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# COMPARATIVE STUDY OF ISOTHERMAL AND NON-ISOTHERMAL THERMOKINETIC PROCESSES

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## Abstract

In this paper a graphical and analytical method is presented for generating reaction isotherms from a set of non-isotherms and *vice versa*. The method was tested by using computer generated curves. The method was also checked by studying the kinetics of dehydration of calcium oxalate in a static atmosphere. The reaction was monitored in both non-isothermal (with nine heating rates between 0.5 and 60°C min$^{-1}$) and isothermal modes (at 150, 160 and 170°C). The 160°C isotherm obtained experimentally was compared with that obtained by graphical method from non-isotherms determined experimentally and the differences of $\alpha$ were less than 3%.

**Keywords:** isotherm, kinetic, non-isotherm

## Introduction

Thermoanalytical methods for the determination of kinetic parameters in both isothermal and non-isothermal regimes are well known in the literature. The results depend on the precision of the experimental data and also on the mathematical modeling of the process. Although isothermal kinetic data are sometimes used together with non-isothermal ones for the computation of kinetic parameters, there has been discussion regarding the equivalence between the reaction progress at constant temperature or under a variable temperature regime.

The stepwise elevation of temperature and the performance of the process at constant reaction rate have led to two different working techniques, quasi-isothermal analysis (QIA) [1, 2] and stepwise isothermal analysis [3], which have recently been improved [4–6].

A graphical and analytical method for generating reaction isotherms from a set of non-isotherms, and *vice versa*, is presented in the present work.

The method has been tested by using computer-generated isotherms and non-isotherms and experimentally for the dehydration of calcium oxalate.

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## Results and discussion

The changes in a system can be studied either in time, at constant temperature, or as a function of temperature at constant heating rate β. The reaction rate depends upon the shape of the function f(α), the kinetic parameters *n*, *A* and *E*, and, in a regime of variable temperature, the heating rate β.

As long as the reaction mechanism does not change in the given temperature range, one can consider the isothermal regime of reaction progress as an extrapolation of the non-isothermal regime at a heating rate equal to zero. Similarly, the increase in the extent of the reaction in response to a linear temperature increase can be thought of as a change in the system with a stepwise temperature increase under the condition that the steps are sufficiently small to approximate to a linear increase.

On the other hand, for a given process, two systems having the same α are in the same stage of reaction progress if they are at constant temperature or in a regime of variable temperature. It is obvious that the increase in the system energy with temperature must be such that a distribution of the energy excess over all internal freedom degree becomes possible.

In order to avoid debate regarding the equivalence or non-equivalence of the process, the isotherms have been obtained directly from non-isotherms and *vice versa*. The thermoanalytical curves were generated theoretically according to the following integral equations:

$$\text{– isothermal regime: } -\ln(1-\alpha) = A\exp(-E/RT)t \qquad (1)$$

$$\text{– non-isothermal regime: } -\ln(1-\alpha) = \frac{A}{\beta}\int_0^T e^{-E/RT}\,dT \qquad (2)$$

with $n=1$, $A=10^{12}$ min$^{-1}$ and $E=40$ kcal mol$^{-1}$.

The passage between the two regimes characterizing the reaction progress must be performed graphically, so that it does not depend on either the kinetic parameters $A$ and $E$ or the reaction mechanism ($n$).

## Obtaining non-isotherms from isotherms

Starting from a set of $N$ isotherms $(\alpha,t)_{T_i}$ of temperatures $T_i$, were $i=\overline{1,N}$, one seeks a non-isotherm corresponding to a heating rate $\beta=\Delta T_i/\Delta t_i$. The passage between two successive isotherms $(T_{i-1},T_i)$ with $T_{i-1}<T_i$, can be accomplished at constant α, the system remaining on each isotherm for a period of time $\Delta t_i=\Delta T_i/\beta$. The variation in α as a function of $T$ can be obtained by summing the α, $T$ increases for each isotherm (Fig. 1).

For $f(\alpha)=1-\alpha$, for a stepwise passage, by summing $k_i\Delta t_i$ for each isotherm, one obtains:

$$-\ln(1-\alpha_1) = A\exp(-E/RT_1)\Delta t_1 = k_1\Delta t_1$$

where $\Delta t_1$ represents the time corresponding to the variation in $\alpha$ between zero and $\alpha_1$ for isotherm $T_1$. The $\alpha_1$ value is as low as possible.

$$-\ln(1-\alpha_2) = -\ln(1-\alpha_1) + A\exp(-E/RT_2)\Delta t_2 = k_1\Delta t_1 + k_2\Delta t_2$$

$$-\ln(1-\alpha_3) = -\ln(1-\alpha_2) + A\exp(-E/RT_3)\Delta t_3 = k_1\Delta t_1 + k_2\Delta t_2 + k_3\Delta t_3$$

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$$-\ln(1-\alpha_N) = -\ln(1-\alpha_{N-1}) + A\exp(-E/RT_N)\Delta t_N = \sum_{i=1}^{N} k_i\Delta t_i \tag{3}$$

with $\Delta t_i=\Delta T_i/\beta=(T_i-T_{i-1})/\beta$, $i=\overline{2,N}$.

On eliminating time in Eq. (3) we obtain:

$$-\ln(1-\alpha_i) = \frac{1}{\beta}\sum_{j=1}^{i} k_j\Delta T_j, \qquad i=\overline{1,N} \tag{4}$$

If the isotherms are equally spaced, that is $\Delta T_1=\Delta T_2=\ldots=\Delta T_N=\Delta T$, the system remains for equal time intervals on each individual isotherm:

$$-\ln(1-\alpha_i) = A\sum_{j=1}^{i}\exp[-E/R(T_1+j\Delta T)]\Delta t, \quad i=\overline{1,N} \tag{5}$$

where $i=(T_N-T_1)/\Delta T$.

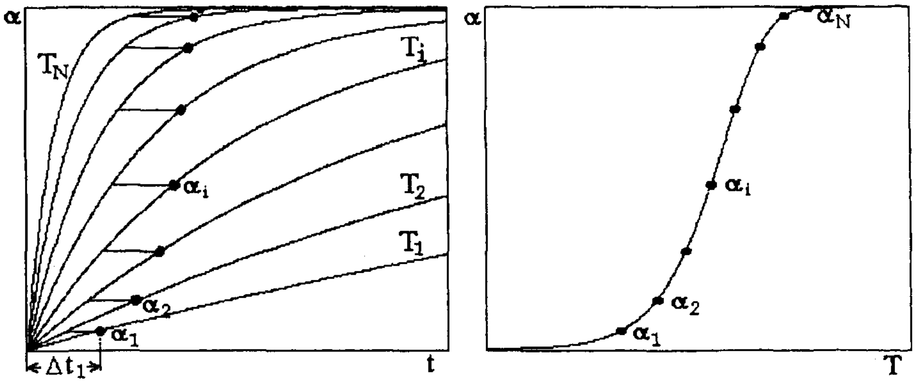

**Fig. 1** Graphical illustration of how the non-isotherm is obtained from a set of isotherms $(\alpha,t)_{T_i}$, $i=\overline{1,N}$

By comparing Eq. (4) with the non-isothermal integral Eq. (2), one obtains another approximation for the temperature integral:

$$\sum_{j=1}^{i} \exp[-E/R(T+j\Delta T)]\Delta T = \int_{0}^{T} e^{-E/RT}\mathrm{d}T, \quad i=\overline{1,N}$$

In Table 1, the temperature variation of the conversion degree as obtained by this method is compared with the 'exact' value, using the asymptotic approximation for the temperature integral, as well as some other approximations to be found in the literature. A very good agreement may be observed between the value we have obtained and the one resulting from the asymptotic increase of the temperature integral.

**Table 1** The temperature variation of conversion degree for non-isothermal process. $n$=1, $E$=40 kcal mol$^{-1}$, $A$=10$^{12}$ min$^{-1}$, $\beta$=1°C min$^{-1}$, $T$=10°C

| $T$/K | $\alpha^x$ | $\alpha^a$ | $\alpha^b$ | $\alpha^c$ | $\alpha^d$ |
|---|---|---|---|---|---|
| 610 | .0694 | .06949 | .6949 | .07342 | .0691 |
| 620 | .1191 | .1191 | .1191 | .1257 | .1181 |
| 630 | .1970 | .1970 | .1970 | .2076 | .1948 |
| 640 | .3116 | .3116 | .3116 | .3272 | .3073 |
| 650 | .4650 | .4649 | .4649 | .4855 | .4577 |
| 660 | .6436 | .6436 | .6436 | .6662 | .6338 |
| 670 | .8131 | .8131 | .8131 | .8323 | .8030 |
| 680 | .9321 | .9321 | .9321 | .9430 | .9250 |
| 690 | .9858 | .9858 | .9858 | .9830 | .9830 |
| 700 | .9987 | .9987 | .9987 | .9991 | .9982 |

[a] Simpson method; [b] Integral asymptotic approximation; [c] Coats-Redfern approximation; [d] Doyle approximation; [x] from Eq. (3)

## Obtaining isotherms from non-isotherms

Having given a set of $N$ non-isothermal curves $(\alpha,t)_{\beta_i}$ of heating rates $\beta_i$, with $i=\overline{1,N}$ and $\beta_1>\beta_2>...>\beta_N$, one tries to obtain an isotherm $(\alpha,t)_T$ at a certain temperature $T$ (Fig. 2). The passage between the non-isotherms is performed as before for constant $\alpha$. The time is obtained by summing the time intervals the system spends on each individual non-isotherm.

For the chosen conversion function, by performing a stepwise passage, one obtains:

$$-\ln(1-\alpha_1)=\frac{A}{\beta_1}\int_0^T e^{-E/RT}\mathrm{d}T,\quad t_1=\Delta t_1=(T-T_1)/\beta_1$$

where $T_1$ is the greatest temperature where $\alpha$ on non-isotherm $\beta_1$ is still zero.

$$-\ln(1-\alpha_2)=-\ln(1-\alpha_1)+\frac{A}{\beta_2}\int_{T-\Delta T_2}^{T} e^{-E/RT}\mathrm{d}T,\qquad t_2=t_1+\Delta t_2=t_1+\frac{\Delta T_2}{\beta_2}$$

$$-\ln(1-\alpha_3)=-\ln(1-\alpha_2)+\frac{A}{\beta_3}\int_{T-\Delta T_3}^{T} e^{-E/RT}\mathrm{d}T,\qquad t_3=t_2+\Delta t_3=t_2+\frac{\Delta T_3}{\beta_3}$$

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$$-\ln(1-\alpha_N)=A\sum_{i=1}^{N}\frac{1}{\beta_i}\int_{T-\Delta T_i}^{T} e^{-E/RT}\mathrm{d}T \tag{7}$$

$$t_N=\sum_{i=1}^{N}\Delta t_N=\sum_{i=1}^{N}\frac{\Delta T_i}{\beta_i} \tag{8}$$

$\Delta T_j$ results from the condition of constant $\alpha$:

$$\frac{1}{\beta_{i+1}}\int_0^{T-\Delta T_i} e^{-E/RT}\mathrm{d}T=\frac{1}{\beta_i}\int_0^{T} e^{-E/RT}\mathrm{d}T,\quad i=\overline{1,N}$$

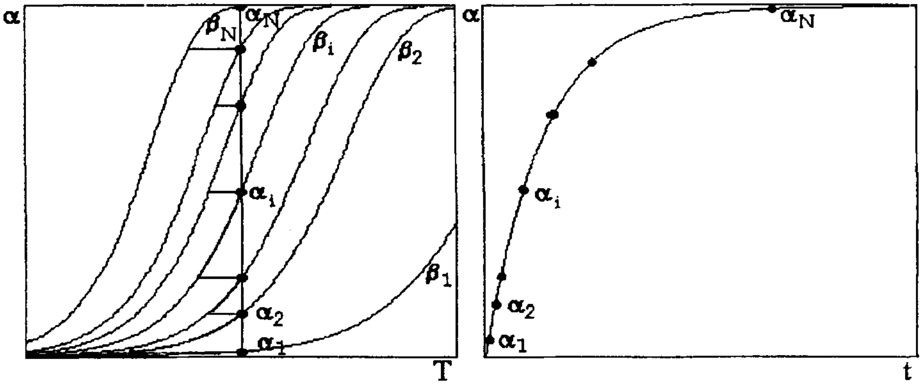

**Fig. 2** Graphical illustration of how the isotherm is obtained from a set of non-isotherms $(\alpha,T)_{\beta_i}$, $i=\overline{1,N}$

The contribution of the temperature integral for each non-isotherm is equal to

$$\int_{T-\Delta T_i}^{T} \exp(-E/RT)\mathrm{d}T = \frac{\exp[-E/R(T-\Delta T_i)] + \exp(-E/RT)}{2}\Delta T_i = \mathrm{e}^{-E/RT}\Delta T_i \qquad (9)$$

Substituting the results obtained in (4) and (9) into Eq. (7):

$$-\ln(1-\alpha_i) = A\mathrm{e}^{-E/RT}\sum_{j=1}^{i}\frac{\Delta T}{\beta_j} = A\mathrm{e}^{-E/RT}\sum_{j=1}^{j}\Delta t_j,\quad i=\overline{1,N}$$

which is the isotherm equation.

**Table 2** The time variation of the conversion degree for isothermal process. $n=1$, $E=40$ kcal mol$^{-1}$, $A=10^{12}$ min$^{-1}$, $T=700$K

| $t$/min | $\alpha^a$ | $\alpha^b$ |
|---|---|---|
| 0.3648 | 0.1062 | 0.1012 |
| 0.6791 | 0.1885 | 0.1832 |
| 1.2640 | 0.3222 | 0.3091 |
| 3.2528 | 0.5152 | 0.4976 |
| 4.3790 | 0.7401 | 0.7223 |
| 8.1515 | 0.9186 | 0.9079 |
| 15.1720 | 0.9406 | 0.9881 |
| 28.2400 | 0.9998 | 0.9997 |

[a] from Eq. (1), [b] from Eq. (4)

The values obtained according to this procedure are comparable (Table 2) with those calculated directly from the isotherm (Eq (1)).

It is worth noting here that the graphical procedure presented requires a passage between two successive curves to be performed at similar values, and the system should spend a certain time on each isotherm or non-isotherm.

If the last condition is negligible, the isoconversion curves are obtained:

$$\text{– for isotherms: } \Delta\ln(t) = \frac{E}{R}\Delta\left(\frac{1}{T}\right)$$

$$\text{– for non-isotherms: } \Delta\ln(\beta) = \frac{E}{R}\Delta\left(\frac{1}{T}\right)$$

If $t$ in the isotherm equation is replaced by the expression obtained from Eq. (5), we have:

$$-\ln(1-\alpha)=\frac{A}{\beta}\frac{RT^2}{E}\mathrm{e}^{-E/RT}$$

which represents the non-isothermal equation in the Coats-Redfern approximation.

The method has been tested experimentally by studying the kinetics of dehydration of calcium oxalate in a static atmosphere by means of a 1090 DuPont Thermal Analyser. The reaction was monitored thermogravimetrically (951 TGA module) in both non-isothermal (at nine heating rates ranging between 0.5 and 60°C min$^{-1}$) and isothermal modes (at 150, 160 and 170°C). The isothermal runs were performed by ramp heating up to the desired temperature, with heating rates of 10, 20 and 30°C min$^{-1}$ for the 150, 160 and 170°C isotherms, respectively. The sample mass chosen was around 40 mg. We are aware of the need to use a specially selected fraction of substance particles for real kinetic experiments; however, this is not so important for our purpose, because the isothermal and non-isothermal experiments are run with one and the same sample. Only the strictly isothermal part of the curve of mass loss is selected in the analysis by means of the 'Extended Playback V2.0' plots of the real-time stored experiments.

Table 3 shows explicitly how the 160°C isotherm is obtained from non-isotherms, in comparison with the experimental one.

The two sets of values are satisfactorily comparable and demonstrate the direct applicability of the method for the experimental curves.

We consider that, as the proposed method has been derived from a theoretical point of view and verified experimentally, it can be successfully applied in both isothermal and non-isothermal kinetics.

**Table 3** The time variation of the conversion degree for calcium oxalate isothermal dehydration at 160°C

| $\alpha_N$ | $\beta_i$ | $T_i$ | $t=\sum_{i=1}^{j} T_j/\beta_j$ | $\alpha_i^{exp}$ | $\frac{\alpha_i-\alpha_N}{\alpha_i}$/% |
|---|---|---|---|---|---|
| 0.0295 | 60 | 30 | 0.5000 | 0.0333 | 11.5 |
| 0.0551 | 40 | 9.5 | 0.7375 | 0.0541 | –1.68 |
| 0.0840 | 20 | 7 | 1.0875 | 0.0833 | –0.79 |
| 0.1125 | 10 | 4 | 1.4875 | 0.1125 | 0. |
| 0.1779 | 5.0 | 6 | 2.6875 | 0.1791 | 0.706 |
| 0.2991 | 2.5 | 7 | 5.4875 | 0.3083 | 2.99 |
| 0.5489 | 1.8 | 7 | 9.3760 | 0.5250 | –4.55 |
| 0.6652 | 1.0 | 3 | 12.376 | 0.6416 | –3.66 |
| 0.9914 | 0.5 | 10 | 32.376 | 0.9916 | 0.027 |

$\alpha_N$ from Eq. (7), $\alpha_i^{exp}$ determinated experimental

## Conclusions

The possibility of correspondence between an isothermal and a non-isothermal development of a process is presented.

The imposed condition is that the passage between two successive thermoanalytical curves is to be performed at the same value. With graphically applied experimental thermoanalytical curves, the method allows isotherms to be obtained directly from the non-isotherms, and *vice versa*, with no need to know the conversion function.

For numerical calculations, $f(\alpha)=1-\alpha$ has been considered; the values calculated by this method practically fit those obtained from the exact integral equations.

The method was tested experimentally on the reaction of dehydration of calcium oxalate in both isothermal and non-isothermal regimes.

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