

CRITICAL COMMENTS CONCERNING EXTENSION OF THE PUBLISHED KINETIC RESULTS OF SOME THERMAL DECOMPOSITION MEASUREMENTS

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The "trial and error" method was used for a kinetic evaluation of the first DTG peaks of the alanine complexes of four lanthanide isothiocyanates (La, Ce, Pr and Nd) after well-organised preparation, sample control and TG measurements [1]. According to the authors, from 19 alternative possibilities, the reaction follows Eq. 18, with second-order kinetics. They also conclude that the decomposition processes of the four complexes are identical, as the corresponding parameters of the kinetic compensation effects (CE) are approximately the same. The correlation coefficient of the CE, however, is greater than 0.99 in each case (Table 10 [1]), so it is arbitrary to choose the second-order "mechanism" from the 19 examined alternative possibilities as the rate-determining one [2]. Similar arbitrary conclusions are frequently observed in the literature.

In strict connection with the dimensionless evaluation, the following equation is suitable for characterisation of the thermal processes [3]:

$$\ln A \cong \overline{(1/RT)_i} E_i - n \overline{\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i}$$

It is also based on the analogies between the heat, the component and the momentum streams [3]. $A=1$ and $n=1$ are the original conditions for elimination of the physicochemical preconceptions relating to the inseparable partial processes besides the chemical one. TG measurement data can be used directly for calculation of the equation parameters. A formal analogy exists with the CE ($\ln A = aE \pm b$), for a is the tangent α and b is the ordinate intercept in the CE-like relation:

$$a \cong \overline{1/RT}_i \quad \text{and} \quad b \cong -n \overline{\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i}$$

This equation, however, obviously differs from the CE. It is not an indefinite phenomenon only, but characterises both the thermal process and the relations of the measured data directly. It allows a quantitative determination of the similarities and differences in the various measurements. This is illustrated by the table below.

The measured T_i , α_i and $(d\alpha/dT)_i$ data on the La, Ce, Pr and Nd compounds (p. 1438, Table 5 [1]) were recalculated with the above equation for comparison with the published kinetic data (Tables 6–11 [1]), as follows:

	For the published kinetic data				For the published measured data			
	$1/RT$	E	b	K	$1/RT$	E	b	K
La	0.24622	23.19	-5.7094	488.5	0.25234	20.39	-5.1488	476.6
Ce	0.24236	23.71	-5.7468	496.3	0.25037	21.71	-5.4457	480.4
Pr	0.24514	23.85	-5.8473	490.6	0.25196	19.10	-4.8173	477.4
Nd	0.24183	25.64	-6.1997	497.4	0.25590	22.11	-5.6676	470.0

(The published interval of E is 227.24–100.48 kJ mol⁻¹.) The characteristic temperature (K) of the measurements seems to be in a functional connection with the atomic weight of the lanthanide. The significantly greater $(d\alpha/dT)_i$ causes the relatively small E value of the Pr compound (19.10 kJ mol⁻¹). With the average $(d\alpha/dT)_i$ for the La, Ce and Nd compounds the corresponding value is 21.83 kJ mol⁻¹, which poses the question of whether E is also a function of the atomic weight or why there is a higher process velocity for the Pr compound.

References

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- 2 Z. Adonyi and G. Kőrösi, *Thermochim. Acta*, 60 (1983) 23.
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