁰ Strong argument supporters irreducibility are considered mathematical theorems Gödel. However, this theorems asserts only that higher can not be derived from a lower *in full volume*.

are becoming more complex. Physics has explained the Periodic Law and the nature of the chemical bond. Biological chemistry study the reactions in living organisms, discovered the structure and mechanism of action of the genetic code.

For clarity, the science can be arranged in the form of a “stairway”:

sociology
biology
chemistry
physics
mathematics

As a result of the expansion of the underlying sciences into frontier areas of the sciences located above, both the upper and lower borders of each science have shifted toward the complexity of objects. In short, there is a parallel (simultaneous) shift of frontiers of sciences (Imyanitov 2003b). Therefore, the reduction to physics of the frontier areas of chemistry cannot result in the full absorption of chemistry by physics. Keep in mind that at the same time chemistry has absorbed the border area of biology. As a result, the objects of chemical study become more complicated, and chemistry remains irreducible to physics as a science in general. In the same way dialectic reducibility/irreducibility exists for physics in the mathematics–physics–chemistry, and for biology in the chemistry–biology–sociology systems (Imyanitov 2003b).

To conclude this section, it is important to emphasize that dialectics is an essential part of modern scientific paradigm. However, it is often present in an implicit form and therefore remains unmentioned. This also applies to the synergetics though it develops ideas of dialectics.

Chemical aspects of synergetics will be discussed later.

Synergetics

As noted in the Introduction, synergetics is a concrete application of the dialectics which serves as a mediator between universal dialectical laws and specific scientific knowledge (Poddubnyj 1999). It was originated in mid twentieth century, two and a half millennia after appearance of dialectics. Synergetics is less speculative than philosophy (dialectics). It uses mathematical models; some of results of the synergetics have been strictly proven in the form of mathematical theorems.

Synergetics is an interdisciplinary area of research; it aims to reveal general laws and principles that underlie the processes of self-organization in systems of very different nature (i.e., physical, chemical, biological, technical, economic, social).

This paper is limited to consideration of the chemical facets of synergetics. In chemistry, the synergetics can be exemplified by the oscillatory reactions in which self-organization occurs in the space or time, or both in space and in time. In chemical oscillatory reactions self-organization is shown as periodic changes in the concentrations of substances or related characteristics.

A significant part of this vast area are processes in which the determining role is played by physical factors, such as heterogeneity of the system, the phenomena of supersaturation, or temperature fluctuations in the exothermic process. If we restrict our consideration by

homogeneous isothermal reaction, the self-organization may occur: *in a stirred medium*, temporal oscillations in the concentrations of intermediate or catalyst species; *in an unstirred medium*, traveling spatial waves or zones of chemical reaction; and, *in a continuous-flow stirred tank reactor* (CSTR), bistability or even tristability, hysteresis, excitability, and deterministic chaos (Field 1989). A number of introductory texts exist on the subject (Epstein and Pojman 1998; Scott 1994; Gray and Scott 1994). Some general information about oscillations in the concentrations is presented below.

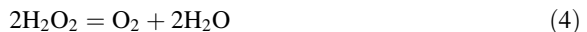
The dramatic story of the discovery of oscillatory reactions. The origination of synergetics (Pechenkin 2005; Tabony 2006; Temkin 2012)

Usually, chemical reactions run continuously and monotonically. However, as early as in seventeenth century, Robert Boyle observed periodic flashes of lights in the oxidation of phosphorus vapor (Harvey 1957). In 1834 Munk published a paper on the study of this reaction (Munk 1834), which is often considered the first article on the oscillatory reaction.

In 1850 and 1855 Runge published two books (Runge 1855; Pechenkin 2005) titled “To the chemistry of color. Samples for friends of the beautifulness” and “Substance in a tendency to formation”. He impregnated with salt solutions a filter paper and placed in its center a drop of another salt. Certain combinations of reactants then started to form concentric tracers. The “Substance in a tendency to formation”, despite its great age, can be found on the Internet (Runge 1855).

Liesegang (1896) obtained rings from the precipitate $\text{Ag}_2\text{Cr}_2\text{O}_7$, placing a drop of AgNO_3 solution in the middle of the plate from the gelatin hydrogel containing $\text{K}_2\text{Cr}_2\text{O}_7$ (Fig. 6).

In 1921 it was reported that the reaction of decomposition hydrogen peroxide



proceeds periodically at a constant temperature when HJO_3 is used as a catalyst. To avoid heterogeneity caused by the formation of bubbles of oxygen, the reaction rate was lowered by decreasing the temperature. The oxygen is produced so slowly that it diffuses out of the solution without the formation of bubbles. Since in this case the oscillations are not disappearing, it was concluded that completely homogeneous purely chemical oscillatory reaction was carried out for the first time (Bray 1921). It described below under the title “Bray–Liebhavsky reaction.”

However, information on oscillatory reactions remained on the periphery of chemical science. Chemists have seen in these reactions something atypical, exotic and perhaps even erroneous (Pechenkin 2005). It seemed incredible that under constant conditions the reaction proceeds in the forward, then backward.¹¹ It was customary to think that the oscillations are caused by the associated physical processes: temperature leaps in exothermic gas phase reactions or heterogeneous steps in the liquid phase. It should be noted that in many cases these doubts turned to be true (Bowers and Noyes 1985; Griffiths 1985). Indeed, upon the formation of rings Liesegang (Fig. 6), the reaction system involves a combination of reaction, diffusion and precipitation.

Up to 1965 there were just a few publications of oscillatory reactions (Fig. 7). This period is well described by the outstanding expert in oscillation reactions, Noyes (1990):

¹¹ It's really incredible, and in oscillatory reaction is not happening. Concentration of the intermediate specie is oscillated. The intermediate is then accumulated, then consumed. Here, too, had to overcome the stereotype: the principle of quasi-stationary concentrations of intermediate species are widely used in the analysis of the reaction mechanisms kinetics, but only under certain restrictions.

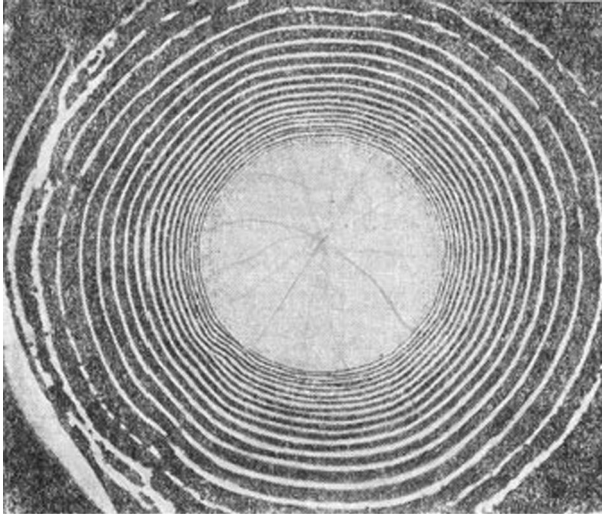


Fig. 6 Typical Liesegang patterns: silver-chromate rings formed in a gelatine layer

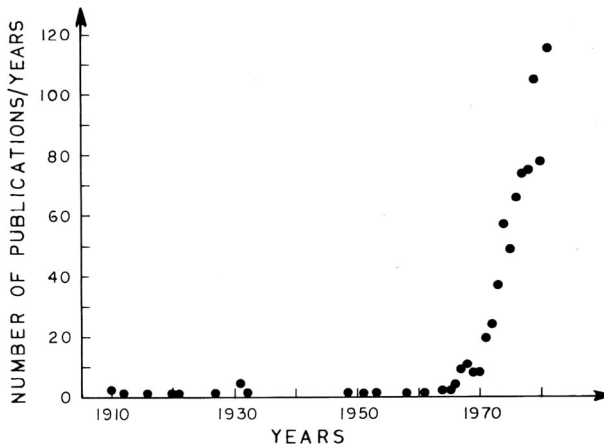


Fig. 7 Annual production of publications, in oscillating reactions, 1910–1981 (Burger and Bujdoso 1985, p. 568)

“most chemists including myself either had never heard of oscillatory reactions or else believed that the few alleged examples were artefactual”.

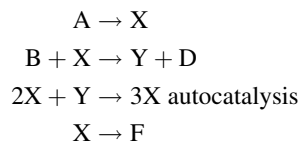
So when Belousov in 1951 tried to publish an article about the discovery of the oscillatory reaction, the reviewer claimed that his “supposedly discovered discovery” was quite impossible (Winfree 1984). This article describes the multiple color changes from colorless (Ce^{3+}) to yellow (Ce^{4+}) and backwards upon the oxidation of citric acid. Oxidation was carried out in a homogeneous aqueous solution under the influence KBrO_3 in acidic medium. Cerium ions served as a catalyst.

This article was twice rejected by the editors of reputable journals; Belousov eventually managed to publish it in reduced form only eight years afterwards in the “Collection of

abstracts on radiation medicine” (Belousov 1959), the journal with a very small readership. Only 30 years later, this article (Belousov 1981, 1982, 1985) was made available.

Nevertheless, this work attracted the attention of Shnol’ (Winfree 1984; Zhabotinskii 1985; Pechenkin 2005; Viter 2008). In 1961 he offered to his university graduate student Zhabotinskii to continue investigations of Belousov. Zhabotinskii made a substantial contribution to the elucidation of the kinetics and mechanism, as well as to the mathematical modeling of this reaction (Zhabotinskii 1964a, b, 1974; Zaikin and Zhabotinsky 1970). As a result, this reaction became known as Belousov–Zhabotinskii reaction. Experts consider studies of Belousov and Zhabotinskii as a beginning of the modern era of research in this area (Field 1985, p. 55).

A powerful incentive for the development of studies of these reactions has been also formed outside chemistry. The synergetics, an interdisciplinary research area aimed to study complex, capable of self-organization systems, began to form as distinct discipline (Nicolis and Prigogin 1977; Haken 2012). It needed models complicated enough to be adequate, but nevertheless sufficiently simple to be analyzed by strict mathematical methods. The group led by one of the founders of synergetics, Prigogine, has utilized for this purpose a hypothetical sequence of reactions (Prigogine and Lefever 1968; Nicolis and Prigogin 1977, p. 93).



where A and B are precursor reactants, D and F are final products, X and Y are intermediate species. This model is called trimolecular (based on its stage of autocatalysis) or «Brusselator» (by city name where it was developed). It describes the oscillations in the concentrations of intermediate species. The mathematical study of this model produced general concepts regarding the regularities of oscillating reactions, and, more broadly, regarding the principles of self-organization of all complex systems in various branches of science. For this works Prigogine was awarded the Nobel Prize.

While Brusselator has a speculative design and is not based on a real chemical reaction, «Oregonator» (from the state of Oregon, the place of its creation) was developed based on the Belousov–Zhabotinskii reaction (Field and Noyes 1974; Field 1975; Taylor 2002). So chemistry and synergetics mutually contributed to the progress of each other. Since 1965, there has been intensive advancement in the research of oscillating reactions (Fig. 7). Chemical oscillators have become to be regarded as paradigmatic examples of complex systems, which are the focus of modern science. The synergetics significantly increased the role of chemistry in the system of fundamental scientific knowledge (Pechenkin 2005).

Basic concepts of synergetics

The main concepts of synergetics are self-organization, open systems, and non-linearity. Self-organization is a spontaneous ordering, a transition from chaos to order. It occurs during the formation and evolution of structures. In chemistry, self-organization is seen in the form of temporal oscillations in the concentrations of intermediate or catalyst species, traveling spatial waves or zones of chemical reaction, etc. (see above).

Self-organization can occur only in the far-from-equilibrium systems. First of all, the system has to be open. Its remoteness from equilibrium ensures the supply of energy and/or

matter (precursor reactants, e.g. A and B, see above in «Brusselator») from the outside. In closed systems, the ability of self-organization will disappear at the approach to equilibrium.

Nonlinearity takes place, when the reaction rate is described by the equation with variables in degrees greater than one, or with coefficients depending on the properties of the medium. Nonlinear equations have several solutions, hence the above-mentioned bistability or even tristability.

There is a proven theorem stating that self-organization in time is impossible in a reaction sequence involving two variable intermediates if the reaction steps are only uni- and bimolecular (Nicolis and Prigogin 1977, p. 90, 94). Accordingly, while designing Brusselator it was necessary to use a trimolecular step (see above, autocatalysis). It should be noted that true trimolecularity is not mandatory: it is enough that the kinetic equation would contain X^3 or X^2Y . In systems with three or more intermediates for the self-organization, the trimolecularity is no longer necessary (Nicolis and Prigogin 1977, p. 192).

Stage $2X + Y \rightarrow 3X$ in the Brusselator (see above) deserves special attention. It reflects the autocatalytic formation of intermediate X. Autocatalysis is the cause of the most common type of non-linearity, resulting in oscillating reactions (Gray and Scott 1994, pp. 5, 7–15; Barragán 2015).

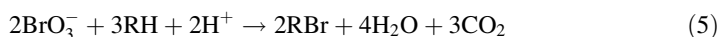
The conditions required for the implementation of the oscillations are analyzed in more detail in the monograph (Temkin 2012). 21 simple nonlinear kinetic models are considered; thermodynamic, chemical and mathematical conditions are formulated on this basis. Examples of thermodynamic conditions include remoteness from equilibrium and unstable stationary states. Mandatory chemical conditions include the presence of non-linear stages or significant complexing of catalyst with precursor reactants, final products, intermediate species or inhibitors.

Next, let's consider chemical individual homogeneous isothermal oscillatory systems.

Individual homogeneous oscillatory systems

Belousov–Zhabotinskii reaction

Belousov–Zhabotinskii reaction is the most famous chemical oscillator. Different variants of demonstration of the color variations of this reaction can be viewed in the Internet (Oscillating Chemical Reaction 2007). This reaction includes the catalyzed oxidation and bromination of organic species by acid bromate ion (Tyson 1985; Toth and Taylor 2006)



where RH is malonic acid, $\text{CH}_2(\text{COOH})_2$; instead malonic acid one can use brommalonic, citric, and malic acids, as well as ketones or other compounds (Zhabotinskii 1974, p. 90; Field 1985, p. 81; Taylor 2002).

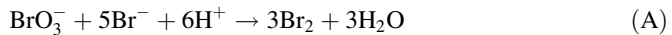
It utilizes as catalysts the transition metal ions, which have two oxidation states differing by one electron: $\text{Ce}^{4+}/\text{Ce}^{3+}$, $\text{Mn}^{3+}/\text{Mn}^{2+}$, and complexes of ruthenium, iron (ferroin/ferriin), chromium, cobalt, copper, nickel, osmium and silver, with 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen) ligands (Taylor 2002; Field 1985, p. 79).

Oscillatory regimes, bistability, packets oscillations, separated by non-oscillatory stationary states, quasi-periodic and chaotic oscillations, traveling waves and spatial structures have been experimentally established for Belousov–Zhabotinskii reaction (Temkin 2012; Taylor 2002).

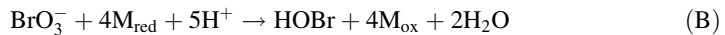
The mechanism and kinetic model were firstly proposed for the $\text{KBrO}_3\text{--Ce}(\text{SO}_4)_2\text{--H}_2\text{SO}_4\text{--malonic acid}$ system (Zhabotinskii 1964b, 1974; Vavilin and Zhabotinsky 1969). They described the causes for occurrence of an induction period and oscillations in a closed system.

Later Field, Koros and Noyes (FKN) published a more detailed mechanism consisting of 11 reactions and 7 intermediates (Field et al. 1972). The kinetic model based on this mechanism was called Oregonator (see above). More detailed mechanism, which included 80 reactions and 26 intermediate species, was suggested in 1990s (Györgyi et al. 1990). Corresponding model contained 42 stages and 22 intermediates (Turanyi et al. 1993).

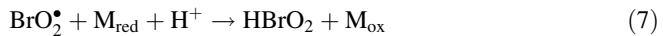
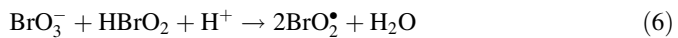
The above FKN mechanism can be split into the three discrete processes, each of which consists of several reactions (Toth and Taylor 2006; Taylor 2002; Tyson 1985). Process (A)



proceeds until the concentration of Br^- has fallen to a critical value such that the rate of Process (B) becomes significant (Fig. 8c)



where M_{red} and M_{ox} refer to the reduced and oxidised forms of the catalyst respectively. Process (B) includes autocatalytic stages



Br^- inhibits autocatalysis, destroying HBrO_2 .

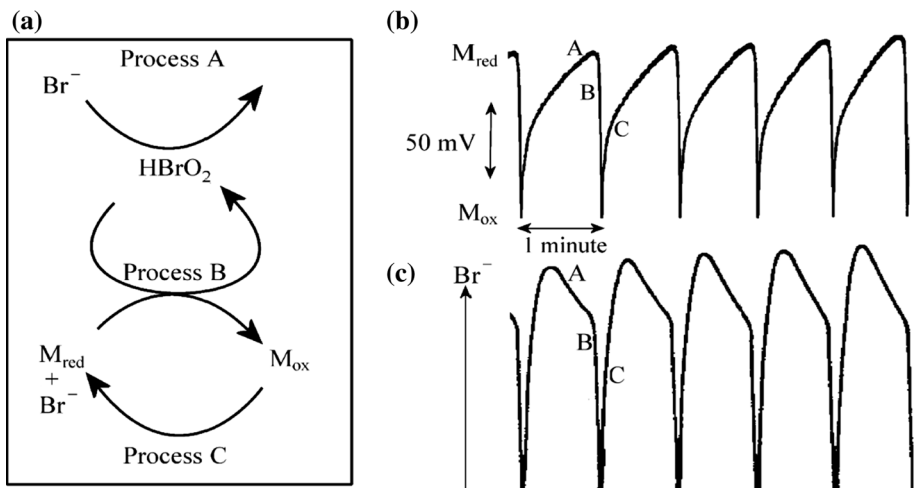
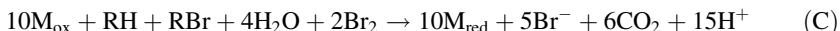


Fig. 8 a Schematic of the FKN mechanism where M_{ox} and M_{red} represent the oxidised and reduced form of the catalyst respectively. Potential oscillations in the Belousov-Zhabotinsky reaction with b a platinum electrode, c a bromide-selective electrode. A, B and C refer to FKN Processes A, B and C respectively (Toth and Taylor 2006)

The M_{red} and Br^- are regenerated in Process C (8b, c), in which the organic species, RH, acts as a reducing agent



where RH is malonic acid, $\text{CH}_2(\text{COOH})_2$. So begins a new oscillation (Fig. 8a–c).

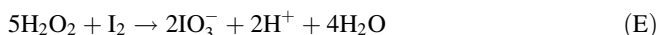
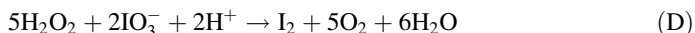
The growth in the concentration of Br^- results in a suppression (8) of autocatalysis (6)–(7) in Process (B) and acceleration of Process (A). Process (A) then replaces Process (C) (Fig. 8). The concentration of Br^- is a switch that provides the shift of the processes. The change in oxidation state of the catalyst during the reaction is accompanied by a colour and redox potential changes (Fig. 8b).

The mechanism of the Belousov–Zhabotinskii reaction was discussed in depth in reviews (Taylor 2002; Toth and Taylor 2006). The survey on the applications of this reaction can be seen below in “Use of chemical oscillators” section.

Bray–Liebhavsky reaction

As mentioned above, this reaction was described in 1921. It is often noted that this is the first known purely chemical homogeneous oscillating system. However, the existence of a heterogeneous (physical) stage of this reaction has been suspected time and again since its discovery up to the present time.

The catalytic cycle of decomposition of hydrogen peroxide by Bray–Liebhavsky reaction (4) can be described in two combined Processes (Furrow 1985; Treindl and Noyes 1993; Noyes et al. 1995; Ren et al. 2008).



The net result of Processes (D) and (E) is five times reaction (4). In Process (D) H_2O_2 acts as a reducing agent, in Process (E)—as an oxidant. The processes (D) and (E) alternately dominate the system, resulting in iodine oscillations (Fig. 9) and periodic

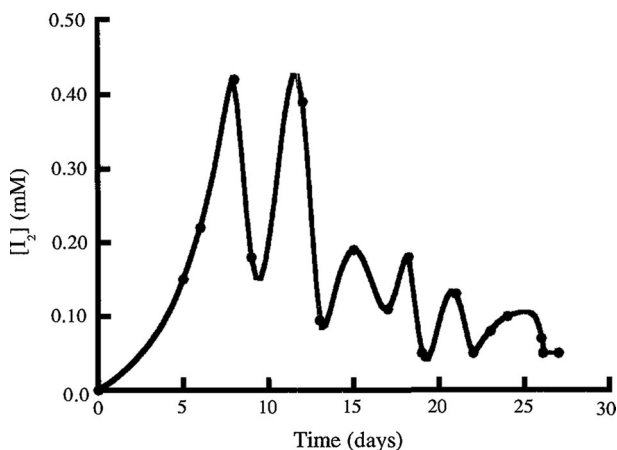


Fig. 9 Oscillations in the iodine concentration in the Bray–Liebhavsky reaction at 25 °C. (Bray 1921; Epstein and Pojman 1998, p. 7)

oxygen gas evolution. Each of these processes consists of several reactions. In current views, the total number of these reactions is about ten (Treindl and Noyes 1993; Noyes et al. 1995; Szabo and Sevcik 2013).

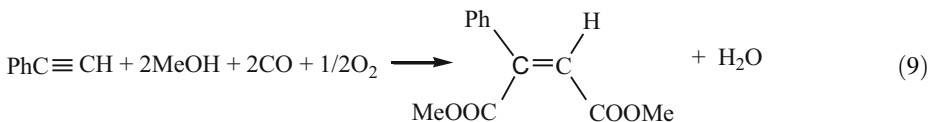
The explanation of the reasons for oscillations that was based on homogeneous reactions (Bray 1921) initially met skepticism (see above). Instead, the heterogeneous reaction occurring on the surface of dust particles, “a very unusual combination of chemical and physical factors”, including volatilization of iodine, or exposure to the light, were proposed as the underlying mechanism (Furrow 1985, p. 172). These assumptions became unnecessary upon research of Belousov–Zhabotinskii reaction, when the existence of homogeneous chemical oscillators was recognized (see above; Furrow 1985).

However, the development of mathematical models describing quantitative aspects of Bray–Liebhavsky reaction resulted in the reinvention of the physical component. In particular, there are proposed scenarios in which O_2 is considered a reactive intermediate, and the transport of oxygen from the solution to atmosphere will influence the overall reaction (Treindl and Noyes 1993; Noyes et al. 1995; Kissimonova et al. 2001; Olexova et al. 2010). But on the basis of high-precision measurements of gas production, this version is put into question (Szabo and Sevcik 2013). A mechanism involving iodine interphase transport has also been suggested (Valent et al. 1998; Szabo and Sevcik 2013).

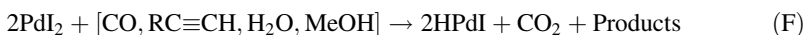
Oxidative carbonylation of alkynes

The first report on a palladium-catalysed oxidative carbonylation of an alkyne in the presence of an iodine-containing catalyst was presented in 1962 (Grosjean et al. 2008). The oscillations during oxidative carbonylation of acetylenes were discovered by Temkin and co-workers in 1983–1985 (Temkin 2012).

Unlike all other known oscillating chemical systems, the oxidative carbonylation of alkynes involves converting relatively simple substrates into complex molecules. With phenylacetylene and catalyst system PdI_2 –KI, the reaction proceeds according to the equation (Temkin 2012; Malashkevich et al. 1997).



This reaction is known to have (Fig. 10) oscillations of the platinum electrode potential, pH, and rate of gas ($CO + O_2$) absorption. Oscillations can be explained (Temkin 2012) by alternately proceeding combined Processes (F) and (G). (F) is a reduction.



Process (G) is an oxidation.



Process (F) includes the formation oxidative carbonylation catalyst Pd_2I_2 ($Pd_2I_4^{2-}$) by reactions



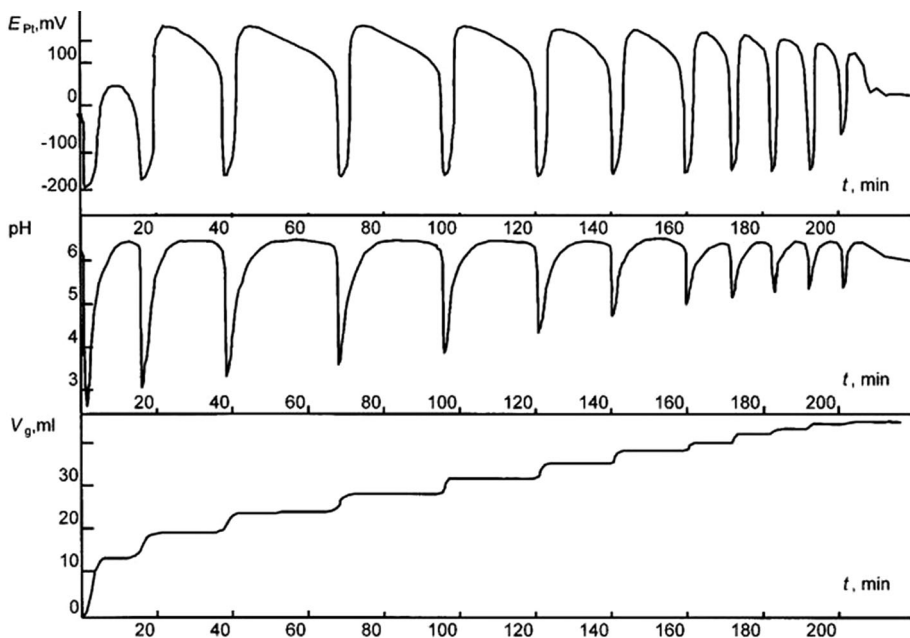
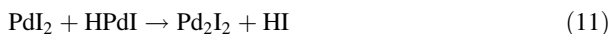
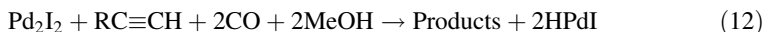


Fig. 10 Oscillations of the platinum electrode potential (E_{Pt}), pH, and volume of the gas mixture CO–O₂ (V_g) consumed in the course of phenylacetylene oxidative carbonylation (Temkin 2012; Malashkevich et al. 1997)

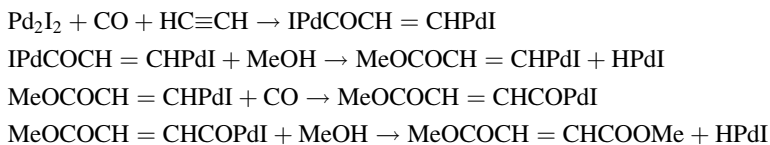


Kinetic model of reaction (9) includes 7 stages (Temkin 2012), and the autocatalysis is represented by reactions (11) and (12).



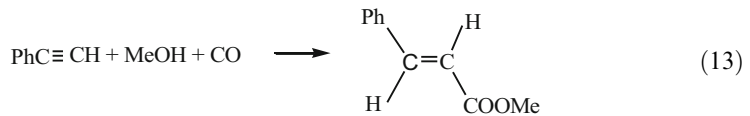
The calculated periodic curves are close to the experimental ones. A number of similar models have been proposed resulting in oscillations (Gorodskii et al. 2003; Temkin 2012; Parker and Novakovic 2013).

Reaction (12) involves the following steps (Temkin and Bruk 2003).



Mechanisms with intermediate formation of Pd⁰ can also explain oscillations (Gorodskii et al. 2003; Parker and Novakovic 2013).

Oxidative carbonylation reaction of phenylacetylene was very sensitive to traces of water. When dry methanol was used, hydrocarboxylation (13) was observed instead of oxidative carbonylation (9) (Parker and Novakovic 2013).



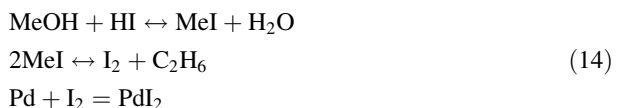
It is reasonable to assume that the water influences the synthesis of oxidative carbonylation catalyst Pd_2I_2 during the stages (10, 11). Since water is formed by the reaction (9), this can be defined as an autocatalysis by water.

The oxidative carbonylation of phenylacetylene was studied in order to determine the product distribution and reaction conditions, which resulted in oscillatory versus non-oscillatory behaviour (Grosjean et al. 2008; Gorodskii et al. 2001, 2003). The reaction was carried out in a calorimeter, and variations in heat release and pH were recorded (Novakovic et al. 2007). Unambiguous identification of the products was undertaken (Grosjean et al. 2008). It demonstrated that when operating in an oscillatory pH regime, product formation may be suppressed until oscillations occur after which there is a steep increase in the formation of dimethyl ester for the above reaction (9). When operating the reaction in oscillatory mode, a high selectivity was observed (Novakovic et al. 2008a; Grosjean et al. 2008).

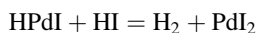
The same authors conducted a thorough study of gas–liquid mass transfer in a reaction. Simulation work revealed that at the previously reported operating conditions, mass transfer of CO is limited due to its poor solubility in methanol. The influence of gas–liquid mass transfer rates on reactant conversion and the dynamics and selectivity of product formation as well as the occurrence of oscillatory behaviour in this reaction system, was established (Novakovic et al. 2008b). This work is presented only in the form of conference abstract, so it is not clear to which extent the oscillations are determined by mass transfer or by chemical reaction.

Oscillations in the oxidative carbonylation, in addition to phenylacetylene, occur with acetylenes $\text{RC}\equiv\text{CH}$, where $\text{R}=\text{H}$, CH_3 , $n\text{-C}_7\text{H}_{14}$, HOCH_2 , $\text{HOC}(\text{Me})_2$ (Temkin 2012; Gorodskii et al. 2003; Gorodskii et al. 2001), as well as with mono alkyne-terminated poly(ethylene glycol) methyl ether (Donlon and Novakovic 2014).

All the above oxidative carbonylation reactions are carried out using an oxidizing agent. Oxygen, on the one hand, provides stoichiometry: it binds two “unnecessary” hydrogen atoms in the reaction (9). On the other hand, the oxidizer closes the catalyst cycle: it returns HPdI formed by the reaction product synthesis (F), to the initial PdI_2 by means of reaction (G). Nevertheless, it has been found that it is possible to conduct oscillatory carbonylation of phenylacetylene in the absence of externally supplied oxidant. The authors speculated that in this case the oxidizing agent was iodine (Donlon et al. 2014).



However, the reaction (14) is described as a photochemical process (Harris and Willard 1954), so it is more likely in this case to represent the reaction (Chiusoli et al. 2003).



The study of oscillations in the oxidative carbonylation of acetylenes was initially conducted only in Lomonosov Moscow State Academy of Fine Chemical Technology (Russia). Then these studies were actively joined by the Department of Chemical Engineering and Advanced Materials, Newcastle University (United Kingdom). Currently, this work is being done in collaboration by both organizations (Gorodskii and Novakovic 2011; Gorodskii 2011).

Other oscillating reactions

For a long time, iodates and bromates have been considered to be essential components in oscillating reactions. Studies conducted since the 1970s (Fig. 7) have greatly extended the number of reagents and a diversity of reactions. Figure 11 provides some description of the progress in this field, where the systematization is done by “families” such as the bromate, iodate, chlorite, permanganate and thiosulfate based reactions.

Oscillatory reactions on heterogeneous catalysts were carried out only in the early 1970s. I would mention here only the decomposition of N_2O on the copper oxide and CO oxidation with oxygen, and suggest for further reading the review (Imbihl 2008) and the book (Slin'ko and Jaeger 1994).

Use of chemical oscillators

In the initial stage, from the mid nineteenth century, chemical systems that exhibited rhythmical oscillations, were seen as fascinating but obscure phenomena which were purely of aesthetic interest. In the second period, starting from the second half of the twentieth century, these systems served as models for the study of self-organization in systems of very different nature. For example, it is shown that the Belousov–Zhabotinsky reaction is an excellent model of the neural dynamics (Gentili 2013). The above models, such as «Brusselator» and «Oregonator», contribute to the basis of synergetics.

In the third stage, at the beginning of the twenty first century, the development of novel biomimetic or smart materials was added to aesthetics and modeling (Yoshida 2010; Yashin et al. 2010; Zhou et al. 2011). The structure of one of such materials is shown in Fig. 12. This polymer operates as a gel, and ruthenium ions catalyze Belousov–Zhabotinsky reaction. When this reaction occurs, Ru^{3+} rhythmically converts to Ru^{2+} and backwards. Since Ru^{3+} has a higher hydrophilicity, these transformations result in cyclic swelling-deswelling alterations of the gel (Yoshida 2010).

It is suggested to use changes in the volume of a gel at a swelling-deswelling alterations for development of a self-beating micropump, peristaltic micro-/nanoactuator, pacemaker, etc. (Yoshida 2010). It is also possible to design self-propelled soft robots, micro-machines, coatings for damage detection, membranes for selective transport, etc. (Yashin et al. 2010). In particular, an autonomous mechanical pumping intestine-like system was obtained by fabricating self-oscillating gel in a tubular shape (Shiraki and Yoshida 2012).

Belousov–Zhabotinsky reaction was carried out in the presence of a strong acid and using a strong oxidizing agent (see above). Such a system cannot be applied to living organisms. To resolve this problem, it was suggested to fix the acid (more precisely, the $-SO_3H$ group) and the oxidant ($-Me_3N^+BrO_3^-$ group) on the same polymer as done for the ruthenium ions. Polymer similar to that shown in Fig. 12, but containing these groups, was obtained by copolymerization. Self-oscillation under biological conditions where only the organic acid (malonic acid) exists was actually achieved (Yoshida 2010).

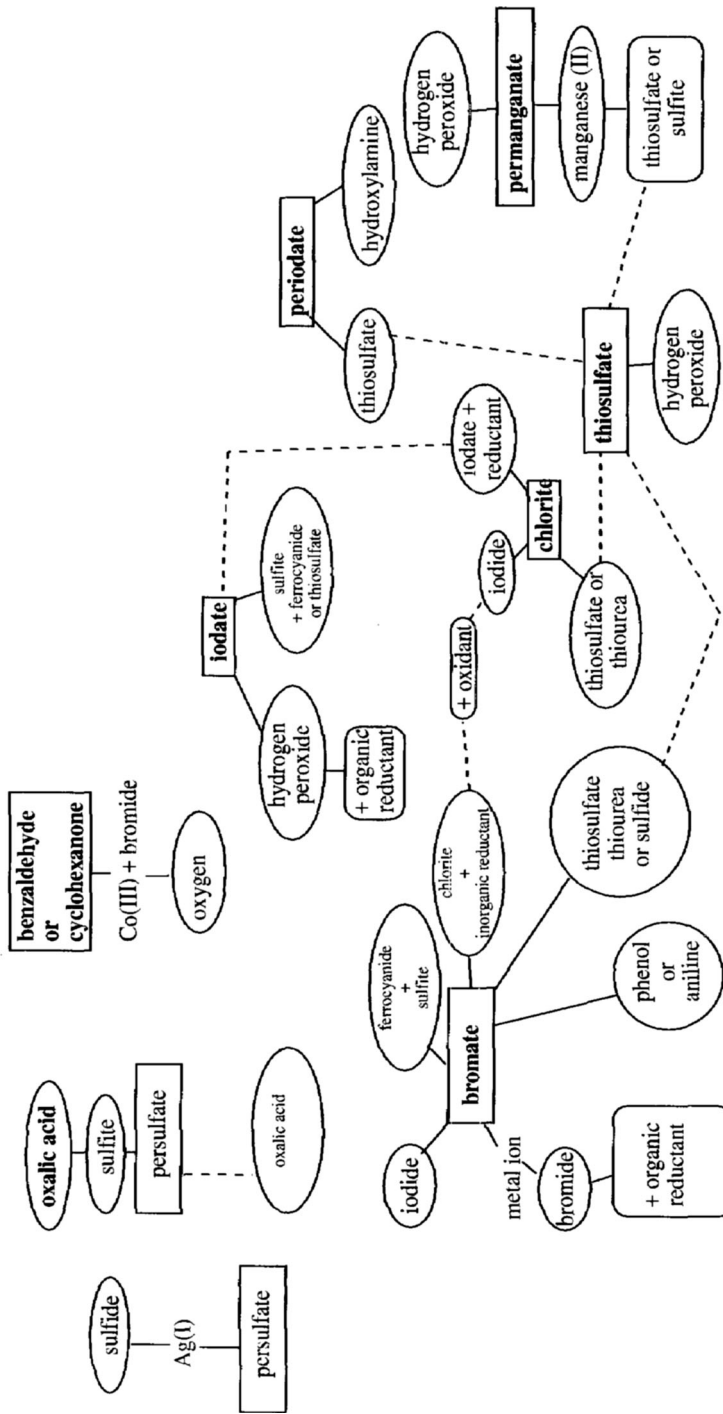


Fig. 11 A taxonomy of chemical oscillators. *Dashed lines* indicate family relationships, that is, oscillating reactions that fall into both families (Epstein and Pojman 1998, pp. 81, 82)

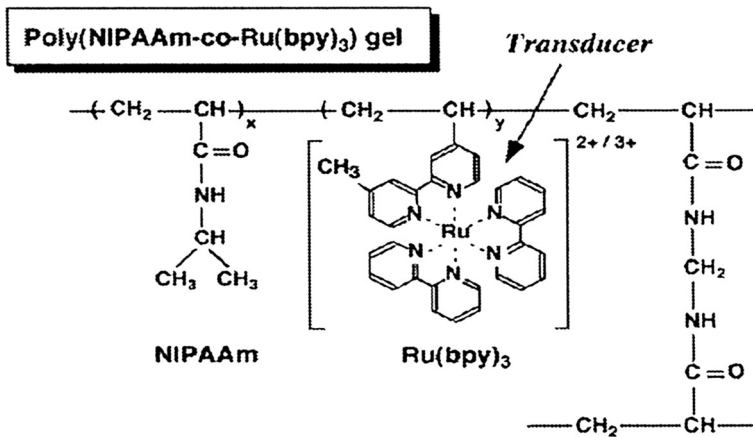
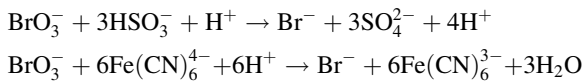


Fig. 12 Chemical structure of smart material, which functioning is based on the Belousov–Zhabotinskii reaction (Yoshida 2010)

In simpler versions of the use of chemical oscillators the components of the oscillatory reaction are not a part of the polymer. As an example, consider the system of the pH-oscillator and pH responsive hydrogel. Polymer methacrylic acid was used as hydrogel. A weak polyacid such as polymethacrylic acid will, at low pH, be essentially charge-neutral, because the degree of dissociation of the carboxylic acid groups is relatively weak. In these circumstances hydration for polyacid is small and the gel collapses. However, as the pH is increased, COOH is converted into COO^- and the polymer acquires a net charge. Hydration is great and mutual repulsion between the charged chains causes them to stretch away from each other. As a result, the hydrogel increases in volume (Crook et al. 2002).

As pH-oscillator, the second component of the described system, Landolt reaction was utilized (Rabai et al. 1990).



The first process¹² serves as the proton production mechanism, while the second acts as reaction consuming protons.

Combining the described pH-oscillator with the pH responsive hydrogel results in the development of chemically driven synthetic muscle (Crook et al. 2002; Howse et al. 2006).

Dialectics in oscillating reactions

Oscillations occur as a result of the conflict of opposites, alternating predominance of one against the other. The opposites exist in unity: the elimination of one of them results in the cessation of oscillations. This is a manifestation of the law of the unity and conflict of opposites. In synergetics, instead of “conflict of opposites” it is common to call it “interplay between positive and negative feedback.” (Epstein and Pojman 1998; Scott 1994; Gray and Scott 1994). Mathematical analysis has demonstrated that delayed feedback plays

¹² It goes autocatalytically: initially takes place $\text{HSO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_3$, because H_2SO_3 reacts faster with BrO_3^- than HSO_3^- (Rabai et al. 1990).

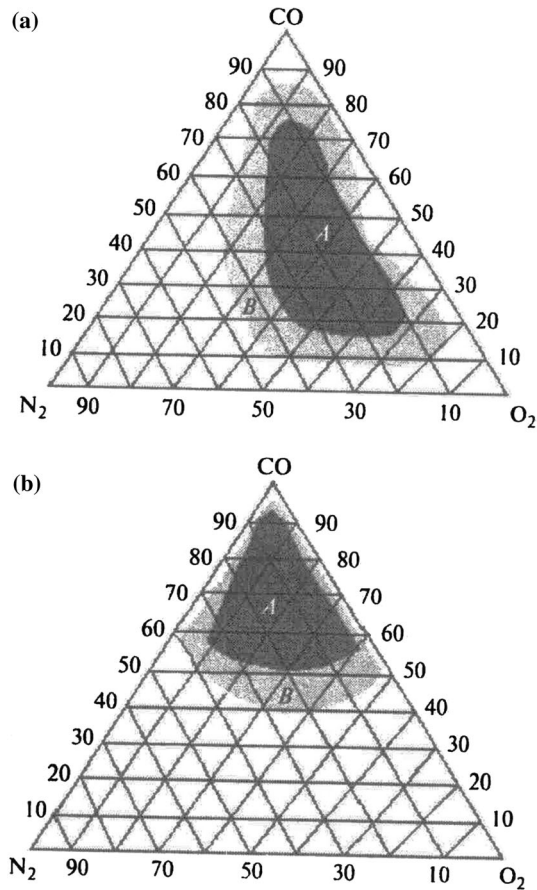


Fig. 13 Regions of existence of oscillations in the oxidative carbonylation of methylacetylene (a) and phenylacetylene (b): A is the region of stable oscillations; B is the region of rapidly damping oscillations (Gorodskii et al. 2003)

a key role in most, if not all chemical oscillators (Epstein and Luo 1991). This is an example of the development and concretization of dialectic relationships by synergetics.

In Bray–Liebhavsky reaction the opposites are represented by the Processes IO_3^- reduction (D) and iodine oxidation (E). Their unity is achieved through the unity (coexistence) of oxidation and reduction properties of hydrogen peroxide.

The relationship between the opposites is more complex in the Belousov–Zhabotinskii reaction. Process C, on the one hand, is the opposite of Process A. The first increases Br^- concentration, which is a switch. Process A, on the contrary, reduces the concentration of Br^- (see above).

On the other hand, Process C is also opposed by Process B: the first reduces M_{ox} in M_{red} , the second conducts inverse transformation (Fig. 8a).

Upon oxidative carbonylation of acetylenes, the opposites are the Processes of reduction (F) and oxidation (G).

Oscillations are impossible for relatively simple reactions, but as the number of intermediates increases, the oscillations become real (see above). Oscillations require a certain

combination of the quantities (concentrations) of reagents (Fig. 13). Different concentrations often correspond to different types of oscillations. The above examples illustrate the law of the passage of quantitative changes into qualitative changes.

Oxidation step in the above reactions gives way to the reduction step, then oxidation occurs again. With the progressive change in the concentration of reactants oscillatory regimes are initially missing, then appear, then disappear (Fig. 13). Complete homogeneity in Bray–Liebhavsky reaction was initially denied on the basis of incorrect underlying considerations, however became recognized later. Specific heterogeneous stages were defined after that upon the development of mathematical models (see above). This exemplifies the law of the negation of the negation.

More broadly, the long history of non-recognition of the existence of oscillatory reactions testifies to the need of dialectical thinking. It is important to avoid the dogmatism, excessive straightness and rejection of all the new when it does not fit into the established ideas.

Conclusion

Dialectics is an essential part of modern scientific paradigm. However, it is present in the latter in a somewhat implicit form. This situation has arisen historically for political (ideological) reasons and needs to be corrected.

Dialectic approach makes it possible to consider the objects comprehensively, in interrelationship with other objects and its history. Dialectics warns against orthodoxy, stereotypical thinking. At the same time one should not forget that philosophy provides a method for cognition and is in no way a substitute for scientific research, experiment.

Chemical regularities are an ideal material for illustration and application of the laws of dialectics. The laws of dialectics remain appropriate at the level of atoms, and at the level of molecules, and at the level of the reactions, and at the level of ideas. In particular, fundamental representation of the Periodic Law can be made in the form of spiral with breaks and jumps (Fig. 4, 5). Further, if desired, the spiral can be simply transformed (by compression, bending, cutting) into many other graphic representations, including tables.

Small changes in the conventional Periodic Table on the basis of previously rejected options allow reflecting secondary and additional periodicity (Table 1).

Despite the obvious fact of the reduction of the frontier areas of chemistry to physics, one cannot expect the full absorption of chemistry by physics. Keep in mind that the frontier areas of biology are transferred to chemistry at the same time. As a result, the objects of chemistry become more complicated, and chemistry remains irreducible to physics as a science in general. In the same way dialectic reducibility—irreducibility exists for physics in the mathematics–physics–chemistry, and for biology in the chemistry–biology–sociology systems. In short, there is a parallel (simultaneous) shift of frontiers of sciences.

Classical conservation laws can be considered as a special case of the recently proposed fourth law of dialectics, in which *Development of one property can occur only at the expense of the degradation of another property*. Thus, the development and degradation are interdependent.

Synergetics, similarly to dialectics, is dedicated to the studies of general laws of evolution. Synergetics is an interdisciplinary area of research. It aims to obtain the knowledge on the general laws and principles that underlie the processes of self-organization in

systems of very different nature: physical, chemical, biological, technical, economical, social.

The interrelation between dialectics and synergetics are the subject of debate. The most plausible definition of the position of synergetics assumes that it provides concrete examples and applications for dialectics and plays a role of mediator between universal dialectical laws and specific scientific knowledge.

To study the complex and capable to self-organization systems, synergetics needs complex models to provide the adequacy. At the same time, the models have to be relatively simple so that they can be studied by strict mathematical methods. The examples of such models include oscillating chemical reactions, which consist of a large number of stages. For example, one of the models of Belousov–Zhabotinsky reaction consists of 11 stages and 7 intermediates.

Oscillating reactions can be viewed as models of complex systems, which are in the focus of modern science. Chemical oscillators have become, in essence, a “testing ground” for new ideas and concepts. The role of chemistry in the system of fundamental scientific knowledge has increased due to synergetics. The chemistry and synergetics mutually stimulate their progress.

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