

Synergistic Phenomena in Chemistry

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Abstract

New classification of synergistic effects in chemistry of five categories, every contains two or three types of synergism has been worked out. The classification covers all the cases of synergism in static and dynamic conditions of chemical form of substance existence.

Synergistic effects (SE)¹ and phenomena were first discovered in biology and medicine and were defined as a non-additive increase of action of two (or more) biologically active compounds (medicine) at their combined using.

Later, synergistic phenomena were noted in different fields of chemistry and also in physics, other sciences and in technical developments. However, the problem of synergism as a phenomenon in modern chemistry is not developed at all, there are only some, not connected with each other, reports about synergism effects in physical, biological, pharmaceutical, analytical and other direction of chemistry. Thanks to the works of the authors [2,3] and articles of scientists of Russia and Belgium this phenomenon had been studied in catalysis little more in details.

The literature on synergism analysis shows that in present there has been still no any general conception, which generalizes odd data; scientifically – confirmed methods for solving of both general – methodological and theoretical – instrumental problems of the phenomenon have not been found.

The first attempts of consideration of the mechanism of originating non-additivity of two or more component system properties show that synergistic phenomenon is a particular (and the most simple) case of synergetic – the science about multifactor processes in complicated mechanical, physical, chemical, biological and other self – organizing systems [1].

Author of this work has tried to classify these phenomena in chemistry on the base of previous developments on catalysis on this sphere [3], and introduced

a number of new ideas and definitions of SE.

SE (or phenomena), as it was mentioned above, is a non-proportional increase of some characteristics of chemical systems at variation of concentration (relation) of its components or at effect of external physical factors.

Since synergism in the articles on chemistry is currently used for determination of different effects of non – additive variations of many characteristics of two- (or more) component systems we consider it is necessary and expedient to accept the following five category classification of synergistic effects:

- I. By the origin of a synergistic effects onto three types:
 - a) Synergism due to chemical causes including structural and kinetics (dynamic)
 - b) Synergism due to physical, electrochemical and other factors.
 - c) Synergism due to mixed – chemical and physical (or other) factors.
- II. By functional characteristics of the particles participating in synergistic effects onto three classes (Fig.1):
 - a) Synergism in 'substrate – substrate' system ($S_1 - S_2$) (Fig.1, curve a);
 - b) Synergism in 'substrate - non- substrate' system ($S-X$) (Fig.1 Curve b);
 - c) Synergism in ' non-substrate – non-substrate' system ($X_1 - X_2$) (Fig.1, curve c).

¹ The terms "synergism" and "synergistic" should not be mixed [1], though they come from the same Greek word "sinergeia", which means cooperation.

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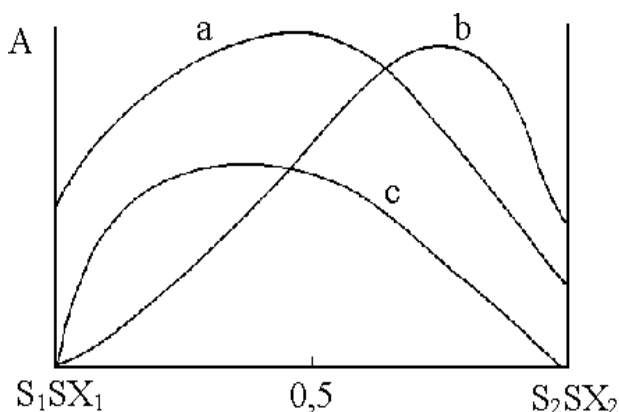
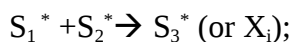


Fig.1

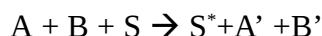
Effect of the composition of a two component synergistic system on its characteristics (A, α).
a,b,c – synergistic curves

III. By the character of interaction between the components of synergistic couple and nonstoichiometrical components of the systems onto three types:

a) Formation of new compounds with synergistic properties:



b) Paralell effect of internal and external synergistic partners on the substrate:



Where A, B are external factors including physical (heat, light, radiation, electromagnetic waves, sound etc.) or internal (unstoichiometrical) components – solvents, admixtures and so on. S^* is substrat with synergistic properties;

c) Consecutive effect of external or internal synergistic partners:



Where S' is substrate with additional (or changing) properties, 'channels'.

IV. By the hierarchy of synergistic effect origin – onto two types:

- primary,
- secondary

V. By character of the causes of synergistic effect origin onto two types:

- intrinsic (internal),
- induced (external) There are some explanations to definitions and terms in the given classification.

I. The nature of SE origin may be determined by the chemical components - new chemical compound formation or new reaction way origin, which leads to the observed non-additivity of the system properties. The physical components – the change in the surface, porosity, form of the particles and other characteristics of the system, which lead to non-additivity of properties. Types 1a and 1b can cooperate in action.

II. As a substrate we accept the compound substance (S), the property of which (α) varies synergistically at mixing with other component (or at effect of it by the physical factor). In other words, S originally has a certain property α , contrary to non-substrate (for instance, solvent, carrier external factor), that doesn't have it. It may be clearly seen from Fig. 1.

Sometimes synergistic curves have complicated form – two maximums or maximum and minimum (inhibition) (Fig.2) [47].

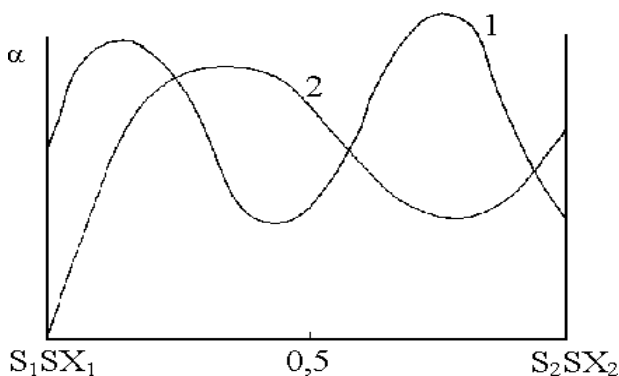


Fig.2

Tips of the synergistic (inhibition) curves

III. Interaction of S and other components (factors) with each other results in change of structural, thermodynamic and dynamic (kinetic) properties, that is the origin of SE, defined by paragraphs 4 and 5.

IV. At the formation of new compounds from molecules (atoms, ions, complexes) of synergetic partners (S and X according to p.2) they, as a rule, appeared to have new *primary* often *non-additive properties*: structural characteristics, sizes of crystals (the distance between atoms, molecules, fragments), molecular volume, density etc. change. The thermodynamic characteristics (ΔH , ΔG , ΔS) change synergis-

tically.

The change of the properties, determined by primary changes – that is kinetic activity, optical and adsorptive characteristics, solvency or solvent capacity, viscosity electric – and photochemical properties, biological activity, is classified as *secondary* SE.

V. The *intrinsic* (or *internal*) SE are determined (generated) by S_1 , S_2 and $S+X$ partners, while the *induced* SE originate of combined effect of external chemical partners and (or) physical factors (X_1 and X_2 – thermal, luminous, radiative, electromagnetic, ultrasonic, chemical etc.)

We suppose that the classification covers all the known synergism cases in chemistry and hope, that it will help to understand the mechanism of origin of non-additivity better, and go the mechanism of formation and functioning of the complicated chemical systems. The classification is worked out on the base of our own results and date of the world publications on different fields of chemistry (catalysis, physical chemistry, analytical chemistry etc.)

There are some examples of synergism in physical chemistry.

This field of chemistry, like catalysis, abounding in synergistic phenomena, since both structural (primary) and dynamic (secondary) characteristics of the substance and processes are present widely, it concerns and cooperates closely with all the other fields of chemistry.

For example, synergistic phenomena reflect, apparently, the majority of diagrams of “composition-property” type [4-8], which are determined by component interaction practically on all the levels from sub-micro – to macro-level (primary and secondary SE). As an example we take well – studied binary systems, for instance, $\text{SnCl}(\text{Br})_4 - \text{R}_2\text{O}$, causing as a result of acid-basic interaction the formation of the complex compounds of different composition (from 2:1 to 1:2). $\text{SnCl}_4 - \text{Bu}_2\text{O}$ system shows synergism at the change of such properties as molecular mass, chemical shift, isotherms of viscosity, activation energy of viscous flow, conductivity, steam pressure. The same precise synergetic curves were obtained in the systems $(\text{C}_2\text{H}_5)_2\text{O} -$, $\text{RCOOH} - \text{SnCl}_3$, $\text{HClO}_4 - \text{H}_2\text{O}$, $\text{H}_2\text{O}_2 - \text{H}_2\text{O}$ [9,10].

M.I. Usanovich describes viscosity curves ($\lg\eta$) by the general equation [10].

$$\lg\eta = \frac{\lg\eta_B + x(\lg\eta_A - \lg\eta_B) - y(\lg\eta_A + \lg\eta_B - \lg\eta_{AB})}{1 - y}$$

Where AB is compound from A and B components, x , y are fractions of the compounds.

The author came to the conclusion that this equation is true for many different isotherms of viscosity, which determined by the relation between η_A , η_B , η_{AB} and K , which is balance of AB formation reaction constant.

The dependencies “composition–property” have wore complicated composition in metallic binary alloys, where the compounds in liquid and solid states often form in systems; including chemical compounds, compounds of different composition. It results in the significant changes of some properties (fusing temperature, viscosity, strength, fluidity, microhardness, flexibility and superflexibility) [11 – 13]. Many technical characteristics of hard alloys strongly depend on the regime parameters of hardening, conditions of cooling and crystallization [13].

The synergistic effects present in the alloys of mercury with metals – amalgams [14]: the form of system liquids, for example, Hg–Ga clearly indicates the formation of compound of composition 1:1 [15], and with it the fusing temperature alloy T_f rises by 160-250°C in comparison with T_f of individual metals. The interaction of alkali metals with mercury confirmed except high heats of alloy formation also high change in volume and viscosity of amalgams, the results of steam pressure measurement.

The potentials of amalgams ϕ of these metals differ significantly from ϕ of the corresponding pure metals [14, 16].

It is shown that the systems with the acutely expressed interaction, leading to the synergism, are typical for the metals, having completely unfilled outer d-shell (Li, Na, K, Rb and Cs) [14].

All the given instances are the typical examples of the synergism of type $S_1 - S_2$ (2a), the primary (type 4a) and intrinsic (type 5a) synergism. The so-called function of stability of hard solution $F(x)$ also passes the maximum in the system $\text{PbF}_2 - \text{SrF}_2$ [17]. With it, the maximum value is reached with the comparison ~ 60% SrF_2 when the difference between temperatures of liquidus and solidus approaches to the highest. From the synergistic curve it follows that homogeneous single crystals PbF_2 are impossible to obtain when the SrF_2 content is more than 10%.

It was shown, that the change in composition of hard solution $\text{Co}_{1-x}\text{Cu}_x\text{O}_n$ to the synergistic change in the parameters of the elementary lattice in the interval 0,1-0,3x [18]. But the substitution of matrix atoms by admixture atoms occurs more easily when they differ

by mass not very much [19].

Water–dioxane solution has interesting properties. It was shown before that in the solution at 60–80 mas. % of dioxane the maximum activity of catalytic system Pd(II) – Cl(Br) was observed at oxidation of CO in CO₂ by benzoquinone and other quinones [20]. It is shown in [21] that the values of the density, viscosity and the enthalpy of mixing ΔH pass the maximum in the same concentration range, and ΔH is equal to zero at 50% (mole) of dioxane, i.e. in this case all the bonds H...O in the water are broken, i.e. aqueous associations have decomposed under C₄H₄O₂ molecules effect.

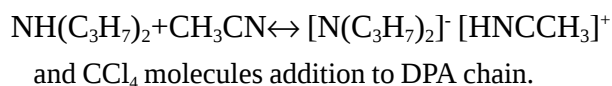
It is discovered that the synergistic and other effects are often observed near the critical points of mixtures, in particular, solvent [22]. For example, the critical azeotrop has a number of unique properties as a dissolving medium; volumetric and thermal effects, connected with solvating, increase several times, and it leads to the synergism.

Formation of new compounds, associates, new phases and specific interactions between mixture component result in the change in thermodynamic characteristics of the system. One may also suppose that, on the contrary, due to thermodynamics the initial characteristics of mono-component mediums (at their mixing) changing, that leads to observe effects, including the synergistic ones. It is discovered, for example, in the liquid alloys of system Na – Cd (ΔH , Q) [23], SiO₂ – CaO (H°) [24], Na – Sn (ΔH) [25], NH₃ – O₂ (yield of NO_x) [26], CH₃OH – (CH₃)₂CO (ΔH of CuL_n) [27], H₂O – CH₃OH (t-BuOH) (dissolving heat of aniline) [28] etc. [29]. The thermodynamic probability of one of the A_nB_m compounds in the systems MgO – TiO₂, CaO – SiO₂ and CaO – V₂O₅ obtaining, defined as the change in Gibbs energy and other parameters, is also described by synergistic curve at variation of the concentrations of these components [30].

The concentration dependence of the chemical shifts of the protons of formamide amino group (FA) for the cis- and trans-protons at interaction with N, N-demethylformamide (DMFA) pass the maximum at FA = 0,5 as a result of their weak complexing [31]. The excessive enthalpy of FA and DMFA mixture has the identical form.

The mixing enthalpies and the molar volume of Na and Tl in liquid alloys of the same system are determined synergistically by metal-metallic bond between the components (balance constant K = 25,7 at 800 K), which form the compound of NaTl composition [32].

The excessive thermal capacity (C_p^E , J/mole .K) of solutions of dipropylamine (DPA) and tetrachlorethane, DPA and acetonitrile at 298,15 K depend on the mixture composition similarly [33]. It occurs as a result of association owing to the acid–basic interaction (CH₃CN – is the effective acceptor of proton):



Among the other examples of SE origin in Physical chemistry consider the non-additive change in thermodynamic and concentration dependencies in the mixed solvents: the excessive enthalpy of mixing of H₂O dimethylsuloxide (DMSO) solution [34], “dramatic” increase in NbO_x solubility in the water – oxalic acid (Ox) mixture with the further sharp fall at [Ox] = 0,1 weig. fraction owing to the niobium oxalate settling out [35], the influence of internal and external molecular hydrogen bonds on the synergistic solubility effects [36].

The causes of synergistic change in the kinetic characteristics of reactions may be – the changes in the innerspherical parameters of the intermediate complexes, for example, the central ion of Cu(II) surrounding by the molecules of amine (piperidine) – a reducer at its dilution by acetonitrile [37]. Reaction rate is rising as non-symmetrical complexes are forming; it leads to the synergistic dependencies.

The kinetic of sootformation is described by the synergistic curve at variation of relation of initial products – ethylene and propane [38], acetylene and benzene, acetylene and hydrogen [39]. SE explanations are based on the complicated consecutive – parallel stages of molecule decomposition on the surface and in the volume. Often the causes of synergism are not cleared up [40].

The adsorptive, absorptive, kinetic and other characteristics of different systems very often depend synergistically on the medium pH, since acidity determines the surface and dynamic properties of these systems and formed intermediates [41,42]. One may say that the so-called induced synergism realizes in this case owing to the OH[–] and H⁺ ion participating in the structural and dynamic transformations.

Physical and chemical causes determine the synergism of ultra-small particles of CaCO₃ and M₂O₃ (M is metal) on the explosive characteristics of organoaluminium mixtures: at the optimal relation of admixtures the pressure exponent and combustion rate increase [43].

Apparently, it is caused by physical causes a kind of synergism of ice formation from the cloud of water streams at the combined effect of such organic compounds as phenasine (or phloroglucin) and anthraquinone, and at it the yield of ice crystals increases by more than an order in comparison with individual compound effects [44]. It was discovered that similar effect is caused by the formation of smaller crystals of these organic embryos of new (solid) phase of H_2O .

Finally, the synergism origin in KCl powder (conglomeration of F and M painting centers) is discovered at their simultaneous radiation by protons and electrons of energy from 30 to 100 keV (SE on submicrolevel) [45]. It is considered that in this case the energy of these two moities is summarized and as a result originated effects consolidate better, the depth of the defective layer increases (induced synergism).

An strange "synergy", originated between the magnetic interaction and spin location in the Fe (II) complexes with organic radicals as ligands, in particular, for bis (cis-1, 2-diciano-1, 2-ethylene-dithialato) [2-p-N-methylperidinium)-4,45,5-tetramethylmidasoline-1-oxile]-ferrum (III) addition, is may be classified as the same type [46]. According to the introduction as a result two types of molecular magnetism, viz.: the intermediate spin state, the so-called "spine crossover", and magnetic interaction appear simultaneously in the same compound.

Thus, one can discover practically all the types and classes of synergism, covered by the above-mentioned classification in physical chemistry. Sometimes synergistic curves have complicated form – several maximums and minimum. The latter may indicate inhibition i.e. negative synergism.

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