

A KINETIC COMPENSATION EFFECT ESTABLISHED FOR THE THERMAL DECOMPOSITION OF A SOLID

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Two causes for the kinetic compensation effect (KCE) were recognized for a given solid-state reaction at various heating rates. One is due to any change in the range of reaction. This KCE is quantitative and meaningful, provided that $F(\alpha)$ remains constant under the given conditions. The other is due to misestimation of the appropriate rate law, which in turn leads to a superficial KCE. It was also shown that the existence of an isokinetic point does not necessarily imply the occurrence of a meaningful KCE.

It is well known that the rates of solid-state decompositions are extremely difficult to interpret in terms of elementary steps. The time behavior is controlled not only by the molecularity or chemistry, but also by the geometry of the system, the mass and heat transfers, and so on [1, 2]. Although the physical meaning of the Arrhenius parameters for such solid-state reactions may be dubious [3, 4], the occurrence of a linear relationship between the logarithm of the preexponential factor A and the apparent activation energy E has been reported for many and diverse heterogeneous reactions [5-14]. This is the kinetic compensation effect (KCE), which is expressed as

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$$\log A = a + bE \quad (1)$$

where a and b are the compensation constants. On account of this effect, a comparison of the kinetics of homologous solid-state reactions in terms of E alone seems less meaningful [15].

Zsako stressed that the KCE is real and the compensation constants are more significant than the values of E and A [3]. Krug *et al.* reported, however, that, when the data are plotted in a usual way, the true functional dependence, if any, is usually masked by a dominant statistical compensation pattern that arises solely from experimental errors [16]. Manche and Carroll have pointed out that many of the linear relationships obtained in the thermal decomposition of solids, which have been ascribed to possible chemical factors, are open to question [17]. It is also true that not a few articles on the KCE are less meaningful or even sterile, from which one cannot extract any knowledge useful for a better understanding of the kinetics of solid-state reactions. It is evident that extensive KCE studies based on elaborate physical measurements are required to gain a deeper comprehension of such reaction kinetics [7, 18].

The Arrhenius parameters can be obtained on the basis of the "isokinetic hypothesis", i.e. the kinetic obedience remains constant. Nevertheless, most arguments for the KCE have so far been made independently of the kinetic rate equation assumed to obtain the apparent Arrhenius parameters. By introducing the "isokinetic hypothesis" to the examination of the KCE, we reported that the quantitative KCE, which is established provided the rate law is constant under the given experimental conditions, is useful for comparing the kinetic obedience between the isothermal and nonisothermal runs of a solid-state reaction [11-14]. One of the important findings is that the rate constant k determined isothermally is in good agreement with that calculated in terms of the KCE for the corresponding nonisothermal reaction at various heating rates, when the same rate law is valid for both isothermal and nonisothermal runs of a given solid-state reaction. Table 1 illustrates the comparability of k for several reactions between the isothermal and nonisothermal runs, in which each rate law is valid for both runs [11, 13, 14]. It was also shown that the k value differs considerably between the runs when the rate law is changed or "misestimated".

It is also worth analyzing theoretical plots of the fractional reaction α against time t (for the isothermal runs) and against temperature T (for the nonisothermal runs), drawn with the help of a computer. It was hoped that such an approach could generalize the above relationship, which in turn would enable us to understand the complicated kinetic behavior of solid-

Table 1 Comparison between rate constants k determined isothermally and in terms of KCE for the corresponding nonisothermal reaction at various heating rates

Reaction	$F(\alpha)$	Temp., °C	Rate constant k , 1/s		Ref.
			isothermally	from KCE ^{*1}	
CaC ₂ O ₄ → CaCO ₃ + CO	A _{1.43}	415.0	6.66 · 10 ⁻⁴	7.01 · 10 ⁻⁴	11
SrC ₂ O ₄ → SrCO ₃ + CO	R _{1.54}	450.0	2.00 · 10 ⁻⁴	2.10 · 10 ⁻⁴	11
CuCl ₂ · 2H ₂ O → CuCl ₂ + 2H ₂ O	R _{1.2}	77.0	1.13 · 10 ⁻³	1.03 · 10 ⁻³	13
CaC ₂ O ₄ · H ₂ O → CaC ₂ O ₄ + H ₂ O	A _{1.9}	165.0	1.33 · 10 ⁻³	1.31 · 10 ⁻³	14

*1 Calculated in terms of the equation, $\log A = a + bE$, with the value of $\log A$ determined isothermally

state reactions at the most fundamental level possible. The present article concerns the kinetics of a solid-state reaction at various heating rates, including the isothermal reaction, analyzed by integral methods.

Theoretical TA curves

For the isothermal decomposition of solids, the following equation can be assumed:

$$F(\alpha) = kt, \quad \text{with } k = A \exp(-E/RT) \quad (2)$$

where $F(\alpha)$ is a kinetic model function, R is the gas constant and T is the absolute temperature. Table 2 lists various $F(\alpha)$ used to describe the kinetics of solid-state decompositions. The theoretical isothermal TA curves are obtained in terms of Eq. (2) by specifying the $F(\alpha)$, Arrhenius parameters and temperatures. If the reaction were described by the contracting envelope law: $1 - (1 - \alpha)^{1/2} = kt$ with $E = 170$ kJ/mol, $\log A = 21.5$ 1/s and $T_n = 340 + 5n$ K ($n = 0, 1, 2, 3$ and 4), we could obtain the theoretical isothermal TA curves as shown in Fig. 1.

Table 2 Kinetic model functions, $F(\alpha)$

Model	$F(\alpha)$	label
one-dimensional diffusion	α^2	D ₁
two-dimensional diffusion	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	D ₂
Jander	$[1 - (1 - \alpha)^{1/3}]^2$	D ₃
Ginstling-Broushstein	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$	D ₄
contracting geometry	$1 - (1 - \alpha)^{1/n}, \quad n = 1, 2, 3$	R _n
Avrami-Erofeyev	$[-\ln(1 - \alpha)]^{1/m}, \quad m = 1, 2, 3, 4$	A _m

As concerns the dynamic process at a heating rate β , on the other hand, the following equation holds [19]:

$$\ln(AE/\beta R) = \ln F(\alpha) - \ln p(E/RT) \quad (3)$$

where $p(x) \doteq \exp(-x)x^2$ according to Doyle [20]. We assume here the numerical values of E at a given β , as listed in Table 3 in accordance with the general trend of E at different β [21]. We can derive $\log A$, in terms of Eq. (1), by giving numerical values of a and b . The $\log A$ values thus derived

are included in the last column of Table 3, assuming $a = -4.0$ 1/s and $b = 0.15$ mol/kJ·s. Figure 2 shows the compensation plot assumed, in which the Arrhenius parameters given for the isothermal process also fit the compensation line. By assuming that the R_2 law is also appropriate for the dynamic process, the TA curves are obtained as shown in Fig. 3, using Eq. (3) and the values given in Table 3.

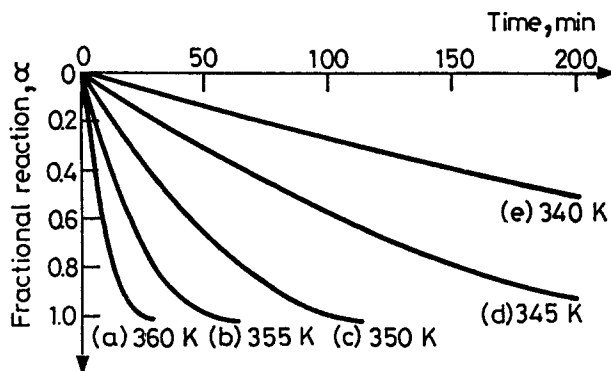


Fig. 1 Theoretical isothermal TA curves obtained by assuming $1 - (1 - \alpha)^{1/2} = kt$ with $E = 170$ kJ/mol and $\log A = 12.5$ 1/s

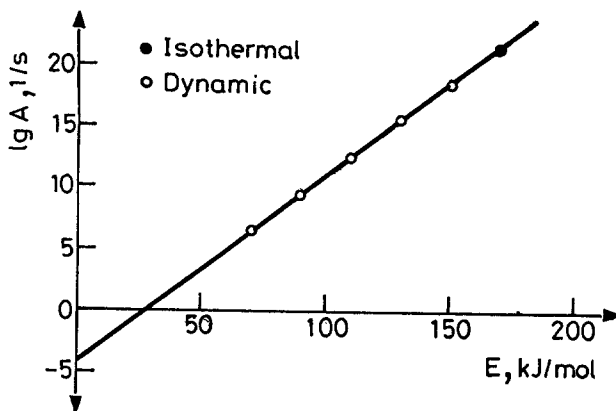


Fig. 2 The $\log A$ vs. E plot for the reaction assumed at various β

Table 3 The E values assumed at given heating rates β and the $\log A$ values derived in terms of $\log A = a + bE$ with $a = -4.0$ and $b = 0.15$

curve	β , deg/min	E , kJ/mol	$\log A$, 1/s
A	0.5	150	18.5
B	1.0	130	15.5
C	2.0	110	12.5
D	4.0	90.0	9.50
E	8.0	70.0	6.50

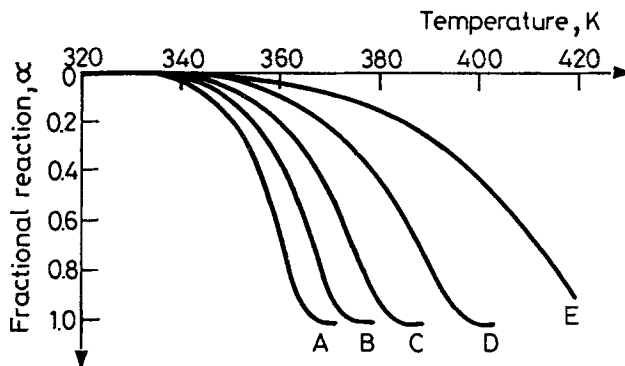


Fig. 3 Theoretical dynamic TA curves obtained by assuming $R_2 = 1 - (1 - \alpha)^{1/2}$ with numerical values of E , $\log A$ and β as listed in Table 3

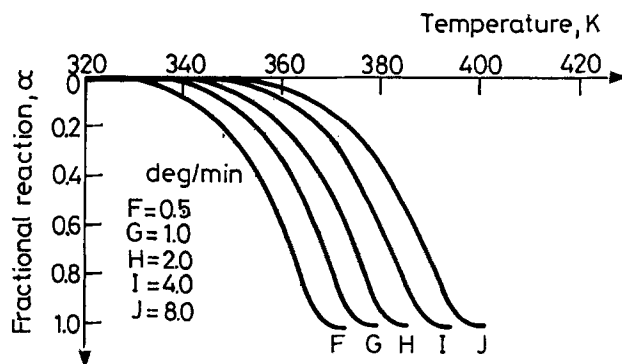


Fig. 4 Theoretical dynamic TA curves obtained by assuming $R_2 = 1 - (1 - \alpha)^{1/2}$ with $E = 110$ kJ/mol and $\log A = 12.5$ 1/s

In addition, it is interesting to draw nonisothermal TA curves, supposing that the Arrhenius parameters do not change independently of β . Figure 4 shows such curves obtained by assuming $F(\alpha) = R_2$ with $E = 110$ kJ/mol and $\log A = 12.5$ 1/s for all curves at different β .

Calculation of Arrhenius parameters

The values of E and $\log A$ were recalculated for the isothermal TA curves in Fig. 1 in terms of all the $F(\alpha)$ in Table 2. The Arrhenius parameters for the nonisothermal curves in Figs 3 and 4 were calculated in terms of the eleven $F(\alpha)$ by assuming the equation of Coats and Redfern (CR) [22]:

$$\ln [F(\alpha)/T^2] = \ln (AR/\beta E) [1 - (2RT/E)] - (E/R)(1/T) \quad (4)$$

In addition, the values of E for the nonisothermal curves in Figs 3 and 4 were calculated according to the following equation [12]:

$$\ln (\beta/T^2) \doteq -E/RT + \ln (R/\Theta E) \quad (5)$$

where Θ is the generalized time [23-25].

Results and discussion

Isothermal analysis

Figure 5 shows the plots of $F(\alpha)$ against t , in terms of all the $F(\alpha)$ examined, for a typical TA curve (curve *b* in Fig. 1). Although the correct $F(\alpha)$ should be selected to some extent from the linearity of the $F(\alpha)$ vs. t plot, it seems difficult because an incorrect $F(\alpha)$ also shows fairly good linearity, as can be seen from Fig. 5. We have pointed out that, in practice, determination of the correct $F(\alpha)$ is much more difficult because of a possible change in a rate-limiting step and the concurrent processes, which depends on α , T , and so on [21].

Table 4 lists the Arrhenius parameters calculated in terms of the eleven $F(\alpha)$ for the theoretical isothermal TA curves in Fig. 1. The Arrhenius parameters estimated isothermally, irrespective of the $F(\alpha)$ used, are in good agreement with the values assumed, $E = 170$ kJ/mol and $\log A = 12.5$ 1/s, as observed usually [26].

Table 4 The Arrhenius parameters calculated for the isothermal TA curves in Fig. 1

$F(\alpha)$	E , kJ/mol	$\log A$, 1/s	$-\gamma^{*1}$
D ₁	170±1	21.6±0.1	0.9991
D ₂	170±1	21.5±0.1	0.9991
D ₃	170±1	21.1±0.1	0.9991
D ₄	170±1	20.9±0.1	0.9992
R ₁	170±1	21.6±0.1	0.9991
R ₂	170±1	21.5±0.1	0.9991
R ₃	170±1	21.3±0.1	0.9991
A ₁	170±1	22.0±0.1	0.9991
A ₂	170±1	21.7±0.1	0.9991
A ₃	170±1	21.6±0.1	0.9991
A ₄	170±1	21.4±0.1	0.9991

*¹Correlation coefficient of the linear regression analysis of the Arrhenius plot

Nonisothermal analysis

We see from Fig. 3 that the nonisothermal TA curves shift toward the higher temperature region with increasing β [27], accompanied by decreasing slope. This is a normal pattern for mass loss traces recorded at different β [3]. Table 5 gives the Arrhenius parameters derived from the CR method for the TA curves shown in Fig. 3. It also seems difficult to choose the correct $F(\alpha)$ in view of the linearity of the CR plot. It is indeed difficult, because the kinetic obedience of the thermal decomposition of solids is likely to be affected by β . We also see from Table 5 that the Arrhenius parameters derived for the respective TA curves at different β change depending on the $F(\alpha)$ assumed, in contrast with the consequence of the isothermal analysis [21].

Table 6 lists the compensation constants a and b obtained for the Arrhenius parameters calculated using the CR method for the nonisothermal TA curves in Fig. 3, together with the rate constants k_i and k_n determined isothermally and nonisothermally, respectively. The values of k_i and k_n in terms of the correct R_2 law assumed are nearly equal, whereas those in terms of other $F(\alpha)$ are not. This proves that the quantitative KCE between the isothermal and nonisothermal processes is highly correlated with the correct $F(\alpha)$, which remains unchanged under given conditions. This is in good agreement with the relationship obtained experimentally [11-14]. Such a relationship was used successfully to discuss variations in the kinetic obedience between isothermal and nonisothermal reactions of a solid [21]. It

Table 5 The Arrhenius parameters, E (kJ/mol) and $\log A$ (1/s), calculated by Coats & Redfern Method for the nonisothermal TA curves in Fig. 3

$F(\alpha)$	Heating rate, deg/min														
	0.5			1.0			2.0			4.0			8.0		
	E	$\log A$	$-\gamma^{*1}$	E	$\log A$	$-\gamma^{*1}$	E	$\log A$	$-\gamma^{*1}$	E	$\log A$	$-\gamma^{*1}$	E	$\log A$	$-\gamma^{*1}$
D1	264	35.2	0.9978	227	29.7	0.9975	195	24.6	0.9967	155	18.5	0.9974	119	12.9	0.9975
D2	292	39.2	0.9999	252	33.1	0.9996	213	27.0	0.9996	172	20.7	0.9996	132	14.4	0.9997
D3	327	43.9	0.9996	283	37.0	0.9998	237	30.0	0.9997	193	23.1	0.9997	149	16.1	0.9999
D4	303	40.3	0.9999	262	33.9	0.9999	221	27.6	0.9999	179	21.1	0.9999	138	14.5	0.9999
R1	129	15.5	0.9975	111	12.9	0.9972	94	10.4	0.9964	75	7.5	0.9969	56	4.8	0.9972
R2	152	18.8	1.0000	131	15.6	1.0000	110	12.5	1.0000	88	9.3	1.0000	67	6.0	1.0000
R3	161	19.9	0.9998	138	16.6	0.9998	116	13.2	0.9998	93	9.8	0.9997	71	6.4	0.9998
A1	180	23.3	0.9976	155	19.5	0.9972	129	15.6	0.9959	105	12.0	0.9971	80	8.1	0.9973
A2	86	9.5	0.9973	74	7.7	0.9972	61	5.9	0.9958	49	4.2	0.9969	37	2.3	0.9969
A3	56	4.8	0.9976	48	3.7	0.9979	39	2.6	0.9953	31	1.5	0.9963	22	0.3	0.9961
A4	40	2.4	0.9967	34	1.7	0.9980	28	0.9	0.9946	22	0.1	0.9936	15	-0.7	0.9944

*1 Correlation coefficient of the linear regression analysis of the CR plot

is noted that the kinetics of nonisothermal reaction, which in particular have practical importance but are usually difficult to explain theoretically, can be elucidated and discussed more comprehensively by using this relationship.

Table 6 The compensation constants, a and b , for the nonisothermal processes and comparison of rate constants, k_i and k_n , obtained isothermally and nonisothermally, respectively, for the theoretical TA curves in Figs 1 and 3

$F(\alpha)$	Compensation constants ^{*1}			Rate constant ^{*3} , 1/s	
	$-a$, 1/s	b , mol/kJ·s	γ ^{*2}	k_i	k_n ^{*4}
D1	5.5	0.15	0.9999	$9.23 \cdot 10^{-4}$	$1.45 \cdot 10^{-4}$
D2	6.1	0.16	0.9999	$7.33 \cdot 10^{-4}$	$5.35 \cdot 10^{-4}$
D3	7.1	0.16	0.9999	$2.89 \cdot 10^{-4}$	$7.52 \cdot 10^{-5}$
D4	6.9	0.16	0.9999	$1.96 \cdot 10^{-4}$	$1.03 \cdot 10^{-5}$
R1	3.6	0.15	0.9999	$9.00 \cdot 10^{-4}$	$1.04 \cdot 10^{-3}$
R2	4.1	0.15	0.9999	$6.94 \cdot 10^{-4}$	$7.07 \cdot 10^{-4}$
R3	4.3	0.15	0.9999	$5.41 \cdot 10^{-4}$	$4.98 \cdot 10^{-4}$
A1	4.0	0.15	0.9999	$2.27 \cdot 10^{-4}$	$1.57 \cdot 10^{-4}$
A2	2.9	0.14	0.9999	$1.25 \cdot 10^{-4}$	$5.42 \cdot 10^{-4}$
A3	2.6	0.13	0.9999	$8.81 \cdot 10^{-4}$	$1.90 \cdot 10^{-5}$
A4	4.1	0.20	0.9999	$6.82 \cdot 10^{-4}$	$4.36 \cdot 10^{-2}$

^{*1} For the nonisothermal TA curves in Fig. 3

^{*2} Correlation coefficient of the linear regression analysis of the compensation plot

^{*3} Value at 360 K

^{*4} Calculated using the value of $\log A$ derived isothermally in terms of each $F(\alpha)$

At the same time, it is noted that the linearity of the $\log A$ vs. E plot is fairly good for incorrect $F(\alpha)$ other than R_2 , although the compensation constants are considerably different, depending on the $F(\alpha)$ assumed. This fact suggests that this compensation behavior results, at least in this case, from two causes: variation of β and "misestimation" of $F(\alpha)$. Although it may be argued as to whether or not the KCE results from chemical reasons [4, 10], the effect of β seems to include some chemical or physical reason or any kinetically meaningful factors, and the "misestimation" of $F(\alpha)$ does not. It is likely that the former is closely connected with a shift of the TA curves along the temperature coordinate, accompanied by variation in the slope (see Fig. 3), i.e. change in the range of reaction temperature. This is supported by the linear relationships between the apparent Arrhenius parameters determined in terms of the R_2 law and the reciprocals of the temperature in-

tervals analyzed, ΔT^{-1} , as shown in Fig. 6. This explains a systematic variation in E for solid-state reactions with increasing β , as observed for many solid-state reactions [9, 21]. On the other hand, a typical example of the KCE due to the "misestimation" of $F(\alpha)$ is concerned with a superficial KCE established among the Arrhenius parameters derived in terms of different $F(\alpha)$ [28]. Table 7 lists the superficial compensation constants, a and b , for the Arrhenius parameters obtained by using the eleven $F(\alpha)$ for the respective TA curves in Fig. 3. Although all the compensation plots are nearly linear in this case, such a KCE has no physical sense in formulation of the kinetics and mechanisms of solid-state reactions. In this respect, the linear compensation plots reported so far do not necessarily mean the quantitative KCE which gives valuable information about the reaction kinetics. It also seems that an isokinetic point, which is believed to be a strict criterion of the occurrence of the KCE by many workers [29-31], is not always useful for recognition of the separate causes of the KCE, because a linear compensation plot gives the isokinetic point [32].

Table 7 The compensation constants, a and b , for the Arrhenius parameters obtained by assuming various $F(\alpha)$ for the respective TA curves in Fig. 3

Curve	β , deg/min	Compensation constants		γ^{*1}
		$-a$, 1/s	b , mol/kJ·s	
A	0.5	3.15±0.04	0.1445±0.0002	0.9998
B	1.0	2.93±0.03	0.1421±0.0002	0.9998
C	2.0	2.72±0.03	0.1387±0.0002	0.9997
D	4.0	2.52±0.03	0.1337±0.0003	0.9995
E	8.0	2.36±0.03	0.1253±0.0004	0.9991

*1 Correlation coefficient of the linear regression analysis of compensation plot

It is interesting here to obtain E at various α on the basis of the TA curves in Fig. 3, using the Ozawa method. Figure 7 shows the variation in E with α , calculated using Eq. (5). We see that E decreases with increasing α . This is also due to variation in the ΔT analyzed, i.e. the temperature difference between the reactions at the highest and lowest β at a given α . The relationship between ΔT^{-1} and E is shown in Fig. 8. The plot is also a nearly straight line, as is the case with the E obtained using the CR method (see Fig. 6), which implies that E decreases quantitatively with the increasing temperature region analyzed.

As concerns the TA curves in Fig. 4, in which the Arrhenius parameters were assumed to be constant irrespective of β , we see that the curves show

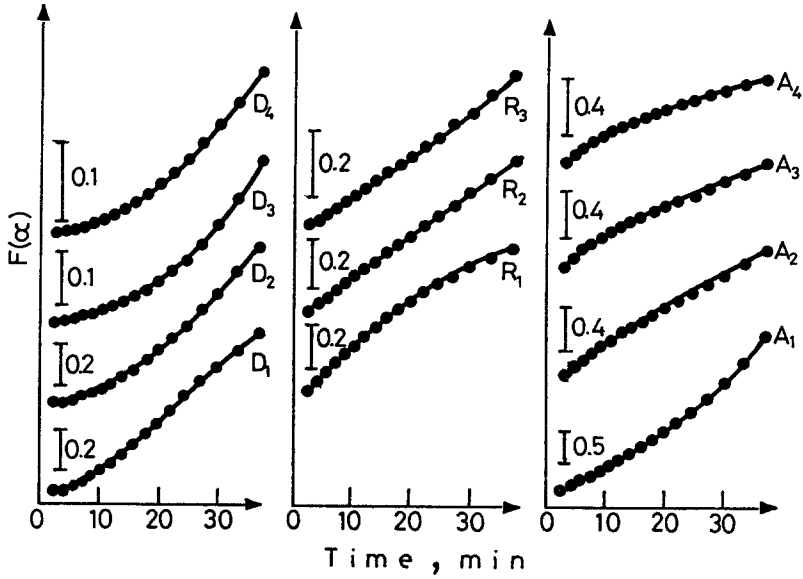


Fig. 5 Typical $F(\alpha)$ vs. t plots for an isothermal TA curve at 355 K

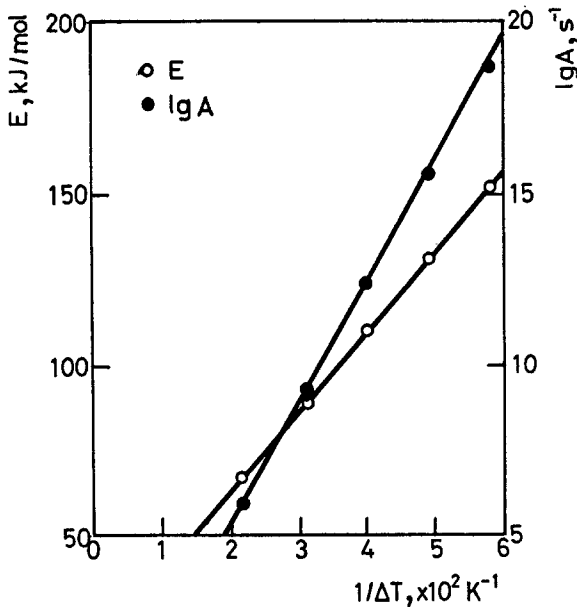


Fig. 6 The plots of E and $\lg A$, obtained using the CR method for the nonisothermal TA curves in Fig. 3, against reciprocals of the temperature interval analysed, ΔT^{-1}

Table 8 The Arrhenius parameters, E (kJ/mol) and $\log A$ (1/s), calculated by Coats & Redfern Method for the nonisothermal TA curves in Fig. 4

$F(\alpha)$	Heating rate, deg/min														
	0.5			1.0			2.0			4.0			8.0		
	E	$\log A$	$-\gamma^*1$	E	$\log A$	$-\gamma^*1$	E	$\log A$	$-\gamma^*1$	E	$\log A$	$-\gamma^*1$	E	$\log A$	$-\gamma^*1$
D1	195	25.0	0.9967	195	24.8	0.9967	195	24.6	0.9967	195	24.3	0.9969	195	24.1	0.9970
D2	213	27.6	0.9994	213	27.3	0.9995	213	27.0	0.9996	213	26.8	0.9998	213	26.5	0.9998
D3	237	30.6	0.9996	237	30.3	0.9997	237	30.0	0.9997	237	29.6	0.9999	237	29.3	0.9999
D4	221	28.2	0.9999	221	27.9	0.9999	221	27.6	0.9999	221	27.3	0.9999	221	27.0	0.9999
R1	94	10.4	0.9964	94	10.4	0.9965	94	10.4	0.9964	94	10.5	0.9968	94	10.5	0.9966
R2	110	12.5	1.0000	110	12.5	1.0000	110	12.5	1.0000	110	12.5	1.0000	109	12.4	1.0000
R3	116	13.2	0.9995	116	13.2	0.9998	116	13.2	0.9998	116	13.2	0.9999	115	13.1	0.9999
A1	129	15.7	0.9959	129	15.6	0.9960	129	15.6	0.9959	129	15.6	0.9962	128	15.5	0.9959
A2	61	5.7	0.9955	61	5.8	0.9955	61	5.9	0.9958	61	6.0	0.9958	61	6.1	0.9959
A3	39	2.2	0.9952	39	2.4	0.9944	39	2.6	0.9953	39	2.7	0.9954	39	2.9	0.9951
A4	28	0.5	0.9935	28	0.7	0.9943	28	0.9	0.9946	28	1.1	0.9936	27	1.3	0.9943

*1 Correlation coefficient of the linear regression analysis of the CR plot

almost no change in slope. In this case, there is little change in the ΔT analyzed, irrespective of β and α . Table 8 lists the Arrhenius parameters obtained, in terms of the eleven $F(\alpha)$, using the CR method for the nonisothermal TA curves at different β (see Fig. 4). As expected, the Arrhenius parameters calculated in terms of a given $F(\alpha)$ are not different for the TA

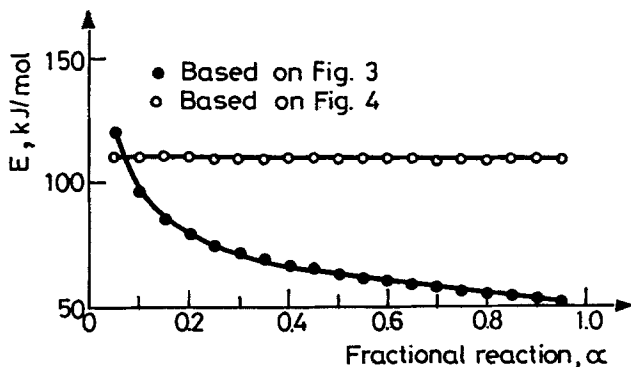


Fig. 7 Activation energies E at different α , calculated by the Ozawa method, for the nonisothermal TA curves in Figs 3 and 4

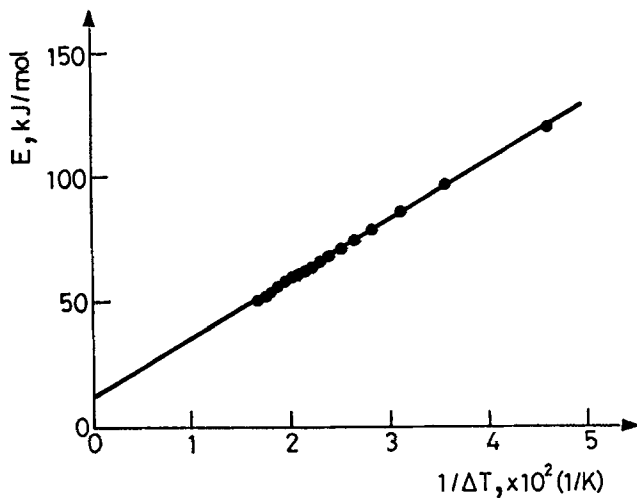


Fig. 8 The plot of E , obtained using the Ozawa method for the theoretical TA curves in Fig. 3, against the reciprocals of the temperature intervals, ΔT^{-1}

curves at different β . If the KCE could be established for the different $F(\alpha)$ for a given β , the compensation constants would not change for the TA curves at different β . Accordingly, this KCE is superficial and due only to the "misestimation" of $F(\alpha)$. It is expected here that the E values derived from the Ozawa method are nearly constant, independently of α . Figure 7 shows the E values at various α from 0.05 to 0.95 in steps of 0.05 for the TA curves in Fig. 4. We note that there is no change in E , irrespective of α .

It is clear from the above results that the variation in apparent E and/or $\log A$ depending on α and β is caused by any changes in the slope of the nonisothermal TA curves. In other words, the KCE is established for a series of nonisothermal TA curves whenever there is a change in the slope of the TA curves [19]. Any variation in E and $\log A$ due to the change in the slope of the dynamic TA curves suggests a drawback of such a kinetic approach [33]. Some problems remain in describing the nonisothermal and/or isothermal rate data of solid-state reactions in terms of E and A [7, 18, 34, 35]. In this respect, such a KCE itself might not have any physical significance in formulating the kinetics of solid-state reactions.

It is well known, on the other hand, that the actual processes of thermal decomposition of those solids, which yield solid and gaseous products, consist of several elementary steps [1, 2]. Such steps regulate the shape of the TA curves [5, 35]. Changes in the slope and/or shape of the nonisothermal TA curves are possible, depending on various sample and measuring conditions, e.g. sample preparation, particle size, sample mass, heating rate, atmosphere, and so on [36]. Accordingly, the KCE is more or less established for all the Arrhenius parameters obtained experimentally for the thermal decomposition of a solid under various conditions. The experimental KCE due to any changes in the slope of the nonisothermal TA curves is rather indirectly correlated with variation in the reaction processes. Although the Arrhenius parameters obtained for solid-state reactions have been explained in terms of a compensation line [29], this seems deficient in consideration of a possible change in $F(\alpha)$ [8, 35, 37]. In other words, such compensation behavior is likely to arise from both meaningful and superficial origins. In this respect, it is important to recognize the separate causes of any appearance of the KCE. The KCE would be quantitative and meaningful only if appropriate processing were made, based on reliable data in terms of the correct $F(\alpha)$, which remains unchanged under the given conditions.

Conclusions

There are at least two causes of the existence of the KCE established for a given solid-state reaction at various β . One is due to any change in the range of the reaction temperature. This KCE is quantitative, provided that $F(\alpha)$ remains constant under the conditions examined. The other is due to possible "misestimation" of the most appropriate $F(\alpha)$, which in turn leads to a superficial KCE. The above results make it possible that the kinetics of a nonisothermal reaction at various heating rates are "viewed" in terms of the kinetics of the corresponding isothermal reaction. The excellent linearity of the compensation plot and the existence of an isokinetic point do not necessarily imply the occurrence of a meaningful KCE. The validity of many articles reported so far on the KCE is likely to be diminished in that not a few workers analyzed the kinetics without considering possible changes in the rate laws, in addition to the possibility that the KCE sometimes arises from the experimental error.

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Zusammenfassung — Für den kinetischen Kompensationseffekt (KCE) für eine gegebene Feststoffreaktion bei verschiedenen Aufheizgeschwindigkeiten wurden zwei Gründe angegeben. Der eine Grund steht in Beziehung zur Änderung der Reaktionstemperatur. Dieser KCE ist quantitativ und von Bedeutung, vorausgesetzt, daß $F(\alpha)$ unter den gegebenen Bedingungen konstant bleibt. Der andere liegt in der falschen Aufstellung des entsprechenden Geschwindigkeitsgesetzes. Es wurde weiterhin gezeigt, daß die Existenz eines isokinetischen Punktes nicht zwangsweise das Auftreten eines bedeutenden KCE beinhaltet.