

# Kinetic compensation effects: a long term mystery and the reality. A simple kinetic consideration

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**Abstract** The paper concerns the most probable physical–chemical reasons of observing the kinetic compensation effects which arise at the experimental kinetic studies of complex stepwise reactions in both homogeneous systems and homological set of solid or heterogeneous systems. It is shown that, in the former case, the reason for such effects is the existence of an ‘isokinetic’ temperature when the change of the rate determining step does occur. In the latter case, the reason of the effects reflects “polychromatic” nature of kinetics of chemical transformations in heterogeneous systems as well as a peculiarity of arranging the experimental kinetic studies of such “polychromatic” processes.

**Keywords** Chemical kinetics · Compensation effect · Isokinetic temperature · Stepwise reactions

## Introduction

Typical studies of chemical transformations aiming to reveal their intrinsic mechanism or to do an optimization of practically interesting processes include variation of principal “external” parameters which control the rate of the transformations, usually the temperature of the process, the reagent concentrations as well as the composition of catalyst, etc.

In the case of the unknown intrinsic mechanism of the process, the first exit parameters of such studies are usually the experimentally detected (apparent) rates,  $v_{\Sigma}$ , of the target chemical transformations within a given temperature range. The experimental data on the apparent rate are analyzed to find both apparent activation energy,  $E_{a\Sigma}$ , which characterizes the temperature dependence of this rate, and the

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slightly temperature dependent apparent pre-exponential factor,  $v_{\Sigma}^o$ , which also characterizes the apparent rate of the transformation and may include concentrations of reagents, etc.:

$$v_{\Sigma} = v_{\Sigma}^o \exp(-E_{a\Sigma}/RT). \quad (1)$$

If the process under study is not an elementary chemical reaction, the experimentally measured parameters  $E_{a\Sigma}$  and  $v_{\Sigma}^o$  may change with the change of the range of the used temperature and reagent concentrations.

The same approach of analyzing the experimental data is used when studying the target chemical transformations in homological heterogeneous systems like transformations over catalysts of different nature or pretreatment. During such studies, the initially obtained parameter of the studies is also the apparent rate  $v_{\Sigma}$  of the transformation, which is preliminarily analyzed also with the use of expression 1. Obviously, in that case, the apparent parameters  $v_{\Sigma}^o$  and  $E_{a\Sigma}$  appear to be dependent of the nature of the system under study.

Yet at the beginning of 1920s, it was unexpectedly found that the experimentally obtained values of parameters  $v_{\Sigma}^o$  and  $E_{a\Sigma}$  appear very often to be closely related via the formula

$$\ln v_{\Sigma}^o \approx \gamma E_{a\Sigma} + b \quad (2)$$

with  $\gamma$  being typically of the order of  $0.3 - 0.5 (kJ/mol)^{-1}$ , while  $b$  is a constant [1, 2].

Comprehensive studies of numerous homological processes which occur with the participation of a variety of heterogeneous components like, e.g., catalysts, heterogeneous surfaces or the reagent “confining” solid matrixes confirmed the existence of the same effect. As a result, this quite general phenomenon received the name of the “kinetic compensation effect” and was the subject of numerous speculations, which unfortunately did not result in a distinctive opinion on the origin of the observed compensation effect in spite of its seemingly evident importance for practice (see, e.g., [3–10]).

Under serious discussion is also a hypothesis that the compensation effect is not of physical–chemical origin but has a totally artificial statistical character originated simply from derivation of the mutually related values of the enthalpy-entropy pair of the process activation from experiments with large experimental errors in the case of precise measuring the temperature of the experiments (see, e.g., [11–13] and references therein). However, this hypothesis may be seriously considered only in the case of experimentations in very narrow temperature range, while the actual situation can be different (see, e.g., [14]).

Sometimes Eq. 2 is represented by the so-called Cremer–Constable relation [8]:

$$\ln v_{\Sigma}^o = \ln v_i + E_{a\Sigma}/RT_i, \quad (3)$$

where  $v_i$  is called an isokinetic constant ( $b = \text{const} = \ln v_i$ ), and  $T_i$  is called the isokinetic or compensation temperature ( $\gamma = 1/RT_i$ ). Here  $R$  is the universal gas constant and index “i” means a set of homological systems “i” under analysis.

Expression 3 is quite often rewritten via apparent rate constants  $k_{\Sigma}^o$  and  $k_i$  which are proportional to parameters  $v_{\Sigma}^o$  and  $v_i$ :

$$\ln k_{\Sigma}^o = \ln k_i + E_{a\Sigma}/RT_i. \tag{4}$$

Due to very dramatic differences in the occurrence of complex stepwise stoichiometric chemical transformations in homogeneous systems from those in heterogeneous ones, one may expect that the origin of the compensation in the mentioned situations should be different too.

Unfortunately, until now, both displays of the kinetic compensation effect remain incompletely understood being, frankly speaking, a sort of a mystery for chemical kinetics, catalysis, topochemical reactions, etc.

In this paper, we present simple physico-chemical kinetic considerations which may explain the origin of both types of kinetic compensation effects at least in some simple situations.

Note from the beginning that typical observations of the compensation effects are attributed to studies of so-called stoichiometric stepwise (net) processes which consist of a set of elementary chemical reactions or even parallel pathways of the transformations. The condition of stoichiometry for overall net processes means that all chemical intermediates of the net transformation exist in constant “steady state” concentrations. Evidently, namely this allows the net processes to be considered as stoichiometric ones.

**Kinetic compensation effects arising due to a change of the rate determining step of a stoichiometric net process at the change of temperature or other “external” parameters**

A typical case of observing the kinetic compensation effect is a kinetic study of a complex stoichiometric stepwise chemical transformation in homogeneous systems at changing external parameters of the process occurrence.

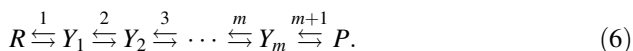
It is well known that the apparent rate of such transformation is a complex function of many dynamic and thermodynamic parameters of elementary chemical reactions; the leading role here is playing by those of the “rate determining step” [15–17].

The rate constants of elementary reactions that compose the overall stoichiometric stepwise process have as a rule different dependence on temperature. For this reason, a probable situation is a change of the rate determining step and, thus, the rate determining parameters when changing the temperature in the temperature range of the kinetic study.

Let us consider the result of such change in the easiest example of stoichiometric net process



This consist of  $m + 1$  consecutive monomolecular transformation:



Here R and P are the initial reagent and final product of the net transformation,  $Y_i$  are intermediates of the transformation ( $i = 1, \dots, m$ ).

The most correct and easiest way for the analysis of occurrence of such stationary stepwise reaction is to follow the so-called thermodynamic representation of chemical kinetics [13, 14]. In such representation in a general case, the stationary rate of the stoichiometric net transformation 5 is expressed via very simple “Horiuti–Boreskov” relation:

$$v_{\Sigma} = -\frac{d[R]}{dt} = \frac{d[P]}{dt} = \varepsilon_{\Sigma}(\tilde{R} - \tilde{P}).$$

Here [R] and [P] are the concentrations of reagents R and P, while in thermodynamically ideal systems:

$$\tilde{R} = [R] \exp(\mu_R^o/RT),$$

$$\tilde{P} = [P] \exp(\mu_P^o/RT).$$

Here  $\mu_i^o$  is the standard chemical potential of reagent i.

The parameter  $\varepsilon_{\Sigma}$  is an effective so-called “truncated” rate constant equal to

$$\frac{1}{\varepsilon_{\Sigma}} = \sum_{i=1}^{m+1} \frac{1}{\varepsilon_i}.$$

Here  $\varepsilon_i \equiv \frac{k_B T}{h} \exp(-\mu_i^{o\neq}/RT)$  are the temperature dependent “truncated” rate constants of step i,  $k_B$  and  $h$  are the Boltzmann and Plank constants,  $\mu_i^{o\neq}$  is the “standard chemical potential” of the transient state of step i. Indeed,  $\varepsilon_i$  are proportional to the classic rate constants  $k_i$  of elementary steps (for the explanation see [16, 17]).

The rate determining step in this situation is that with the smallest truncated rate constant  $\varepsilon_{\min} = \min\{\varepsilon_i\}$ ,  $i = 1, \dots, m + 1$  (note, not the minimal  $k_i$ !). At this situation,  $\varepsilon_{\Sigma} = \varepsilon_{\min}$ , and since the dependence of each  $\varepsilon_i$  on temperature may be different, the rate determining step may change with the change of the temperature: at the temperature elevation the values of  $\varepsilon_i$  rise according to the Arrhenius rule and thus the new rate determining step will be that which rise slowly. The results of such changes which lead to the kinetic compensation effect is comprehensively considered in [17] in terms of thermodynamic representation of chemical kinetics, the principal point here being the “isokinetic temperature”  $T^*$ , at which the value of parameter  $\varepsilon_i$  of a previous limiting step “lim1” equals to that of the new one “lim2”:

$$\varepsilon_{\text{lim}1}(T^*) = \varepsilon_{\text{lim}2}(T^*).$$

It is quite easy to demonstrate the appearance of such compensation with the use of the conventional kinetic language too in the situation when the net process 5 occurs far from equilibrium and thus it is kinetically irreversible:



In such a situation, the apparent rate  $v_{\Sigma}$  can be easily expressed via standard kinetical parameters:

$$v_{\Sigma} = k_{\text{lim}} \prod_{i=1}^{\text{lim}} K_i [R] \equiv k_{\Sigma} [R]. \tag{8}$$

Here  $k_{\text{lim}}$  is the classic rate constant of the rate determining step “lim”,  $k_{\Sigma}$  is apparent “conventional” rate constant of the overall net process 7, while  $K_i$  are the equilibrium constants of steps, preceding the rate-determining one (see, e.g., [16, 17]). It is well known that the rate-determining step is the first (from left to right) kinetically irreversible step in set 6, while all the preceding steps can be considered as being in a dynamic (partial) equilibrium. The kinetic irreversibility means simultaneously that the transformation at this step occurs far from equilibrium, i.e., the current change of Gibbs energy of the transformation at this step,  $\Delta_r G_{\text{lim}}$ , is larger than  $RT$ , where  $T$  is temperature of the system (in the thermodynamic representation this means also that the value of  $\varepsilon_{\text{lim}}$  is the minimum one).

As the result, expression 8 can be rewritten as

$$v_{\Sigma} = v_{\Sigma}^o \exp(-E_{a\Sigma}/RT) = k_{\Sigma} [R] = k_{\Sigma}^o \exp(-E_{a\Sigma}/RT) [R],$$

$v_{\Sigma}^o$ ,  $k_{\Sigma}$  and  $k_{\Sigma}^o$  are apparent pre-exponential factors, which depend only slightly on the temperature, and  $E_{a\Sigma}$  is the apparent activation energy.

It is well known that

$$E_{a\Sigma} \approx E_{a\text{lim}} - \sum_{i=1}^{\text{lim}} \Delta_r H_i^o.$$

Here  $E_{a\text{lim}}$  is the activation energy of an elementary transformation, which coincides with the rate determining step, and  $\Delta_r H_i^o$  are the enthalpy changes of all the steps preceding the rate-determining one.

Let us remind, that the rate determining step “i” is the first (from left to right) kinetically irreversible one in set 6. In other words, this is the first step for which the change of the Gibbs potential at the elementary transformation,  $\Delta_r G_i$ , exceeds  $RT$ . Since the value of  $\Delta_r G_i$  at any step  $i$  is temperature dependent:

$$\Delta_r G_i = \Delta_r H_i - T \Delta_r S_i,$$

the change of temperature may results in the change of the rate determining step that leads to the change of the apparent activation energy  $E_{a\Sigma}$ , too.

Let us consider the results of such the change in more detail.

Let the rate determining step be step “lim1” at a given temperature  $T$ , while at the elevation of temperature up to value  $T_1^*$  the rate determining step becomes step “lim2”. Evidently, at this temperature  $T_1^*$ , it will be no jump of the overall rate of net process 7, but below temperature  $T_1^*$  (temperature  $T_1$  in Fig. 1) the overall rate is expressed as:

$$v_{\Sigma} = v_{\Sigma 1}^o \exp(-E_{a\Sigma 1}/RT) = k_{\Sigma 1}^o \exp(-E_{a\Sigma 1}/RT)[R].$$

Here  $E_{a\Sigma 1} = E_{a \text{ lim } 1} - \sum_{i=1}^{\text{lim } 1} \Delta_r H_i^o$ , while over temperature  $T_1^*$  (temperature  $T_2$  in Fig. 1), it is expressed as:

$$v_{\Sigma} = v_{\Sigma 2}^o \exp(-E_{a\Sigma 2}/RT) = k_{\Sigma 2}^o \exp(-E_{a\Sigma 2}/RT)[R].$$

Here  $E_{a\Sigma 2} = E_{a \text{ lim } 2} - \sum_{i=1}^{\text{lim } 2} \Delta_r H_i^o$ .

Evidently too,  $E_{a\Sigma 2} < E_{a\Sigma 1}$  holds since the new rate determining step depends on temperature slowly that the preceding one.

The temperature  $T_1^*$  can be called “isokinetic temperature”, since at this temperature:

$$v_{\Sigma} = v_{\Sigma 1}^o \exp(-E_{a\Sigma 1}/RT_1^*) = v_{\Sigma 2}^o \exp(-E_{a\Sigma 2}/RT_1^*) \quad (9)$$

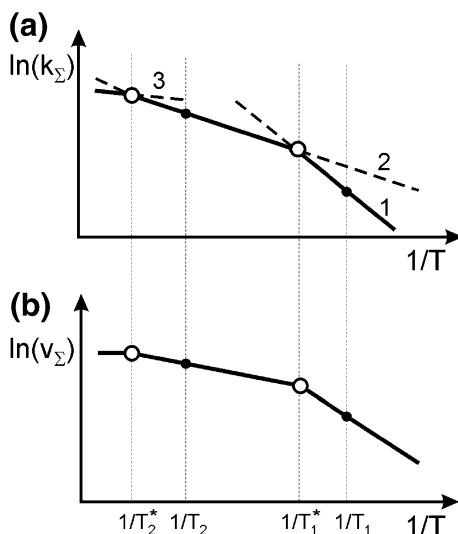
(In fact, the change of the overall rate at the change of the rate determining steps occurs quit smoothly rather than stepwise. However, at analyzing the experimental data, it looks typically as a simple stepwise change.)

Equation 9 corresponds to the following equations:

$$\ln v_{\Sigma 1}^o - E_{a\Sigma 1}/RT_1^* = \ln v_{\Sigma 2}^o - E_{a\Sigma 2}/RT_1^*, \quad (10)$$

or

**Fig. 1** Arrhenius graphs illustrating appearance of kinetic compensation effect in net process 5–7 at passing the temperature via isokinetic temperatures  $T_1^*$  and  $T_2^*$ : **a** the change of apparent values of  $k_{\Sigma}$  ( $i = 1, 2, 3$ ); **b** the change in the corresponding apparent values of  $v_{\Sigma}$



$$\ln k_{\Sigma 1}^0 - E_{a\Sigma 1}/RT^* = \ln k_{\Sigma 2}^0 - E_{a\Sigma 2}/RT^* \tag{11}$$

These are totally equivalent to Eqs. 2–4.

In a complex process at the continuation of the temperature elevation, a next change of the rate determining step from  $\text{lim}2$  to  $\text{lim}3$  is possible at passing the next isokinetic temperature  $T_2^*$ , etc. (see Fig. 1). Taking into account a not very large difference in temperatures of the experiments and thus in the values of  $T_1^*$ ,  $T_2^*$ , etc. and significant experimental errors when measuring  $v_\Sigma$ , we obtain a general approximate relation:

$$\ln v_{\Sigma i}^0 \approx \gamma E_{a\Sigma i} + b \tag{12}$$

or

$$\ln k_\Sigma^0 \approx \gamma E_{a\Sigma} + b' \tag{13}$$

Here  $\gamma = 1/RT^*$ , the value of  $T^*$  being reflect the temperature range of the experiments. At  $T^*$  locating inside the range of 300–500 K and when measuring  $E_{a\Sigma}$  in  $\text{kJ/mol}$ , the value of  $\gamma$  is relatively constant:  $\gamma \approx 0.3\text{--}0.4$ .

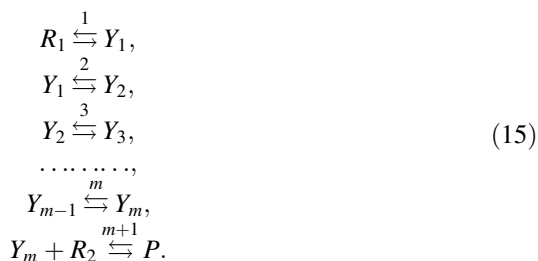
It is evident that relations 12 and 13 correspond to the existence of the compensation effect, which is under discussion: the change in the value of apparent activation energy is “compensated” by a rather distinctive change of the value of apparent pre-exponential factor of either overall rate or rate constant of the net reaction under study. It is evident, however, that the real reason of arising the mentioned compensation is continuity of the change of the resulting overall rate  $v_\Sigma$  of the net process at the continuous change of external parameters of the process occurrence (in our case—temperature).

Analogous “compensation” effects can be observed at the change of rate-determining steps in more complex schemes of net transformations. Moreover, these can be observed not only at the change of temperature but also at the change of the concentration of reactants which can be considered as “external” in respect to the intermediates.

For example, let us consider a stoichiometric net process:



This process is assumed to occur according to the following scheme:



Here  $R_1$  and  $R_2$  are the initial “external” reagents,  $P$  is the final product, and  $Y_i$  ( $i = 1, \dots, m$ ) are intermediates with stationary concentrations.

It is shown in [16, 17], that for this scheme in the thermodynamic representation the overall rate equals to:

$$v_{\Sigma} = -\frac{d[R_1]}{dt} = -\frac{d[R_2]}{dt} = \frac{d[P]}{dt} = \varepsilon_{\Sigma}(\tilde{R}_1 \cdot \tilde{R}_2 - \tilde{P}).$$

Here  $\varepsilon_{\Sigma} = \frac{\varepsilon_{eff} \varepsilon_{m+1}}{\varepsilon_{eff} + \varepsilon_{m+1} \tilde{R}_2}$  and  $\frac{1}{\varepsilon_{eff}} = \sum_{i=1}^m \frac{1}{\varepsilon_i}$ . In addition,  $\varepsilon_{\Sigma}$ ,  $\varepsilon_i$ ,  $\varepsilon_{eff}$  as well as  $\tilde{R}_1$ ,  $\tilde{R}_2$  and  $\tilde{P}$  have the same meaning as before.

At this in the case  $\varepsilon_{m+1} \tilde{R}_2 \ll \varepsilon_{eff}$ , the rate determining step is reaction  $m + 1$ , while at  $\varepsilon_{m+1} \tilde{R}_2 \gg \varepsilon_{eff}$  the rate determining step is one of the steps  $i = 1, 2, \dots, m$  with the smallest value of  $\varepsilon_i$ .

The same as for the earlier example, the change of temperature may cause different changes in the values of parameters  $\varepsilon_i$  (note, that the value of  $\tilde{R}_2$  is also temperature dependent) and, as a result, lead to not only change of  $E_{a\Sigma}$ , but also to the change of apparent molecularity of the overall net process. The above changes may be caused even at constant temperature when changing the concentration of  $R_2$ , if only the last change causes the change in ratio of terms in the denomination of expression for  $\varepsilon_{\Sigma}$ . The concentration of  $R_2$  at the moment of this change can also be considered as an “isokinetic concentration”  $[R_2]^*$ . The final result for the overall kinetics will be the same: for concentrations of  $R_2$  smaller and larger the value of  $[R_2]^*$  the apparent values of  $E_{a\Sigma}$  will be related by the “compensation” relations similar to expressions 12 and 13.

Note that usually in literature, the change in values of  $E_{a\Sigma}$  is related to a change of the mechanism of the net transformation, while in reality, one should relate this with the change of the rate-determining step only.

Thus, the change of the concentration of initial reagent  $R_2$  can follow in the change of the rate determining step. If the net reaction process from left to right far from equilibrium and thus is kinetically irreversible ( $\tilde{R}_1 \cdot \tilde{R}_2 \gg \tilde{P}$ ).

$$\text{At } \tilde{R}_2 \ll \varepsilon_{eff} / \varepsilon_{m+1} = \tilde{R}_2^*$$

$$v_{\Sigma} \approx \varepsilon_{m+1} \tilde{R}_1 \cdot \tilde{R}_2,$$

$$\text{at } \tilde{R}_2 \gg \varepsilon_{eff} / \varepsilon_{m+1} = \tilde{R}_2^*$$

$$v_{\Sigma} \approx \varepsilon_{eff} \tilde{R}_1.$$

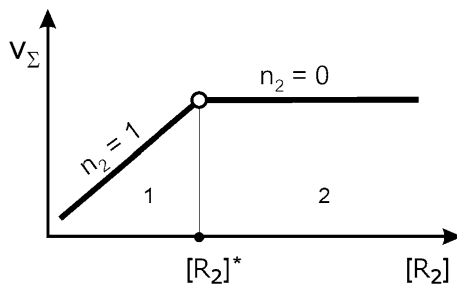
This means that the apparent molecularity (the order) of the net process with respect to reagent  $R_2$ ,  $n_2$ , is equal to zero at  $[R_2] > [R_2]^*$ , while at  $[R_2] < [R_2]^*$  the apparent molecularity  $n_2$  equals to unity (see Fig. 2).

Note that the value of  $[R_2]^*$  at which the change of the rate determining step does occur depends on the temperature of measuring the reaction order.

The values of apparent activation energy, which are measured at segments 1 and 2 of Fig. 2 at the same temperature T, can appear different. However, if take into account that at the isokinetic concentration  $[R_2] = [R_2]^*$



**Fig. 2** The change of the apparent molecularity (order),  $n_2$ , of stoichiometric net reaction 14–15 with respect to the concentrations of reactant  $R_2$  at a fixed temperature at passing the isokinetic concentration  $[R_2]^*$



$$v_{\Sigma}^o = k_{\Sigma 1}^o \exp\left(-\frac{E_{a\Sigma 1}}{RT}\right) [R_1] [R_2]^* \approx k_{\Sigma 2}^o \exp\left(-\frac{E_{a\Sigma 2}}{RT}\right) [R_2]^*.$$

We receive once again a rigid relation between apparent values of  $k_{\Sigma 1}^o$  and  $k_{\Sigma 2}^o$ :

$$\ln k_{\Sigma 1}^o - \ln k_{\Sigma 2}^o + \ln[R_1] = \frac{1}{RT} (E_{a\Sigma 1} - E_{a\Sigma 2}).$$

So, in this case, we also have to observe the kinetic compensation effect with  $\gamma = 1/RT$ , where T is temperature of the experiment occurrence.

The presented examples can be, indeed, extended to any complicated scheme of stoichiometric net chemical reactions which allows the presentation of the apparent rate of the reaction as, e.g.,

$$v_{\Sigma} = k_{\Sigma}^o \exp\left(-\frac{E_{a\Sigma}}{RT}\right) \prod_i [R_i]^{v_i}.$$

Here  $k_{\Sigma}^o$  is a slightly temperature dependent pre-exponential factor, and  $v_i$  are apparent molecularities of the reactions in respect to reagents i.

It is evident that in any cases of changing the temperature and/or concentration of initial reagents, we have to observe the compensation effect of a type 12 or 13 with  $\gamma \approx 1/RT$ , where T is the temperature within the interval of the studies.

Much more amusing seems to be the origin of kinetic compensation effect, which is observed at studies of the same or similar chemical transformations in different but homological systems, e.g., in the presence of different catalysts, etc.

### The origin of kinetic compensation effect which is observed at studying chemical transformations in different, but homological systems

In the previous part of the paper, we have shown that appearance of the kinetic compensation effect is a natural sequence of changing the rate determining steps in complex stepwise reactions at changing the “external” parameters. During that consideration, the reactive system was assumed to be chemically uniform and homogeneous.

The situation with chemically reactive solid and/or heterogeneous systems could be much more complicated in comparison with what we have considered earlier, since here we have to take into account not only the change of the rate determining steps, but also the possibility of “polychromacity” of the kinetics of the overall transformation of a registered target (or key) substance. Indeed, due to the absence of sufficient reactant mobility, in solid systems, the rate constants for reacting substances may depend either on distance between the spatially “frozen” reactants or reactive centers or their mutual orientation, or on the intrinsic reactivity of the reactive centers, etc.

A classical example is low temperature redox reactions which occur in solid matter via long distance tunneling electron transfer. The kinetics of such reactions was comprehensively studied by Zamaraev et al. [18]. It was found that due to absence of mobility of reagents and dramatic (exponential) dependence of the constant rate  $k$  of the tunneling electron transfer between the reacting species on the distance  $r$  between them, the consideration of the overall transformation in the system has to take into account the sum of individually reacting pairs of reagents:

$$v_{\Sigma} = -\frac{d[C]_{\Sigma}}{dt} = \int_{\nu} k(r) n(r) 4\pi r^2 dr.$$

Here  $[C]_{\Sigma}$  is the overall concentration of the reacting pairs,  $k(r)$  is the distance dependent rate constant,  $n(r)$  is the density of the spatial distribution of reacting species located on the distance  $r$ , the integration is made over all the specimen volume,  $\nu$  [19].

As the result, the experimentally recorded kinetics of the overall transformation is not described by simple kinetic laws with one rate constant and thus is exhibited as a “polychromatic” transformation with the very “long tail” of activity. The linearization coordinates in this particular case appear to be quite unusual for chemical kinetics, the overall concentration  $[C]_{\Sigma}$  being linearly diminished with the logarithms of time of the concentration measurements. The time scale for the respective studies was unusually large: from several milliseconds for nearly a year, and for any time the systems were not kinetically silent!

The same feature may be characteristic for topochemical reactions or reactions between species confined in solid matrixes. The apparent rate of such reactions (attributed to, e.g., a unit volume of the system) can be in the easiest case expressed as the sum of nearly independent concurrent chemical transformations, which are described by a variety of rate constants  $k_i$ ,  $i = 1, 2, \dots$ . The registered kinetics of the overall transformation of a key substance  $C$  is dependent in this case on those transformations which make the largest contribution to the kinetics at particular conditions of the experiment:

$$\frac{d[C]_{\Sigma}}{dt} = \sum_i k_i(T) n_i(t).$$

Here  $n_i$  are the concentrations of reactants  $i$  which contribute to the change of the concentration of key substance  $C$ .

Indeed, since  $k_i(T)$  are temperature dependent, the exhibition of the process for a spectator will much dependent on the temperature, sensitivity of the process occurrence detector, as well as the time scale of the observation.

The systems under study which appear below those sensitivity and time scale are everywhere considered as chemically silent or inert. Since the reactivity of species typically increases with temperature, in order to avoid “kinetic silence” of the system, the experimenter increases the temperature to do the transformation visible with the use of available equipment.

The same situation is valid for heterogeneous catalysis, where typically a large variety of nearly independent catalytically active centers are operating simultaneously thus resulting in “polychromatic” kinetics for the overall catalytic transformation of a substance under study. As a consequence, in this case, the catalytic system is usually considered as nonactive in the situation when the depth of the transformation at the time of the reaction study occurs lower than the sensitivity of a detector utilized. In order to make the catalytic process visible, the experimenter elevates the temperature to accelerate the process and make it visible by the registration system in the experimental set up. So, at such studies one may expect that any device used for the experimentation can be characterized by a virtual constant which is usually the minimal visible rate,  $v^*$ , of the transformation under study.

Following this idea, the author of this paper has tried to analyze some details of experiments of classical papers [1, 3], where the first observations of the compensation effect were announced.

So, it was found in paper [1] (the details of the experiments were disclosed in paper [2]) that the critical time scale for testing the decomposition of alcohol over a set of copper catalysts with different pretreatment in a flow-through reactor was one hour, which has been considered as the time needed for the experimentally recorded establishing of the steady state. Simultaneously, the sensitivity of the respective catalytic tests of the reaction under study was a bubble of hydrogen evolved in a special recording equipment. So, here one hour was a characteristic time  $\tau^*$  for the set up used.

It means that the occurrence of the reaction was detected if its rate was no less than one bubble per hour. Otherwise, at lower temperature, the system was considered as catalytically inert.

Another classical example is presented by an early work [3], which studied the  $N_2O$  decomposition also over a set of copper catalysts in a static nearly gradientless system. In this work, the rate of the catalytic processes was calculated as the depth of conversion during 1 min starting from the initial pressure of  $N_2O$  50 mm Hg with the sensitivity of the process occurrence around several percent of the pressure increase from its initial value. If a raise of the pressure was not recorded during 1 min, the system was considered as inactive one. So, here time 1 min was the characteristic time  $\tau^*$ .

One can examine in the same way more recent experimental data too.

If the rate of the process is lower than the critical one, the heterogeneous systems are considered as kinetically silent or inactive. However, in fact, even the rate of the transformation is smaller, than this fixed value, the system cannot

be considered as silent since one can obtain a sufficient transformation at larger time of the observation due to a “polychromacity” of the kinetics. In other words, the activity of a reactive system should be related everywhere with the time scale of its expectation. For example, catagenic processes of the organic fossils transformation in the Earth crust occur in the time scale of many millions years, while in conventional life of our civilization with the time scale up to thousands of years, we consider the fossils as totally inactive for their self-occurring transformations.

The possibility of the occurrence of two or more concurrent catalytic reactions over heterogeneous catalysts, which can lead to polychromacity of the apparent kinetics, was considered already by Cremer [4].

When supposing, as earlier, that the rate  $v_{obs}$  of detected “polychromatic” transformations of a key substance in the mentioned complex system  $i$  can be approximated via the simple Arrhenius equation:

$$v_{obs} = v_i^o \exp\left(-\frac{E_{ai}}{RT}\right). \quad (16)$$

Here  $v_i^o$  is the slightly temperature dependent pre-exponential factor, and  $E_{ai}$  is the apparent activation energy, one can state that, at the elevation of temperature, the visible transformations in such system can be detected first at

$$v_{obs} \approx v^*.$$

Here the value  $v^*$  is a constant dependent of the design of the experimental set up. When taking into account Eq. 16, we obtain:

$$\ln v_i^o - \frac{E_{ai}}{RT_i} \approx \ln v^* = \text{const.}$$

This suites relation 3 and thus expresses the existence of the “compensation”.

Since usually at studies of homological systems the values of  $T_i$  lie in quite short interval, one may select the value of  $T^*$  inside this interval for which:

$$\ln v_i^o - \frac{E_{ai}}{RT^*} \approx \ln v^* = \text{const.}$$

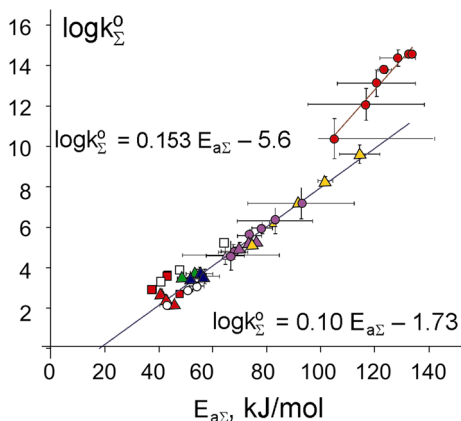
If, for example,  $T^* \approx 500 \text{ K}$ , the coefficient is:

$$\gamma = \frac{1}{RT^*} \approx 0.25 \text{ (kJ/mol)}^{-1} \quad (17)$$

This is declared in the most papers which discuss the compensation effects in catalytic processes. The compensation temperature detects quite precisely the middle of the range of experimental temperatures [4].

An example of the experimental observation of the compensation effect is given in Fig. 3. Note that the data marked by black circles were received at lower temperatures than the other ones, and thus the slope for the former data are sharper.

**Fig. 3** Experimentally observed correlations between the values of apparent activation energy  $E_{a\Sigma}$  and pre-exponential factor  $k_{\Sigma}^0$  for reduction of copper oxides of different nature with hydrogen (according to [20]). The values of  $k_{\Sigma}^0$  are expressed in units of  $s^{-1}$



## Conclusions

The above consideration evidences that kinetic compensation phenomena have to be quite typical at studying kinetics in a large variety of chemically reactive systems and reflect, at least, two main “conservative” factors. First, at studying the occurrence of chemical transformations in one and the same system at different external conditions like temperature, reagent concentrations, etc., the compensation phenomenon is a sequence of existing a temperature (or concentration) at which the change of the rate determining step does occur. Second, at studying the occurrence of either a chemical transformation in a set of homological systems (like heterogeneous catalysts of close nature, etc.) or, vice versa, homological transformations, the compensation phenomenon reflects the existence of a constant parameter of sensitivity of the kinetics measuring devices. Typically, this is a minimal rate (and, thus, typical time of the transformation) which can be detected by the device.

The experimental errors in complex experiments and logarithmic scale of the experimental data representation are shading, indeed, some misbalances of the found correlations.

Indeed, both mentioned reasons of the origin of compensation phenomena do not exclude the possibility of some correlations between enthalpy and entropy in the dynamic parameters of chemical transformations under study. A large variety of such correlations are well known in chemical thermodynamics of homological objects.

In spite of the above not so optimistic comments on the possible nature of the kinetic compensation phenomena, one has to emphasize, nevertheless, a significant practical importance of studying such phenomena: these are reflecting the temperature at which the target chemical transformation can occur with a practically acceptable rate.

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