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Special Review

ISOPARAMETRIC KINETIC RELATIONS FOR CHEMICAL TRANSFORMATIONS IN CONDENSED SUBSTANCES (ANALYTICAL SURVEY). II. REACTIONS INVOLVING THE PARTICIPATION OF SOLID SUBSTANCES

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Various manifestations of the kinetic compensation effect are considered in reactions involving the participation of solid substances under isothermal and nonisothermal conditions, as well as manifestations of other isoparametric correlations. It is shown that isoparametric correlations can be used for the analysis of solid-phase reactions and the exclusion of artefacts in nonisothermal kinetics.

1. Introduction

In part I of our survey [1] we considered the work concerning various aspects (formal, statistical and physicochemical) of the theory of isoparametric correlations (predominantly those of the compensation effect, CE) and showed that these aspects are rather well developed in the kinetics of homogeneous reactions. It is advisable that the success attained in this field be used to make a breakthrough in the study of the much more complicated problems of solid-phase reaction kinetics.

It is known [2–5] to be much more difficult to interpret the parameters reflecting the kinetics of reactions involving the participation of solid substances than those of homogeneous reactions. Correspondingly, the CE analysis for solid-phase reactions runs into great difficulties. The experimentally measured values of E and A may be unnaturally high (up to 10^{92} s^{-1} for A [6]) or low (negative E), and for this reason they cannot be considered as characteristics of the reaction energy barrier.

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In most cases, the changes of the Arrhenius parameters under different experimental conditions may be attributed to a narrow experimental temperature range and, consequently, to long-range extrapolation in finding A [7, 8]. The use of data yielded by different methods has allowed [9] this temperature range to be extended considerably, and variations of the characteristic time of explosive decomposition by almost 9 orders of magnitude can be covered. The experimental data for each explosive, characterized by greatly different values of A and E, appeared to be grouped in a narrow band whose boundary lines differ from the mean value of E by 1 to 2 kcal/mol. The value of A was in all cases close to $10^{13.6}$ s^{-1}, i.e. the theoretical value for monomolecular gas-phase reactions. $A = 10^{13.6}$ s^{-1} in [9, 10] is referred to the transformation of molecules at a frequency of the valence vibrations of the characteristic groups of 1000 to 1700 cm^{-1}, irrespective of the state of substance aggregation.

Application of the activated complex theory to the thermolysis reactions of solids seems to be problematic [11], yet it may explain a change of A by 10 to 12 orders of magnitude [12, 13]. The other publications surveyed in [4] explain much wider ranges of A as well. Although interesting approaches to the problem have been found of late [14], on the whole there is no satisfactory theory to explain the activation energy and pre-exponential factor as applied to solid-phase reactions. According to [15], the decomposition of solids does not give rise at all to a discrete activated state, and the absence of statistical energy distribution precludes the use of the Arrhenius equation. One may hope that the analysis of isoparametric relations in the kinetics of reactions in solids will promote progress in this field, just as it has in the kinetics of homogeneous reactions.

2. Isothermal conditions

The value of E observed for the total process in reversible reactions of the type

$$A_{sol,} \rightleftarrows B_{sol,} + C_{gas} \tag{1}$$

is the sum of the reverse reaction activation energy, the absorption heat of the gaseous product, and a fraction of the thermal effect of the reaction. This value of E is dependent on the degree of approximation of the pressure (P) of gas C to the equilibrium pressure (P_0) [4]. When these pressures are equal, $E \to \infty$. It is typical for isobaric decompositions according to Scheme 1 to manifest the CE, without which "...a satisfactory theory of reversible topochemical reactions can hardly be worked out" [4]. Whether in high vacuum or at supersaturation, P_0/P being maintained constant during the isothermal experiment, the activation energy has the same value independently of P_0/P, because the reverse reaction does not affect the activation energy, and the height of the reaction energy barrier is constant. However, the value of A grows with supersaturation since it affects the nucleation rate [4, 16]. The analysis of the specific features of reactions of type (1) proceeding in the kinetic region may enable one to conclude that it is the chemical stage rather than nucleation that exerts the decisive influence on the most important kinetic laws of a topochemical reaction [4]. References on the CE in solid-phase reactions are given in [4]. Papers [17–19] are among the new publications that deserve attention. They consider the Arrhenius equation as a correlation in terms of projective geometry. This has helped to reveal mutually correlated magnitudes and to determine the number of possible correlations, many of which were unknown or little studied. The above papers also prove a number of known relations and correlations, e.g. between the isokinetic temperature and CE parameters, and show an interdependence between the CE and the Zavadsky–Bretschneider relation known in topochemistry (this interdependence is not always strictly unambiguous [4], but just as in the case of the connection between isoparametric relations and Hammett-type equations [1], this does not belittle its importance at all).

Many isoparametric relations (IR) can be represented graphically if the initial (Arrhenius, Hammett, etc.) equations involving the product of two variables are represented as hyperbolic paraboloid [20–21], so that the mathematical aspect of the above relations is quite trivial, and the most common conclusion [4, 5, 17–19] that the CE is mathematically based on the Arrhenius equation proper cannot be called into question. However, when the CE is not a computational artefact [1], no mathematical analysis in itself can point to the cause of change of empirical A and/or E because these causes are most apparently of a physico-chemical nature, though they may not be related at all to the changes of the potential reaction surface characteristics. Besides, one ought to understand the physico-chemical nature of these changes and their regular pattern of occurrence corresponding to the CE.

The value of B in the CE equation is related to the structure of and defects in the starting material [17],

$$\log A = B + eE \qquad (2)$$

or, to be more precise, to the mobility of the crystal lattice, which determines the "system mobility" for (1), i.e. how far it is from the equilibrium state when the reaction proceeds in the temperature range typical for it: in fact, it is related to the position of this range on the temperature scale [22]. The value of B for the reactions of this type is close to zero [4, 16, 17]. For irreversible nitro compound decomposition reactions, both these constants are other than zero. In liquid and solid-phase processes, the corresponding constants are similar, which may be due to partial melting of the nitro compounds [23], but they differ substantially from their values for gas-phase thermolysis reactions [24]. On the whole, these constants are different for one and the same reaction in the melt and in the solid phase (2);

polymorphic transformation ($SrCO_3$) does not upset the CE during thermolysis [4, 25].

The fact that the temperature of the corresponding e is in the experimental temperature range may be an indication of an apparent CE [1, 22]. On the other hand, the experimental isoparametric point that can be reached as mentioned above [1] is a most reliable criterion for the observance of CE-type relations. A certain contradiction between these two statements may be explained as follows. The first statement should not be regarded as a sufficient criterion of the apparent CE, but only as a requisite one, whereas the second statement is a sufficient condition for the true CE, i.e. for an effect when an approximate equality of the rate constants is attained at an isokinetic temperature or rates, provided the kinetic equation and α are constant. The realization of this situation is in no way connected with our notion about the essence of the process under study and interpretation of the kinetic parameters to be determined, which is a subjective basis for characterizing this effect as a "true" one. The observed kinetic parameters rather than true ones can correlate according to Eq. (2). Correspondingly, we have every reason to speak about the true CE (IR) for empirical kinetic parameters.

Let us consider the measure to which the kinetic data for solid-phase reactions correspond to the CE truth criterion as we understand it. The Arrhenius lines given in [16, 17, 26] converge to form a pencil. Further, it has been pointed out that the reaction rate at a definite stage is independent of the pressure of the gaseous product [27] so that the isoparametric point can practically be reached in some instance. So long as we are interested in the fundamentals of the problem, we shall confine ourselves to the above examples of CE satisfiability. It would also be of interest to bring out the instances of the real passage through the isoparametric point, which is known to be accompanied by a transformation of the reactivity series. In the reactions under consideration (1), this transformation corresponds to a change in the role the gaseous product plays when its pressure varies, which, for example, takes place in the case of the Smith–Topley effect [28, 29]. On the whole, this effect cannot be reduced to any concrete form of the IR. In definite ranges of the variables (P and T), however, there may occur a situation when at some temperature water vapour will accelerate rather than decelarate dehydration, which at least is in qualitative agreement with the CE. The physico-chemical basis of the Smith–Topley effect is the simultaneous effect of water vapour on dehydration in two opposite directions: deceleration (due to "impedance" [30]) according to an equilibrium shift in (1), and acceleration due to the positive effect of the amorphous layer of the solid, which retards dehydration, on the crystallization process. Another reason for acceleration—the hydrolytic effect of water—is also concerned, as has been proved experimentally by the example of the dehydration of polyphosphates [31, 32], which are thermodynamically unstable with respect to H_2O because of their chemical bonding [33]. A combination of the reverse effect of water vapour on the rate of polyphosphate dehydration has the result that the pattern of the water vapour effect on dehydration changes [31] in the temperature range corresponding approximately to the point at which the Arrhenius lines intersect [26]. A spasmodic change of the kinetic characteristics of the process is reported in [34], which does not necessarily upset the IR and change the process mechanism [35–37]. According to [38], there may be certain deviations from the Arrhenius equation and specific temperature points at which the reaction rate changes dramatically in the temperature-dependence of the rate of a simple chemical reaction in the condensed (particularly solid) phase.

On the whole, many crystalline hydrates have a "critical" temperature around 100°, above which water vapour accelerates the process, and below which decelerates it [4, 31]. For example, if a substance decomposes at a temperature above the "critical" one, dehydration is accelerated [27, 32]. A comparison of the values of e (0.48 to 0.64) in [4] and corresponding to $\Theta \approx 180-70^\circ$ with the "critical" temperature shows that these temperatures are identical (allowing for a definite uncertainty of the "critical" temperature [31] and difficulties in the exact determination of Θ [1]). Therefore, the dehydration of crystalline hydrates manifests isoparametricity conditioned by a complex pattern of transformations in the solid.

The data on the effects of temperature and H_2O vapour on dehydration given in [4, 31, 34] may lead to the assumption that an isoparametric pressure point—isokinetic pressure—may also be attained, which corresponds to $E=0$.

The CE is reported to be observed in the reduction by hydrogen of solid solutions of oxides characterized by different ratios of components [39]. The reasons for the CE being observed in the reactions of gases with carbon materials which are homogeneous in terms of crystal chemistry, nonporous and highly reactive, have recently been reported [40, 41]. Entropy and bond energy are found to correlate in a series of carbon compounds, in rather close agreement with [42]. According to such a correlation, the entropy may change by more than 6 orders of magnitude. By using (2) for two series of reactions and estimating the limit of variations of the frequency factor incorporated into A, the author come to the conclusion that the contribution of the CE to the entropy factor change is predominant. This sort of conclusion helps establish some similarity in the interpretation of the CE in the kinetics of homogeneous and heterogeneous reactions. The CE observed during coal oxidation is reported in [43]. In the case of catalytic coal oxidation, the CE is explained by two reactions proceeding concurrently [44].

Correlation (2) between apparent activation parameters for a group of reactions of the same type, characterized by similar or close values of the true activation parameters, has been analysed in [22]. It is shown that the reaction temperature range defined by the true values of E and A corresponds to such a group. Insignificant variations of the reaction rate in this group and of its temperature-dependence due to the activation energy temperature-dependence, diffusion, etc., have practically no effect on the above temperature range. They do, however, influence the effective activation energy E_{ef} and determine its magnitude. In this case

$$\Delta E_{ef}/\Delta \log A_{ef} = 2.3\, RT_m \tag{3}$$

where T_m is the temperature corresponding to the reaction rate maximum and characterizing the reaction temperature range.

New information on the CE in condensed phases is provided in [45]. The author analyses the origin of extremely high values of E which, when associated with energy barriers, are insurmountable in a chemical act. He considers the variations of E and A within reasonable ranges to be quite trivial, because they can be explained by entropy-enthalpy compensation (and in these cases as well this may be attributed to the CE of anomalously great variations of E and A). The survey of a wide range of phenomena with CE manifestations made it possible to conclude that the CE ought to be explained by diffusion mechanisms rather than chemical kinetics, viz. the rate of unit chemical changes in the condensed phase is limited by steric difficulties, and by the deficit of free space rather than that of energy, the accumulation of which cannot ensure the requisite mobility of reacting particles and enable the latter to penetrate the dense barrier made by their nearest neighbours. Only local entropy fluctuations (packing of particles) can ensure a duly oriented contact between the reagents. The Arrhenius reaction rate relation can be simulated by a diffusion temperature-dependence (packing fluctuation density) and the mobility of the particles participating in the process, including rotational mobility, whose temperature-dependence corresponds to that for the sequential diffusion coefficient. Correspondingly, the observed reaction rates are determined by the equilibrium density of such fluctuations or their arising frequency dependent on molecular mobility, while the CE is cooperative in nature and is affected by the steric difficulties of unit chemical change. In specific manifestattions of the CE considered above, it is caused by the temperature-dependence of E [46] related to unfrozen molecular mobility, or the CE of diffusion. As a result, the author draws the very important methodological conclusion that reactions in the condensed phase should be analysed from the aspect of the entropy rather than the energy factor. In particular, the former may be related to the matrix rigidity. The quantitative assessment of its effect on solid-phase reactions is considered to be a most important problem [47]. The importance of molecular mobility in the kinetics of polymer reactions is reported in [48, 49].

3. Nonisothermal conditions

[22, 24, 50–54] compare the IR for isothermal conditions and for a linear rise in the temperature most widely used in thermal analysis, and describe their agreement. In the absence of such agreement, the conclusion is made that some version of the thermal analysis conditions cannot be correct [24]. In general, the correlation between isothermal and nonisothermal kinetics is a fairly complex problem and requires special consideration [55–60]. We shall only note the techniques developed for scaling nonisothermal data in terms of isothermal data [61].

The problem of whether some most important postulates of nonisothermal kinetics are correct is still to be decided; its methods are therefore not recommended for solving the inverse kinetics problem [62–65].

The previous discussion (refer to [55]) convinced one author [66] of the validity and correct use of the equation

$$d\alpha/dt = k(T)f(\alpha) \tag{4}$$

or its transformed form $d\alpha/dT = k(T)/\beta f(\alpha)$ in nonisothermal kinetics, although the problem has not as yet been solved, and even more so for complex polymers at high heating rates [56, 67–74].

The possibility of separating the variables in (4) ought to be confirmed in each particular case, by testing the temperature-invariance of the reaction zone configuration and kinetic regime. In isothermal kinetics, this is done through the use of special experimental techniques of "separation" and affine transformation (for the use of the latter during linear heating, see [75]). Temperature variations may change the reaction kinetic regime [76] and, in fact, the space where it proceeds [57, 77]. In the case of dynamic heating, the reaction temperature range is sufficiently wide [78]. The narrowing of this temperature range involves the higher uncertainty of the kinetic parameters [8]. A change in the heating rate displaces this temperature range, which may condition the course of different reactions, particularly in the case of complex objects, and cause a formal dependence of the kinetic parameters E and A on α and the heating rate [67, 79, 80]. Equations with unseparated variables are used in general cases [81].

The interpretation of $k(T)$ and $f(\alpha)$ is problematic, as is the separation of the variables in (4). It was noted in [15, 38] that the Arrhenius law can hardly be used for solid-phase reactions; nevertheless, it is usually satisfied, since the unit chemical changes of which the total process is composed are of an activation nature. Just as in homogeneous processes, it is advisable to take into account the pre-exponent temperature-dependence [82].

There is another aspect of using the Arrhenius equation which is formulated mathematically as the incorrect statement of inverse problems [83] characterized by poor grounds (the information matrix determinant is close to zero) and an unstable solution. Such inverse problems are solved nonuniquely unless special methods are employed [84–86]. The overall extremum of the criterion function is difficult to find, and therefore the estimates of the equation parameters may be shifted somewhat. This problem as analysed for dynamic thermogravimetry conditions in [87–89]. Poor grounds in finding A and E result in a greatly extended domain on the surface of dispersion, so that, even in the case of small experimental errors (± 1.5 K [88]), the experimental findings can be described accurately in terms of the parameters A and E, which vary widely within this domain. The CE will pose as a computational artefact. In this case, the parameters A and E, calculated in different ways, characterize the mathematical method used rather than the reaction proper. This is also testified to in [50, 80, 90–93]. The artefact can be eliminated, though partially, through transformation of the Arrhenius equation [1] by introducing a new variable, $T^* = (T - \langle T \rangle)/T$ for example, which improves the statement of the problem. The mathematical aspects of such transformations, as applied to the Arrhenius equation, are considered in [94], and elimination of the CE during a computer search for kinetic parameters in nonisothermal kinetics in [95, 96]. The authors of [97] hold that, as a computational artefact, the CE does not impede extrapolation to the domain close to the experimental temperature range. One may agree to this, provided the E and A variation range is narrow. However, if this range is wide or remote extrapolation is performed even with small variations of E and A, then the extrapolation uncertainty caused by such CE makes the former meaningless. In practice, this is a most “annoying” aspect of the computational CE (another “unpleasant” aspect is that E cannot be used in the capacity of a reactivity characteristic [98]).

No matter how important the consequences of interaction of the parameters in the Arrhenius equation may be, it should be borne in mind that the CE may be the result of something else. It is found in [99] that variations of A and E cannot be mutually compensated in full. These variations are also due to a change in the shape of the thermoanalytical curve, i.e. they are related to the change of $f(\alpha)$ or n. Thus, we come to understand the important role played by the second function (4) in the CE. It is often represented in the form of $f(\alpha) = (1-\alpha)^n$, with the result that a rather flexible, yet formal model is obtained:

$$d\alpha/dt = A \cdot \exp(-E/RT) \cdot (1-\alpha)^n \tag{5}$$

whose parameters have no clear physico-chemical meaning. Moreover, they cannot be determined uniquely as, for the reasons considered above in [87–89], there is no unambiguous agreement between the experimental curve and the model parameters: different sets of A, E and n can all describe this curve perfectly well [100–104]. Probably this conditions the correlations between E and n [105–107] and A

and n (the confidence range, a hyperellipsoid within parameters A, E, n is detailed in [88]).

A wide range of thermoanalytical experimental conditions, for example the weight and shape of the sample ($CaCO_3$), the heating rate, and the type of instrument, is reported in [108–110]. Further different differential equations have been used in [108–110] to describe the reaction rate, with different methods to calculate A and E. By varying different factors, one could observe the CE, the correlation between the Arrhenius parameters and the kinetic constants (m, n, p) of reaction order type, as well as the correlation between the latter. Moreover, the polynomial of the sixth power, used for the description of the DTG curve, was also correlated (on change of the number of experimental points) in terms of the CE. The authors [108–110] make the substantiated conclusion that the quantitative description of the thermoanalytical data is formal, and the structure of this description leads to the aforementioned correlations. As long as the kinetic parameters are correlaed, they can only be used as a set, three parameters being enough to form a set. A and n in the base dependence can be assumed to be unity in order to compare the TGA data for different conditions. Then, the quantities A and n will be parameters determined by experimental conditions to transform such curves to the base dependence. The fact that the CE and the greater descriptive ability of Eq. (5) make possible quantitative assessment of the similarity of TG data, even for a nonlinear dependence of $\log k$ on $1/T$, justified the use of CE and Eq. (5) in nonisothermal kinetics [108–110].

It is noteworthy that the parameters of the CE found through the use of various equations change with changing experimental conditions. Therefore, to a certain extent they characterize these conditions. However, no precise regularity in the changes of the CE parameters has been established [109–112]. This may be due to the fact that the range of variations of some factors was very wide. For example, the $CaCO_3$ weighed amount increased 4550-fold [109, 110], which might have resulted in control of the rate of the reversible process by CO_2 diffusion. It may also be possible that the CE was affected by the compensation of the parameters m, n and p. In order to understand the above regularity, it is advisable that only one of these parameters be varied. Again, definite conditions are required under which the reverse reaction can be ignored. Lastly, the varying conditions should not alter the nature of the limiting stage. The contribution of the changing equilibrium pressure of CO_2 to the CE during $CaCO_3$ decomposition under nonisothermal conditions is considered in [113].

The correlations between E and n, and A and n. may be regarded as an isoparametric condition for (5). The latter should have the form

$$\log k = \gamma - \zeta n \tag{6}$$

i.e. $n = (\gamma - \log A)/\zeta + E/2.3\,R\zeta T$, from which it is seen that (6) actually corresponds to a definite relationship between the formal quantities n, A and E. Note that isoparametric relation (6) confirms the existence of values of α at which the rate is independent of n, i.e. it is numerically equal to the rate constant. In such a context, the rate constant is an isoparametric quantity. The trivial realization of such a statement corresponds to $\alpha = 0$ (then $\zeta = 0$), as is seen from (5). Since the quantities n, A and E under consideration are formal, one may assume that (6) is also satisfied at ζ, $\alpha \neq 0$, i.e. the changes of n correspond to variation of E and A, or k, which compensate for the former. Such a situation underlines most conspicuously the formal character of n, k, E and A and, at the same time, points to the necessity of using other invariants of the reaction. In particular, the numerical value of $\gamma = \log\left(\frac{d\alpha}{dt}\right)_\zeta$ in the case of an isoparametric value of $\log(1-\alpha) = \zeta$ independent of n can be interpreted as a rate constant logarithm rather than an analogy term from (5) and (6). The temperature-dependence γ should yield invariant E and A.

Model (4) is considerably improved in content when $f(\alpha)$ is plotted in accordance with definite notions about the process mechanism [66]. However, a comparison of the sets of functions $f(\alpha)$ commonly used in such cases [11] with the theoretical ones considered in [114] shows that they are limited and the integrated $f(\alpha)$ functions are simplified. Expansion of a set or complication of $f(\alpha)$ is quite an undertaking, because many $f(\alpha)$ of a wide set of these functions are hard to discriminate. This can be illustrated by the results obtained in [115]. As shown here, the Kolmogorov–Erofeev topokinetic equation can be used for approximation in a wide range of α of thirteen equations most widely used in heterogeneous kinetics. In a number of cases, the value of the basic parameter of this equation, n, is the same or almost the same for different equations. The latter are therefore hard to discriminate. Consequently, conventional or computer selection [116] of $f(\alpha)$, based on the most correct criteria for the experimental curve in a wide range, cannot solve the problem. A preliminary informal selection of a mathematical model has to be made, based on a study of the subject under investigation and the knowledge of the basic features of the reaction [2, 66, 114, 117]. The widely used technique of linearization of expression (4) and (5)

$$\ln (d\alpha/dt)/f(\alpha) = \ln A - E/RT \tag{7}$$

yields an unsatisfactory $f(\alpha)$ discrimination, since the fact of strightening is in weak dependence on the nature of this function owing to the strong temperature-dependence $d\alpha/dt$ [118]. This remark also holds for the integral mehod [119–121]. The methods which do not require a knowledge of $f(\alpha)$ are also vulnerable to criticism [66].

We have accentuated some drawbacks in the methods of nonisothermal kinetics, just to show the formal character of the relations and parameters, including the CE, obtained with their use. It is therefore more logical to analyse such relations and parameters within the framework of formal theories and, in particular, of the one considered in [1]. We are far from criticizing formal kinetics, which is the only means of kinetic description of most complex processes [122]. It should be noted that the success of nonisothermal kinetics is based above all on consistent application of classical methods of the theory of burning and thermal explosion [61, 118, 123–126] and consideration of the real peculiar features of topochemical reactions for solids [66] established by independent methods [65].

Just as in many cases thus far considered [1], the CE in nonisothermal kinetics can be interpreted as approximate coincidence of the temperature ranges of reactions of the same type [22, 127] or of the corresponding peak maxima (T_m) [128] on the temperature scale. If the reaction rate constants are close in value a T_m, this corresponds to partially satisfied isokineticity. The relationship between the CE and the formal theory is considered in [1] and is further touched upon in [129].

In principle, there may be a random set of individual reactions that will satisfy the described CE [130]. It is obvious, however, that the Arrhenius lines may as well be obtained from a set of rate constants of different reactions by a mechanistic approach. In combinations of reactions that may proceed in complex objects and hardly under the investigator's control, the Arrhenius relation and the CE for a certain series of reactions may equally be indefinite in their sense. Therefore, it might seem more correct to interpret the CE version under consideration as follows. The temperature range of a reaction is specified by the uniformity (general origin) of reactions, by the closeness of their true activation energies correlating, as was noted in [1], with the energy of dissociation chemical bonds [22, 42, 127, 131, 132].

It should be borne in mind, however, that this correlation has very limited generality [66, 133], and the CE, which appears due to varying experimental conditions (sample holder position [88], heating rate [49, 53, 54, 93, 134, 135], sample mass, shape and packing [53, 100–102], dispersity [53, 135, 136], synthesis conditions [137] and reaction product pressure [53, 54, 113, 138], may be conditioned by different factors. These are different rates of self-heating or self-cooling (Bio criterion > 1), increasing deviations of the process from the quasi-stationary state on exceeding 0.1 of the dimensionless heating rate, the similar and considerable dependence of the errors in E and A determination on the Frank–Kamenetsky criterion of the dependence reaction formal order and, consequently, of E [105–107] on the dispersity, a changed diffusion contribution and the effect of the distance from equilibrium [66, 139]. Hence, the CE is a formal consequence of the description of the entire kinetic curve by Eq. (5), neglecting the influence of secondary factors and changes in the process pattern on decomposition [87, 88, 133]. It also follows from the above that the average values of the kinetic parameters obtained by varying the experimental conditions

[100–102] are almost meaningless. As empirical indices of the reaction rate temperature-dependence though, they can correlate with the chemical properties in a series of compounds, and more so if the average values specified for this series vary in accordance with the CE, i.e. in a regular manner. The corresponding compensation parameters may be regarded as empirical characteristics of some property common to the entire series of compounds.

The reported unrealistic values of the kinetic parameters stipulating the CE more often than not are criticized directly or indirectly for having no physical meaning. It should be noted in all fairness that those reporting such values did not, as a rule, confirm the reverse. On the contrary, the formal character of such values is invariably stressed, and their relationship in the form of the CE is considered as the relation between the empirical parameters of the kinetic curve rather than between the true E and A of the chemical stage. In this case, the CE is real, as its parameters characterize a set of experimental kinetic curves as such. Generally speaking, this characteristic is not only reduced to prescribing a reaction temperature range and the corresponding value of $\log k$ [139]. This is easy to understand, for the isokinetic point is not necessarily to be within this range and may as well be outside it, on extrapolated sections of the Arrhenius lines. However, the problem of whether the isoparametric point may be outside the experimental reaction range can only be solved experimentally [127]. Formal modelling of the situation [139] does not take into consideration, for example, the possible correlation between the parameters B and e [21] beause of which the effects of B and e on the set of kinetic curves are levelled. Having analysed ample experimental material, the authors of [100–102, 140–142] reach the conclusion that the point of view expressed in [127, 131], as to e being determined by the reaction temperature range, is valid. To be precise, e corresponds to a temperature of $\alpha = 0.1$ [100–102, 143], i.e. roughly to the beginning of the reaction. It is known that the initial reaction temperatures resulting from definite standardization of the experimental conditions can be compared and they have a definite physical meaning [66, 100, 101, 142]. The e from the CE relation with definite T in the reaction temperature range predetermines the dependence of e on β owing to the thermoanalytical curves being displaced on the temperature axis on change of the rate β of sample heating. However, experimental findings [22, 24, 50–52] show that e may remain the invariant characteristic of the process under isothermal and nonisothermal conditions (probably because of the insignificant temperature range shifts that may be observed in these cases), i.e. it characterizes the temperature range as such and, depending on the set of curves it stands for, corresponds approximately to the initial decomposition temperature in one case, and to the medium decomposition temperature in another. On the whole, the parameters B and e can only be compared for same-type sets of experimental curves that may be obtained for same-type substances and processes. The occurrence of points off straight line (2) is usually interpreted as a deviation from the mechanism typical for a given series, because they correspond to other sets of kinetic curves and/or other T_m. However, there is no guarantee that (2) will have the same values of B and e [24] under widely varied experimental conditions, with the reaction mechanism being constant. Therefore, in a general case, the parameters B and e cannot be considered as truly invariant characteristics of the process. Certain restrictions in varying the experimental conditions are to be imposed to make these parameters invariant. Such restrictions may also provide invariant "true" values of A and E, whose constancy is not a trivial consequence of the fixed experimental conditions. It is determined by the nature of a chemical reaction that must be a limiting stage, thus imposing rigid experimental restrictions. A change in the experimental conditions within these restrictions no longer involves A and E variations.

We noted above factors which may cause a formal change of the kinetic parameters. They are dwelt upon in greater detail in [66]. Along with the critical selection of the subjects of inquiry, methods of calculation that take into account the topochemical features of the process, and elimination of the effect of such factors, may give A and E for a chemical reaction on the reagent-product interface [66, 144–146. For such A and E, the CE can only be obtained by varying the chemical properties of the reagent determined by its composition and structure (doping, defects, heterophasal additives), or its nature in the series of cognate compounds [66, 132, 147]. In these cases, when the Arrhenius straight lines tend to form a pencil, one may consider the CE to be "true", although this truth is also relative, as alternative kinetic equations [148] are hard to discriminate and the values of A and E for solid-phase reactions are conditional.

A chelate series was dehydrated and some techniques of experimental data processing were analysed in [66] to check the CE validity in nonisothermal kinetics. The author concludes that the CE will be observed only in a series of non-isostructural compounds similar in the structure and composition of the coordination sphere if the total chemical reaction in this series includes a different number of similar elementary reactions (entropy-enthalpy reasons for satisfying (2) in such cases are considered in [42]). In the same manner as the true value of the transmission coefficient κ [1] can be found from the CE for a homogeneous reaction proceeding in various solvents, we have estimated κ to be 10^{-14} and 10^{-16} (two series of solids) for the solids studied in [66] and different in the structure of the crystals. The author [66] emphasizes that isoenthalpy and isoentropy series and those with isokinetic temperature should be clearly separated when comparing the kinetic stability of solids during thermolysis. He also gives examples of the series in which the reaction rate is controlled by both enthalpy and entropy factors (most often by the latter).

The presence or absence of isokinetic temperature is one of the most important conditions which predetermine whether it is possible or not to draw a parallel between kinetic and thermodynamic stability, as well as to use some simplified kinetic characteristics of the type of the thermal transformation initial temperature [149]. For example, the choice of temperatures in the isokinetic region for the evaluation of the kinetic lability of some substances makes it possible to compare only activation energies, which is not enough for the purpose [66, 150, 151], for on reaching the kinetic temperatures the stability series transform as a result of a transition from enthalpy control of the reaction rate to entropy control, or vice versa.

4. Other isoparametric relations for reactions involving the participation of condensed substances

Chemical kinetics deals not only with isoparametric relations of type (2), i.e. those for activation parameters, but also with other correlations, based, for example, on polylinear dependences [1] containing the Hammett equation constants, or the E and n correlations we have so far mentioned. A detailed structure of the E and n values observed for one-way heterogeneous catalytic reactions is given in [152], which emphasizes the importance of the analogy in the expressions for these parameters. In [153–155], a negative correlation of type (6) is established between the parameters in the Kolmogorov–Erofeev topokinetic equation. This correlation is analysed in [156, 157]. Although n and k in (6) and in the above equation are not identical, they are nevertheless related [158] in a complicated manner. In general, this correlation may be viewed as a realization of a definite variant of (6) in which, due to changed values of k and n, γ and ζ are expressed in terms of α and time, respectively.

The dependence of the burning rate (u) of heterogeneous condensed systems on pressure is formally described by the power law

$$u = \beta_p P^{\nu} \tag{8}$$

The parameters β_p and ν are related by the negative correlation [159, 160]

$$\log \beta_p = a - b^{\nu} \tag{9}$$

which is an isoparametric relation [161]. Therefore, the dependence of the rate on P and the factors affecting β_p and ν can be represented as a polylinear expansion [21, 162]. Correlation (9) may be used for estimation of the burning rate control limits [163]. The physico-chemical basis of (9) is the close similarity of the physical properties of same-type heterogeneous condensed systems in some series, as well as that of the kinetic and thermal characteristics of the total chemical reaction taking place during burning of these systems [159]. The values of β_p and ν change in this case, possibly owing to a change in the effect of the processes proceeding in the gas and condensed phases on the burning rate [160, 164].

A correlation similar to (9) can also be obtained for the parameters of the Freindlich equation, which describes absorption isotherms. This equation is similar to (8) [165–167].

It should be noted that the validity of isoparametric correlations evidences a complex formal behaviour of the variables (type E, A, n, v and others) in these correlations. The variables cannot be identified with simple kinetic characteristics of elementary chemical acts or even separate reaction stages. At the same time, it is a definite step forward in the reconstruction of such characteristics that these correlations can be obtained. Everything said above can evidently be confirmed by the method widely used in enzymology to determine the individual constants of enzymatic reaction rates. These constants are described by the Michaelis–Menten equation in the form of effective kinetic parameters. By selectively affecting the rates of separate stages of a stationary enzymatic process by the effector, one can vary these effective parameters. A pencil of lines results from variations of the effector and substrate concentrations in the Lineweaver–Berke coordinates. The coordinates of the pencil centre are expressed in terms of the individual constants of the separate stages [168, 169]. It is easy to see that an isoparametric correlation of the effective kinematic constants of the said equation corresponds to this pencil of lines. Therefore, the constants of the separate stages appear to be isoparametric quantities.

The use of "supercorrelation" dependences, i.e. the correlations between parameters B and e from (2), a and b from (9) etc., is a definite step towards the construction of physically more meaningful kinetic characteristics from experimental data on the kinetics of complex transformations. As is shown in many works, such quantities can be expressed in terms of one another; it is also to be noted that they can be variables. These two facts convincingly point to a possible correlation between the above parameters. However, experimental data, particularly kinetic ones, that confirm the existence of such correlations are limited, although a correlation between B and e (in reactions of different types and therefore of formal character) was observed long ago [170]. It is easy to understand why these data are limited: a very great bulk of experimental material is required for the reliable detection of a "supercorrelation". Only through the classification of a great number of references in [171] was it possible to establish [21, 172] the correlation

$$B = \log \hat{A} - \hat{E}e \tag{10}$$

A correlation of type (10) is obtained in [172] from the entire data file [171], i.e. for different reactions and catalysts. For separate reactions proceeding on same-type catalysts, correlation (10) is rather close [21]. It represents the Arrhenius equation for isoparametric values of the rate constant ($\hat{k}$) because $B = \log \hat{k}$, and the validity of (10) is likely to imply the presence of an invariant stage characterized by

$\log \hat{A}$ and $\hat{E}$ in the complex chemical transformation of related substances. An example of such a stage in the heterogeneous catalytic decomposition of formic acid, considered in [21], may correspond to a process related to reorganization of the C—H bond remote from the catalyst surface and therefore not very sensitive to the change of its activity. This process (k_2) defines the total level of the reaction rate in some temperature range, whereas the primary reversible stage of catalytic decomposition with the equilibrium constant K, the formation of surface formate ions, which proceeds on interaction between the HCOOH molecule carboxyl moiety and the active catalyst centres [173, 174], determines the temperature-dependence of the acid decomposition on a given catalyst, as it is sensitive to the properties of the catalysts. If k_2 is approximately constant on different catalysts at effective rate constant

$$k = K \cdot k_2 \tag{11}$$

then one may make certain that (10) is the Arrhenius equation for k_2.

A pencil of straight lines (10) can also be obtained from the data in [171] for reactions related in this way or some other to the breaking of C—H bonds in the presence of metallic catalysts. The corresponding isoparametric temperature (about 1000 K) is comparable with the initial temperature of C—H bond thermal dissociation (during methane pyrolysis). Transitions from (2) to (10) and then to a pencil of lines (10) comprise the algorithm of transition to ever more definite characteristics [175]; therefore, the above facts do not seem to be random.

Other experimental findings may be analysed in the same light. A CE with different values of compensation parameters B and e in hydrocarbon polymers and teflon is observed [46] during the recombination of radicals in irradiated polymers. As a result, straight lines (2) intersect. The approximate coordinates of the intersection point are $(\log \hat{A}; \hat{E}) = (-18; 5)$, with A measured in cm^3/s and E in kcal/mol. These values of A and E are within a comparatively narrow bracket of typical kinetic parameter values for reactions of the most diverse radicals in a liquid medium [176]. The above values of $\log \hat{A}$ and $\hat{E}$ should therefore be considered as averaged parameters of recombinations of radicals in molten hydrocarbon polymers and teflon, obtained through close extrapolation of the experimental data. It is known [46, 48, 49] that reactions in polymers are effective at temperatures close to their melting point.

Other examples can be given when (10) is satisfied. Using the data found for the thermolysis of a great variety of related cobalt complexes [177, 178], one can find (10), with one missing point though.

The next example concerns the dehydration of chelates $CaML.nH_2O$ (M = Mn, Co, Ni, Cu, Zn, Cd; L = EDTA ligand) [66]. This example from the field of nonisothermal kinetics attracts attention, because the author of [66] devoted thorough consideration to all minor factors that may cause the apparent CE. Two pencils of Arrhenius lines with their centres on the Arrhenius straight line for the Cu chelate are plotted during the investigation of the above complexes. The latter is therefore a "supercorrelation" straight line (10). The suggested consistent mechanism of thermolysis includes the equilibrium stage of formation of a symmetric binuclear complex $[(H_2O)_nCaLM]$ and the subsequent stage of its deactivation when the Ca—OH_2 bonds break. In contrast to the former, the latter is probably subjected to the influence of M to a lesser degree. Therefore, for all chelates it can be characterized by approximately similar kinetic parameters set by straight line (10). That is coincides with the Arrhenius line for the copper chelate may be conditioned by the peculiar composition of this compound, due to which the first stage is kinetically insignificant.

The picture so far considered is close to the one for HCOOH catalytic decomposition. Thus, relation (10) may be observed when the reaction rate constant under consideration can be represented as a product of type (11) constants, one of which (k_2) remains almost constant in the series of related objects.

If stage 2 is not a limiting one, then (11) is not satisfied, and (10) degenerates; the centre of the pencil of lines (10) in coordinates $\log A$ versus E is at the origin of coordinates. Such a regularity is most important for isobaric decomposition according to (1) under isothermal conditions [4, 17]. The latter is a simplified version for an instance when one of the reversible stage reactions limits the entire process (a more precise thermolysis chart is $A_{sol.} \rightleftarrows [B_{sol.}+C_{ads.}] \rightarrow B_{sol.}+C_{gas}$). Correlation (11) is satisfied and $B \neq 0$ as "supercorrelation" in the form of the Arrhenius dependence for the second stage will characterize desorption of the product C when the experiment runs, for example, in a derivatograph, with decomposition controlled by removal of the gaseous product. In fact, the carbonates of some metals complying with the above regularity yield $B \neq 0$ under linear heating conditions [91]. Crude estimation of $\hat{E}$ from data presented in [91] yields a value within 16 to 56 kJ · mol^{-1}, which corresponds to low-activation processes such as desorption and diffusion.

A type (10) correlation has been established and analysed for the recrystallization of alloys in [179]. It was used to evaluate the intermolecular energy barrier height (E_T) for conductivity in organic semiconductors, which in turn permitted estimation of the effective mass of the activated electron (together with the energy barrier height E_T and width; the latter determines the isoparametric temperature for electrical conductivity in the case of CE) [180]. It is important that even in this simplest process (reversible excitation electron tunnelling) the dependence of electrical conductivity on temperature is expressed as a product of three exponential functions with alternating exponent signs comprising the constant E_T and variable energy level at which electron tunnelling takes place. Such an expression for electrical conductivity satisfies Eq. (11) in the Arrhenius form complying with the possibility of a correlation chain: Arrhenius equation →(2)→(10). It can thus be concluded that the validity of type (11) correlations is a rather general prerequisite for correlation (10).

Lastly, let us analyse the use of (10) when the CE is a computational artefact. It was noted in [1] that the latter can be eliminated, partially at least, by transforming the Arrhenius equation in terms of new variables. The invariant characteristics of the process can also be calculated by developing a statistical model of the process in the form of a polynomial. A method based on (10) is suggested in [181] and can be used in both approaches. Thanks to (10), this method appears to be very simple in terms of computation. It can clearly be interpreted, which promotes an understanding of the physical meaning of the invariants.

The method is based on the intersection of the confidence intervals of type (2) correlations (each of them being greatly ambiguous in the determination of A and E) derived under varying experimental conditions. The intersection of these confidence intervals defines a smaller size of the total (common to all initial) confidence interval. The values of A and E can clearly be seen to become more certain.

In estimating the possible use of this method, one should bear in mind that a change in the heating rate is a real chance of having (10) satisfied in the case of an artefact CE, because this change leads to a displacement of the thermoanalytical curve, i.e. to a change in the reaction temperature rate and, consequently, in e. A change in the technique of calculating A and E or in the process model $f(\alpha)$ only leads to an artefact CE, as we can see from the data presented in [182]. Using the data from [183], we are convinced that, in general, this method does not lead to average values of A and E.

The method of A and E determination corresponds to a transformation of the original equation of nonisothermal kinetics (4), the shortcomings of which are shown clearly in [87, 88], i.e. to reduction of this equation to a three-exponential equation of the form

$$\mathrm{d}\alpha/\mathrm{d}t = \hat{A}\cdot\exp(-\hat{E}/R\hat{T}_v)\cdot\exp(E_j/R\hat{T}_v)\cdot\exp(-E_j/RT)\cdot f_j(\alpha) \qquad (12)$$

($\hat{T}_v = 1/2.3\,Re_v$; v is the β_v heating rate number). Here, $\hat{T}_v$ for a given substance actually characterizes the experimental conditions, and E_j the kinetic function and calculation method [184]. If $f_j(\alpha)$ is correctly selected, the exponents containing $\hat{T}_v$ cancel out and Eq. (12) reduces to (4). The two last exponents cancel out if k is determined at $T = \hat{T}_v$. As will be shown later, additional exponential terms make the solution of the inverse problem less ambiguous.

Models $f_j(\alpha)$ can be discriminated with the use of log $\hat{A}$ and $\hat{E}$ and Eq. (4) with which the design values of $\frac{\mathrm{d}\alpha}{\mathrm{d}t}$ are found. When n of the i-th exponential values $\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i$

is available, the residual sum of squares can be found for each $f_j(\alpha)$:

$$(n-1)S_{jv}^2 = 1/\beta^2 \sum_{j}^{n} [(\mathrm{d}\alpha/\mathrm{d}t)_i - \hat{A}\cdot\exp(-\hat{E}/RT)\hat{f}_j(\alpha_i)]^2$$

and then the most probable function $f(\alpha)$ can be selected with respect to the minimal approximation error $\langle S \rangle = (\sum_{v} S_{jv})/v$ mean for all heating rates v.

Closer examination [185] shows that the above method of $\hat{E}$ and $\hat{A}$ determination is a peculiar variant of a rather general technique used to describe multi-parameter relations by polynomials and to decrease the interdependence of mathematical model parameters by introducing a transformed independent variable, which reduces the value of nondiagonal elements in the information matrix.

According to [185], the polynomial corresponding to the set of the Arrhenius equation and (2) and (10) has the form

$$f(x_1, x_2, x_3) = f(x_1^0, x_2^0, x_3^0) + a_1x_1 + a_2x_2 + a_{23}x_2x_3 + \\ + a_{12}x_1x_2 + a_{123}x_1x_2x_3 \tag{13}$$

where $f(x_1, x_2, x_3) \equiv \log k$, $x_1 \equiv T^{-1}$, x_2 is the variable causing a change of A and E in accordance with the CE, x_3 is the variable causing a change of B and e according to (10), and x_i^0 are the values of variables selected as standard ones. This polynomial is a particular case of the nonhomogeneous polylinear function considered in [1]. Thus, one can observe a relationship between the formal theory of isoparametric correlations and the method of finding kinetic invariants from nonisothermal data.

As to the general technique of decreasing the interdependence between the parameters of the mathematical model, its efficiency depends on how successfully the independent variable has been transformed. The substitution of relations (2) and (10) into the Arrhenius equation is equivalent [185] to the transformation of x_1 to $x_1^* = (x_1 - \hat{x}_1)/\hat{x}_1$, where $\hat{x}_1$ is the isoparametric value of x_1 dependent on x_3. The dependence of x_1^* on x_3 reveals the specific feature of the transformed variable, i.e. of x_1^*. The transformed variable being used, the information matrix for the transformed model becomes nondegenerate, and the dependence of x_1^* on x_3 increases the value of the matrix determinant. As a result, the worst estimates of the model parameters appear to be displaced to a lesser degree and the statement of the problem conditions improves.

On the whole, the conclusion may be drawn that the use of (10) eliminates the CE as a computational artefact.

5. Conclusions

There may be different reasons for the kinetic compensational effect (CE). Therefore, the CE can be correctly interpreted and used only when such reasons are properly examined. Several kinds of CE can be discriminated, depending on what has conditioned them. The first is known as the "apparent" CE. It unites several varieties of the CE. Some of them are caused by statistical peculiarities of isoparametric correlations (statistical CE), the specificity and difficulty of solving inverse problems, i.e. they are a computational artefact. Others are conditioned by the complex effect of the experimental conditions on the parameters under measurement, and by the difficulty of their determination. This variety of CE's can be termed an experimental artefact. Still others are known as "true" CE's. As chemical reactions in a condensed phase are complex processes and the kinetic parameters to be determined are some effective quantities, one can state that the most widely spread version of the true CE is the one in which, according to (2), effective parameters (empirical or effective CE) correlate. Realization of a total reaction in which the growing influence of one process on the ultimate rate is due to a weaker influence of the other process, is probably the physical basis of the effective CE. A reversible reaction [4] or parallel reactions [186] are the simplest examples.

The CE is true if it has been caused by entropy-enthalpy compensation. Kinetic nonequivalence of the reacting particles, i.e. their entropy-energy distribution, may be its basis in a solid. Experience shows that this distribution can be different and fail to correspond to (2) [49]. In this connection, it should be noted that, in a general case, (2) can assume an anticompensational ($e<0$) or an isoentropic ($\log A = B$) form.

Entropy-enthalpy compensation has a simple physical meaning should this regularly be considered in a series of related compounds. In the final analysis, it is reduced to a thermodynamic CE: the higher the energy of interaction between particles in related condensed systems, the higher the degree of their ordering. This regularity holds true for both liquid and solid states, i.e. the true CE has a common basis in these phases. Also common are the reasons for an effective CE, as well as the difficulties concerning an apparent CE. All this calls for a much closer relationship and interaction between appropriate areas of homogeneous and heterogeneous kinetics. So far, such areas have been called 'isokinetics' [187]. For example, a wide use should be made of homogeneous kinetic statistical methods for the analysis of isoparametric correlations and the calculation from them of true transmission coefficients and true values of $\Delta G^{\neq}$ and $\Delta S^{\neq}$.

The formal theory of isoparametric correlations, developed for homogeneous reactions, is not used in practice in the kinetics of reactions involving the participation of solids. "Supercorrelations", i.e. isoparametric correlations of much higher order, can be interpreted within the framework of this theory. The capacities of "supercorrelations" have not as yet been studied in full. The use of high-order isoparametric correlations consists in finding invariant values by varying the effects of the factors which impede the determination of the values, rather than by eliminating the effects (which is not always possible to do).

Certain successes so far attained and analysed in our survey (parts I and II) allow us to believe that isokinetics can really become a useful section of the chemical kinetics of condensed substances.

List of Symbols

Symbols	
Section 2	Isothermal conditions
A_{ef}; E_{ef}	effective activation parameters
P	pressure
T_m	temperature corresponding to reaction maximum
Section 3	Nonisothermal conditions
m; n; p	kinetic parameters
T_m	temperature of maximum in DTA curve
T^*	variable that improves statement of inverse kinetic problem
β	rate of heat raising
γ, ζ	parameters of linear correlation of $\log k$ on n
Section 4	Other isoparametric relations for reactions involving the participation of condensed substances
a; b	parameters of linear correlation of β_P on ν
$\hat{A}$; $\hat{E}$	invariant activation parameters
$\hat{f}(\alpha)$	most probable kinetic function
K	equilibrium constant
$\hat{k}$	isoparametric constant of action
S^2_{iv}	residual sum of squares
$\langle s \rangle$	mean approximation error
$\hat{T}_v$	isoparametric value of temperature
u	combustion rate
v	heating rate number
$\hat{x}$	isoparametric value of variable
x^*	transformed variable in polylinear relation
β_P; ν	parameters of empirical combustion law

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Zusammenfassung — Verschiedene Erscheinungen des kinetischen Kompensationseffektes bei unter Beteiligung von festen Substanzen unter isothermen und nichtisothermen Bedingungen verlaufenden Reaktionen werden erörtert, ebenso Erscheinungen anderer isoparametrischer Korrelationen. Es wird gezeigt, daß isoparametrische Korrelationen zur Analyse von Festphasenreaktionen und zum Ausschluß von Artifakten in der nicht-isothermen Kinetik herangezogen werden können.

Резюме — Рассмотрены различные случаи проявления кинетического компенсационного эффекта в реакциях с участием твердых веществ, протекающих в изотермических и неизотермических условиях, а также случаи проявления других изопараметрических соотношений. Показана возможность использования изопараметрических соотношений при анализе реакций твердых веществ и исключения артефактов в неизотермической кинетике.