

COMPUTATIONAL THERMAL AND KINETIC ANALYSIS

Complete standard procedure to evaluate the kinetic triplet form non-isothermal data

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Advanced software (TKS-SP2.0 version) for thermal and kinetic analysis, for determining the non-isothermal kinetic parameters of heterogeneous processes has been developed. The dynamic handle of conversion degree steps and ranges, heating rates and kinetic models, makes the evaluation of the kinetic parameters much faster, for TG, TPR and dilatometry experiments. The standard procedure for evaluating the kinetic triplet was implemented; several linear isoconversional methods (from generalized KAS to FWO, Li-Tang and Friedmann methods), IKP method, Perez-Maqueda *et al.* criterion (both by Differential equation) and Master plots method. The software is designed mainly for data processing of experimental files, but may also import other already transformed numeric data.

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

Introduction

Early papers on the automatic obtaining of non-isothermal kinetic parameters reported the application of different single-heating rate methods [1–5], procedures to discriminate between various forms of kinetic models [6, 7] or CRTA methods [8]. Recently developed software packages, doubled by further progress in the field, allow the evaluation of the kinetic triplet $\{E, A, f(\alpha)\}$ in a much more adequate and user-friendly manner [9–17].

After a review of the single constant-heating rate methods for kinetic parameters evaluation [18–21], it was concluded that they provide only erroneous results, thus decided the need to use multi-constant-heating rate methods, for example isoconversional methods. For constant isoconversional activation energies, advanced kinetic methods like IKP are used in order to provide the pair (E_{inv}, A_{inv}) [22]. Although IKP method offers significant information about the range of the right conversion function, it cannot straight provide it. 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 [23]. Discrimination criteria like Perez-Maqueda *et al.* [24] or Master plot methods [25–30] may be used in order to establish the true conversion function and therefore the kinetic triplet.

Methodological aspects of non-isothermal kinetics in heterogeneous systems

Starting from the progress rate equation, various methods for non-isothermal kinetic parameters evaluation were developed. Budrugaec [31] 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 any 'model-free' kinetic (MFK) method.

The various 'model-free' kinetic methods (linear/non-linear, integral or differential) are usually followed by discrimination procedures like Invariant Kinetic Parameters method [22] (IKP – for determining the pre-exponential factor), Master plots method [25–30] (for identifying the true conversion function of each linear non-isothermal process), Perez-Maqueda *et al.* criterion [24] (a heating-rate independence criterion – for establishing the entire kinetic triplet of a process) or combined with isothermal and SCTA (CRTA, HRTG, etc.) experiments [32].

'Model-free' kinetic (MFK) methods

Although most of the MFK methods are isoconversional, there were developed also other types of MFKs (like Popescu isothermality method [33]). TKS-SP2.0

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package, the advance version of TKS-SP1.0 [17] (comprising of KAS [34, 35] and FWO [36, 37] methods), contains also other integral (1), differential (2) and conversion rate-integrated (3) isoconversional methods, which use (1) the conversion data (Generalized KAS [38, 39], Tang *et al.* [40], Starink 1 [41, 42], Starink 2 [42], Madhusudanan *et al.* 1 [43], Madhusudanan *et al.* 2 [44], Madhusudanan *et al.* 3 [44], Tang and Chen [45] and Ortega [46]), (2) the conversion rate data (Friedmann [47]) and again, (3) the conversion rate data (Li-Tang [48–50] methods). Starink [41, 42] and Madhusudanan *et al.* [43, 44] methods should provide similar results to those of KAS method, since they rely on very close equations. Tang and Chen [45] method and Ortega [46] method are both average-linear integral methods, their results being different from the last and should provide similar results with those of the non-linear integral methods. By using the reaction rate data, Friedmann [47] and Li-Tang [48–50] proved during the time to be the worse methods, even if they do not assume any approximations. When E depends on α , the complexity of the process may be identified from the shape of this dependence [51]; 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.

Invariant kinetic parameters (IKP) method

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 . In order to determine the invariant kinetic parameters (E_{inv} and A_{inv}), the upgraded version of TKS-SP package (version 2.0) does not chose any of the $f(\alpha)$ conversion function from a pre-established group of kinetic models, and uses the Differential (later to be referred as 'D') method for obtaining the apparent parameters. 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 invariant kinetic parameters (E_{inv} and A_{inv}) are evaluated using the supercorrelation relation (Eq. 1):

$$a_\beta = \ln A_{inv} - b_\beta E_{inv} \quad (1)$$

Using the values of $\ln A_{inv}$, E_{inv} and the progress rate equation, the numerical evaluation of *i.e.* may be performed.

Methods for discriminating the suitable kinetic model

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 [22]. For this reason, it is recommended to make use of Perez-Maqueda *et al.* criterion [24] or Master plots methods [25–30] which may provide the kinetic triplet. The use of Perez-Maqueda *et al.* criterion is simpler for determining E and $\ln A$, and with the help of TKS-SP2.0, Master plots methods may provide more useful information about the true kinetic model, even for single heating-rate experiments.

Results and discussion

Algorithm and software development

In recent years, several papers [52–62] used Budrugaec's standard procedure [31]. This paper presents the advanced software for thermal and kinetic analysis ('Thermal and Kinetic Software' – TKS) by standard procedure (TKS-SP 2.0 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 by a simple change to import files from other thermal equipment. The software is designed mainly for data processing of experimental files, but may also import other already transformed numeric data. The dynamic handle of conversion degree steps and ranges, heating rates and kinetic models makes the evaluation of the kinetic parameters much faster, for TG, TPR, Dilatometry and other experiments (for example the transformed conversion data from DSC experiments). The interpolation of transformed data (α vs. T curves) is made for a certain imposed step of the 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.

For all employed methods by TKS-SP 2.0 software to determine 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. Using the Generalized KAS method, the exponent m value in $\ln \frac{\beta}{T^{m+2}}$ may be set. When $m=0$, Arrhenius theory applies (KAS equation), setting $m=0.5$, the collision theory occurs and for $m \geq 1$ it becomes the case of activated complex the-

ory [38]. For Tang and Chen and Ortega methods, $\Delta\alpha$ interval may be set as well; in this paper, $\Delta\alpha=0.25$ was used for testing the software. The dependence may then be plotted and the mean value for the selected conversion interval provided. The apparent activation parameters of each kinetic model are obtained by means of two integral single constant-heating rate methods (Coats–Redfern [63] or Flynn–Wall [36] – described in [17]) and by means of the differential equation, with variable step of model order (i.e. $s_n=0.01$), and variable step and range of the conversion degree (i.e. $s_\alpha=0.05$, $\alpha=0.2\text{--}0.8$). For the IKP method, the selection of fitting models is made by introducing a performance criterion of the correlation coefficient (i.e. $r>0.9980$). 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 combining the performance criterion (highest correlation coefficient) and the dynamic visual search of the superposing points corresponding to each single constant-heating rate plot and known conversion function. The Master plot method uses a step by step visual fit of the normalized experimental data – $(d\alpha/dt)/(d\alpha/dt)_{\text{selected}}$, by adjusting the $[f(\alpha)g(\alpha)]/[f(\alpha_{\text{selected}})g(\alpha_{\text{selected}})]$ master equation with the appropriate selected conversion degree and conversion function.

Testing TKS-SP 2.0

For testing the software, we made use of the numeric data acquired for the thermal decomposition, in dynamic air atmosphere, of an aromatic azomonoether (2-allyl-4-((4-(4-methylbenzyloxy)phenyl)diazanyl)phenol), with the calculated and computational results being 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 more detailed discussions on the kinetic study (various groups of kinetic models) have been previously reported [64–67].

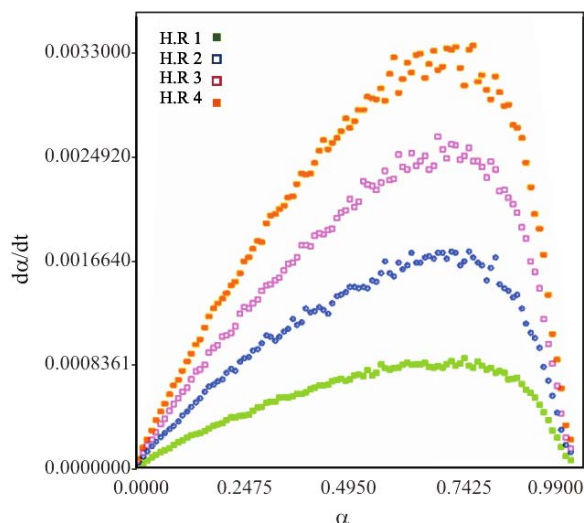


Fig. 1 Conversion rate curves of the thermal decomposition of 2-allyl-4-((4-(4-methylbenzyloxy)phenyl)diazanyl)phenol for the 2, 4, 6 and 8 K min^{-1} experiments

Because of the noisy DTG/conversion rate data (Fig. 1), the activation energy values by Friedmann method are obtained with less accuracy than those by means of Li-Tang (here $\alpha_{\text{initial}}=0.19$ was set) method, which are worse than those obtained by KAS method and in general than every isoconversional integral method.

Table 1 presents the isoconversional activation energy evaluated as function of conversion degree with 0.1 step in the range 0.2–0.8, for the Friedmann and Li-Tang methods in comparison with the KAS method.

$$\begin{aligned} \bar{E}_{\text{Friedmann}} &= 95.6 \pm 4.0 \text{ kJ mol}^{-1} \\ \bar{E}_{\text{Li-Tang}} &= 93.6 \pm 1.7 \text{ kJ mol}^{-1} && \text{calculated} \\ \bar{E}_{\text{Friedmann}} &= 95.7 \pm 4.0 \text{ kJ mol}^{-1} \\ \bar{E}_{\text{Li-Tang}} &= 93.6 \pm 1.8 \text{ kJ mol}^{-1} && \text{computed} \\ \bar{E}_{\text{KAS}} &= 92.8 \pm 1.7 \text{ kJ mol}^{-1} && \text{computed} \end{aligned}$$

The calculated activation energies, compared with those obtained using the TKS-SP 2.0 software are practically identical. The small difference in the accuracy

Table 1 Isoconversional activation energies by Friedmann and Li-Tang ($\alpha_{\text{initial}}=0.19$) methods, calculated and computed by TKS-SP 2.0; comparison with computed results of KAS method

α	$E_{\text{Friedmann}}/$ kJ mol^{-1} calc.	$r_{\text{Friedmann}}$ calc.	$E_{\text{Friedmann}}/$ kJ mol^{-1} comp.	$r_{\text{Friedmann}}$ comp.	$E_{\text{Li-Tang}}/$ kJ mol^{-1} calc.	$r_{\text{Li-Tang}}$ calc.	$E_{\text{Li-Tang}}/$ kJ mol^{-1} comp.	$r_{\text{Li-Tang}}$ comp.	$E_{\text{KAS}}/$ kJ mol^{-1} comp.	r_{KAS} comp.
0.20	92.6	0.99861	92.8	0.99672	91.2	0.99765	91.2	0.99569	90.9	0.99736
0.30	92.0	0.99380	92.0	0.99279	92.1	0.99655	92.1	0.99466	91.3	0.99713
0.40	92.2	0.99578	92.4	0.99398	92.8	0.99650	92.8	0.99442	91.7	0.99693
0.50	93.6	0.99650	93.6	0.99430	93.5	0.99679	93.5	0.99454	92.4	0.99695
0.60	97.6	0.99791	97.5	0.99575	94.4	0.99720	94.4	0.99482	93.4	0.99706
0.70	101.8	0.99647	101.8	0.99404	95.3	0.99732	95.4	0.99601	94.4	0.99708
0.80	99.9	0.99913	100.0	0.99726	96.1	0.99746	96.2	0.99132	95.5	0.99710

of results (correlation coefficients) is due to the different algorithms used by commercial/computing softwares.

In Fig. 2a all range of linear isoconversional methods is covered, from Generalized KAS ($m=2$) to

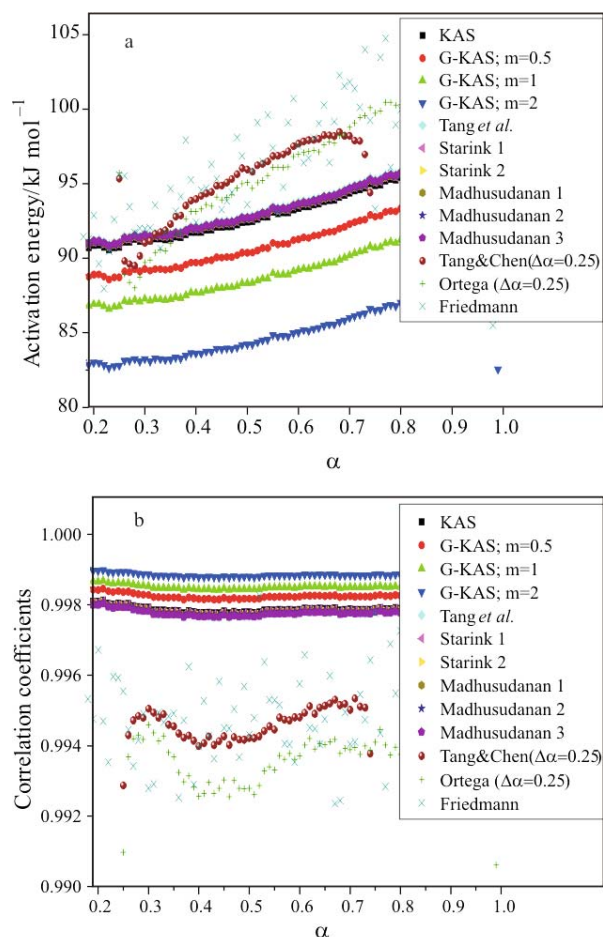


Fig. 2 a – Isoconversional activation energy for several linear methods and the **b** – correlation coefficients in their evaluation

Tang *et al.*, the average linear integral Tang and Chen and Ortega methods, to differential Friedmann method.

In the case of average linear integral methods (Tang and Chen and Ortega), the activation energy values change by different slopes than in the case of normal linear integral methods. Together with Friedmann method, the average linear integral methods provide the most inaccurate results (Fig. 2b). The correlation coefficients have the lower values, and while increasing m , the evaluation improves. 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 [68]. In Table 2, the apparent activation parameters (for all 4 constant heating rates), obtained by means of D method, are presented. Although being obtained with high accuracy, the values change with different heating rates and among conversion functions.

The straight lines $\ln A_{\beta}$ vs. E_{β} for several constant heating rates should intersect in a point (isoparametric point [69]) which corresponds to the true values of the activation energy and natural logarithm of the pre-exponential factor (E_{inv} , $\ln A_{inv}$). Certain variations of the experimental conditions, as well as the straight lines (corresponding to different heating rates) junction at low values, determine a region of intersection rather than a unique point in the $\ln A$ vs. E plot. For 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, computationally obtained by differential method are compared with those previously reported [17] by using Coats–Redfern equation, and listed in Table 3.

Table 2 Apparent activation parameters for all heating rates by D method

Kinetic model	$E_D/\text{kJ mol}^{-1}$ computed	$\ln A_{D,\beta}/\text{s}^{-1}$ computed 2 K min ⁻¹	r_D computed	$E_D/\text{kJ mol}^{-1}$ computed	$\ln A_{D,\beta}/\text{s}^{-1}$ computed 4 K min ⁻¹	r_D computed
F0.45	84.9	14.338	0.99699	88.6	15.348	0.99648
F0.5	89.0	15.383	0.99722	92.6	16.375	0.99642
F0.55	92.9	16.398	0.99735	96.6	17.399	0.99618
F0.6	96.9	17.439	0.99729	100.7	18.436	0.99573
A0.1	1180.3	288.121	0.99235	1215.7	289.800	0.99215
Kinetic model	$E_D/\text{kJ mol}^{-1}$ computed	$\ln A_{D,\beta}/\text{s}^{-1}$ computed 6 K min ⁻¹	r_D computed	$E_D/\text{kJ mol}^{-1}$ computed	$\ln A_{D,\beta}/\text{s}^{-1}$ computed 8 K min ⁻¹	r_D computed
F0.45	93.3	16.430	0.99664	92.3	16.272	0.99638
F0.5	97.5	17.459	0.99661	96.4	17.289	0.99648
F0.55	101.5	18.478	0.99641	100.6	18.306	0.99647
F0.6	105.7	19.503	0.99602	104.7	19.319	0.99632
A0.1	1233.1	288.339	0.99204	1235.8	286.673	0.99208

Table 3 Compensation effect parameters for all selected kinetic models by D and CR methods

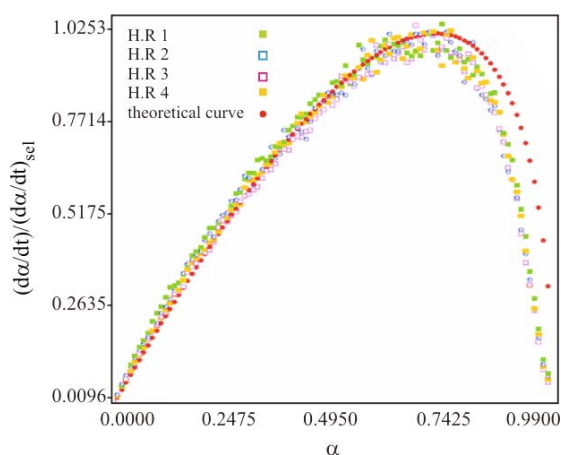
$\beta/\text{K min}^{-1}$	$a_{\beta}A/\text{s}^{-1}$	ASKM/computed D method $b_{\beta}/\text{mol J}^{-1}$	r	$a_{\beta}A/\text{s}^{-1}$	ASKM/computed CR method $b_{\beta}/\text{mol J}^{-1}$	r
2	-6.83320	$2.500 \cdot 10^{-4}$	0.99787	-6.92036	$2.501 \cdot 10^{-4}$	0.99980
4	-6.15242	$2.430 \cdot 10^{-4}$	0.99800	-6.24402	$2.433 \cdot 10^{-4}$	0.99981
6	-5.76681	$2.391 \cdot 10^{-4}$	0.99812	-5.86437	$2.395 \cdot 10^{-4}$	0.99981
8	-5.49443	$2.361 \cdot 10^{-4}$	0.99810	-5.58690	$2.361 \cdot 10^{-4}$	0.99982

Table 4 Invariant kinetic parameters for all selected kinetic models by D and CR methods

IKP computed	$E_{\text{inv}}/\text{kJ mol}^{-1}$	$\ln A_{\text{inv}}/A/\text{s}^{-1}$	r_{inv}
D	96.7	17.353	0.99469
CR	93.2	17.126	0.99452

Table 5 Perez-Maqueda *et al.* kinetic parameters using D and CR methods for F0.55

F0.55 kinetic model	$E_{\text{PM}}/\text{kJ mol}^{-1}$	$\ln A_{\text{PM}}/A/\text{s}^{-1}$	r_{PM}
D	96.8	17.402	0.99379
CR	93.6	16.518	0.99831


Fig. 3 Master plot fit of normalized experimental conversion rate ($\alpha_{\text{selected}}=0.72$) by F0.55 kinetic model

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 4).

Even if model-fitting methods and IKP method select a group of presumed conversion functions, those cannot establish precisely the right and unique model from a certain 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 methods, for every constant heating rate, the true kinetic model should provide both the same constant activation energy as well as the pre-exponential factor. The dynamic visualization of $\{\ln(d\alpha/dt) - \ln f(\alpha)\}$ vs. $1/T$ (D method) and $\{\ln[\beta g(\alpha)/T^2]\}$ vs. $1/T$ (CR method) plots, pointed towards F0.55 as being the right kinetic model. The calculated/computed results of Perez-Maqueda *et al.* criterion, for F0.55 kinetic model are presented in Table 5.

In order to use Master plot method, the conversion rate data must be normalized, by dividing these values to a selected value, usually to the maximum conversion rate (here, the $d\alpha/dt$ values for $\alpha_{\text{selected}}=0.72$). Other values of α may be chosen, many papers reporting on $\alpha_{\text{selected}}=0.5$ as well. A step by step visual fit of the normalized experimental data – $(d\alpha/dt)/(d\alpha/dt)_{\text{selected}}$, by adjusting the $[f(\alpha)g(\alpha)]/[f(\alpha_{\text{selected}})g(\alpha_{\text{selected}})]$ master equation with the appropriate selected conversion degree and conversion function, provides the true kinetic model, for each constant-heating rate experiment. In Fig. 3 is presented the Master plot fit of the 4 experiments, which led to the F0.55 kinetic model to apply and confirmed once more Perez-Maqueda *et al.* results.

The Master plot method applied here must be used together with other methods in order to provide the full kinetic triplet of a certain process.

Conclusions

New software to determine the non-isothermal kinetic parameters of heterogeneous reactions was developed. TKS-SP 2.0 version for Windows, written in C++ under Windows, was designed for kinetic analysis of linear non-isothermal experiments by means of the most known isoconversional methods, IKP method (using Differential, Coats–Redfern and Flynn–Wall) and Perez-Maqueda *et al.* criterion (using Differential, Coats–Redfern and Flynn–Wall). The use of these constant single-heating rate methods provided kinetic triplet of the first thermal decomposition step of an aromatic azomonoether dye to be $\{E \approx 94\text{--}97 \text{ kJ mol}^{-1}$; $\ln A \approx 16.5\text{--}17.5$; $f(\alpha)$: F0.55}, result obtained after both calculated and computational processing with almost identical correlation coefficients. Applying Master plots method, the identification of true kinetic model becomes much faster and easy to establish only

by visual discrimination. By selecting the conversion degree corresponding to the maximum conversion rate and by verifying each kinetic model, we have confirmed F0.55, previously obtained by means of Perez-Maqueda *et al.* criterion.

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