

## **KINETIC COMPENSATION EFFECT BETWEEN THE ISOTHERMAL AND NON-ISOTHERMAL DECOMPOSITION OF SOLIDS**

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A “true” kinetic compensation effect was established using the most appropriate kinetic function  $F(\alpha)$  for the non-isothermal decomposition of solids at various heating rates. It is likely that the correct kinetic mechanism  $F(\alpha)$  is responsible for the “true” kinetic compensation effect, whereas an inappropriate  $F(\alpha)$  would lead to “false” one.

An establishment of such a “true” compensation effect between the isothermal and non-isothermal decompositions of a solid implies that  $F(\alpha)$  used is appropriate for both the isothermal and non-isothermal decompositions.

When the kinetic compensation law,  $\log A = a + bE$ , was applied to the thermal dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  under isothermal and non-isothermal conditions, “true” compensation relations with the highest linearity of the  $\log A$  vs.  $E$  plot were established only in terms of the correct kinetic model functions estimated conventionally. The significance and availability of the “true” compensation effect are discussed.

In the kinetic study of the thermal decomposition of solids the determination of the appropriate mechanistic function  $F(\alpha)$  is one of the most important subjects. In some cases it is not able to single out unequivocally the correct  $F(\alpha)$  by means of the conventional isothermal analysis alone. Recently the importance of a systematic examination, e.g., comparison of isothermal and non-isothermal kinetics for decompositions of powdered and single crystalline materials, has been stressed in finding the actual decomposition mechanism, along with meaningful kinetic parameters [1].

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Another subject of the kinetic investigation is the evaluation of kinetic parameters, i.e., the activation energy  $E$  and the pre-exponential factor  $A$ . It is well known that these parameters vary with the experimental conditions, even if the decomposition mechanism do not change, which is referred to as "kinetic compensation effect". Many workers have so far argued it from the theoretical and experimental points of view [2, 3]. On account of this effect, the comparison of kinetics of homologous reactions in terms of kinetic parameters is complicated and the selection of the correct  $F(\alpha)$  becomes difficult.

It is likely that the kinetic compensation effect is established for the kinetic parameters  $E$  and  $A$  derived under various experimental conditions:

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

where  $a$  and  $b$  are constants. In our previous study this relationship was examined using not only the correct  $F(\alpha)$  estimated but also other  $F(\alpha)$  which were not appropriate, for the thermal decompositions of several oxalates [4]. It was suggested that the "true" compensation law should result from the most appropriate  $F(\alpha)$  alone, which in turn is useful for reviewing the availability of the  $F(\alpha)$  estimated conventionally.

It is interesting to extend such an examination to the thermal dehydration of inorganic salt hydrates, since the kinetic evaluation for such dehydrations is rather difficult and discordant among workers. In the present investigation the isothermal and non-isothermal dehydrations of crystalline powdered  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  were chosen, since this dihydrate is dehydrated to the anhydride in a single step at a relatively low temperature. In addition, the kinetic result reported earlier [5] on the thermal dehydration of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  was reviewed in view of the "true" kinetic compensation effect.

## Experimental

Reagent grade  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was ground and screened to a particle size fraction of 100–170 mesh.

TG measurements were made on a Rigaku Thermoflex TG–DSC 8085 E1 system, in a flow of nitrogen at a rate of 30 ml/min, with ca. 10.0 mg of sample in a platinum crucible of 5 mm diameter and 2.5 mm in height. Isothermal mass-change traces at various temperatures were recorded under identical conditions with the dynamic runs. The kinetic analyses were made in a dehydration fraction  $\alpha$  of 0.3–0.9 throughout, because  $E$  estimated from Ozawa's method [6] varied depending on  $\alpha$  appreciably in the range  $\alpha < 0.3$ .

## Results and discussion

From the conventional isothermal analysis,  $R_{1,2}$  law was deduced for the isothermal dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  into  $\text{CuCl}_2$ . Figure 1 shows a typical  $R_{1,2}$  vs. time ( $t$ ) plot. The kinetic parameters derived from Arrhenius plot over a temperature range of 56.5–68.0° are shown in Table 1. The  $R_{1,2}$  function was in good agreement with the non-isothermal dehydration mechanism derived from Ozawa's method [6], i.e.,  $F(\alpha)$ -generalized time  $\theta$  plot [7], over a heating rate range of 0.57–4.19 deg/min. Table 1 also shows the mechanistic function  $F(\alpha)$  and kinetic parameters derived from Ozawa's method. A typical  $R_{1,3}$  vs.  $\theta$  plot is shown in Fig. 2. This agreement in  $F$  implies that the dehydration mechanism practically does not change between the isothermal and non-isothermal dehydrations examined.

With regard to the kinetic parameters derived from modified Coats and Redfern's method [8] at heating rates of 0.57, 1.01, 2.14, and 4.19 deg/min the best linearity of  $\log A$  vs.  $E$  plot was found in terms of  $R_{1,2}$ . Table 2 lists the compensation parameters  $a$  and  $b$ , together with the correlation coefficients  $\gamma$  of the

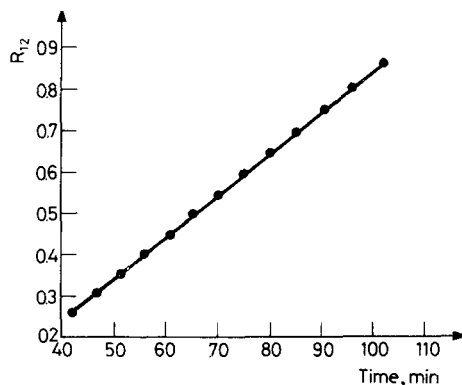


Fig. 1 Typical  $R_{1,2}$  vs.  $t$  plot for the isothermal dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{CuCl}_2$  at 60.0 °C, assuming  $R_{1,2} = 1 - (1 - \alpha)^{1/1.2} = kt$

Table 1 Appropriate  $F(\alpha)$  and kinetic parameters derived isothermally and from Ozawa's method for the thermal dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{CuCl}_2$

Method	$F(\alpha)^{*1}$	$E$ , kJ/mol	$\log A$ , 1/s	$\gamma^{*2}$
Isothermal	$R_{1,2 \pm 0.1}$	$106.3 \pm 2.7$	$12.9 \pm 0.4$	-0.9854
Ozawa	$R_{1,3}$	$83.7 \pm 1.5$	$7.36 \pm 1.89$	0.9997

\*1  $R_n = 1 - (1 - \alpha)^{1/n}$ , where  $n$  is theoretically an integer of 1, 2, or 3.

\*2 Correlation coefficient of the linear regression analysis.

linear regression analysis. It is interesting to compare kinetically the isothermal with the non-isothermal dehydrations in terms of rate constants  $k$  derived isothermally and from the compensation relation along with Arrhenius equation using each  $\log A$  derived isothermally [4]. The rate constants  $k$  at 77.0° are shown in

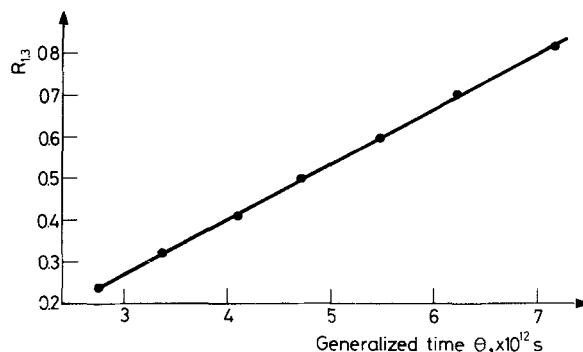


Fig. 2 Plot of  $R_{1,3}$  vs.  $\theta$  for the dynamic dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{CuCl}_2$ , assuming  $R_{1,3} = 1 - (1 - \alpha)^{1/1.3} = A\theta$

Table 2 Kinetic parameters derived isothermally, compensation constants for the non-isothermal runs, and comparison of the rate constants in terms of various  $F(\alpha)$ , for the dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  into  $\text{CuCl}_2$

$F(\alpha)^{*1}$	Isothermal analysis			Compensation constant <sup>*3</sup>			Rate constant, 1/s <sup>*4</sup>	
	$E$ , kJ/mol	$\log A$ , 1/s	$-\gamma^{*2}$	$-a$ , 1/s	$b$ , mol/kJ s	$\gamma^{*2}$	Iso- thermally	From compensa- tion law <sup>*5</sup>
$D_1$	106.3	13.0	0.9856	25.666	0.2506	0.9711	$1.3689 \times 10^{-3}$	$9.4300 \times 10^{-11}$
$D_2$	106.2	12.9	0.9856	6.4676	0.1619	0.9988	$1.1326 \times 10^{-3}$	$1.1127 \times 10^{-5}$
$D_3$	106.1	12.5	0.9856	7.9416	0.1630	0.9987	$4.7196 \times 10^{-4}$	$6.0385 \times 10^{-7}$
$D_4$	106.2	12.3	0.9857	7.3732	0.1622	0.9988	$3.0981 \times 10^{-4}$	$1.6098 \times 10^{-6}$
$R_1$	106.4	12.9	0.9854	3.1527	0.1517	0.9996	$1.1307 \times 10^{-3}$	$1.2836 \times 10^{-3}$
$R_{1,2}$	106.3	12.8	0.9854	3.4806	0.1539	0.9996	$1.1318 \times 10^{-3}$	$1.0348 \times 10^{-3}$
$R_2$	106.2	12.8	0.9854	4.0543	0.1556	0.9994	$9.5579 \times 10^{-4}$	$4.2352 \times 10^{-4}$
$R_3$	106.2	12.7	0.9855	4.4130	0.1567	0.9993	$7.6867 \times 10^{-4}$	$2.5199 \times 10^{-4}$
$A_1$	106.1	13.4	0.9854	4.3891	0.1587	0.9991	$3.4000 \times 10^{-4}$	$4.7444 \times 10^{-4}$
$A_2$	106.3	13.1	0.9857	3.1359	0.1481	0.9993	$1.6454 \times 10^{-4}$	$5.5217 \times 10^{-4}$
$A_3$	106.3	12.9	0.9856	2.3819	0.1376	0.9994	$1.1062 \times 10^{-4}$	$2.1211 \times 10^{-4}$
$A_4$	106.3	12.8	0.9853	2.2353	0.1270	0.9991	$8.3288 \times 10^{-4}$	$1.3771 \times 10^{-5}$

\*<sup>1</sup> See, for example, Ref. [1].

\*<sup>2</sup> Correlation coefficient of the linear regression analysis.

\*<sup>3</sup> For the non-isothermal runs at heating rates of 0.57, 1.01, 2.14, and 4.19 deg/min.

\*<sup>4</sup> Value at 77 °C.

\*<sup>5</sup> Calculated using the value of  $\log A$  derived isothermally in terms of each  $F(\alpha)$ .

Table 2. We see from Table 2 that the rate constants  $k$  in terms of  $R_{1,2}$  are nearly equal. It is clear that the compensation line in terms of  $R_{1,2}$  is best and hence the "true" compensation effect, because of the highest linearity of  $\log A$  vs.  $E$  plot and appropriate dehydration mechanism. Figure 3 shows the "true" compensation plot.

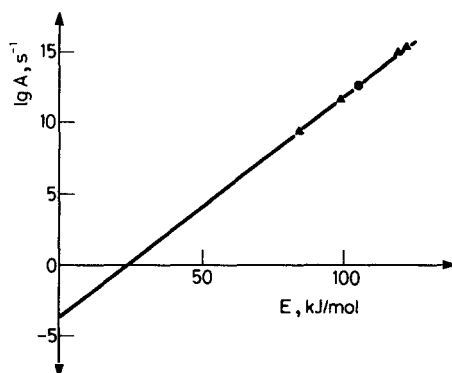


Fig. 3 "True" compensation plot for the thermal dehydration of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to  $\text{CuCl}_2$  in terms of the equation;  $\log A = a + bE$ . ● and ▲ are the points according to the kinetic parameters derived isothermally and from Coats and Redfern's method, respectively

It is mathematically proved that  $\ln k$  vs.  $1/T$  plots assuming Arrhenius equation form a pencil if a linear relationship exists between  $\ln A$  and  $E$  [9]. Namely the "true" compensation line indicates the existence of an isokinetic point, which is the strict criterion of the existence of kinetic compensation effect [10]. In a given run, on the other hand, the shape of TG curve can be reflected by the mechanistic model function  $F(\alpha)$ , whereas the kinetic compensation effect is closely related to the shift of TG curve along the temperature coordinate [11]. Accordingly, an establishment of the "true" compensation effect may support the decomposition mechanism estimated and thus the kinetic parameters.

It is interesting here to use such a "true" compensation effect for reviewing the  $F(\alpha)$  estimated earlier [5]. If the decomposition mechanism did not change under the experimental conditions examined, the "true" compensation relationship should result in terms of the correct  $F(\alpha)$ . In view of the correct  $F(\alpha)$  for the thermal dehydration of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , which was difficult to single out [11], can be reviewed with regard to the two possible kinetic laws  $R_{2,0}$  and  $A_{1,9}$ . Table 3 shows the compensation constants  $a$  and  $b$  including kinetic parameters derived isothermally and non-isothermally for the dehydration of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . We see from Table 3 that the "true" compensation effect is established in terms of  $A_{1,9}$ .

**Table 3** Compensation parameters <sup>\*1</sup> in terms of  $R_{2.0}$  and  $A_{1.9}$  for the thermal dehydration of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  into  $\text{CaC}_2\text{O}_4$ 

$F(\alpha)^{*2}$	$-a, 1/s$	$b, \text{mol/kJ s}$	$\gamma^{*3}$	$\sigma \times 10^{2*4}$
$R_{2.0}$	$2.773 \pm 0.037$	$0.1173 \pm 0.0003$	0.9998	7.2367
$A_{1.9}$	$1.887 \pm 0.014$	$0.1088 \pm 0.0002$	0.9999	3.4196

<sup>\*1</sup> For the equation,  $\log A = a + bE$ .

<sup>\*2</sup>  $R_{2.0} = 1 - (1 - \alpha)^{1/2.0}$  and  $A_{1.9} = [-\ln(1 - \alpha)]^{1/1.9}$ , with  $0.1 \leq \alpha \leq 0.9$ .

<sup>\*3</sup> Correlation coefficient of the linear regression analysis of the  $\log A - E$  plot.

<sup>\*4</sup> Standard deviation of the least square fitting of the  $\log A - E$  plot.

On the other hand, it seems that decomposition mechanism possibly changes with the experimental conditions in the case of "superficial" or "false" compensation effects [4, 7].

## Conclusion

A "true" compensation effect, which shows the highest linearity of  $\log A$  vs.  $E$  plot, was established using the most appropriate kinetic model function  $F(\alpha)$  for the non-isothermal decomposition of solids at various heating rates. It follows from this fact that the correct decomposition mechanism should be closely related with the "true" compensation effect. The concept of "true" compensation effect can also be used for the kinetic comparison of a non-isothermal decomposition with isothermal one, from which the correct  $F(\alpha)$  can be specified.

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**Zusammenfassung** — Für die nichtisotherme Zersetzung von Feststoffen bei verschiedenen Aufheizgeschwindigkeiten wurde unter Zuhilfenahme der geeignetsten kinetischen Funktion  $F(\alpha)$  ein „wahrer“ kinetischer Kompensationseffekt festgestellt. Es kann angenommen werden, daß für den „wahren“ kinetischen Kompensationseffekt der richtige kinetische Mechanismus  $F(\alpha)$  verantwortlich ist, während ein ungeeigneter  $F(\alpha)$  zu einem „falschen“ führen würde. Die Feststellung eines solchen „wahren“ Kompensationseffektes zwischen der isothermen und nichtisothermen Zersetzung von Feststoffen sagt aus, daß der angewandte  $F(\alpha)$  sowohl für die isotherme als auch für die nichtisotherme Zersetzung geeignet ist.

**Резюме** — Используя наиболее подходящую кинетическую зависимость  $F(\alpha)$  для реакции неизотермического разложения твердых тел при различных скоростях нагрева, установлен «истинный» кинетический компенсационный эффект. Вероятно, что правильный выбор кинетической зависимости  $F(\alpha)$  отвечает за истинный кинетический компенсационный эффект, тогда как не подходящая функция  $F(\alpha)$  может привести к «фальши». Введение такого «истинного» компенсационного эффекта между изотермическим и неизотермическим разложением твердого тела означает, что использованная функция  $F(\alpha)$  соответствует как для изотермического, так и для неизотермического разложений.