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COMPENSATION EFFECT AND ISOKINETIC TEMPERATURE IN THERMAL DISSOCIATION REACTIONS OF THE TYPE $A_{solid} \rightleftharpoons B_{solid} + C_{gas}$

INTERPRETATION OF THE ARRHENIUS EQUATION AS A PROJECTION CORRELATION

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It is shown that the Zawadzki — Bretsznajder rule, compensation effect, and isokinetic temperature are simple consequences of interpretation of the Arrhenius equation as a projection correlation. It is established that such an interpretation of the Arrhenius equation allows the discrimination of the deviation factors which impart a definite (although not always simple and recognized) physical sense, to the known empirical correlation. A possibility of deriving new correlation relationships by this method of reasoning is presented.

Thermal dissociation of solids, crystalline starting materials or mineral raw materials is usually carried out to obtain solid products of required chemical and phase compositions, appropriate activity and utilizability for further technological applications, or to obtain desired gaseous products. Typical, trivial examples of such processes are: the thermal decomposition of limestones in the sugar industry and in the production of building materials; the decompositions of chromium(III), magnesium (II), strontium(II), manganese(II) and other carbonates in the production of oxide catalysts; the dissociation of carbonyls and iodides in the preparation of metals of very high purity; the dehydration of crystalline hydrates in the production of surface-active agents; and many others.

The practical utilization of thermal decomposition reactions is responsible for the fact that the knowledge of the mechanisms and the rates of these reactions is one of the most important problems of contemporary chemical investigations. The solution of these problems is a very difficult and time-consuming task, but it allows the intensification of very important technological processes.

The very complex nature of topochemical processes of the type

$$A_{solid} \rightleftharpoons B_{solid} + C_{gas}$$

led to the fact that, since the first Lewis work on this subject (published in 1905), no attempt to give a general theory of such processes has been made until today. However, some regularities concerning the courses of these processes have been known for many years, and more and more attempts towards their theoretical elucidation have been observed recently.

The aim of the present work was to find a relationship between one of these regularities, usually referred to as the Zawadzki–Bretsznajder rule, and the compensation effect, which is recognized as one of the fundamental laws of chemical kinetics. We also aimed to prove that a direct consequence of this rule is the existence of the isokinetic temperature, a knowledge of which allows calculation of the constant term in the compensation equation.

Compensation effect and isokinetic temperature in a thermal dissociation reaction of the type $A_{solid} \rightleftharpoons B_{solid} + C_{gas}$

During studies on the thermal dissociation of calcium carbonate under different pressures of the gaseous reaction product, Zawadzki and Bretsznajder [1] were first to observe that the activation energy of the process was a function of the pressure of the gaseous reaction product

$$E = f(p_{CO_2}) \tag{1}$$

and it increased (in the decomposition of $CaCO_0$ from E = 40 kcal/mole for p = = 10^{-3} mm Hg to E = 376 kcal/mole for p = 45 mm Hg) with increasing CO_2 pressure. Similar relationships were later observed for carbonates, hydroxides, oxides and peroxides, sulfates and basic sulfates, oxalates, ammonium complexes, and crystalline hydrates.

The Zawadzki–Bretsznajder rule was theoretically confirmed by Pavluchenko and Prodan [2] in 1961 after a thorough analysis of a reversible reaction of the type $A_{solid} \rightleftharpoons B_{solid} = C_{gas}$. These workers derived the following expression for the activation energy of thermal dissociation at constant temperature:

$$E = E_2 + \lambda + mQ \frac{p_0^m}{p_0^m - p^m} \tag{2}$$

where E_2 = activation energy of the association process (e.g. synthesis of $CaCO_3$ from CaO and CO_2);
λ = adsorption (or desorption) heat of the gaseous reaction product;
Q = heat of dissociation;
p_0 = decomposition pressure (equilibrium pressure of the gaseous product at the temperature of the reaction);
p = pressure of the gaseous product in the reaction system;
m = constant; $0 \leq m \leq 1$.

For $p^m \to 0$ (i.e. for high vacuum)

$$\lim \frac{p_0^m}{p_0^m - p^m} = 1$$

and:

$$E = E_2 \pm \lambda + mQ \tag{3}$$

whereas for $p^{\mathrm{m}} \to p_0^{\mathrm{m}}$

$$\lim \frac{p_0^{\mathrm{m}}}{p_0^{\mathrm{m}} - p^{\mathrm{m}}} = \infty$$

and:

$$E = \infty . \tag{4}$$

Hence for $0 \leq p \leq p_0$ we have

$$E_2 \pm \lambda + mQ \leq E \leq \infty \tag{5}$$

and Eq. (5) becomes equivalent to the Zawadzki–Bretsznajder rule (1).

Relationships (1) and (5) may be represented in the coordinate system $\ln k, \frac{1}{T}$, i.e. in the Arrhenius diagram, and they can be described by the Arrhenius equation

$$\ln k = A - \frac{E}{RT} \tag{5a}$$

or:

$$k = A \cdot \exp\left(-\frac{E}{RT}\right) \tag{5b}$$

where: k = dissociation rate constant;
A = pre-exponential coefficient;
R = gas constant;
T = absolute temperature.

If, according to Eqs (1) and (5), the value of E increases considerably due to an increase in p, then the increase of E can not be compensated by the increase of T alone, but the value of A in Eq. (5b) must also be changed. The relation between A and E is represented by an empirical equation, usually referred to as the compensation equation [3]:

$$\ln A = a + b + E \tag{6}$$

where a and b are constants.

The compensation equation represents a kind of general relationship, since a compensation effect has been observed in many catalytic reactions, during

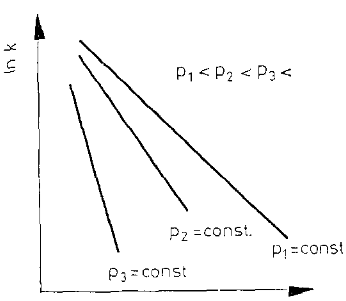

Fig. 1

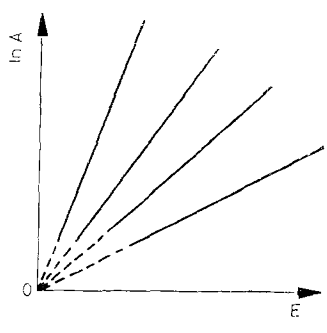

Fig. 2

measurements of viscosity and diffusion, in studies on electric conductance and electron emission, in biological processes and in the thermal dissociations of many solids (see 3 and literature included there). Relation (6) can be represented graphically in the coordinate system $\ln A$, E (Fig. 2).

For reactions of the type discussed here the value of A is usually equal to 0, and the values of b can be found from the slopes of the lines.

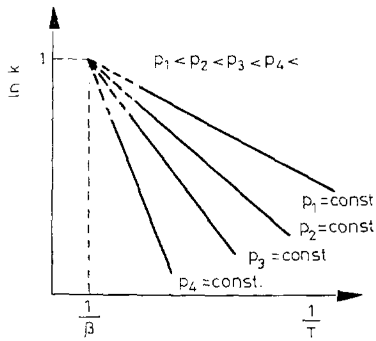

Fig. 3

During studies on the decomposition of carbonates and the dehydration of crystalline hydrates we have observed [4] that for a process carried out at different pressures of the gaseous reaction products it is possible to find a temperature β referred to as the isokinetic temperature, at which the reaction proceeds with a fixed value of the rate constant (Fig. 3).

A knowledge of the isokinetic temperature β allows determination of the coefficient b in compensation equation (6).

At certain temperatures T_1 and T_2 under pressures p_1 and p_2, let $\ln k_1 = \ln k_2$. Hence:

$$\ln A' - \ln A'' = \frac{E'}{RT_1} - \frac{E''}{RT_2}. \tag{7}$$

In order to obtain Eq. (6) it is necessary to assume $T_1 = T_2 = \beta$ in Eq. (7). Then:

$$\Delta \ln A = \frac{\Delta E}{R \cdot \beta} \tag{8}$$

and from Eqs (6) and (8) one obtains

$$b = \frac{1}{R \cdot \beta}. \tag{9}$$

In subsequent parts of the present paper it will be shown that the empirical relations (6) and (9) and their correlation can be theoretically justified if the given process of thermal dissociation can be described by the Arrhenius equation.

Therefore we shall prove that:

(1) the existence of the isokinetic temperature β is a necessary condition for the appearance of the compensation effect;

(2) the appearance of the compensation effect is evidence of the existence of the isokinetic temperature β; which is equivalent to the statement about the existence of a line-pencil relationship between k, E, T and A, provided that these quantities are interrelated by the Arrhenius equation.

Mathematical justification of the existence of the isokinetic temperature and compensation effect

The basis for further considerations will be the Arrhenius equation (5a) rearranged to the following form:

$$\ln k + E \cdot \frac{1}{RT} - \ln A = 0. \tag{10}$$

If we put $\frac{1}{T} = x$ and $\ln k = y$ in Eq. (10), then for given values of A and E ($R = $ const) we obtain a linear equation:

$$y + \frac{E}{R} \cdot x - \ln A = 0. \tag{11}$$

It frequently occurs in practice that, under certain assumptions, the lines (11) have a common point (x_0, y_0) for different values of A and E, i.e. they form a pencil.

In such cases it appears that:

Theorem 1. If the lines represented by Eq. (11) form a pencil, a linear relationship exists between $\ln A$ and E (the compensation equation is valid).

Proof: Let Eq. (11) be fulfilled for certain (y_0, x_0) and $E_1, E_2, E_3, A_1, A_2, A_3$, i.e. let:

$$y_0 + \frac{E_1}{R} x_0 - \ln A_1 = 0 \tag{12}$$

$$y_0 + \frac{E_2}{R} x_0 - \ln A_2 = 0 \tag{13}$$

$$y_0 + \frac{E_3}{R} x_0 - \ln A_3 = 0. \tag{14}$$

By subtracting Eq. (13) from (12) and Eq. (14) from (13), we obtain, after rearrangement:

$$\ln A_2 - \ln A_1 = \frac{x_0}{R} (E_2 - E_1) \tag{15}$$

$$\ln A_3 - \ln A_2 = \frac{x_0}{R}(E_3 - E_2). \tag{16}$$

If it is assumed that $E_1 \neq E_2$ and $E_3 \neq E_2$, we can divide Eq. (15) by $(E_2 - E_1)$, and Eq. (16) by $(E_3 - E_2)$ to obtain the following relation:

$$\frac{x_0}{R} = \frac{\ln A_2 - \ln A_1}{E_2 - E_1} = \frac{\ln A_3 - \ln A_2}{E_3 - E_2} \tag{17}$$

which means that the quotient of differences $\frac{\Delta \ln A}{\Delta E}$ is constant, as the selection of E_1, E_2, E_3 was completely arbitrary.

If the quotient of differences is constant (see Lemma 1 below), the derivative with regard to the variable is also constant, which means (compare Lemma 2 below) that the relationship between the value of the function and the variable is linear.

Hence if $\frac{\Delta \ln A}{\Delta E}$ = const., then $\frac{\partial \ln A}{\partial E}$ = const. too, and for certain constants a and b we have $\ln A = a + bE$, which was to be proved.

Lemma 1. If a quotient of differences $\frac{\Delta f(x_0)}{\Delta x}$ = const. for all x_0, then the derivative $\frac{\partial f}{\partial x}$ = const.

Proof: From the definition of the derivative it is known that:

$$\frac{\partial f(x)}{\partial x} = \lim_{h \to 0} \frac{f(x_0 + h) - f(x_0)}{h}.$$

Let us assume a sequence $h_n \to 0$, such that $h_n \neq 0$ for all n; from Heine's definition of convergence of a function we have:

$$\lim_{h \to 0} \frac{f(x_0 + h) - f(x_0)}{h} = \lim \frac{f(x_0 + h_n) - f(x_0)}{h_n};$$

besides: $$\frac{f(x_0 + h_n) - f(x_0)}{h_n} = \frac{\Delta f(x_0)}{\Delta x}, \text{ where } \Delta x = h_n.$$

From the assumption above, $\frac{\Delta f(x_0)}{\Delta x}$ = const., which means that the sequence $a_n = \frac{f(x_0 + h_n) - f(x_0)}{h_n}$ is constant for all x_0, and the limit of the sequence is a_n for all x_0. Hence, $\frac{\partial f}{\partial x}$ is always constant, which was to be proved.

Lemma 2. Let the derivative $\frac{\partial f}{\partial x}$ be constant; then f is a linear function of x, i.e. for certain constants a and b we have $f(x) = a + bx$ for all x.

Proof: From Lagrange's theorem, on the average it follows that for any quantities x, y there exists a $\theta \in (0,1)$ such that

$$\frac{f(y) - f(x)}{y - x} = f'[x + \theta(y - x)]$$

if the function f is differentiable in the interval $\langle x, y \rangle$. Let us assume an interval $\langle x_0, x \rangle$; for a certain θ we have:

$$\frac{f(x) - f(x_0)}{x - x_0} = \frac{\partial f}{\partial x} [x_0 + \theta(x - x_0)].$$

Since $\frac{\partial f}{\partial x} = b$, where b is a const., then

$$\frac{f(x) - f(x_0)}{x - x_0} = b.$$

The mode of reasoning will not change on changing x_0. In such a case we have $f(x) = f(x_0) + b(x - x_0)$; let $a = f(x_0) - b \cdot x_0$, and hence $f(x) = a + bx$, which was to be proved. It has appeared that Theorem 1 may be reversed.

Theorem 2. If $\ln A$ is a linear function of E, then the straight lines described by Eq. (11) form a pencil.

Proof: Let us have E_1, E_2, E_3, A_1, A_2, A_3 such that for certain constants a and b we can write:

$$\ln A_1 = a + b \cdot E_1$$

$$\ln A_2 = a + b \cdot E_2$$

$$\ln A_3 = a + b \cdot E_3.$$

For given values of E and A we obtain the following linear equations:

$$y + \frac{E_1}{R} x - \ln A_1 = 0 \tag{18}$$

$$y + \frac{E_2}{R} x - \ln A_2 = 0 \tag{19}$$

$$y + \frac{E_3}{R} x - \ln A_3 = 0. \tag{20}$$

If the straight lines represented by Eqs (18–20) are to form a pencil, a necessary and sufficient condition is [7] that the matrix of the system of equations be equal to 0. It should therefore be proved that:

$$\begin{bmatrix} 1, & \frac{E_1}{R}, & -\ln A_1 \\ 1, & \frac{E_2}{R}, & -\ln A_2 \\ 1, & \frac{E_3}{R}, & -\ln A_3 \end{bmatrix} = 0.$$

It should be noted that:

$$\begin{bmatrix} 1, & \frac{E_1}{R}, & -\ln A_1 \\ 1, & \frac{E_2}{R}, & -\ln A_2 \\ 1, & \frac{E_3}{R}, & -\ln A_3 \end{bmatrix} = \begin{bmatrix} 1, & \frac{E_1}{R}, & -a - bE_1 \\ 1, & \frac{E_2}{R}, & -a - bE_2 \\ 1, & \frac{E_3}{R}, & -a - bE_3 \end{bmatrix} = 0$$

since it is a necessary and sufficient condition that a linear relationship exists between the lines or the columns of that matrix. In our case we have:

$$\begin{bmatrix} -a - bE_1 \\ -a - bE_2 \\ -a - bE_3 \end{bmatrix} = -a \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} - bR \begin{bmatrix} \frac{E_1}{R} \\ \frac{E_2}{R} \\ \frac{E_3}{R} \end{bmatrix}$$

which means that the third column is a linear combination of the first and second columns with coefficients $-a$, $-bR$. Since the columns of the obtained matrix are linearly correlated, the matrix is equal to 0, which was to be proved.

Theorems 1 and 2 may be formulated jointly in the following way:

Theorem 3. If the quantities k, E, T, A are intercorrelated by Eq. (10), then: The quantities $\ln A$ and E are linearly correlated if and only if there is a pencil relationship between $\ln k$ and $\frac{1}{T}$ (i.e. the lines (11) form a pencil).

This interesting fact leads to the conclusion that a dual relationship holds here, that is:

Theorem 4. If the quantities k, E, T, and A are intercorrelated by Eq. (10) then:
A pencil relationship between $\ln A$ and E exists if and only if there is a linear relationship between $\ln k$ and $\frac{1}{T}$.

Proof: The proof, intuitively obvious, is analogous to the proofs for Theorems 1 and 2 and requires only some changes in the substitution in Eq. (10). By substitution of $E = x$ and $\ln A = y$ in Eq. (10) we obtain:

$$\ln k + x\frac{1}{RT} - y = 0. \tag{21}$$

In order to prove Theorem 4 we can follow the procedure applied in the proof of Theorem 1. Let us assume that the straight lines (21) form a pencil; then for certain x_0, y_0, k_1, k_2, k_3, T_1, T_2, T_3 the following relationships will hold:

$$\ln k_1 + x_0\frac{1}{RT_1} - y_0 = 0 \tag{22}$$

$$\ln k_2 + x_0\frac{1}{RT_2} - y_0 = 0 \tag{23}$$

$$\ln k_3 + x_0\frac{1}{RT_3} - y_0 = 0. \tag{24}$$

By following the procedure applied above for Eqs (12–14), we get:

$$-\frac{x_0}{R} = \frac{\ln k_3 - \ln k_2}{\frac{1}{T_3} - \frac{1}{T_2}} = \frac{\ln k_2 - \ln k_1}{\frac{1}{T_2} - \frac{1}{T_1}} \tag{25}$$

which means that the quotient of differences $\frac{\Delta \ln k}{\Delta \frac{1}{T}}$ is always constant, as the values k_1, k_2, k_3, T_1, T_2, T_3 were selected completely arbitrarily. Upon making use of Lemmas 1 and 2, we may conclude that $\ln k$ and $\frac{1}{T}$ are linearly correlated.

On following a procedure analogous to that applied in the proof of Theorem 2, we assume that $\ln k$ and $\frac{1}{T}$ are linearly correlated. Let us take k_1, k_2, k_3, T_1, T_2, T_3 such that $\ln k_1 = a + b\frac{1}{T_1}$, $\ln k_2 = a + b\frac{1}{T_2}$ and $\ln k_3 = a + b\frac{1}{T_3}$, where a and b are constants.

For k and T thus selected we have the following linear equations:

$$\ln k_1 + x\frac{1}{RT_1} - y = 0 \tag{26}$$

$$\ln k_2 + x\frac{1}{RT_2} - y = 0 \tag{27}$$

$$\ln k_3 + x\frac{1}{RT_3} - y = 0. \tag{28}$$

Similarly as in Theorem 2, straight lines represented by Eqs (26–28) form a pencil if and only if :

$$\begin{vmatrix} \ln k_1, & \frac{1}{RT_1}, & -1 \\ \ln k_2, & \frac{1}{RT_2}, & -1 \\ \ln k_3, & \frac{1}{RT_3}, & -1 \end{vmatrix} = 0.$$

Making use of the fact that the first column is a linear combination of the second and the third columns, we have:

$$\begin{vmatrix} \ln k_1, & \frac{1}{RT_1}, & -1 \\ \ln k_2, & \frac{1}{RT_2}, & -1 \\ \ln k_3, & \frac{1}{RT_3}, & -1 \end{vmatrix} = \begin{vmatrix} a+b\frac{1}{T_1}, & \frac{1}{RT_1}, & -1 \\ a+b\frac{1}{T_2}, & \frac{1}{RT_2}, & -1 \\ a+b\frac{1}{T_3}, & \frac{1}{RT_3}, & -1 \end{vmatrix} = 0$$

and:

$$\begin{bmatrix} a+b\frac{1}{T_1} \\ a+b\frac{1}{T_2} \\ a+b\frac{1}{T_3} \end{bmatrix} = -a\begin{bmatrix} -1 \\ -1 \\ -1 \end{bmatrix} + Rb\begin{bmatrix} \frac{1}{RT_1} \\ \frac{1}{RT_2} \\ \frac{1}{RT_3} \end{bmatrix}$$

hence the straight lines (26)–(28) form a pencil, which was to be proved.

Theorems 3 and 4 lead to the formulation of very interesting definitions.

Definition 1. A pair of quantities (or parameters) (x_1, x_2) is correlated with a pair of quantities (y_1, y_2) if and only if there exist real functions f_1, f_2, g_1, g_2 such that:

(1) quantities $f_1(x_1), f_2(x_2)$ are linearly correlated if and only if a pencil correlation exists between $g_1(y_1), g_2(y_2)$;

(2) quantities $g_1(y_1)$, $g_2(y_2)$ are linearly correlated if and only if a pencil correlation exists between $f_1(x_1)$, $f_2(x_2)$.

The functions f_1, f_2, g_1, g_2 will be referred to as measuring scales (or in short scales) for the quantities x_1, x_2, y_1, y_2, respectively [5].

On the basis of Definition 1 and Theorems 1–4 we can present the above proved relationship in the form of the following theorem.

Fundamental theorem 1. If the quantities k, E, T, A are intercorrelated by Eq. (10), then the pair (A, E) is correlated with the pair (k, T).

Proof: Let us have $f_1(x) = \ln x$, $f_2(x) = x$, $g_1(x) = \ln x$, $g_2(x) = \frac{1}{R \cdot x}$, and $x_1 = A$, $x_2 = E$, $y_1 = k$, $y_2 = T$. Interpretation of Definition 1 conforming to the contents of Theorems 3 and 4 means that the conditions of Definition 1 are fulfilled, which is to say, that condition 1 is equivalent to Theorem 3, and condition 2 is equivalent to Theorem 4, which was to be proved.

One can also suppose that the derived correlation is related with the form of Eq. (10), which means that in the given empirical situation many more similar correlations can exist. The Arrhenius equation is very frequently applied, and not only in the field of chemical reactions, so an answer to the above given question would be of very general significance.

In searching for the answer to this question, our bases will be the dual relationships [6] well known in the field of mathematics, as well as certain conceptions of projection geometry [7]. With the Arrhenius equation regarded as a projection correlation it will be shown that the proofs ot Theorems 1–4 become a simple consequence of fundamental conceptions of projection geometry thus leading to new and surprising conclusions.

The Arrhenius equation in projection coordinates. New correlation relationship

In numerous considerations of analytical geometry problems, a much higher degree of generalization and elegance may be achieved by replacing the Cartesian coordinates by uniform coordinates or by projection coordinates in general. Such coordinates make it possible to represent points, lines, planes, and, more generally, hyperplanes.

There is no analytical difference between projection coordinates of points and corresponding Plucker coordinates of lines. The treatment of these coordinates depends merely on the method of interpretation.

The points of the n-order Cartesian space R^n are ordered systems (series of n in length) of numbers $(y_1, y_2, \ldots, y_n)$.

Let us relate this system with a system of $n+1$ numbers: $1, y_1, y_2, \ldots, y_n$, and with all systems proportional to it of general form $\lambda, \lambda y_1, \lambda y_2, \ldots, \lambda y_n$, where: λ = any number different from zero. The systems $\lambda, \lambda y_1, \lambda y_2, \ldots, \lambda y_n$ will be referred to as uniform (common) coordinates of point $y = (y_1, y_2, \ldots, y_n)$ in the space R^n.

The coordinates defined in this manner are determined with a precision corresponding to the coefficient $\lambda \neq 0$, and this property is taken into account when they are called the uniform coordinates.

A point with uniform coordinates $x_0, x_1, \ldots, x_n$ will be denoted as $\{x_0, x_1, \ldots, x_n\}$. In order to represent in Cartesian coordinates a point with given uniform coordinates, it is sufficient to change the system $x_0, x_1, \ldots, x_n$ into the system $1, \frac{x_1}{x_0}, \ldots, \frac{x_n}{x_0}$, if $x_0 \neq 0$, as in Cartesian coordinates a point is represented as $\left(\frac{x_1}{x_0}, \ldots, \frac{x_n}{x_0}\right)$.

It is also interesting to point out the geometrical sense of uniform coordinates $x_0, x_1, \ldots, x_n$, when $x_0 = 0$.

If L is a line in space R^n, which is determined by a point $a = (a_1, \ldots, a_n)$ and a vector $\vec{a} = (\alpha_1, \alpha_2, \ldots, \alpha_n)$, then the line in the space R^n is identical with a set of points $p(t) = a + t \cdot \vec{a} = (a_1 + t \cdot \alpha_1, \ldots, a_n + t \cdot \alpha_n) = \{1, a_1 + t \cdot \alpha_1, \ldots, a_n + t \cdot \alpha_n\} = \left\{-\frac{1}{t}, -\frac{a_1}{t} + \alpha_1, \ldots, -\frac{a_n}{t} + \alpha_n\right\}$, where: $t \neq 0$. If $(t) \to \infty$, the point $p(t)$ departs unlimitedly from a, and its uniform coordinates tend to the values $0, \alpha_1, \alpha_2, \ldots, \alpha_n$. It is therefore intuitively conceivable that such a system may be regarded as a point in infinity, i.e. as a so-called improper point of line L. Parallel lines have a common improper point, and non-parallel lines have different improper points. A line supplemented by its improper point is referred to as a projection line.

A projection line differs from a Cartesian line (Euclidean line) by a single additional point which terminates it in a certain sense, thus making the line similar to a circle of "infinite" radius.

A transition from a Cartesian to a uniform system may often be effected by adding unity at the end of the series of numbers representing the Cartesian system. Thus, if the Cartesian coordinates are represented by $(y_1, y_2, \ldots, y_n)$, the uniform coordinates become $(y_1, y_2, \ldots, 1)$. The use of another analytical representation of a point facilitates the analysis of a linear equation on a plane, and it makes it possible to derive conclusions essential for the considerations presented on p. 3.

If in Cartesian coordinates an equation of a line in plane (R^2) has the form $Ax + By + C = 0$ (where $A^2 + B^2 > 0$), then the transformation to projection coordinates $\{(x, y)\} \to \{x, y, 1\} \to \{x_1, x_2, x_3\}$ changes the linear equation to the form $Ax_1 + Bx_2 + Cx_3 = 0$, since the system $\{x, y, 1\}$ is proportional to the system x_1, x_2, x_3; hence $x = \frac{x_1}{x_3}$ and $y = \frac{x_2}{x_3}$, and inversely. Hence, in any system of uniform coordinates (projection coordinates) every line in a plane may be represented by the equation $(m)\ a_1x_1 + a_2x_2 + a_3x_3 = 0$, in which not all the values a_1, a_2, a_3 disappear, i.e. $|a_1| + |a_2| + |a_3| = 0$.

If in equation (m) we replace the coefficients a_1, a_2, a_3 by numbers propertional to these coefficients the result is the same straight line, since by multiplying equation (m) by $\lambda \neq 0$ $(b_1 = \lambda \cdot a_1;\ b_2 = \lambda \cdot a_2;\ b_3 = \lambda \cdot a_3$ we obtain the equation $(m\ m)\ b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 = 0$, and if x_1, x_2, x_3 fulfil the conditions of equation $(m\ m)$, then by dividing them by α we can conclude that x_1, x_2, x_3 satisfy equation (m). And inversely, if x_1, x_2, x_3 satisfy equation (m), they also satisfy equation $(m\ m)$, which means that equations (m) and $(m\ m)$ represent one and the same line.

In an analogous way as for a point, it is possible to derive for lines coordinates $\{a_1, a_2, a_3\}$, which are the Plucker coordinates of a line within the proportionality precision limit.

In this case an equation of the type $a_1u_1 + a_2u_2 + a_3u_3 = 0$ (where $|a_1| + |a_2| + |a_3| \neq 0$) may be given the following interpretation:

(1) the equation is a necessary and sufficient condition for a point of coordinates $\{x_1, x_2, x_3\}$ to belong to a line of coordioates $\{a_1, a_2, a_3\}$, and

(2) the equation represents a pencil of lines passing through a point $\{a_1, a_2, a_3\}$ of coordinates $x_1, x_2, x_3\}$, and for this reason it may also be referred to as an equation of a point.

Thus, we can regard the equation $a_1u_1 + a_2u_2 + a_3u_3 = 0$ either as the equation of a line or as the equation of a pencil of lines in the same coordinates, depending on whether the coordinates $\{a_1, a_2, a_3\}$ are treated as coordinates of a line or of a point.

The projection geometry approach may also be applied to the transformed Arrhenius equation (10). Multiplication of Eq. (10) by R gives:

$$R \cdot \ln k + E \cdot \frac{1}{T} - R \cdot \ln A = 0. \tag{29}$$

Relation (29) is equivalent to a projection equation of a line. It enables the construction of the following correlation table:

Table 1

No. \ Coordinates	a_1	a_2	a_3	u_1	u_2	u_3
1	R	E	$\ln A$	$\ln k$	$\frac{1}{T}$	R
2	$\ln k$	E	$\ln A$	R	$\frac{1}{T}$	R
3	R	$\frac{1}{T}$	$\ln A$	$\ln k$	E	R
4	R	E	R	$\ln k$	$\frac{1}{T}$	$\ln A$

The results of the correlation table are:

Theorem 5. The quantities (E, A) are correlated with the quantities (k, T).

Proof: Equation (29) is simultaneously an equation of a line and an equation of a pencil of lines, depending on whether (a_1, a_2, a_3) or (u_1, u_2, u_3) are cooordinates of a point or of a line.

Let us assume, therefore, that for different a_1, a_2, a_3 the quantities u_1, u_2, u_3 are constants and satisfy the projection equation, which means that for certain k_0, T_0 the quantities $\ln k$, $\frac{1}{T_0}$ are constant for different A and E. Let u_1, u_2, u_3 be coordinates of a line. In such a case the projection equation establishes a linear relationship between A and E. If at the same time we settle A and E in this equation and we regard a_1, a_2, a_3 as coordinates of a line, we can get a line from a pencil that establishes a relationship between $\ln k$ and $\frac{1}{T}$.

In an analogous way it is possible to establish the other correlations too.

Theorem 6. The quantities (k, E, A) are correlated with (T).
Proof: Second line of Table 1.

Theorem 7. Quantities (A, T) are correlated with (k, E).
Proof: Third line of Table 1.

Theorem 8. The quantity (E) is correlated with (k, T, A).

Proof: Fourth line of Table 1.

The method of constructing a table leading to the above theorems is as follows: from each term in Eq. (29) we take one factor to obtain the values a_1, a_2, a_3, and the remaining quantities are treated as u_1, u_2, u_3. In this way we obtain 8 relations, among which 2 pairs are of dual type, so it is sufficient to take into consideration only four of them.

The starting Eq. (10) may also be multiplied by T to give a projection equation $T \cdot \ln k + E \cdot \frac{1}{R} - T \cdot \ln A = 0$, for which a new table of correlation relationships may be constructed.

Examples of empirical relationship. Deviation factor (physical sense) of correlation

Upon analyzing the Arrhenius equation as an equation of a projection correlation, we have stated, among others that the pairs of quantities (A, E) and (k, T) are intercorrelated in appropriate scales. This means that, for a certain pair (k_0, T_0), often referred to as the isokinetic pair, and for any values of (A, E) the transformed Arrhenius equation (29) is fulfilled. According to the earlier findings therefore we can treat the quantities $\left\{\ln k_0, \frac{1}{T_0}, R\right\}$ as the Plucker coordinates of a line represented in Fig. 4.

An analogous line has been obtained by one of us [8, 9] after it had been established that points on the line correspond to different values of the pressure (p) of the gaseous reaction product under the experimental conditions.

In the previous sections we have established that, if there is a linear relationship between (A, E), then (k, T) must remain in a pencil relationship (in appropriate scales). This is the result of a different look at the triplet $\left\{\ln k_0, \frac{1}{T_0}, R\right\}$, now regarded as the projection coordinates of a point, which is equivalent to the treatment of Eq. (29) as an equation of a pencil (Fig. 5) with a common point of coordinates $\left(\frac{\ln k_0}{R}, \frac{1}{RT_0}\right)$.

An identical pencil has also been found experimentally [8, 9]. In this case different lines correspond to different values of the pressure of the gaseous reaction product under experimental conditions.

It is possible to state, therefore, that the pressure is the deviation factor (it decides about the physical sense) of this correlation, as different points in the line in Fig. 4 and different slopes of the lines in Fig. 5 correspond to different values of pressure. This statement conforms fully with considerations presented above.

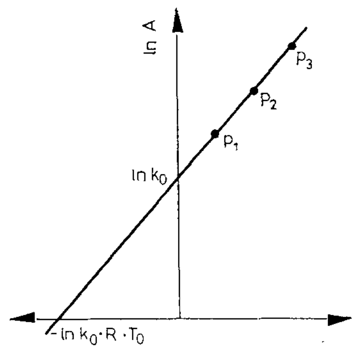

Fig. 4

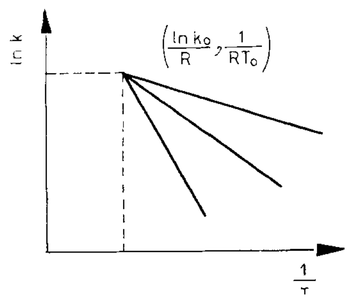

Fig. 5

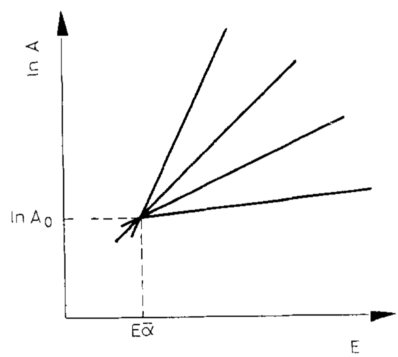

Fig. 6

It should further be mentioned that in the case under consideration the pressure of the gaseous reaction product (as a deviation factor) is also decisive for the motive modulus of the process $\Delta p = p_0 - p$, and it may be a measure of the remoteness of the reaction system from the state of equilibrium.

If we assume that a pencil relationship exists for (A, E) (Fig. 6), then for certain (A_0, E_0) a linear relationship also exists for (k, T).

This case, too, has been studied experimentally [8, 9]. It permitted us to formulate a hypothesis that the theoretically postulated deviation factor of that correlation is a very complex parameter. It seems very probable that it is connected with both the crystalline structure of the reaction substrate and the degree of its defectiveness.

The presented examples demonstrate that every correlation is accompanied by two different deviation factors (that seem to be responsible for the existence of that correlation) but in many cases their nature (physical sense) is not completely clear. It seems to be advisable, however, to introduce such parameters, as they are measurable quantities. Hence:

Definition 2. If in appropriate scales a pair of quantities (x_1, x_2) is correlated with a pair (y_1, y_2), then the slope of lines in the pencil of one relation of this correlation will be referred to as a measure of the deviation factor of that relation.

Conclusion

The representation of the Arrhenius equation and of known empirical relationship in the form of projection correlations is a first attempt to simplify fundamental problems of chemical kinetics with the aid of the less familiar and apparently more complicated theory of projection geometry.

Such an approach not only makes it possible to prove that the Zawadzki–Bretsznajder rule, compensation effect and isokinetic temperature are merely simple consequences of interpretation of the Arrhenius equation as a projection correlation, but it also indicates the existence of new and evidently not investigated relations and their mutual correlations.

The theoretical considerations presented in this work have been illustrated with experimental data on topochemical reactions of thermal dissociation of solids of the type $A_{solid} \rightleftharpoons B_{solid} + C_{gas}$. It seems, however, that the character of the Arrhenius equation and of relationships derived from this equation is decisive for a high degree of generalization of the problems under consideration.

Transformation of the Arrhenius equation to the form (29) that enables its presentation as a projection correlation leads to theoretical discrimination of eight deviation factors which impart to the correlations a definite (although complicated and not always recognized) physical sense. On the basis of earlier works [3, 8, 9] we have indicated that three of these factors may be decisive for the course of thermal dissociation. One may assume, therefore, that all the remaining factors (amounting to $2^3 = 8$) are combinations of the three fundamental ones. Thus, it may be concluded that the Arrhenius equation is a good model of a process so far as the kinetics of this process are controlled by the fundamental deviation factors.

The above hypothesis seems to be confirmed by application of the presented procedure to a more precise (with respect to the Arrhenius equation) relation:

$$k = A \cdot T^m \cdot e^{-\frac{E}{RT}}$$

which after transformation to the form:

$$R \ln k - R \ln A - R \ln T^{m} + E \cdot \frac{1}{T} = 0 \tag{30}$$

becomes a projection correlation in space R^3 between a linear relation and a pencil relation of planes. There are eight such correlation and sixteen corresponding deviation factors. It seems that in model (30) it is possible to discriminate four fundamental deviation factors, and all the others (amounting to $2^4 = 16$) would be some combinations of them.

Such reasoning leads to the conclusion that the form of a mathematical model depends on the intention of its author, such or another number of factors influencing the course of the process being taken into account during the construction of the model.

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Résumé — On présente la justification mathématique de l'existence de la température isocinétique et de l'effet de compensation, ainsi que de la relation de ces quantités avec la loi de Zawadzki–Bretsznajder.

Zusammenfassung — Der mathematische Beweis für die Existenz der isokinetischen Temperatur und des Kompensationseffekts sowie für den Zusammenhang dieser Größen mit der Zawadzki – Bretsznajder-schen Gesetzmäßigkeit wird erbracht.

Резюме —Показано, что правило Завадского-Бретснайдера, компенсационный эффект и изокинетическая температура являются простым следствием уравнения Аррениуса, как отражающая корреляция. Установлено, что такая интерпретация уравнения Аррениуса позволяет различить факторы отклонения, которые придают определенный (хотя и не всегда простой и устанавливаемый) физический смысл известной эмпирической корреляции. Представлена возможность установления новых корреляционных соотношений на основе этого способа рассуждения.