

Kinetic compensation effect as a mathematical consequence of the exponential rate constant

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Abstract

It is shown that the kinetic compensation effect mathematically results from the exponential form of the rate constant. A change of activation energy is thus compensated by the same change in temperature or in the logarithm of the pre-exponential factor.

INTRODUCTION

In the field of kinetic study on solid-state processes, the physical meaning of Arrhenius parameters is rather dubious [1,2], because of the occurrence of a linear relationship between the logarithm of the apparent pre-exponential factor $\ln A_{\text{app}}$ and the activation energy E_{app} obtained experimentally [3], even if the process proceeds with a negligible change in sample and measuring conditions. This fatal problem is known as the kinetic compensation effect (KCE) and many workers have so far tried to solve it from theoretical [4–9] and experimental [10–14] points of view. This problem was originally pointed out by Zawadski and Bretzsnajder [15] for the thermal decomposition of CaCO_3 under various pressures of CO_2 . They determined the dependence in the form $E_{\text{app}} = p(P_{\text{CO}_2})$. Afterwards it was theoretically explained by Pavlyuchenko and Prodan [16], reinvestigated by Wist [17] and analysed from the viewpoint of chemical statistics by Roginskij and Chajt [18]. In fact, this is in agreement with a known dependence of the rate of the process $d\alpha/dt = \dot{\alpha}$ upon the pressure P , which is expressed in the form of a multiplying function $p(P)$ to the rate constant $k(T)$. Another aspect of the KCE is the effect of varying defect concentrations as shown by Olejnikov et

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al. [19] for the formation process of Mg-ferrite under different partial pressures of oxygen. Associated findings were noticed by Solymosi et al. [20] and Dollimore and Rogers [21]. Guarrini et al. [22] pointed out that the non-linearity of the Arrhenius plot increases with the sample mass, and recommended the extrapolation to zero mass. Hullet [23] made a search for the reasons for possible non-linearity, determining that any deviation from a straight line in the plot $\ln k(T)$ vs. reciprocal absolute temperature $1/T$ is to be considered as almost certain evidence that the observed process is complex. The alternative paths of two or more simultaneous processes with different E values are concave upwards while those for the consecutive case are concave downwards. Exner [4] first pointed out that it is not correct to determine the KCE by a linear regression of E_{app} vs. $\ln A_{app}$ because these quantities are mutually dependent, both being derived from the original kinetic data.

The deficiencies in the Arrhenius equation have been pointed out as a cause of the KCE [24–26]. At the same time, experimental and computational errors have also been suggested by some authors [27,28]. In contrast to these critical contributions to the present kinetic treatments of solid-state processes, some authors have explained the KCE in connection with various physicochemical factors [11,14]. One of the most important points under discussion is whether or not the existence of the KCE implies some physicochemical significance. Recently, Agrawal proposed to divide the KCE into two sets by the existence of an isokinetic point on the $\ln k(T)$ vs. $1/T$ coordinate: one arising from physicochemical factors and the other from computational and experimental artifacts [29]. Since $k(T)$ and T can be independently determined, the plot of $\ln k(T)$ vs. $1/T$ is statistically correct. However, Agrawal's procedure [29] of distinguishing a false KCE from a true one was criticized by Šesták [30] and shown by Zsakó and Somasekharan [31] not to be correct. Moreover Pysiak and Sabalski [32] had already mathematically proved that an isokinetic point appears whenever a linear relationship is observed between $\ln A_{app}$ and E_{app} . Accordingly, although it is reasonable to exclude the KCE which does not exhibit an isokinetic point from the present argument, there is no physical explanation for the KCE which does exhibit an isokinetic point resulting from physicochemical factors [30]. On the other hand, Agrawal emphasized the usefulness of the KCE in kinetic research by following up on the previous studies which explained the KCE in connection with various physicochemical factors [33]. It seems to be necessary to inspect the background of the KCE to confirm the possibility of using the relation for chemical research.

In this study, we attempt to prove mathematically that the KCE is latent in the present orthodoxy on the kinetics of solid-state processes. On the basis of the mathematical consequence, the possibility of using the KCE for chemical research is briefly discussed.

MATHEMATICAL CONSEQUENCES

For the kinetic description of heterogeneous processes, the following equation can be applied [3]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)p(P) \quad (1)$$

where α is the fractional reaction, $f(\alpha)$ is a kinetic model function derived on the basis of physico-geometrical assumptions [3,34] on the development of the reaction boundary between the initial substance and the product, and $p(P)$ is the pressure constant possibly dependent on other force-fields (intensive properties) [3,6]. From eqn. (1) we can obtain the equation

$$k(T) = \frac{d \ln k(T)}{dT} \frac{\phi}{F(\alpha)} \frac{1}{p(P)} \quad (2)$$

with

$$F(\alpha) = \frac{df(\alpha)}{d\alpha} \quad (3)$$

where ϕ is the constant heating rate and the property of the $F(\alpha)$ function is shown elsewhere [34,35]. The temperature term $k(T)$ usually takes the form of the Arrhenius equation [3]:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

The symbols A , E and R are conventionally the pre-exponential factor, activation energy and gas (or Boltzmann) constant, respectively. Taking the first derivative of $\ln k(T)$ with respect to T , we can obtain the following from eqn. (4):

$$\frac{d \ln k(T)}{dT} = \frac{E}{R} \frac{1}{T^2} \quad (5)$$

Replacing the term $d \ln k(T)/dT$ in eqn. (2) by eqn. (5)

$$k(T) = \frac{E}{R} \frac{1}{T^2} \frac{\phi}{F(\alpha)} \frac{1}{p(P)} \quad (6)$$

From eqns. (4) and (6)

$$A \exp\left(-\frac{E}{RT}\right) = \frac{E}{R} \frac{1}{T^2} \frac{\phi}{F(\alpha)} \frac{1}{p(P)} \quad (7)$$

Taking logarithms of eqn. (7) we can obtain the equation

$$\ln A = \frac{E}{RT} + \ln \left[\frac{E}{R} \frac{1}{T^2} \frac{\phi}{F(\alpha)} \frac{1}{p(P)} \right] \quad (8)$$

Equation (8) can be reproduced as

$$\ln A + \Delta \ln A = \frac{E + \Delta E}{T + \Delta T} \frac{1}{R} + \text{const.} \quad (9)$$

In eqn. (9) if the E term is constant, i.e. $\Delta E = 0$, the value of ΔT decreases with increasing $\Delta \ln A$. On the contrary, the value of ΔT increases with ΔE if the $\ln A$ term is constant, i.e. $\Delta \ln A = 0$. These relationships deduced from eqn. (9) are in good agreement with the previous studies for the relationship between $\ln A$, E and T by using the theoretical plots of α against T [36–38].

On the other hand, if the T term is constant, i.e. $\Delta T = 0$, a linear relationship can be observed between $(\ln A + \Delta \ln A)$ and $(E + \Delta E)$. Then eqn. (9) is equivalent to the well-known kinetic compensation equation

$$\ln A = aE + b \quad (10)$$

Some important consequences already noticed by Šesták [36] follows from eqn. (9) for the calculated value of E if the temperature is measured incorrectly. For example, in TG the temperature sensor is often positioned close to but not touching the sample, so that the difference ΔT between the correct (sample) and the measured (sensor) temperatures depends on the heating condition and the surface reflectance of the sample holder. In general, ΔT is positive for endothermic and negative for exothermic reactions, and ΔE and/or $\Delta \ln A$ are affected by the variation in ΔT , cf. eqn. (9). For uncontrolled changes of temperature $\Delta T \neq \phi \Delta t$, the value of E is found to follow the same trend with the resulting (apparent) value being a certain mean value.

In contrast to the requirement of a wide temperature interval for reliable determination of the Arrhenius parameters, a narrow range of temperature is sometimes necessary to satisfy a practical requirement. Over such a small temperature interval the temperature term in eqn. (9) seems to be constant and $\ln A$ and E become interdependent according to eqn. (10). In addition, when eqn. (10) is satisfied by more than one set of the apparent Arrhenius parameters obtained for a series of processes, the temperature term in eqn. (9) is apparently equivalent to the so-called isokinetic temperature T_{iso} . Then eqn. (8) can be rewritten

$$\ln A = \frac{E}{RT_{\text{iso}}} + \ln \left[\frac{E}{R} \frac{1}{T_{\text{iso}}^2} \frac{\phi}{F(\alpha)} \frac{1}{P(P)} \right] \quad (11)$$

The logarithmic term in the right-hand side of eqn. (11) is equivalent to the logarithm of the isokinetic rate constant $\ln k_{\text{iso}}$. Thus we can finally obtain the equation

$$\ln A = \frac{1}{RT_{\text{iso}}} E + \ln k_{\text{iso}} \quad (12)$$

It is clear from eqn. (12) that the KCE can be defined as the linear relationship between $\ln A_{\text{app}}$ and E_{app} , with a slope of $1/RT_{\text{iso}}$ and an intercept of $\ln k_{\text{iso}}$. It should be noted from eqn. (11) that in a strict sense this effect relies upon the “isokinetic hypothesis”, i.e. the kinetic obedience

remains constant. This explains the empirical fact that the KCE, which is established provided the rate law is constant, is more quantitative [39,40]. In addition, eqn. (9) apparently includes not only terms of $\ln A$ and E , but also at least one T term, as the variable. In this sense, the KCE, eqn. (10), can be understood as a projection of the interrelationship between $\ln A$, E and T onto the $\ln A$ vs. E plane. Although it is necessary to investigate the physical meaning of the T term, it seems to be connected not only to the absolute temperature but also to the working temperature interval [30,40].

DISCUSSION

As can be seen from the above results, the existence of the KCE and/or isoparametric relationship itself can be explained as a mere mathematical consequence. It should also be considered, however, that the KCE can be created by projecting the effect of change in some physicochemical factors and/or errors of measurements. This is dependent on the sample and measuring conditions, i.e. on the T term, and affects the simple relation expressed by eqn. (10) through the mathematical background described above. In order to remove this odd effect it is necessary to throw light on the projection system mathematically, because any physicochemical explanation for the apparent Arrhenius parameters is not fully quantitative without considering the KCE.

On the other hand, some interesting attempts to detect differences in the kinetics of homologous reactions by using the KCE have been reported [41]. Among them it is worth noting the studies of kinetic comparison by using the compensation parameters a and b , and the isokinetic point ($\ln k_{\text{iso}}$, $1/T_{\text{iso}}$) [33,42]. These attempts are based on the premise that the kinetics of a given process can be characterized by the isokinetic point. If the projection system expressed by eqn. (9) were a mathematical law, it should be possible to detect the kinetic difference in these processes under qualitative comparison. However, since the KCE is a mere mathematical consequence, it is difficult to discuss quantitatively the difference in the KCE between homologous reactions as a direct consequence of various physicochemical factors. Moreover, as discussed elsewhere, thermoanalytical data include inevitable errors [36,43–46]. It should be understood that variations in the shape and position of the thermoanalytical curves with slight changes in the sample and measuring conditions, which are the direct cause of the KCE, are the sum of the change in some physicochemical factors and experimental errors. Accordingly, the isokinetic point is the characteristic point depending not only on the process itself but also on the working condition.

It has been reported that “mis-estimation” of kinetic obedience is also responsible for the KCE [6,9]. If we obtained the Arrhenius parameters by assuming various $f(\alpha)$ including a correct one, these sets of Arrhenius parameters would show the KCE [47–49]. This is an example of the KCE

observed among the true and false kinetic model functions. Using the false kinetic model $h(\alpha)$ instead of the required one $f(\alpha)$, the following equation is obtained, cf. eqns. (1) and (4):

$$\frac{d\alpha}{dt} = A_{\text{app}} \exp\left(-\frac{E_{\text{app}}}{RT}\right) h(\alpha) \quad (13)$$

From eqns. (1) and (13), it follows that

$$\Delta \ln A = \frac{\Delta E}{RT} + \left\{ \ln f(\alpha) + \ln \left[\frac{p(P)}{h(\alpha)} \right] \right\} \quad (14)$$

if $\Delta \ln A = 0$

$$\Delta E = -RT \left\{ \ln f(\alpha) + \ln \left[\frac{p(P)}{h(\alpha)} \right] \right\} \quad (15)$$

or if $\Delta E = 0$

$$\Delta \ln A = \ln f(\alpha) + \ln \left[\frac{p(P)}{h(\alpha)} \right] \quad (16)$$

where $\Delta \ln A = \ln A_{\text{app}} - \ln A$ and $\Delta E = E_{\text{app}} - E$. Equation (10) leads to the relationship

$$\Delta \ln A = a \Delta E \quad (17)$$

where $a = 1/RT_{\text{iso}}$. From eqns. (14) and (17) the distortion in the Arrhenius parameters by missing $p(P)$ or false $h(\alpha)$ terms can be expressed as follows

$$\Delta E = \frac{RTT_{\text{iso}}}{T - T_{\text{iso}}} \left\{ \ln f(\alpha) + \ln \left[\frac{p(P)}{h(\alpha)} \right] \right\} \quad (18)$$

and

$$\Delta \ln A = \frac{T}{T - T_{\text{iso}}} \left\{ \ln f(\alpha) + \ln \left[\frac{p(P)}{h(\alpha)} \right] \right\} \quad (19)$$

Agrawal [33] stated that the use of incorrect model relations has to be explained before the KCE can be discussed as an artifact. We think that one of the most important problems is whether or not the solid-state processes can be fully described by the present oversimplified kinetic model functions $f(\alpha)$ [34]. In addition, the correct $f(\alpha)$ is sometimes difficult to ascertain in a practical study [40] and generally can only be established on the basis of the predetermined value of E [35] (i.e. from several runs using the Kissinger [50] or Ozawa [51] method). Similarly, the "mis-use" of the calculation methods beyond their implicit restriction can be recognized as a cause of the KCE [28,45]. These two problems in kinetic calculation are likely to distort the projection system itself.

The simple relationship of eqn. (10) seems to result from complex interaction of more than one cause [52,53], which is supported by the fact

that the compensation parameters can also change depending on the range of experimental conditions examined for the process under study [49]. In order to discuss the KCE more quantitatively and in connection with the respective causes, it is necessary to examine these effects at predetermined experimental and computational conditions. At least, the examination of KCE among the Arrhenius parameters obtained by different authors using different TA systems, and computational methods under different sample and experimental conditions, would be meaningless for any further quantitative discussion.

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