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COMPUTATIONAL THERMAL AND KINETIC ANALYSIS
Software for non-isothermal kinetics by standard procedure

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A software package to determine the non-isothermal kinetic parameters of heterogeneous reactions has been developed. The dynamic handle of conversion degree step and ranges, heating rates and kinetic models makes the evaluation of the activation parameters much faster. The standard procedure: 'model-free' kineitc, IKP and Perez-Maqueda *et al*. methods, is applied for the determination of the kinetic triplet corresponding to thermal induced transformations. The software is designed mainly for thermogravimetric, temperature programmed reduction and dilatometry data processing, but may also import already transformed numeric data.

Keywords: *computational kinetic analysis, IKP method, 'model-free' kinetics, Perez-Maqueda et al. criterion*

Introduction

Early papers on the automatic obtaining of non-isothermal kinetic parameters were reporting the application of different single constant-heating rate methods [1–5], procedures to discriminate between various forms of kinetic models [6, 7] or CRTA methods [8]. Recently developed software, doubled by progress in the field, allows the evaluation of the kinetic triplet in a much more adequate and user-friendly manner [9–16].

Experimental data for the kinetic analysis of heterogeneous processes can be obtained under different temperature profiles; for a single heterogeneous process, Eq. (1) describes the progress rate:

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/RT} \qquad (1)$$

where α is the conversion degree, ($d\alpha/dt$) is the reaction rate, A is the frequency factor, E is the activation energy, $f(\alpha)$ is the differential conversion function and R is the universal gas constant. After a review of the single constant-heating rate methods for kinetic parameters evaluation [17–21], it was concluded that they are providing only erroneous results, thus decided the need to use multi constant-heating rate methods. Taking into account the impossibility to separate the reaction dependence on the temperature and on the conversion, almost every conversion function may describe the experimental data [22]. To discriminate among them, various isoconversional methods (linear/non-linear, integral or differential) must be used, followed if possible by discrimination procedures (invariant kinetic parameters (IKP) method [23] and Perez-Maqueda *et al*. criterion [24]) or combined-temperature regimes to be applied (isothermal, CRTA, HRTG, etc.) [25].

Methodological aspects of non-isothermal kinetics in heterogeneous systems

Starting from Eq. (1) various methods of non-isothermal kinetic parameters evaluation were developed. Budrugeac [26] reviewed a number of recent publications in the field, analyzed the procedural errors in the kinetic triplet [E, A, $f(\alpha)$] evaluation and proposed a general algorithm to be applied. According to this algorithm, the kinetic analysis must begin with the evaluation of the dependence of E on α, that may be performed by an isoconversional method. If E is independent of α, no matter which isoconversional method (linear or non-linear) is used, the frequency factor must also be constant, and can be determined by means of the IKP method or Perez-Maqueda *et al*. criterion. Any integral or differential method, based on a single constant-heating rate experiment can be used. The IKP method does not suppose the choice of any $f(\alpha)$ function from a pre-established group of kinetic models. Considering a group of conversion functions that do not compulsory contain the true kinetic model, for each heating rate, the apparent activation parameters and corresponding compensation effect parameters (a_β and b_β) are determined. The in-

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variant kinetic parameters (E_{inv} and A_{inv}) are evaluated using the supercorrelation relation (Eq. (2)):

$$a_\beta = \ln A_{\mathrm{inv}} - b_\beta E_{\mathrm{inv}} \qquad (2)$$

Using the values of $\ln A_{\mathrm{inv}}$, E_{inv} and the progress rate equation (Eq. (1)), the numerical evaluation of f_{inv} may be performed. In order to discriminate the kinetic model, the shape of f_{inv} *vs.* α curve is compared with the profile of $f(\alpha)$ *vs.* α curves corresponding to all known kinetic models. Despite the fact that the true kinetic model can be obtained by successive application of the IKP method, the values of the calculated f_{inv} are especially affected by errors in ln*A* evaluation [26]. For this reason, it is recommended to make use of discrimination criteria. Perez-Maqueda *et al.* criterion (kinetic parameters should be independent on the heating rate), may provide the kinetic triplet; the results are close to those of IKP method (for *E* and ln*A*). The use of Perez-Maqueda *et al.* criterion is simpler for determining *E* and ln*A*, compared with Master plot method, which provide more useful information about the true kinetic model, even for single heating-rate experiments. However, Master plots [27, 28] require the use of derivative curves and in the case of nucleation models it proved to be much more difficult to apply. When *E* depends on α, the complexity of the process may be identified from the shape of this dependence [29]; if *E* increases with α, the process involves parallel reactions. If *E* decreases with α and the curve is concave, the process has reversible stages; if the curve is convex, the process changes the limiting stage. Therefore, the IKP method can be applied only if *E* (isoconversional) remains constant during the progress of the investigated process. Because the IKP method gives kinetic parameters strongly dependent on the heating rate, these results are close to the isoconversional ones only when *E* is independent of α.

Results and discussion

Algorithm and software development

In recent years, several papers [30–40] used Budrugeac's standard procedure [26]. This paper presents a software for thermal and kinetic analysis ('Thermal and Kinetic Software' (TKS)) by standard procedure (TKS-SP 1.0 version for Windows), written in C++ under Windows. The software was designed to use experimental data obtained on a 'Diamond Differential/Thermogravimetric' Analyzer from Perkin-Elmer Instruments, but it is possible to import already transformed conversion data, and by a simple change even to import files from other thermal equipments. The interpolation of transformed thermogravimetric, temperature programmed reduction and dilatometry data (α *vs.* *T* curves) is made for an imposed step of conversion degree. The interpolated conversion curves, as well as the use of already transformed temperature-conversion curves are possible to be saved, respectively imported and furthermore computed.

Because all employed methods by TKS-SP 1.0 software (Kissinger–Akahira–Sunose [41, 42], Flynn–Wall–Ozawa [43, 44], IKP [23] and Perez-Maqueda *et al.* [24]) are linear ones, for determining the optimal parameters of every straight-line involved, the least squares method was used. For the isoconversional methods, the activation energy is evaluated for each imposed conversion degree step. The dependence may then be plotted and the mean value for the selected conversion interval provided. The apparent activation parameters are obtained by means of two integral single constant-heating rate methods (Coats–Redfern [45] or Flynn–Wall [43]), for each kinetic model, with variable step of model order (i.e. s_n=0.01), and variable step and range of the conversion degree (i.e. s_α=0.05, α=0.2–0.8). For the IKP method, the selection of fitting models is made by introducing a performance criterion of the correlation coefficient (i.e. r>0.9990). The compensation effect parameters (a_β and b_β), corresponding to each constant-heating rate are determined from the selected kinetic models that accomplish the performance criterion. The identification of the true kinetic model by Perez-Maqueda *et al.* criterion is made by a dynamic visual search of the superposing points corresponding to each single constant-heating rate plot and known conversion function.

Testing TKS-SP 1.0

For testing the software, we made use of the numeric data acquired for the thermal decomposition in dynamic air atmosphere (TG data), of an aromatic azomonoether, with the calculated and computational results compared. The comparison was made for the first oxidative decomposition step, for the constant heating rates of: 2, 4, 6 and 8 K min^{-1}. The thermal behavior and thermal parameters, as well as a more detailed discussion on the kinetic study (various groups of kinetic models) have been previously reported [46]. Table 1 presents the isoconversional activation energy evaluated as function of conversion degree in the range 0.2–0.8 with 0.05 steps. As usual, because of the different approximations of the temperature integral, the values obtained by FWO method are higher than those obtained by KAS method. The results of the manual evaluation compared with those obtained using the TKS-SP 1.0 software are identical. The small difference in the accuracy of results (correlation coefficients) is due to the different algorithms used by commercial/computing softwares.

Table 1 Comparison between isoconversional activation energies by KAS and FWO methods

α	E_{KAS}/kJ mol^{-1}	r_{KAS}	E_{KAS}/kJ mol^{-1}	r_{KAS}	E_{FWO}/kJ mol^{-1}	r_{FWO}	E_{FWO}/kJ mol^{-1}	r_{FWO}
	calculated		computed		calculated		computed	
0.20	90.8	0.99777	90.9	0.99736	93.8	0.99811	93.9	0.99834
0.25	90.7	0.99769	90.7	0.99727	93.8	0.99804	93.8	0.99822
0.30	91.3	0.99752	91.3	0.99713	94.4	0.99791	94.4	0.99804
0.35	91.3	0.99728	91.3	0.99701	94.4	0.99771	94.5	0.99798
0.40	91.7	0.99717	91.7	0.99693	94.9	0.99762	94.9	0.99788
0.45	92.0	0.99723	92.1	0.99699	95.3	0.99766	95.3	0.99796
0.50	92.4	0.99719	92.4	0.99695	95.7	0.99763	95.7	0.99790
0.55	93.1	0.99731	93.1	0.99704	96.3	0.99774	96.4	0.99798
0.60	93.3	0.99734	93.4	0.99706	96.6	0.99776	96.6	0.99800
0.65	93.8	0.99739	93.8	0.99708	97.0	0.99780	97.0	0.99799
0.70	94.3	0.99742	94.4	0.99708	97.6	0.99783	97.7	0.99794
0.75	94.9	0.99745	94.9	0.99710	98.1	0.99786	98.1	0.99793
0.80	95.4	0.99744	95.5	0.99710	98.7	0.99784	98.8	0.99790

calculated – $\overline{E}_{KAS}$=92.7±1.5 kJ mol^{-1}, $\overline{E}_{FWO}$=95.9±1.6 kJ mol^{-1}; computed – $\overline{E}_{KAS}$=92.7±1.6 kJ mol^{-1}, $\overline{E}_{FWO}$=95.9±1.7 kJ mol^{-1}

Since the activation energy remains almost constant, the IKP method may be applied in order to determine the invariant parameters. All known kinetic models were used, but only those fulfilling the performance criterion were kept for further IKP calculations. An additional elimination of the diffusion functions was taken into consideration, because their contribution to such types of decompositions is less probable, providing increased errors [47]. In Tables 2 and 3, the apparent activation parameters (for the heating rate of 2 K min^{-1}), obtained by means of Coats–Redfern and Flynn–Wall methods, are compared. Although being obtained with high accuracy, the values change with different heating rates and among conversion functions.

The straight lines lnA_β *vs*. E_β for several constant heating rates should intersect at a point (isoparametric point [48]) which corresponds to the true values of the activation energy and natural logarithm of the frequency factor (E_{inv}, lnA_{inv}). Certain variations of the experimental conditions, as well as the straight lines (corresponding to different heating rates) junction at low values, determining a region of intersection rather than a unique point in the ln$A$ *vs*. E plot. For

Table 2 Apparent activation parameters for 2 K min^{-1} by Coats–Redfern method

Kinetic model	E_{CR}/kJ mol^{-1}	lnA_{CR}, A/s^{-1}	r_{CR}	E_{CR}/kJ mol^{-1}	lnA_{CR}, A/s^{-1}	r_{CR}
		calculated			computed	
$F_{0.45}$	88.8	15.215	0.99996	88.7	15.191	0.99979
$F_{0.5}$	90.5	15.679	0.99999	90.4	15.656	0.99990
$F_{0.55}$	92.2	16.149	0.99999	92.2	16.133	0.99992
$F_{0.6}$	94.0	16.624	0.99997	93.9	16.613	0.99983
$A_{0.1}$	1161.2	283.265	0.99905	1160.1	282.995	0.99887

Table 3 Apparent activation parameters for 2 K min^{-1} by Flynn–Wall method

Kinetic model	E_{FW}/kJ mol^{-1}	lnA_{FW}, A/s^{-1}	r_{FW}	E_{FW}/kJ mol^{-1}	lnA_{FW}, A/s^{-1}	r_{FW}
		calculated			computed	
$F_{0.45}$	91.9	16.300	0.99997	91.8	16.308	0.99978
$F_{0.5}$	93.6	16.727	0.99999	93.6	16.722	0.99990
$F_{0.55}$	95.2	17.160	0.99999	95.1	17.154	0.99992
$F_{0.6}$	96.9	17.601	0.99997	96.8	17.609	0.99983
$A_{0.1}$	1111.3	279.286	0.99906	1110.4	279.272	0.99886

Table 4 Compensation effect parameters for all selected kinetic models by CR method

β/K min^{-1}	ASKM (calculated)			ASKM (computed)		
	a_β, A/s^{-1}	b_β/mol J^{-1}	r	a_β, A/s^{-1}	b_β/mol J^{-1}	r
2	–6.91791	$2.499\cdot10^{-4}$	0.99998	–6.92036	$2.501\cdot10^{-4}$	0.99980
4	–6.24377	$2.434\cdot10^{-4}$	0.99997	–6.24402	$2.433\cdot10^{-4}$	0.99981
6	–5.86453	$2.385\cdot10^{-4}$	0.99997	–5.86437	$2.395\cdot10^{-4}$	0.99981
8	–5.58681	$2.364\cdot10^{-4}$	0.99998	–5.58690	$2.361\cdot10^{-4}$	0.99982

Table 5 Invariant kinetic parameters for all selected kinetic models by CR and FW methods

	$E_{\text{inv–CR}}$/kJ mol^{-1}	ln$A_{\text{inv–CR}}$, A/s^{-1}	$r_{\text{inv–CR}}$	$E_{\text{inv–FW}}$/kJ mol^{-1}	ln$A_{\text{inv–FW}}$, A/s^{-1}	$r_{\text{inv–FW}}$
Calculated	96.0	17.101	0.99752	94.1	16.873	0.99771
Computed	96.1	17.120	0.99926	94.2	16.871	0.99868

Table 6 Perez-Maqueda *et al.* kinetic parameters using CR and FW methods for $F_{0.55}$

	$E_{\text{PM–CR}}$/kJ mol^{-1}	ln$A_{\text{PM–CR}}$, A/s^{-1}	$r_{\text{PM–CR}}$	$E_{\text{PM–FW}}$/kJ mol^{-1}	ln$A_{\text{PM–FW}}$, A/s^{-1}	$r_{\text{PM–FW}}$
Calculated	93.6	16.514	0.99840	96.8	17.565	0.99838
Computed	93.6	16.518	0.99831	96.7	17.567	0.99836

these reasons, the evaluation of the invariant kinetic parameters is performed using the supercorrelation equation. For all selected kinetic models (ASKM), the compensation effect parameters (i.e. by CR method) calculated and computed, are listed in Table 4.

The fit of such 'fantastic' apparent activation values, as that of the A0.1 kinetic model, proves once again the high resolution of the IKP method (Table 5).

Even if model-fitting methods and IKP method select a group of presumed conversion functions, they cannot establish precisely the right and unique model from a type of kinetic models (i.e. in our case, all possibilities of F_n type models, with n between 0.4–0.7). According to Perez-Maqueda *et al.* criterion [24], the correct kinetic model corresponds to the independence of the activation parameters on the heating rate. By applying any differential or integral model-fitting method, for every constant heating rate, the true kinetic model shall provide the same constant activation energy, as well as the frequency factor. The dynamic visualization of $\{\ln[\beta g(\alpha)/T^2]\ vs.\ 1/T\}$ (CR method) or $\{\ln[\beta g(\alpha)]+5.331\ vs.\ 1/T\}$ (FW method) plots, pointed towards $F_{0.55}$ as the right kinetic model. The calculated/computed results by Perez-Maqueda *et al.* criterion for $F_{0.55}$ kinetic model are presented in Table 6.

Conclusions

New software to determine the non-isothermal kinetic parameters of heterogeneous reactions was developed. TKS-SP 1.0 version for Windows, written in C++ under Windows, was designed for kinetic analysis of thermogravimetric, temperature programmed reduction and dilatometry data by means of two isoconversional methods – KAS and FWO, IKP method (using CR and FW) and Perez-Maqueda *et al.* criterion (using CR and FW). The use of Coats–Redfern and Flynn–Wall methods provides kinetic triplet of the first thermal decomposition step of an aromatic azomonoether dye (TG data) to be $\{E\approx94–97$ kJ mol^{-1}; ln$A\approx16.5–17.5$; $f(\alpha)$: $F_{0.55}\}$, result obtained with almost identical correlation coefficients, after both calculus in common software or computational processing.

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