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COMPENSATION EFFECT RESULTING FROM THE USE OF MECHANISTIC EQUATIONS, AND ITS PHYSICAL SIGNIFICANCE

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A compensation effect is observed in the activation parameters resulting from various mechanistic equations; the T computed from the slope of the E^* *vs* ln A plot matches the observed DTG peak.

In the Arrhenius equation

$$k = A\exp(-E^*/RT) \tag{1}$$

the activation parameters A and E^*, instead of being independent, have sometimes been found to exhibit a correlation, A increasing with E^* through a series of reactions. Such a compensation effect was first reported in connection with catalytic studies [1]. Evidence for such a kinetic compensation has since been reported in other fields as well [2–11], even though many of the reports have subsequently been disputed. Several theories and explanations that account for such compensation behaviour have also been put forward [2, 4, 7, 12–16].

The kinetic parameters reported for solid-state reactions differ widely; for example, the estimates of the activation energy for the decomposition of calcium carbonate vary between 26 and 377 kcal/mol, while those of the pre-exponential factor vary between 10^2 and 10^{69}. Procedural factors such as the heating rate, sample size, sample pretreatment, container shape and the atmosphere are implicated in the widely differing calculated parameters. Zsakó has suggested [17] that thermal decomposition processes can be better characterized by means of compensation parameters, since the shapes and positions of the TG curves can be greatly influenced by the working conditions, whereas the compensation parameters are independent of them. We have thus been able to identify the mechanisms of thermal decomposition of some copolymers using a compensation parameter $S_p = E^*/\log A$ [18], in spite of the wide scatter in the computed kinetic parameters.

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In our continued quest for a compensation parameter that can be used in place of the widely varying activation energy values, we have observed a compensation effect in the activation parameters resulting from various mechanistic equations.

Results

The thermal dehydroxylation of magnesium hydroxide has been investigated in some detail by Fong and Chen [19]. The experimental data from two thermal curves have been processed by two methods, using 17 mechanistic equations. Of the resultant $(2 \times 2 \times 17) = 68$ E^* and A values presented, we have used 60 sets to look for the compensation effect. Least squares linearization of E^* *vs* ln A gave a good fit (correlation coefficient = 0.99938). The T_z computed from the slope of the straight line was 668 ± 3 K, which matches the observed DTG peak of 667 K in both the curves; T_z differs significantly from the mean experimental temperature of 650 K.

To verify the generality of the finding, we have analysed the data for the decomposition of calcium oxalate, which has been reported in detail [20]. Ninan and Nair studied the effects of heating rate and sample size on the two steps of its decomposition; each data set has been treated by 9 mechanistic equations and by the Coats–Redfern equation. Each set of experimental data has thus provided 10 sets of E^* and A values.

Least squares linearization of E^* *vs* ln A yielded the results given in Tables 1 and 2. Again, the fits are good, as indicated by the correlation coefficients. The values of T_z computed from the slopes again match the observed DTG peaks.

Table 1 Effect of heating rate on the observed T_{max} and the calculated T_z for the decomposition of calcium oxalate

q, deg/min	Stage I			Stage II		
	T_{max}, expt$^+$ K	T_z, calc K	R_{xy}^{++}	T_{max}, expt$^+$ K	T_z, calc K	R_{xy}^{++}
1	413	417 ± 5	0.99936	712	717 ± 6	0.99969
2	419	422 ± 4	0.99971	740	743 ± 6	0.99973
5	429	433 ± 5	0.99944	756	761 ± 6	0.99973
10	446	451 ± 6	0.99936	769	772 ± 7	0.99973
20	456	461 ± 7	0.99915	771	777 ± 7	0.99965
50	479	485 ± 8	0.99895	791	798 ± 24	0.99644
100	496	506 ± 10	0.99850	814	820 ± 8	0.99964

$^+$ Taken from Ref. [23]; $^{++}$ Number of points, $n = 10$.

Table 2 Effect of sample mass on the observed T_{max} and the calculated T_z for the decomposition of calcium oxalate

Weight, mg	Stage I			Stage II		
	T_{max}, expt$^+$ K	T_z, calc K	R_{xy}^{++}	T_{max}, expt$^+$ K	T_z, calc K	R_{xy}^{++}
1.1	425	427 ± 5	0.99955	748	754 ± 7	0.99964
2.5	435	437 ± 5	0.99955	753	760 ± 8	0.99960
5.1	446	451 ± 6	0.99936	769	772 ± 7	0.99969
7.4	449	452 ± 5	0.99943	764	769 ± 7	0.99963
10.0	454	458 ± 6	0.99923	767	772 ± 7	0.99966
15.0	457	464 ± 7	0.99910	769	776 ± 8	0.99957
20.2	472	474 ± 7	0.99901	773	778 ± 8	0.99960

$^+$ Taken from Ref. [23]; $^{++}$ Number of points, $n = 10$.

Discussion

Fong and Chen [19] and Ninan and Nair [20] have linearized

$$\ln\{g(\alpha)/T^2\}\ vs\ 1/T$$

to compute E^* and A values corresponding to each mechanism. If the correlation coefficient is used as the criterion, the fit is nearly perfect in all cases. This may be explained as the insensitivity introduced by the use of the integral forms of the equations, the insensitivity inherent in the log plots, and the insensitivity associated with the use of R_{xy} as the criterion. The fact is that the mechanisms are indistinguishable.

A reaction cannot proceed by all the mechanisms at the same time; hence, most of the equations are incorrect for any set of data. However, the E^* and A values emerging from the apparently incorrect equations all fit the compensation pattern, and they yield a parameter that matches a physical reality (viz. the observed T_{max}).

It appears that there is no independent relevance for the E^* values; E^* attains significance only in association with A. The kinetic parameters (E^* and A) emerging from these equations are points that lead to T_{max}. (It may be added that many of these mechanistic equations represent deceleratory or acceleratory processes, having no T_{max} in conventional isothermal kinetics.)

It has been suggested [21] that inaccurate temperature measurements and the occurrence of large temperature gradients within the sample are the experimental errors that lead to the manifestation of compensation behaviour from computational artefacts. Errors in temperature measurement and the occurrence of large temperature gradients should be more pronounced at higher heating rates and at higher sample masses; Tables 1 and 2 do not show any gradation of CE with heating rate or sample size.

Conclusions

The Arrhenius equation is one of the simplest examples of linear free energy validity. In such an extra-thermodynamic approach, the parameters E, G, H and S are not identified with thermodynamic functions. They follow from the polylinear functions if at least one more x argument is varied with temperature [22]. CE and isokinetic relations need not therefore be discussed thermodynamically. Hence, no physical significance may be attributed to the intercept of the equation

$$E^* = e_0 + RT_z \ln A \tag{2}$$

If the intercept is interpreted as the free energy of activation, this will lead to the unwarranted inference that the mechanistic functions in all the equations are equivalent at $T_{\max}$.

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Zusammenfassung — Bei den sich aus Gleichungen für verschiedene Mechanismen ergebenden Aktivierungsparametern wurde ein Kompensationseffekt beobachtet; der aus der Neigung der Geraden E^* gegen $\ln A$ berechnete T-Wert stimmt mit der Lage des beobachteten DTG-Peaks überein.

Резюме — Компенсационный эффект проявлялся в активационных параметрах, полученных на основе различных механистических уравнений. Величины T, вычисленные из наклона графической зависимости $E^* - \ln A$, хорошо согласуются с наблюдаетмыми пиками ДТГ.