

ISOPARAMETRIC KINETIC RELATIONS FOR CHEMICAL TRANSFORMATIONS IN CONDENSED SUBSTANCES (ANALYTICAL SURVEY). I.

Theoretical fundamentals

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The compensation effect related to isoparametric correlations is analysed within the formal theory, and the statistical and physico-chemical aspects of these correlations are considered.

The greatest difficulty involved in the kinetic analysis of the reactions of condensed substances is the nonuniqueness of the solution of the problem of kinetic parameter reconstruction from experimental data. This usually concerns the form of the compensation effect (CE):

$$\log A = B + eE \quad (1)$$

In nonisothermal kinetics this difficulty is due to Eq. (2)

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (2)$$

with standard notations [1]. The above nonuniqueness of the solution detracts from the value of the kinetic parameters, imparting to them a merely empirical character. Equations (1) and (2) have therefore been criticized and rejected in many publications, most uncompromisingly in [2, 3]. However, the mere rejection of Eqs (1) and (2) is not a solution in itself [4, 5]. In this survey we have endeavoured to throw light on the present-day interpretation of the problem and the application of Eqs (1) and (2) in their interrelation, and to devise a certain approach to the elimination of ambiguity in the kinetic parameters. Earlier contributions concerning the CE in different fields of physical chemistry have been thoroughly surveyed in [6-9].

To be specific, the problem of CE interpretation for solid-state reactions can hardly be solved unless we take into consideration certain advances made in the analysis of the isokinetic reaction (IR)

$$H^\ddagger = g + \Theta\Delta S^\ddagger \quad (3)$$

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for liquid-phase processes similar to (1). Following the traditional situation in chemical kinetics, the level of theoretical CE interpretation is higher in the kinetics of homogeneous reactions than in the kinetics of heterogeneous solid-phase processes. Their certain specificity [10] does not allow one to extend the advances made in the kinetics of homogeneous reactions to the field of heterogeneous processes [11]. However, for want of other grounds, the elementary stages of a chemical event in this field are still being interpreted in terms of the homogeneous transformation theory [12], although this approach is rather questionable. Such a situation in the kinetics has predetermined the pattern of our survey, in which the theory is mainly based on the advances made in the isothermal kinetics of liquid-phase reactions. Nevertheless, the leading problem of the survey is the CE analysis of the kinetics of solid-phase reactions, basically under nonisothermal conditions. This subject is dwelt upon in the second part of the survey, which additionally considers the possibility of a rational use of some approaches from the homogeneous reaction theory. The development of such approaches and their application to heterogeneous process are the concern of refs [13–15].

The expression "isoparametric relations" is based on the terminology suggested by Palm [16]. Their essence is analysed in what follows. An isokinetic relation of the type (1) and (3) is a particular but most important case of isoparametric relations. It should be noted that the term 'isokinetic' may have another meaning [17].

1. Formal aspect

Isoparametric relations appear as natural as they can be in the formal interaction theory cited in monograph [16]. Consider in short the quantitative aspect of this theory. Its mathematical aspects correspond to experimental–statistical methods [18] of planning experiments in particular. The form of the response function f (continuous and monotonic), which expresses the complex dependence of the measured system property on many unknown elementary parameters of x_j composite parts of the system and/or on the ambient conditions, is uncertain; in a rather narrow interval of arguments it is approximated by the polylinear portion of the series expansion

$$f(x_1, x_2, \dots, x_i, \dots, x_n) = f^0(x_1^0, x_2^0, \dots, x_i^0, \dots, x_n^0) + \sum_{i=1}^n a_i x_i' + \alpha \sum_{i=1}^n \sum_{j=1}^n a_j a_i x_i' x_j' + \dots + \alpha^{n-1} \prod_{i=1}^n a_i x_i' \quad (4)$$

where the x_i' are variables depending only on the arguments x_j whose values are controlled by the researcher, their change involving variations of f (the way in which x_i' is introduced is the main specificity of the approximation under consideration); the x_i^0 are the standard argument values at which $f = f^0$; the a_i are the scale factors depending on the x_i' scale standardization conditions (an arbitrary change of the x_i' scale is possible); and α is a constant for the type of interaction of the x_i' parameters. Polylinear functions (4) are linear with respect to any of the x_i' arguments. Their form is preserved on substitution of an arbitrary set of arguments x_i' by a new argument

whose form corresponds to Eq. (4) for m terms (without f^0), which means that each x'_i corresponds to some set of true arguments x_i . These functions may be represented as the product

$$f = f^0 \dots \alpha^{-1} + \alpha^{-1} \prod_{i=1}^n (1 + \alpha a_i x'_i) \quad (5)$$

If the constants in (4) may be expressed as α exponents, then the function is homogeneous (it is nonhomogeneous with mutually independent constants). The homogeneity of the polylinear function may be judged either from the results of the regression analysis of the experimental data, permitting determination of the coefficients in the f expansion, or from the findings for the successive correlation series [19] in the case of the correlation of factors responsible for unsteady solution and displaced estimates of the coefficients. The homogeneous and nonhomogeneous polylinear functions are mathematically equivalent if f is only expressed as the dependence on two x'_i arguments. For a greater number of arguments the nonhomogeneous polylinear function is of the form

$$f = f^0 + \sum_i a_i x_i + \sum_{i < j} a_{ij} x_i x_j + \sum_{i < j < l} a_{ijl} x_i x_j x_l + \dots \quad (6)$$

A formal quantitative interaction theory is constructed on the basis of the polylinear expansion and its properties. A unique homogeneous polylinear function (certain α) is consistent with the intensity for a certain formal homogeneous interaction. With the additive contribution of different formal interactions and one variable factor with the number w , Eq. (4) reduces to

$$f = f_w^0 + \varphi_w x_w \quad (7)$$

whence the numerical value may be obtained for x_w , i.e. a parameter characterizing numerically the contribution of the factor w to the prescribed type of interaction. f_w^0 and φ_w are prestandardized. Numerical characteristics such as these may be obtained for each variable factor.

Equation (5) yields the isoparametric property: the product in (5) vanishes if any of the x'_i arguments becomes $x'_i = -\frac{1}{\alpha a_i}$, called an isoparametric point for the parameter x'_i . Traversing of this point (with changing x'_i) changes the product sign in (5), i.e. it results in change in the orientation of the effect of any remaining argument to f . The isoparametric value of f is $f^0 - \alpha^{-1}$. For the nonhomogeneous polylinear function more widely used in practice, only pair isoparametricity may occur, which is the f independence of a single argument at an isoparametric value of some other one. If such a function is three-parametric, then the pair isoparametricity is represented by an isoparametric line; in the case of a four-parametric function, it is a surface; etc.

It is evident that the isoparametricity observed experimentally is a reality independent of the manner in which the phenomenon is interpreted, while the factors traversing zero values with changing signs can neither be considered invariant charac-

teristics of the process nor have a certain physical meaning. Thus, one may speak of an isoparametricity paradox, as such factors include, in particular, the activation energy E , Hammett constants ρ , etc. Indeed, if the energy ϵ or free energy G are functions as f , then polylinear functions result in linear energies or free energies (LFE).

It follows from (7) that

$$\epsilon_{l,i} = a + b\epsilon_{m,i} \quad (8)$$

(i is the number of the variable factor; l and m are two different combinations of all remaining factors affecting ϵ ; $b = \varphi_l/\varphi_m$, φ depending, in particular, on the α characterizing the isoparametric point; $a = \epsilon_l - b\epsilon_m^0$), with a similar expression for G or ΔG . A LFE (linear free energy), in turn, yields Brønsted, Hammett and other equations. Moreover, the Arrhenius and Van't Hoff equations are also regarded as the simplest example of LFE validity:

$$\log k = \log A - \frac{E}{2.3 R T} \quad (9)$$

where $\frac{1}{T}$ is the x_w parameter (of (7)); E is independent of T . The same may be said about the relation

$$G = H - TS \quad (10)$$

with H (enthalpy) and S (entropy) independent of T .

In such an (extrathermodynamic) approach the parameters E , H , S and G are not identified with thermodynamic functions: isokinetic or isoequilibrium relations similar in their meaning to CE (1) need not therefore be discussed thermodynamically. They follow immediately from the polylinear functions if at least one more x argument is varied along with temperature:

$$\begin{aligned} \Delta G &= \Delta G^0 - \alpha^{-1} + \alpha^{-1}(1 + \alpha a_1 x)(1 + \alpha a_2 T) = \\ &= \Delta G^0 + a_1 x + (1 + \alpha a_1 x)a_2 T, \end{aligned}$$

i.e.

$$-(1 + \alpha a_1 x)a_2 = \Delta S; \quad \Delta G^0 + a_1 x = \Delta H$$

and

$$\Delta H = -\frac{1}{\alpha a_2} \Delta S + \Delta G^0 - \alpha^{-1},$$

which may be written in the form of an isokinetic relation $\Delta H = g + \Theta \Delta S$; here $g = \Delta G^0 - \alpha^{-1}$; $\Theta = -\frac{1}{\alpha a_2}$ (ΔG^0 should not be confused with the standard variation of the isobaric-isothermal potential). On the whole, the isokinetic relation is a mathematical requisite for the validity of all other LFE laws [16]. Isoparametricity is observed when cross term in the f expansion are significant, i.e. when f is markedly affected by the perturbations of the factors which the x_i arguments correspond to.

If the process is governed by a multiparametric nonhomogeneous polylinear function, then the location of isoparametric points for two-parametric relations will depend on the level at which the values of the remaining parameters have been fixed. This accounts for a variable or random character of the values of isokinetic temperature Θ for reactions with similar mechanisms, for which one might expect constant values of this magnitude. Therefore, Θ can hardly be related to the nature of the process, this also being true of the values of the type E , ρ , etc. In particular, real isoparametricity including transformation of the activity series was observed in the systems governed by the Brønsted equation [20]; Brønsted coefficients cannot therefore describe a simple and specific physical meaning (cf. [21]). As invariants, one may consider the coefficients of the cross terms of the nonhomogeneous polylinear function, the validity of which in a wide range of arguments, rather than the constancy of the sensitivity coefficients of the type E , ρ , etc. in partial linear relations, must be regarded as a criterion of a constant process mechanism. It has been emphasized that no theoretical models have as yet been developed for the above invariants, this being an urgent problem [16].

The grounds for the above approach (that can be applied not only in the case of carbon compounds and their simple reactions [22, 23]), as well as the reliability of the subsequent conclusions, have been comprehensively exemplified in [16], including real traversals of isoparametric point. Such traversals are also dealt with in recent contributions [24–28]. The available data on the interdependence of the reactivity (ρ) and isokinetic temperature [29–31] do not contradict the above general conclusion on variable Θ , as in particular cases the effects of some ignored factors on the reactivity may be insignificant, or they were kept at the same level [32]. Critical analyses of one- and multiparametric correlations are made in [33–36].

Thus, 'isoparametricity' may be applied as a general term to describe the property of the polylinear function in assuming one and the same (isoparametric) value if any of the arguments reaches a certain (isoparametric) point. The change of the arguments at that point has no impact on the function value.

The isoparametricity of the simplest function

$$z = y \pm qx \quad (11)$$

mathematically implies the linear interdependence of y and q

$$y = r \mp eq \quad (12)$$

where r and e are constant under definite conditions. Relation (12) is the condition of the formation of a pencil with the centre $(x, z) = (e, r)$ by straight lines (11) with variation of the parameter q ; this can easily be verified by elementary analytical geometry procedures.

Equation (11) may also serve as an isoparametric relation, provided there exists the real dependence

$$Z = z \mp xX \quad (13)$$

with constants z and x . In the same way, Eq. (12) may function as (11), provided that there exists the isoparametric dependence

$$r = R \pm Qq \quad (14)$$

Such a mathematically trivial approach, along with an inductive method, may yield from the fact of isoparametricity a definite hierarchy of isoparametric relations, initiated in our case by Eq. (13). The information available in physical organic chemistry (partly dwelt upon above) shows that isoparametricity is by no means a "nuance of a mathematical game" [16, 37]. It has been shown recently that the above hierarchic structure is also possible [13].

As for a formal CE analysis, intriguing contributions [38–40] have been made regarding the Arrhenius equation as a correlation from the position of projective geometry. This permitted the revelation of the intercorrelated values and the determination of the number of possible correlations, many of which had been little studied, if at all. These works also provide arguments for a number of well-known relationships, for example, between the isokinetic temperature and the CE, as well as the interdependence of the CE and the Zavadski–Bretschneider law, well documented in topochemistry (the interdependence is not always unambiguous [41], but this does not diminish its significance for the problem, just as in the case of the IR with the Hammett equations).

For orientation among the possible relationships between interdependent magnitudes (as, for example, in the Arrhenius equation), it seems reasonable to use the mathematical principle of duality. Many of these relationships are rather obvious, provided that the reference equations of type (9), including the product of two variables, are represented as a hyperbolic paraboloid [13, 42]. Thus, the mathematical aspect of these relationships is trivial and the conclusion [38–41, 43] that the mathematical basis of the CE lies in the equation of type (9) itself is beyond doubt. It is important that long-range extrapolation is performed when calculating A (or $\log A$), which enhances the correlation of A and E in a limited range of experimental temperatures and rate constants [44]. However, when the CE is not a computational artifact, no mathematical analysis alone can indicate the reason for the changing of empirical A and E , as these reasons are quite obviously purely physico-chemical, though they may not be associated at all with the changing properties of the potential reaction surface. Besides, it is necessary to understand physico-chemically why these changes are regular and conform to the CE.

2. Statistical aspect

The development of rigorous quantitative statistical criteria for the CE validity is the most important problem in CE analysis. The development has three aspects. The first is represented by contributions [45–47] identifying the reality of the CE with the functional validity of Eq. (1) and using dispersion analysis as the main statistical approach. The functionality of Eq. (1) may be masked by experimental errors, and the Arrhenius lines will therefore intersect not at one point, but in some domain

$\Delta x \cdot \Delta \ln k$ ($x = 1/T$), whose dimensions are determined by the accuracy measurements. As the most probable coordinates of the above point are prescribed (1) as the regression equation

$$\widetilde{\ln A} = \overline{\ln k}_e + eE \quad (15)$$

the required functionality condition (1) will be satisfied provided that the deviation of $\ln k_{e_i}$ (i.e. $\ln k_e$ for the i -th experimental series at a point $x = e$) from the mean value of $\ln k_e$ (i.e. from $\overline{\ln k}_e$) does not exceed the errors of $\ln k_{e_i}$ estimation, which is solved with the use of the Fischer criterion. Otherwise, the CE is apparent even in the case of an approximate linear dependence in $\ln A$ vs. E coordinates, a weaker correlation corresponding to it. Here, the regression coefficient e is also consistent with the minimum deviation of $\ln k_{e_i}$ from $\overline{\ln k}$. The sufficient conditions for CE reality, requiring that preexponential factors and activation energies be essentially different in different series, are determined in the same way. If only the required condition is fulfilled, then the CE may be due to experimental errors: the minimum dispersion of $\ln k_i$ will correspond to the point \bar{x} , while the apparent CE will be written as

$$\ln A = \overline{\ln k} + \bar{x}E \quad (16)$$

($\overline{\ln k}$ is the mean over all the experiments). In this case, for all i Arrhenius lines a mean value of A or E may be taken. The CE decrease due to experimental errors may be attained by extending the temperature range, increasing the number of measurements close to the edge of this range and the mean experimental temperature. It must be remembered that the validity of Eq. (16) is not strict evidence of the apparent CE, as the experiments might have been performed in a temperature range where $\bar{x} = e$. The validity of this equality can only be verified experimentally. When only the condition of essential difference is fulfilled, the CE may also be apparent (despite the correlation coefficient r ($\ln A, E$) being close to unity), because of the narrow range of k_i and x_i measurements for a series of reactions or catalysts. The appropriate CE will be $\widetilde{\ln A} \cong \overline{\ln k} + \bar{x}E$. Along with the essential differences in E , the narrow range results in the maximum approach of the Arrhenius lines just within this range. The verification of the proposed criteria has shown [46] that they may help to distinguish the functional CE even at low (0.42) correlation coefficient r ($\ln A, E$) obtained at $e = 0$, i.e. when Eq. (1) degenerates to become $\log A = B$ and A is independent of E . In other cases of the functional CE under study, the r ranged between 0.82 and 0.999. The regression analysis in the $\log A$ vs. E coordinates is only regarded as semiquantitative. The method under consideration is comparatively simple, yet it yields a displaced estimate for e . Therefore, in [47] its complicated modification is suggested, comprising iterative procedures and relying upon the application of the χ^2 criterion. This version may be used in most general cases when the number of points, the accuracy of their estimation and the location along the T^{-1} axis are different in different experimental series.

The second aspect is based on the linear regression analysis and is the concern of the studies surveyed in [7]. Comparison of Eqs (3) and (10) shows that (3) acts as an

isoparametricity condition with respect to (10), while g has the meaning of the Gibbs energy (ΔG), and Θ is the absolute temperature. It follows from (3) and (10) that the linear relationship between any two magnitudes of the set ΔG^\ddagger , ΔH^\ddagger and $T\Delta S^\ddagger$ means a linear dependence of the third one on each of the other two magnitudes. In this sense, the three relations obtained are equivalent. This does not mean, however, that they are statistically equivalent. Relation (3) may only be due to the errors in the ΔH^\ddagger and ΔS^\ddagger determination because they are correlated. For k_1 and k_2 estimated at T_1 and T_2 , the isokinetic relation gives the expression

$$\log k_2 = a + b \log k_1 \quad (17)$$

and $\Theta = T_1 T_2 \frac{1-b}{T_1 - b T_2}$. Following (17), b and hence Θ may be estimated in two independent experiments, which eliminates correlated errors. The above and a number of other simple methods of Θ determination are considered in [16] and are not dwelt upon here.

As the variables $\log k$ and $1/T$ are also determined individually, the Arrhenius dependences may be used to find Θ and to estimate its statistical value. It is important that the error in the $\log k$ measurement is essentially less than the errors of the $\log A$ and E indirect measurements. The latter errors have magnitudes of the same order, but the confidence interval in the appropriate coordinates is an ellipse with large eccentricity and the major axis is directed close to the harmonic mean temperature. This proximity must arouse suspicion, for in this case IR may only be due to the errors in the A and E measurements. Thus, the algebraically equivalent expressions turn out to be statistically nonequivalent. To be specific, with no correlation in the coordinates $\log k_1$ vs. $\log k_2$, a fine correlation in the coordinates $\log A$ vs. E may be obtained. In [7] some particular examples are analysed and it is shown that the dependence of the type $\log A$ vs. E cannot be used in the general case to find the isokinetic temperature. Its crude estimation in the first stage of analysis may be performed in accordance with (17), but the plot E vs. $\log k$ is preferable for narrow temperature ranges ($\sim 10^\circ$).

In the course of regression analysis as in (17), the question arises as to which of the two regression lines (17) should be taken for calculations, $\log k_1$ to $\log k_2$, or $\log k_2$ to $\log k_1$. Minimization of the deviations yields for the resulting line (17) the slope $b = \tan \varphi$, with $\tan 2\varphi = \frac{2S_1 S_2 r_{12}}{S_1^2 - S_2^2}$, where S_1 and S_2 are the standard deviations of $\log k_1$ and $\log k_2$; $r_{12} = r(\log k_1; \log k_2)$, the correlation coefficient. The most exact and correct approach, however, implies a statistically correct solution to the problem of intersection of the series of l Arrhenius lines at the point x_0, y_0 ($x \equiv T^{-1}$; $y \equiv \log k$) in the second stage. The details of this analysis are given in [48, 49]. The problem was solved by minimizing the squared deviations of each i -th regression line ordinate from the assumed intersection point. The obtained set of $l+2$ nonlinear equations had an exact solution only when the experimental values for all the regression lines were obtained at the same (but not necessarily equidistant)

values of x . In a more general case, the problem is solved numerically by finding the residual sum of the squares at arbitrary abscissa values and successive estimation of the minimum of this sum.

In what follows we shall cite in short the algorithm proposed in [7, 48] for the case when the measurements in all the runs are performed at equal temperatures. This algorithm may be recommended for solving particular problems dealing with the CE.

For calculations, some auxiliary values should be determined, such as:

$$X = \frac{1}{m} \sum_j (x_j - \bar{x})^2 = \frac{1}{m} \sum_j u_j^2;$$

$$Y = m \sum_i (\bar{y}_i - \bar{y})^2 = \frac{1}{m} \sum_i \left(\sum_j \log k_{ij} \right)^2 - \frac{1}{ml} \left(\sum_{ij} \log k_{ij} \right)^2;$$

$$Z = \sum_{ij} (y_{ij} - \bar{y})^2 = \sum_{ij} (\log k_{ij})^2 - \frac{1}{ml} \left(\sum_{ij} \log k_{ij} \right)^2;$$

$$P = m \sum_i p_i = \sum_{ij} u_j \log k_{ij};$$

$$Q = m \sum_i p_i^2 = \frac{1}{m} \sum_i \left(\sum_j u_j \log k_{ij} \right)^2;$$

$$U = 2m \sum_i (p_i - \bar{p})(\bar{y}_i - \bar{y}) = \frac{2}{m} \sum_i \left(\sum_j u_j \log k_{ij} \sum_j \log k_{ij} \right) - \frac{2}{ml} \left(\sum_{ij} u_j \log k_{ij} \right) \left(\sum_{ij} \log k_{ij} \right),$$

where

$$u_j = T_j^{-1} - \frac{1}{m} \sum_j T_j^{-1}; \quad p_i = \frac{1}{m} \sum_j u_j \log k_{ij}.$$

They may help to obtain the deviation of the value, an inverse of the isokinetic temperature, from the mean measured inverse temperature

$$u_0 = \Theta^{-1} \sum_j \frac{T_j^{-1}}{m} = \frac{Q - \frac{P^2}{ml} - XY - \sqrt{\left(Q - \frac{P^2}{ml} - XY \right)^2 + XU^2}}{U}$$

the inclinations of the Arrhenius lines

$$b_i = \frac{p_i + u_0 \left(y_0 - \frac{1}{m} \sum_j \log k_{ij} \right)}{X + u_0^2}$$

the intersection point abscissa corresponding to the isokinetic temperature,

$$x_0 = \Theta^{-1} = u_0 + \bar{x},$$

and its ordinate

$$y_0 = \frac{1}{ml} \left(\sum_{ij} \log k_{ij} + \frac{u_0 P}{X} \right)$$

The significance of the hypothesis of the single intersection point is estimated by comparing the residual sum of the squares (S_{00}) for normal regression lines with the similar sum (S_0) on the assumption that all the lines intersect at one point:

$$S_{00} = Z - Y - \frac{Q}{X}$$

with the number of degrees of freedom

$$f = (m - 2)l;$$

$$S_0 = Z - \frac{Q + \frac{P^2}{ml} + XY + \sqrt{\left(Q - \frac{P^2}{ml} - XY\right)^2 + XU^2}}{2X}$$

with $f = (m - 1)l - 2$ degrees of freedom. S_0 characterizes the standard deviation at the point $1/\Theta$. If the difference between S_{00} and S_0 is significant ($S_{00} < S_0$); for intersection strictly in a point ($S_{00} = S_0$), then the hypothesis of the single intersection point is rejected. Finally, the S_u function characterizing the confidence interval for $1/\Theta$ is calculated and built as

$$S_u = Z - \frac{Q - uU + u^2 \left(Y + \frac{P^2}{ml} X \right)}{X + u^2}$$

with $f = (m - 1)l - 1$ degrees of freedom. Here, i is the line index, j is the line point index, and m is the number of line points. The S_u function has asymptote S_∞ parallel to the x axis, with a minimum at the point $u = u_0$ ($S_u = S_0$) and a maximum within the domain of the experimental points. If $x = T^{-1}$ is taken as the abscissa, then this function has its minimum at the point standing for the most probable value of Θ^{-1} . This is also true of the standard deviations s_u and s_0 corresponding to the residual sum of the squares. The graphic representation of the analysis results is completed with the indication of the value of S_{00} (or s_{00}) and the $\log k$ experimental measurement error. Such a comparison of the difference in s_0 and s_{00} values with an experimental error, and determination of the confidence interval for Θ , is most visual. The program for computer-aided calculation using the suggested method is reported in [50].

The situation is possible when the hypothesis of the single point of intersection cannot be rejected even at a poor minimum. This is interpreted as the presence of an IR for which Θ cannot be determined with the required degree of accuracy from the above runs. On the whole, in accordance with [7, 51], the isokinetic temperature has no simple physical meaning and its measurement, usually in a wide confidence interval, is not the main goal in the isokinetic problem. The latter implies verification of IR validity for the reaction series. Depending on the value of Θ , the reaction series are subdivided into isoentropic ($\Theta = \infty$), isoenthalpic ($\Theta = 0$), anticompensation ($\Theta < 0$) and compensation ($\Theta > 0$) types. The correct assignment to a reaction series, asided by the comparison of the S_0 , S_{00} and S_∞ type values, promotes the elucidation of the process mechanism, which is often regarded as constant within a series for which an IR is fulfilled. Exner gives particular examples of IR analysis by the method he suggested [7, 48, 49].

The third aspect of the statistical CE analysis allows investigation of both the linear and nonlinear relations [52–54]. Following [52, 54], the real relationship between the activation parameters is always concealed by the existing and dominating statistical CE generated by random experimental errors exceeding the changes in these parameters, which has been pointed out in earlier works but has not been proved statistically. The correlation coefficient (ρ) for the estimates $\Delta\tilde{H}$ and $\Delta\tilde{S}$ in the absence of extrathermodynamic effects is

$$\rho = \frac{\sum \frac{1}{T}}{\sqrt{n \sum \left(\frac{1}{T}\right)^2}} = \lim_{n \rightarrow \infty} r$$

(summation with respect to all n experimental values $1/T$, r being the correlation estimator), i.e. it depends only on the choice of the test temperature range, is close to unity when the range is narrow, and the experimental errors exceed the ΔH and ΔS changes. For real entropy–enthalpy relations the value of r is lower, since its proximity to unity points either to no real effect or to its masking by a much stronger statistical effect. The elliptic confidence interval in the ΔH vs. ΔS plane is determined by the following ratio of the ellipse axes a and b :

$$\frac{a}{b} \approx \sqrt{\frac{n}{\sum \left(\frac{1}{T} - \langle \frac{1}{T} \rangle\right)^2}} \gg 1$$

(typical values of $a/b \sim 10^4$). If the ΔH and ΔS changes are small compared with the errors, then they are superimposed by this ellipse ($\langle \rangle$ stands for a mean value). The inclination of the major ellipse axis is $\langle 1/T \rangle^{-1} = T_{hm}$, i.e. the $\Delta\tilde{H}$ and $\Delta\tilde{S}$ estimates are distributed along the line with slope T_{hm} , which is exactly an erroneous estimate of the isokinetic temperature when ΔH^\ddagger and ΔS^\ddagger are found from the linearized Arrhenius equation by the least-squared method. Correspondingly, the statistical CE has the form $\Delta H^\ddagger = \Delta G_{T_{hm}}^\ddagger + T_{hm} \Delta S^\ddagger$ and is only useful for verifying the zero-

hypothesis $H_0: \Theta = T_{hm}$. The significant deviation of Θ from T_{hm} may be interpreted as manifestation of real compensation. The estimate $(1 - \alpha)$ 100% of the confidence interval for $\tilde{\Theta}$ may be obtained from the formula

$$\tilde{\Theta} \pm t_{m-2, \frac{\alpha}{2}} \sqrt{V(\tilde{\Theta})},$$

where

$$\tilde{\Theta} = \frac{\sum(\Delta H - \langle \Delta H \rangle)(\Delta S - \langle \Delta S \rangle)}{\sum(\Delta S - \langle \Delta S \rangle)^2}, \quad V(\tilde{\Theta}) = \frac{\sum(\Delta H - \Delta \tilde{G}_{\Theta} - \Theta \Delta S)^2}{(m-2) \sum(\Delta S - \langle \Delta S \rangle)^2}$$

and m is the number of pairs of $(\Delta H, \Delta S)$ data. The zero-hypothesis cannot be rejected if T_{hm} is within the above interval. The analysis of the reported data performed in such a manner in [53] has shown that the number of real CE-type relations is much lower than is reported.

The uncorrelated parameters of the Arrhenius equation are obtained [52, 53] from its transformation

$$\ln k = \left(\ln A - \frac{E}{RT_{hm}} \right) - \frac{E}{R} \left(\frac{1}{T} - \left\langle \frac{1}{T} \right\rangle \right) \quad (18)$$

It is easily seen that such a transformation is a mere use of new independent variables of the scaling type [55], which in general may be different [56, 57].

The authors of [53] deal with some shortcomings of the above and other methods suggested by Exner [7], associated with the use of the linear regression alone, restrictions in the choice of $\log k$ at two-three temperatures and the required a priori knowledge of the errors in the k value, as well as the low accuracy of the Θ determination. It is also shown that the neglect of the restrictions of ordinary regression analysis in analysing ΔH vs. ΔS yields worse rather than better parameter estimates. When transformation (18) is used, $\ln k_0 - E/RT_{hm}$, being the measure of $\Delta G_{T_{hm}}^{\ddagger}$, and E/R , are noncorrelated (statistically independent):

$$\rho_{\Delta H^{\ddagger}, \Delta G_{T_{hm}}^{\ddagger}} = \frac{\sum\left(\frac{1}{T} - \left\langle \frac{1}{T} \right\rangle\right)}{\sqrt{n \sum\left(\frac{1}{T} - \left\langle \frac{1}{T} \right\rangle\right)^2}} = 0,$$

as the estimates for $\Delta \tilde{G}_{T_{hm}}^{\ddagger}$ are obtained at $T = T_{hm}$. Thus, of the possible ΔH , ΔS and ΔG pairs of values related by Eq. (10), $\Delta \tilde{G}_{T_{hm}}$ and $\Delta \tilde{H}$ may only be used to seek extrathermodynamic relations. Denoting $1/(1 - T/\Theta)$ in terms of γ gives one of them, which is necessary for further analysis, in the form $\Delta H = \gamma \Delta G + (1 - \gamma) \Delta G_{\Theta}$. The theory and algorithm of the modified regression of two variables determined with some error, which may be applied for linear and nonlinear relations, are given. In the case of linear relations for $\Delta \tilde{G}_j^{\ddagger}$ and $\Delta \tilde{H}_j^{\ddagger}$ (linearity is verified graphically), formulae are obtained to estimate isoparametric values from j data series with $\Delta \tilde{G}_j^{\ddagger}$, $\Delta \tilde{H}_j^{\ddagger}$ and residual sums of squares S_j^2 obtained a priori for each of the series from the regression

In k over $(1/T - \langle 1/T \rangle)$:

$$\Delta \tilde{G}_j^\ddagger = -RT_{hm} \tilde{\xi}_{1,j} + \left\{ RT_{hm} \ln \left(\frac{k_B T_{hm} e}{h} \right) - RT_{hm} \right\};$$

$$\Delta H_j^\ddagger = -R \tilde{\xi}_{2,j} - RT_{hm};$$

$$\tilde{\xi}_{1,j} = \frac{\sum_{i=1}^n \ln k_{ij}}{n}; \quad \tilde{\xi}_{2,j} = \frac{\sum_{i=1}^n \ln k_{ij} \left(\frac{1}{T_i} - \langle \frac{1}{T} \rangle \right)}{\sum_{i=1}^n \left(\frac{1}{T_i} - \langle \frac{1}{T} \rangle \right)^2}$$

$$S_j^2 = \frac{\sum_{i=1}^n \left(\ln k_{ij} - \tilde{\xi}_{1,j} - \tilde{\xi}_{2,j} \left\{ \frac{1}{T_i} - \langle \frac{1}{T} \rangle \right\} \right)^2}{n-2}.$$

These formulae are of the form:

$$\Theta = \frac{T_{hm}}{1 - \frac{1}{\tilde{\gamma}}}; \quad \Delta \tilde{G}_\Theta = \frac{\tilde{a}}{1 - \tilde{\gamma}}$$

where

$$\tilde{\gamma} = \frac{S_{HH} - \lambda S_{HG}}{2S_{HG}} \pm \sqrt{\left(\frac{S_{HH} - S_{HG}}{2S_{HG}} \right)^2 + \lambda};$$

$$a = \frac{\sum \frac{\Delta H_j}{S_j^2} - \tilde{\gamma} \sum \frac{\Delta G_j}{S_j^2}}{\sum \frac{1}{S_j^2}}$$

$$\lambda = \frac{\left(\sum \frac{1}{T} \right)^2}{n \sum \left(\frac{1}{T} - \langle \frac{1}{T} \rangle \right)^2}$$

$$S_{HH} = \sum \frac{\Delta H_j^2}{S_j^2} - \frac{\left(\sum \frac{\Delta H_j}{S_j^2} \right)^2}{\sum \frac{1}{S_j^2}};$$

$$S_{HG} = \frac{\sum \frac{\Delta H_j \Delta G_j}{S_j^2}}{\sum \frac{1}{S_j^2}} = \frac{\sum \frac{\Delta H_j}{S_j^2} \sum \frac{\Delta G_j}{S_j^2}}{\sum \frac{1}{S_j^2}}$$

Upper and lower boundary estimates are obtained for Θ_d^u and $\Delta \tilde{G}_d^u$ to find the $(1 - \alpha)$ 100% confidence interval:

$$\tilde{a}_d^u = \frac{\sum \frac{\Delta H_j}{S_j^2} - \tilde{\gamma}_d^u \sum \frac{\Delta G_j}{S_j^2}}{\sum \frac{1}{S_j^2}}; \quad \tilde{\gamma}_d^u = \sqrt{\lambda} \tan \tilde{\Phi}_d^u$$

where

$$\tilde{\Phi}_d^u = \tilde{\Phi} \pm \frac{1}{2} \sin^{-1} \left[2t_{\frac{\alpha}{2}, m-2} \sqrt{\frac{\lambda(S_{HH}S_{GG} - S_{HG}^2)}{(m-2)\{(\lambda S_{GG} - S_{HH})^2 + \lambda S_{HG}^2\}}} \right];$$

$$\tilde{\Phi} = \tan^{-1} \left(\frac{\tilde{\gamma}}{\sqrt{\lambda}} \right); \quad S_{GG} = \frac{\sum \frac{\Delta G_j^2}{S_j^2}}{\sum \frac{1}{S_j^2}} - \frac{\left(\sum \frac{\Delta H_j}{S_j^2} \right)^2}{\sum \frac{1}{S_j^2}}$$

For γ the zero-hypothesis will be $H_0: \gamma = 1$: the deviation of this hypothesis in the confidence interval $(\tilde{\gamma}_u, \tilde{\gamma}_d)$ is due to the presence of a linear extrathermodynamic relation with the significance level determined by α .

The above method is successfully used in [58]. Its comparison with Exner's method is exemplified in [59]. Other approaches have been developed to find the intersection point for a family of straight lines based on the least-squares method [60].

It must be emphasized, however, that inclusion of Θ in the temperature range chosen for the experiment is a necessary but not sufficient condition to ascribe only statistical meaning to Θ , as instance of real intersection of the Arrhenius lines within this interval are known to reliably evidence IR validity [7, 16, 48]. A "real traversal through isoparametric points is a challenge to . . . physico-chemical ideas on the nature of the processes under study" [16].

When the isokinetic temperature is passed, the significance of the ΔH^\ddagger and ΔS^\ddagger contributions to ΔG^\ddagger changes. Consequently, one may speak about the enthalpy or entropy control of the reaction rate. Simple regression analysis is suggested [61] to elucidate the dominating contribution of either enthalpy or entropy factor.

Elimination of the effect of confidence domain extension on the kinetic parameters is also the concern of refs [62, 63], suggesting the transformation of the linear model parameters, for instance (9), $y = a + bx$, with the aid of earlier obtained values of the parameters a_1 and b_1 : $\xi_1 = a_1 + b_1(\bar{x} - S_x)$ and $\eta_1 = a_1 + b_1(\bar{x} + S_x)$, which reduce this model to give

$$y = \xi + \frac{\eta - \xi}{2S_x} (x - \bar{x} + S_x),$$

with the confidence domain in the form of a circle

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}; \quad S_x^2 = \frac{\sum_{i=1}^n x_i^2}{n} - \bar{x}^2.$$

In [62] this version is considered from more general viewpoints.

One more situation which hinders the statistical analysis of the relations under consideration is the displacement of estimates in model linearization analysed in [64–66], or the equivalent transformations [67] and model inadequacy [68]. As $\log \epsilon(k | 1/T) \neq \epsilon(\log k | 1/T)$ (ϵ being the operator of mathematical expectation), it is first necessary to decide which of the values, k or $\log k$, satisfies the regression analysis prerequisites [69]. Consequently, either a nonlinear or a linear model may be adequate. These complications are often neglected for no reason at all.

3. Physico-chemical aspect

A profound CE analysis is necessitated concerning its relation to the fundamentals of the dynamics of chemical changes. In this respect, the contribution [70] is significant in pointing out physical and mathematical uncertainties in the deviation of the basic equation (in the theory of absolute reaction rates the Eyring equation), the limitedness of its version for nonideal systems (the Brønsted–Bjerrum equation), and the unjustified equating of the transmission coefficient κ to the unit discrepancy, inherent in a more general theory of monomolecular reactions RRKM [71]. In the theory of reaction rate constants in nonideal and condensed systems, the author of [70] uses a view that is more profound than that in the Eyring–Polanyi theory; this is the idea of the excited A molecule decay implying the difference between the active complex A^\ddagger and its transient (activated) state A^+ [71]. The basic starting principles of the theory are the quantum-mechanical energy-time uncertainty ratio, the concept of local equilibration underlying nonequilibrium thermodynamics, and the Boltzmann principle, which is the relation for entropy and thermodynamic probability, well-known in statistical physics (this is insignificant in practice [72], cf. [73]). However, the Boltzmann formula valid for the system in both equilibrium and nonequilibrium states permits the expression, in particular, of the ratio of thermodynamic probabilities of the two states through ΔG nonequilibrium states (observing the conditions of local equilibrium) [70]. If the thermodynamic probabilities of these

states are proportional to the frequencies of their onset, this ratio may give an expression for the frequency of onset of one of the states. In this expression, the frequency of onset of the other state is determined by the universal frequency scale found from the above uncertainty relation. The extension of this theory to the reaction involving the stages of A^\ddagger and A^+ formation yields an equation for the rate constant which only formally differs from the Eyring equation by the constant factor in the transmission coefficient $\kappa = 4\pi e\kappa'$. Here, e is the base of natural logarithms; κ is the transmission coefficient for the probability of onset in the active complex A^\ddagger of the transient state A^+ , i.e. having a different meaning from that of the same coefficient in the Eyring equation; the value of κ consistent with κ' is very small [74]. The other terms of the equation which formally coincide with the terms of the Eyring equation also have essentially different meanings. The frequency factor is the maximum frequency at which a closed macrosystem or quasistationary microsystem can change its energy for $k_B T$ (k_B being the Boltzmann constant); the term $\exp(-\Delta G^\ddagger/RT)$ characterizes the relative probability of the active complex onset without the conditions of thermodynamic equilibrium of a conventional system. The active complex here is considered as a nucleus formed by reactant molecules in a solvate shell; it is thus included in the state A^\ddagger , and its formation may be expressed in terms of chemical reactions proceeding at some degree of completeness ξ . ΔG^\ddagger and κ may change due to changing composition and properties of this shell. The conclusion is drawn that A^\ddagger and A^+ can be studied experimentally. On the basis of the above concepts, the isokinetic effect theory has been developed, providing the method of κ estimation and being of immediate interest. In short, it involves the following [75]. For some reaction q under consideration with empirical (i.e. found on the assumption of $\kappa = 1$) ΔH_q^\ddagger , $\Delta G_{q,\text{emp}}^\ddagger$ and $\Delta S_{q,\text{emp}}^\ddagger$ ($\Delta H_q \equiv \Delta H_{q,\text{emp}}$), the A^\ddagger formation process is r natural reactions (formation of an active complex nucleus, rearrangement of the medium around A^\ddagger , excitation of A^\ddagger molecules). The change in the completeness degree ξ_α ($\alpha = 1, 2, \dots, r$) for these reactions or in their kinetically independent linear combinations ζ_β provides an unstable state to cause chemical changes. The state of a nonequilibrium system is characterized by external (T, P) and internal (ξ_α and ζ_β) variables. If there are f such systems, and at definite T and P a reaction q of one and the same type proceeds in them through an active complex of volume v formed by a reaction ζ_β different from q common to all f systems (the first sufficient CE condition), then the thermodynamic functions of a closed area v are equal for all f systems and only depend on ζ_β . The reaction completeness degree β during A^\ddagger formation in the i -th system is denoted as $\zeta_{\beta_i}^\ddagger$ and, in a general case, is different for different i ($i = 1, 2, \dots, f$). The change in G^\ddagger of reaction q in the i -th system is given as

$$\Delta G_{q_i}^\ddagger = G_q' \Delta \zeta_{\beta_i}^\ddagger \quad (19)$$

where G_q' is the change in G if any of f systems with ζ_β changing by unity; $\Delta \zeta_{\beta_i}^\ddagger$ is the change in $\zeta_{\beta_i}^\ddagger$ necessary for the i -th system to achieve an active state. Similar expressions are also obtained for other thermodynamic functions. If, in this case,

the values of G'_q type are approximately equal for all the systems where reaction q proceeds (the 2nd CE condition), then, as the relation between real and empirical activation parameters are prescribed as

$$\Delta G_q^\ddagger = \Delta G_{q,\text{emp.}}^\ddagger + RT \ln \kappa \quad (20)$$

$$\Delta S_q^\ddagger = \Delta S_{q,\text{emp.}}^\ddagger - RT \ln \kappa \quad (21)$$

using the equation of type (19) for the i and j pair from f similar reactions of the series q , we arrive at

$$\frac{\Delta S_{\beta_i}^\ddagger}{\Delta S_{\beta_j}^\ddagger} = \frac{\Delta H_{q_i}^\ddagger}{\Delta H_{q_j}^\ddagger} = \frac{\Delta S_{q_i,\text{emp.}}^\ddagger - R \ln \kappa_{q_i}}{\Delta S_{q_j,\text{emp.}}^\ddagger - R \ln \kappa_{q_j}} \quad (22)$$

If κ_{q_i} for i reactions of q type are similar (the 3rd CE condition) and equal to κ , then (22) gives the CE

$$\Delta H_{q_i}^\ddagger = g + \Theta \Delta S_{q_i,\text{emp.}}^\ddagger \quad (23)$$

with the constants

$$g = -\frac{\Delta H_{q_i}^\ddagger R \ln \kappa}{\Delta S_{q_i,\text{emp.}}^\ddagger - R \ln \kappa} = -\frac{\Delta H_{q_i}^\ddagger R \ln \kappa}{\Delta S_{q_i}^\ddagger}; \quad \Theta = -\frac{g}{R \ln \kappa} = \frac{\Delta H_{q_i}^\ddagger}{\Delta S_{q_i}^\ddagger} \quad (24)$$

For a particular case (23) when $\Delta H_{q_i}^\ddagger = g$, i.e. $\Theta = 0$, the activation enthalpy is independent of the reaction completeness degree β . The true value of κ is determined by Θ and g from (24) (an appropriate statistically correct method should evidently be used for Θ and g estimation). The equality $\kappa_{q_i} = \kappa$ resulting in (23) is considered [70] as a quantitative formulation for the i -th system's belonging to one reaction series q within which the reaction mechanism (composition and structure of the active complex nucleus and its solvate shell) remains constant. The validity of (23) with the violation of this equality is the sign of an apparent CE stipulated by persistent changes in κ . Upon determination of κ from (23) and (24) by formulas (20) and (21), real activation parameters may be estimated. Equation (23) includes $\Delta S_{q_i,\text{emp.}}^\ddagger$, but using (21), the CE may be obtained from (24) for $\Delta S_{q_i}^\ddagger$ ($\Delta H_{q_i}^\ddagger = \Theta \Delta S_{q_i}^\ddagger$) as well, i.e. not only for empirical parameters found at $\kappa = 1$, but also for real activation parameters within one series. In [75] the CE is compared for the latter with the thermodynamic relation $\Delta H = T\Delta S$. The main difference is that Θ is not equal to the T of the system and may be less than zero (here, the term "isokinetic temperature" loses its meaning). At $T = \Theta$ ($\Theta > 0$) we have $\Delta H_{q_i}^\ddagger = T\Delta S_{q_i}^\ddagger$, i.e. $\Delta G_{q_i}^\ddagger = 0$ ($\Delta G_{q_i,\text{emp.}}^\ddagger = -R\Theta \ln \kappa$). Thus, at the isokinetic temperature all reactions of one kind have equal rates with a reversible normal reaction of A^\ddagger formation. The isokinetic temperature Θ has the meaning of the vibrational temperature of the complex A^\ddagger nucleus. In [70, 75] the CE means that local heating of the system (enthalpy growth) involves, as is always the case, local disordering (entropy growth), the latter being true of the A^\ddagger ambient

medium rather than of the complex A^\ddagger itself. Negative values of Θ are possible at $\Delta S_{q_i}^\ddagger < 0$ ($\Delta H_{q_i}^\ddagger > 0$), i.e. with system ordering in the course of formation of nucleus A^\ddagger and its shell. At $\Theta = 0$, the κ values of uniform reactions are different. It is concluded by Shahparonov that profound study of the reaction mechanism (determination of the thermodynamic functions A^\ddagger and κ) requires that isokinetic relations be sought. This problem cannot as yet be solved by other methods. The theory under consideration has already been used to interpret different cases of the IR effect [76–78], including heterogeneous processes [79, 80]. In the latter, Θ is in correlation with the T_{melt} (or T_{boil}) of the absorbent. The development of the theory has shown [37] that, in a general case, the CE is nonlinear and the widespread Hammett and Taft equations may be deduced from the CE in such a manner that the incorporated empirical parameters obtain complete theoretical interpretation. The CE interpretation under consideration is at present one of the most general. However, it has not yet been applied directly to solid-phase reactions. Among other general approaches, the thermodynamic ones considered below are of greatest interest.

It is shown by a number of examples [81] that the entropy change is mainly determined by the number of chemical bonds formed or broken during reaction (cf. Kobosev rule [82]). Therefore, for processes with a changing number of uniform or, more so, similar bonds, there exists a linear dependence between ΔS and ΔH . The angular coefficient in this dependence increases with growing strength of the bond. Similar relationships have been established in the kinetics of heterogeneous catalytic reactions for ammonia oxidation, and the soft and deep oxidation of propylene, the corresponding angular coefficient being in correlation with the experimental values of binding energy for the surface oxygen of oxide catalysts. The chemical bond is loosened, rather than broken in some governing process, and the electronic cloud of the reactant is deformed by the catalyst [83]. Following [81], a similar relationship is preserved between the loosening energy and entropy.

The thermodynamic CE interpretation by Rudakov [84] has remained poorly known. He distinguishes between false (incorrect account of the process mechanism, effect of foreign factors), trivial (of $T\Delta S = \Delta H$ type for phase transitions) and true CEs. The latter without being confined to similar molecules, occur only in condensed systems. Following Rudakov, therefore, the general reason for CEs is to be found in the specificities of collective molecular interactions. In this connection, CEs must show up in the state functions of individual substances and, specifically, when full thermodynamic functions F, U, S are replaced by the interaction functions

$$\hat{F} = F^* - F; \quad \hat{U} = U^* - U; \quad \hat{S} = S^* - S \quad (25)$$

(* stands for the conventional state, namely a quantum ideal gas at T, V and the composition of the real system obeying the same statistics), where F is the Helmholtz energy; and U is the internal energy. The function \hat{F} is equal to the interaction break in the system, i.e. to its transition to the state * at $T, V = \text{const.}$; \hat{U} is the total measure of energy consumption upon interaction break (internal interaction energy); \hat{S} is the measure of system ordering upon the interaction break. To understand the meaning of

\hat{F} , \hat{U} and \hat{S} , it is important to note that their signs are contrary to those of F , U and S . Therefore, as the system ordering increases, so does \hat{S} , which is always ≥ 0 , and the positive value of \hat{U} corresponds to the negative potential energy of the system. In fact, the use of \hat{F} , \hat{U} and \hat{S} resulted in the CE appearing in unique relations for gaseous, liquid and crystal solids. The general CE equation has the form

$$\hat{S} = \hat{S}_0 + \frac{b}{298} \hat{U} \quad (26)$$

\hat{S}_0 and b for the above three aggregate states being 0 and 0.5; 2 and 0.4; and 10 and 0.02, respectively. This emphasizes the generality of all the CEs obtained. To be specific, the CE line for crystals (per lattice node) includes diverse substances such as metals, halides, oxides, nitrides and carbides. The relation is shown for \hat{S}_0 , i.e. model entropy, for which $\hat{U} = 0$, and 'collective entropy' R (universal gas constant): for gases $\hat{S}_0 = 0 \cdot R$, for liquids $\hat{S}_0 = R$, and for solids $\hat{S}_0 \approx 5R$. The quantity b is interpreted as the system compliance to the change in the energy of interaction between structural elements. There is a correlation between \hat{S}_0 and b for the three aggregate states. When the interaction functions are used, the compensation parameters \hat{S}_0 and b become the characteristics of the structure of the given aggregate state. They show, for example, that the liquid state of a substance is closer to a gaseous than to a crystal state. Following [84], the sense of the thermodynamic CE with collective interactions implies variations of the system ordering as the interaction energy of the particles constituting the system changes. Because of the comprehensive character of the particle-to-particle interactions, the CE of this nature extends to kinetic, viscous, sorption and other processes. Hydrophobic interactions, with changes in the entropy and energy of solvation due to long-range parameters rather than direct interaction between a particle and solvate shell, are the only ones where the CE shows itself within the homologous series alone when the change in the chain by $-\text{CH}_2-$ leads to equal increments in \hat{U} and \hat{S} . The author also shows that, in the general case, the CE is nonlinear. The nonlinear CE in terms of interaction functions, as well as its applications, are considered in [85].

Although the reason for the CE as a connection between the ordering and interaction energy had been found earlier [86–90], Rudakov was the first to show this connection quantitatively and in the most general form, thereby adding a clear physical meaning to this relationship.

CE analysis on the basis of statistical thermodynamics [91] shows that there is no linear dependence between ΔG and ΔH . The CE $\Delta S = A_1 \Delta H + B_1$ may be represented as

$$R\Delta \ln \frac{\Theta}{NV} + R\Delta \left[T \frac{\partial \ln \left(\frac{Q}{V} \right)}{\partial T} \right] = A_1 \left\{ \Delta E_0 + R\Delta \left[T^2 \frac{\partial \ln \left(\frac{Q}{V} \right)}{\partial T} \right] \right\} + B_1$$

where Q is the statistical sum; E_0 is the lowest level energy; N is the Avogadro number; and V is the volume. To make it linear it is necessary, for example, that

$$RT \frac{\partial \ln \left(\frac{Q}{V} \right)}{\partial T}$$

be an integral multiple of $R/2$ and that there exist a linear relationship between ΔE_0 and $\Delta \ln (Q/NV)$. The former is possible with the dissolution of gases in a liquid in the case of complete excitation of harmonic oscillator vibrations in a free-volume well in a liquid phase and of translational and rotational movements in a gas phase. The latter occurs if some interaction alters E_0 and, at the same time, the intervals between the vibration levels, thereby changing Q . Upon gas dissolution, E_0 decreases while the intervals between the levels expand, i.e. Q decreases.

A rather general explanation of the CE for various processes has recently been suggested in [92], through the analysis of changes in the potential energy surface and the energy levels of a transient state. These changes are interdependent. Further, shifting of the energy levels involves a variation of the activation entropy, while changes in the potential energy saddle alter the activation energy. Therefore, for example, a reduction of E during adsorption causes entropy losses compensating for this reduction. The explanation is discussed in [93], while an interpretation is given in [94]. CE is considered on the basis of statistical thermodynamics in [95].

Conclusion

Some progress has been made in different fields of physical chemistry in interpreting the isoparametric relation from general standpoints. As a result, this mysterious regularity has been clearly interpreted physically, primarily from the position of thermodynamics, including irreversible thermodynamics. IR permits the determination of a number of quantities which could otherwise hardly be determined, if at all (true activation parameters, transmission factor [70, 96], number of degrees of freedom of activation [97]) and the interpretation of many empirical parameters [37]. Important statistical aspects of the CE relations are elucidated, and correct statistical methods for their detection and distinction from the artefacts widespread in this field are developed. The inherent connection between such relations and formalized descriptions of multiparametric dependences is shown. However, as Part II of our survey will show, these advances are not used practically when analysing compensation relationships for solid-phase reactions. We think that progress can be made in this field by using the advances of other areas of physical chemistry, although this may seem difficult owing to the specific nature of solid-phase reactions. Some endeavours of this kind will be presented in Part II.

List of signs*Symbols*

A	preexponent factor in Arrhenius equation
$B; e$	parameters in compensation relation
E	activation energy
$f(\alpha)$	kinetic function
g	parameter in isokinetic relation
ΔH^\ddagger	enthalpy of activation
ΔS^\ddagger	entropy of activation
t	time
α	degree of substance transformation
Θ	isokinetic temperature
<i>1. Formal aspect</i>	
a, b	parameters in linear energies relation
$a_i; a_j; a_{ij}; a_{ijl}$	scale factors
$f; f(x_1, x_2, \dots$ $\dots, x_i, \dots, x_n)$	response function in polylinear relation
$f^0; f_w^0; f(x_1^0, x_2^0, \dots$ $\dots, x_i^0, \dots, x_n^0)$	standard values of function
ΔG	free Gibbs energy
ΔG^0	standard value of free energy in definite condition
$\epsilon; \epsilon_i; \epsilon_{ij}$	energy at definite factor or combination of factors
k	constant of action
R	universal gas constant
T	temperature
$x_i; x_j; x_l; x_w$	arguments of polylinear relation
$x_i^j; x_j^i; x_l^j$	variables depending on the arguments $x_i; x_j; x_l$
x_i^0	standard value of argument
$Q; R; X; Z;$	
$l; q; r; x; y; z$	interdependent values in series of isoparametric relations
α	constant characterizing kind of interaction in polylinear relation
ρ	Hammett constant
$\varphi_l; \varphi_m; \varphi_w$	scale factors
<i>2. Statistical aspect</i>	
a, b	axis of ellipsis
f	number of degrees of freedom
ΔG^\ddagger	free Gibbs energy of activation
H_0	null-hypothesis

k_e	constant of action determined at point e
l	number of Arrhenius line
m	number line points
r	correlation estimator
S	standard deviation
S_0	residual sum of squares in assumption that all lines intersect at one point
s_0	error corresponding to S_0
S_{00}	residual sum of squares for normal regression lines
s_{00}	error corresponding to S_{00}
S_u	residual sum of squares characterizing confidence interval of intersection point
s_u	standard deviation corresponding to S_u
S_∞	asymptote of S_u
T_{hm}	mean harmonic temperature
$P; Q; U; X; Z;$	
$p_i; u_j; u_0$	auxiliary values in statistical analysis by method [7]
α	value characterizing level of meaningfulness
ϵ	operator of mathematical expectation
η, ζ	parameters of transformed pattern [62, 63]
ρ	correlation coefficient
φ	angle of slope of lines $\log k_1$ on $\log k_2$
χ^2	statistical criterion
$a; S_j^2; S_{GG}; S_{GH}; S_{HH};$	
$V(\Theta); \gamma; \xi_j; \lambda; \Phi$	auxiliary values in statistical analysis by method [53]
a_d^u	upper and lower boundary estimates of different values, for example a
$\overline{\ln k}$	mean values in statistical analysis by method [45–47] and [7], for example $\ln k$
$\langle T \rangle$	mean values in statistical analysis by method [53], for example T
$\widetilde{\ln k}$	estimated values, for example $\ln k$

3. Physico-chemical aspect

A, B	parameters of compensation relation in statistical thermodynamic
A^+	symbol of activated state
A^\ddagger	symbol of active complex
E_0	lowest level energy
F	Helmholtz energy
$F^*; U^*; S^*$	thermodynamic functions for quantum ideal gas
$\hat{F}; \hat{U}; \hat{S}$	thermodynamic function of interaction

f	number of nonequilibrium system
G_q'	change in G if any of f systems with ξ_β changing by unity
N	Avogadro number
Q	statistical sum
q	symbol of reaction type
r	number of natural reactions at formation of A^\neq
$\hat{S}_0; b$	parameters in compensation relation (26)
U	internal energy
V	volume
v	volume of active complex
ξ_β	completeness degree of linear combination of natural reactions β
ξ_β^\neq	completeness degree of reaction q at A^\neq formation
$K; K'$	transmission coefficients
ξ	completeness degree of natural reactions α

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Zusammenfassung — Der sich auf isoparametrische Korrelationen beziehende Kompensations-effekt wird im Rahmen der formalen Theorie analysiert. Statistische und physikalisch-chemische Aspekte dieser Korrelationen werden erörtert.

Резюме — С позиций формальной теории рассмотрен компенсационный эффект, относящийся к разновидности изопараметрических зависимостей. Рассмотрены также статистический и физико-химический аспекты таких зависимостей.