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SOLID-PLASTIC TRANSITIONS KINETICS BY DSC
Application to alcohols derived from neopentane

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The kinetic parameters of solid-plastic transitions on alcohols derived from neopentane were determined using differential scanning calorimetry (DSC) by a single or multiple scan analysis. The methods studied (Borchard-Daniels, Ellerstein, Multilinear law, Freeman-Carroll, Ozawa, Kissinger), never used before for that kind of transition, imply a single Arrhenius behaviour. These methods werre applied to 2,2-dimethyl 1-propanol (DP), 2,2-dimethyl 1,3-propanediol or neopentylglycol (NPG), 2-hydroxymethyl 2-methyl 1,3-propanediol or pentaglycerine (PG), and 2,2-dihydroxymethyl 1,3-propanediol or pentaerythritol (PE). A simple isothermal test is recommended to check the validity of activation energies experimentally obtained and Arrhenius frequency factors. Taking some restrictions on the heating rate for the heat evolution methods, the results are in agreement with the data obtained by isothermal tests. We have noted a linear dependence of the activation energy values on the number of hydroxyl groups with the exception of pentaerythritol. Isothermal simulations of the solid-plastic transition are an example of industrial applications.

The existence of plastic crystal highly disordered rotary phases, where the molecules trundle rapidly in the solid while maintaining their positional order in the lattice, was first recognized by Timmernans [1], who defined two criteria for this behaviour, one on thermodynamic, the other on structural grounds.

The plastic crystals are characterized by a high melting point and a high vapor pressure in the solid state. Most of the disorder in the liquid phase occurs first in the plastic phase and induces a higher entropy of the solid-plastic transitions compared to the melting entropy (usually less than 21 $J \cdot mol^{-1} \cdot K^{-1}$).

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From a structural view point, Timmernans pointed out that plastic behaviour was characteristic of gobular-component, nearly spherically shaped molecules.

The crystalline solid to plastic crystal transition involves the formation of a large symmetrical structure (genarally cubic in the plastic phase).

A number of experimental and theoretical investigations have contributed to a better understanding of this mesocrystalline or plastic phase, and the results, including crystallographic, N.M.R., calorimetric, and dielectric constant data, have been summarized in several reviews [1-5].

This work is a kinetic study of potential candidate materials for thermal energy storage [6, 7] at a constant transition temperature (well below their melting points). Industrial processes often depend on the kinetic behaviour of systems undergoing phase transformations, and knowledge of the kinetic parameters is necessary to perform isothermal simulations.

Experimental

Procedure and calibration

The apparatus, a Setaram DSC 111 differential heat flux scanning calorimeter, coupled with a Hewlett Packard 86 microcomputer, was calibrated using several scanning rates with various standards (nitromethane, benzoic acid, aluminium, tin, lead and zinc).

All qualitative data were obtained at a heating rate of 5 $K \cdot min^{-1}$ for heat evolution methods and included between 2 and 10 $K \cdot min^{-1}$ for peak maximum evolution methods.

Two calibration modes were used for kinetic studies: one with extra-pure benzoic acid for high temperature (m.p. 122.4°) and the other with nitromethane (m.p. –28°).

Thermal analysis samples consisting of carefully weighed (~20 mg) [8] powdered compounds (mesh: 0.16 mm) were sealed in an aluminium cruicible.

Materials studied

Unpurified pentaerythritol (PE) or 2,2-dihydroxymethyl 1,3-propanediol and pentaglycerine (PG) or 2-hydroxymethyl 2-methyl 1,3-propanediol, obtained from Aldrich Chemical Company, were used, respectively, with a purity of 99% Gold Label and 99%; neopentylglycol (NPG) or 2,2-dimethyl 1,3-propanediol and (DP) or 2,2-dimethyl 1-propanol were obtained, respectively, from Fluka Chemical Company (>98%) and Merck Chemical Company (>99%).

The large reversible solid-plastic transition enthalpy at low temperature makes these organic materials attractive candidates for thermal energy storage. However, the temperature and enthalpy of crystal transformation of these compounds are very sensitive to impurities, including trace amount of water which appears to be bound in the interlamellar spaces of the layered structure [6].

The fixed transition temperature of the pure compounds (PE: 186°, PG: 81°, NPG: 40°, DP: -31°) limits their use in thermal storage applications, and an adjustment of the transition temperature can be obtained by mixing the components such as PG/NPG [6-8]; for the proportion 20/80, 50/50 and 80/20 of PG/NPG mixtures studied, we have, respectively, a transition temperature of 16, 27 and 57°.

Kinetic methods

Our objectives are to show the domain of validity for kinetic methods presented and the determination of the kinetic parameters (reaction order (n), activation energy (E_a), rate constant (k) and degree of conversion (α)), to develop a better understanding of the molecular processes involved in solid-plastic transitions.

The solid-plastic transition, as described above, corresponds to a "preliminary fusion organised in the solid state", and as it is commonly used for a physical transformation, the order of the reaction is assumed to be one.

The activation energy characterises the energy barrier to be overcome to transform the solid phase into a plastic phase.

One of the outcomes of this kinetic study is the characterisation of the solid-plastic transition mechanism occurring in the solid state. Thus, it is assumed that the reaction mechanism is the same throughout the dynamic scan, whatever the scanning rate may be. In these conditions, the mechanism follows the Arrhenius equation:

$$k(T) = k_0 \exp(-E_a/RT) \qquad (1)$$

with: k_0 the preexponential factor (s^{-1}); E_a the activation energy ($J \cdot mol^{-1}$); R the gas constant ($8.31\ J \cdot mol^{-1} \cdot K^{-1}$) and T the absolute temperature (K).

This law suggests that an equilibrium exists between "passive" molecules of a reacting species and "active" molecules formed from normal molecules by the absorption of energy [9].

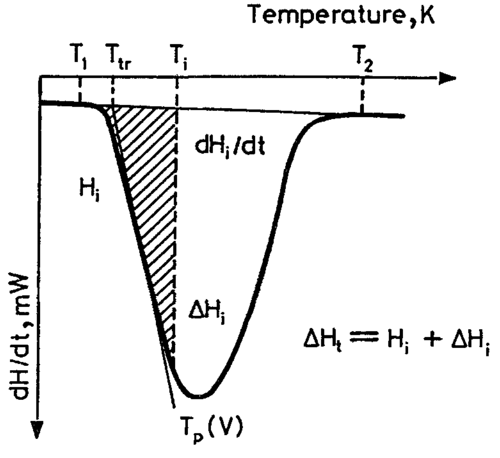

Fig. 1 Thermal curve of a typical solid-plastic transition presenting the kinetic parameters for the two types of methods: T_i, dH_i / dt, ΔH_i and ΔH_t) for methods using a single DSC scan; (T_p and V) for methods using a series of DSC scans

Assuming the general law of homogeneous kinetics, we have:

$$d\alpha / dt = k(T) \cdot (1-\alpha)^n \tag{2}$$

with $d\alpha / dt$ the reaction rate (s^{-1}); k the specific rate constant (s^{-1}); α the degree of conversion (from 0 to 1); n the reaction order and t the time (s).

For a temperature T_i the degree of conversion α_i is obtained by calculating the partial area H_i to total area ratio ΔH_t (Fig. 1).

Note that using the Johnson-Mehl-Avrami equation [10], the reaction rate:

$$d\alpha / dt = n(1-\alpha)[-\ln(1-\alpha]^{(n-1)/n} \cdot k(T) \tag{3}$$

becomes in our case ($n = 1$):

$$d\alpha / dt = (1-\alpha)k(T) \tag{4}$$

that is the same expression obtained from the Eq. (2) for $n = 1$.

On the other hand, in the case of the solid-plastic transition, the function $f(\alpha)$ becomes: $f(\alpha) = 1-\alpha$.

Heat evolution methods

The methods using a single DSC scan (Borchardt-Daniels [11], Ellerstein [12], Freeman-Carroll [13] and the multilinear law [14, 15] use the same basic Eqs (1) and (2) but vary in their mathematical treatment.

For all these methods used, for a fixed temperature T_i, the partial area is H_i, the total area ratio ΔH_t and the peak height $\mathrm{d}H_i / \mathrm{d}t$. Isothermal simulations are possible with the knowledge of the kinetic parameters (n, k_o and E_a) by integration of Eqs (2) or (3).

Using the Freeman-Carroll method, for an interval of integration determined, we have: –The reaction order n:

$$n = \frac{\dfrac{\ln[(\mathrm{d}H/\mathrm{d}t)_{i+2}/(\mathrm{d}H/\mathrm{d}t)_i]}{1/T_i - 1/T_{i+2}} - \dfrac{\ln[\mathrm{d}H/\mathrm{d}t)_{i+1}/(\mathrm{d}H/\mathrm{d}t)_i]}{1/T_i - 1/T_{i+1}}}{\dfrac{\ln[\Delta H_i/\Delta H_{i+1}]}{1/T_i - 1/T_{i+1}} - \dfrac{\ln[\Delta H_i/\Delta H_{i+2}]}{1/T_i - 1/T_{i+2}}} \tag{5a}$$

–The reaction rate k_i, calculated form Eqs (1) and (2), with $\alpha_i = H_i/\Delta H_t$:

$$\ln k_i = \ln[(\mathrm{d}H_i/\mathrm{d}t)\cdot\Delta H_t^{n-1}/\Delta H_i^n] \tag{5b}$$

E_a is determined from the linear slope $-E_a/R$ and $\ln k_o$ by the y axis intercept; when we plot $\ln k$ *vs.* $1/T$, obtained from Eq. (1) that becomes:

$$\ln k = -E_a/RT + \ln k_o \tag{5c}$$

Peak maximum evolution methods

The methods using a series of DSC scans of the sample, run at different heating rates V, show different values for the temperature of the endothermic peak maximum T_p. This shift of temperature *vs.* heating rates is used by the Ozawa [16] and Kissinger [17] methods to determine the activation energy.

Whatever V may be, it is assumed that the degree of conversion is always the same at the maximum point of the DSC curves, for the peak temperature T_p.

For example, in the case of the Kissinger method, E_a is calculated from the linear slope $-E_a/R$ obtained by the equation:

$$\mathrm{d}\log(V / T_p^2) / \mathrm{d}(1 / T_p) = -E_a / R \tag{6}$$

However, we specify that for the Kissinger model, it is not necessary to know the law governing the kinetic reaction [18,1 9], but it will be useful to determine whether this law of homogeneous kinetics is applicable to describe the solid-plastic transition.

Results

For the Ozawa and Kissinger methods, the mean results of these dynamic curve experiments using scans rate of 2, 4, 5, 7 and 10 $\mathrm{K \cdot min^{-1}}$ are listed in Table 1 and an incertitude of 1 K on top temperature peak measurements was estimated.

Table 1 Peak temperature values from DSC experiments at several scanning rates for the pure compounds

V $\mathrm{K \cdot mn^{-1}}$	DP (Ttr 242 K) T_p, K	NPG (Ttr 313 K) T_p, K	PG (Ttr 354 K) T_p, K	PE (Ttr 459 K) T_p, K
2	247.8	317.3	357.2	463.5
4	250.1	321.9	360.7	467.0
5	251.2	322.8	362.6	468.9
7	252.8	325.5	365.6	470.4
10	254.6	327.3	367.4	471.8

From Eq. (6) and the results summarized in Table 1, we have plotted $\ln(V / T_p^2)$ *vs* $(1/T_p)$ for NPG, in the example shown in Fig. 2. The plot obtained is linear with a slope of $-E_a / R$ where the E_a value is 132 $\mathrm{kJ \cdot mol^{-1}}$. For the Ozawa and Kissinger methods, the obtention of a linear plot with a good correlation coefficient justifies their claims to describe the solid-plastic transition of the compounds studied.

Typical but not exhaustive results of our measurements on the activation energies of the materials studied and their mixtures are summarized in Table 2:

Table 2 Kinetic parameters for pure compounds and their mixtures

Sample	KISSINGER / OZAWA 2, 4, 5, 7, 10 K·min^{-1}		FREEMAN-CARROLL 5 K·min^{-1}				
	E_a, kJ·mol^{-1}	r	α	n	$\ln k_0$	E_a	r
PE	332/323	0.9945/0.9948	24-80	1.00	59	247	0.9997
PG	158/157	0.9926/0.9931	17-80	1.09	42	139	0.9969
NPG	132/130	0.9976/0.9978	20-80	1.08	41	123	0.9999
DP	117/115	0.9900/0.9907	10-80	1.04	44	100	0.9996
PG/PPG = 20/80			43-80	0.97	28	83	0.9911
PG/PPG = 50/50			35-80	1.07	48	140	0.9999
PG/PPG = 80/20			18-80	0.99	38	124	0.9997

No more than one unity precision on E_a was obtained because there remains an incertitude of ca 4% on the reproducibility of the activation energy values even with the complete computerisation.

Table 2 shows a discrepancy lower than 3% for the activation energy values calculated form the Ozawa and Kissinger methods.

For the methods using a single DSC scan, thermal curves have been generally integrated for α included in [0.2, 0.8] [20]. This interval of integration determines the most representative region where the solid-plastic transition takes place with a reaction order value very close to one.

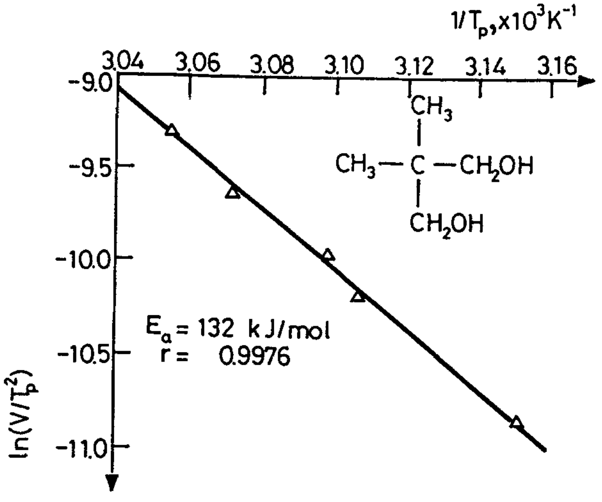

Fig. 2 Kissinger's plot for NPG at different scanning rates (2, 4, 5, 7 and 10 K·min^{-1})

However, these methods present a decrease in the activation energy with the increase in the heating rate. It seems that the general law of homogenous kinetics is not elaborate enough to describe the complex process of the solid-plastic transition; in fact, as mentioned above, the high vapor pressure of these compounds [21] and the scarce residual water in the interlamellar spaces of the layered structure [6] can affect the determination of the activation energy [22].

Also, with a heating rate of 5 K·min^{-1} single scan methods, applied with success to all compounds (except to PE which have a high transition temperature so the sublimation and the vaporisation effects are much more pronounced), are in accordance with the Ozawa and Kissinger models (Table 2).

Effectively, if we compare the activation energy obtained by the two types of methods, we can see the increased linearity described by the activation energy values *vs.* the hydroxymethyl group number related to the breakage in the number of hydrogen bonds during solid-plastic phase transition, except for the high symmetrical molecule of PE characterized with a black symbol (Fig. 3).

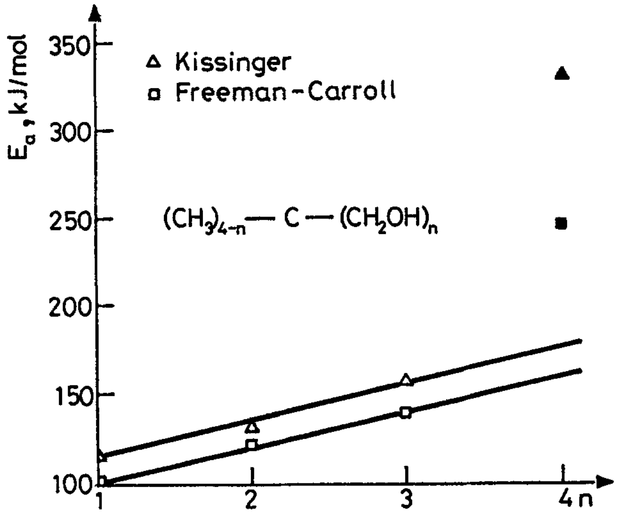

Fig. 3 Activation energy evolution *vs.* the hydroxymethyl group number for Kissinger and Freeman-Carroll methods.
For n = 1 to 4, the compounds are respectively DP, NPG, PG and PE (black symbol)

Secondly, knowing the kinetic parameters we performed isothermal simulations in order to validate the kinetic parameters [22].

With the primitive and initial conditions ($\alpha = 0$ for $t = 0$), we obtain respectively:
from Eqs (1) and (2):

$$\alpha = 1 - [1 + (n-1)k_0 \cdot t \cdot \exp(-E_a/RT)]^{1/(1-n)} \quad \text{with } n \neq 1 \qquad (7)$$

from Eqs (1) and (4):

$$\alpha = 1 - \exp[-k_0 \cdot t \cdot \exp(-E_a/RT)] \quad \text{with } n = 1 \qquad (8)$$

Isothermal tests were performed using the calorimeter block of the DSC at a fixed temperature, with preheating of the sample (5 K under the temperature transition).

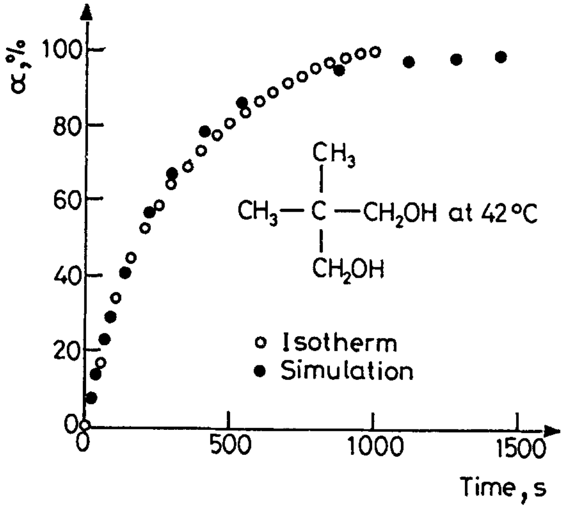

Fig. 4 Degree of conversion, obtained by isotherm and simulation, for NPG placed at 42°C

We plotted on Fig. 4 the fraction transformed α of a sample of NPG, placed at 42° (transition temperature 40°), *vs.* time to compare with the isothermal simulation using Eq. (7) and the kinetic parameters, calculated with the Freeman-Carroll method ($n = 1.08$, $\ln k_0 = 41$, $E_a = 123$). In this case, a difference of no more than 2% was evaluated taking the Eq. (8) for isothermal simulations, and the general law of homogeneous kinetics can describe the transformation of NPG (taking some restrictions on the heating rate).

For the mixtures, we have a low value of the activation energy when the proportion of one of the two compounds is in small quantity; also this small quantity can be considered as an impurity in the lattice of the principal compounds, and diminishing the cohesion forces helps to break the hydrogen bonds during the solid-plastic transition.

Benson [23] has studied the effect on E_a of carbon as nucleation agent on PG, using the results of Thomas and Clarke [24] with scans of 5 and 20 K·min^{-1}, for a first order reaction where at any temperature within the peak, the instantaneous value of $k(T_i)$ is equal to the ratio of the thermal power being absorbed to the amount of the total energy not yet absorbed.

As we have shown for $n = 1$, the Eq. (2) becomes Eq. (4):

$$\mathrm{d}\alpha_i / \mathrm{d}t = k\,(1 - \alpha_i) \qquad \text{with} \quad \alpha_i = H_i / \Delta H_t \qquad \text{and} \quad \Delta H_t - H_i = \Delta H_i$$

where $k(T_i) = (\mathrm{d}H_i/\mathrm{d}t)/\Delta H_i$, so E_a is calculated from the linear slope $-E_a/R$ by the logarithmic plots of k *vs.* reciprocal temperature. They found an activation energy of 124 kJ·mol^{-1} for PG, with a manual practice on a curve scanned at 5 K·min^{-1}, which is in good agreement with our value of 139 kJ·mol^{-1} calculated by the Freeman-Carroll method (Table 2) taking account into the incertitudes related to manual practice as mentioned below.

Table 3 Kinetic parameters for NPG from a thermogram (5 K·min^{-1}) using weight* and numerical integrations**

NPG	α %	n	r	$\ln k_0$	E_a kJ·mol^{-1}
BORCHARDT*	24.5-79.5	1.02	0.9999	46.93	115.35
ELLERSTEIN*	24.5-79.5	1.01	0.9998	37.52	114.41
REGRESSION*	24.5-79.5	1.01	–	38.02	114.25
THOMAS*	24.5-79.5	1.00	0.9999	37.55	113.00
FREEMAN*	24.5-79.5	1.02	0.9999	38.22	115.81
FREEMAN**	20.0-80.0	1.08	0.9999	41.38	122.89

Obtained with heat evolution methods by using weight for the curve integrations, the results for NPG in good agreement among themselves, are summarized in Table 3.

The activation energy calculated from the manual integrations allows no greater precision than 5% (weight measures, cutting up of the curve area, ten points plotted instead of one thousand points with a complete computerisation which modifies effectively the slope precision).

The observed values of activation energy (E_a) are in good agreement for any methods using weight integrations, with a very good correlation coefficient, and we decided to automatize only the Freeman-Carroll method. In Table 3, we can see the difference between the manual and computerized practice as the activation energy of NPG (6% on the slope) for the Freeman-Carroll method.

Using the Thomas-Clarke method, we have found an activation energy of 113 kJ·mol^{-1} for NPG that is in accordance with the other methods using weight integrations.

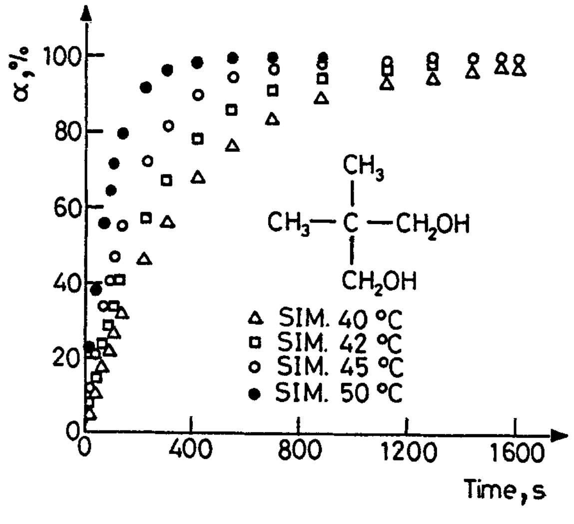

Fig. 5 Degree of conversion for NPG placed at 40,42,45 and 50°C, pbtained by isothermal simulations

For application in storage energy, there is some interest is possible determination of the time-temperature dependence of the degree of transformation.

By simulation, it is easy to observe the different temperature rates of transformation of the compound, depending on the temperature of the simulation (equal to or higher than the transition temperature). In Fig. 5, we have reported the fractional conversion (α) *vs.* time for NPG placed at 40, 42, 45 and 50°.

Conclusion

The Ozawa and Kissinger methods, not necessarily based on the general law of homogeneous kinetics, seem more adapted to describe the kinetics of the solid-plastic transition in alcohols derived from neopentane.

Taking care with the heating rate, the heat evolution methods, using the general law of homogeneous kinetics, are in accordance, except for PE, with the Ozawa and Kissinger methods, because the curve area, in these conditions, concerns only the solid-plastic transition with still less sublimation or water vaporisation effects.

The results of these measurements show the increase of the activation energy (DP < NPG < PG < PE) supported by a mechanism, from the solid state, which involves reversible breaking of nearest-neighbour hydrogen resonance bonds in the molecular crystals at the transition temperatures. The binary mixtures of these alcohols exhibit also solid state transformations which appear to occur by the same kinetic mechanism. To check the validity of these kinetic models, isothermal simulations were performed and compared with isothermal treatments, especially for NPG. In this way, this procedure guarantees that the kinetic parameters obtained from anisothermal experiments should also be valid to describe isothermal kinetics and vice versa.

Knowing the kinetic parameters, isothermal simulations are the most attractive illustration in order to optimize the process conditions for industrial applications of these phase change materials.

A study of the influence of the structure on the activation energy value for this solid-plastic transition, on such tetrahedral substances as neopentane, pentaerythrityl fluoride, and on other plastic crystals, is in progress using kinetic methods presented here and other thermokinetic models in order to describe the whole process.

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Zusammenfassung — Mittels DSC wurden in einem Single- bzw. Multiscananalyse die kinetischen Parameter der fest-plastischen Umwandlung einiger von Neopentan abgeleiteten Alkohole bestimmt. Die untersuchten Verfahren (Borchard-Daniels, Ellerstein, Multilineares Gesetz, Freeman-Carroll, Ozawa, Kissinger), die noch nie für diese Umwandlung angewendet wurden, lassen auf ein einfaches Arrheniussches Verhalten schließen. Diese Verfahren wurden bei 2,2-Dimethyl-1-propanol (DP), 2,2-Dimethyl-1,3-propandiol oder Neopentylglykol (NPG), 2-Hydroxymethyl-2-methyl-1,3-propandiol oder Pantaglycerin (PG) sowie bei 2,2-Dihydroxymethyl-1,3-propandiol oder Pentaerythrit (PE) angewendet. Es wird ein einfacher isothermer Test vorgeschlagen, um die Gültigkeit der experimentell ermittelten Aktivierungsenergien und der Arrheniusschen Frequenzfaktoren zu überprüfen. Unter einer gewissen Einschränkung der Aufheizgeschwindigkeit stimmen die Ergebnisse mit denen des isothermen Testes überein. Mit Ausnahme von Pentaerythrit konnten wir einen linearen Zusammenhang zwischen den Werten für die Aktivierungsenergie und der Anzahl der Hydroxylgruppen feststellen. Die isothermen Simulierungen von fest-plastischen Umwandlungen sind Beispiele für industrielle Anwendungen.