Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

KINETIC ANALYSIS OF CHEMICAL REACTIONS FOR NON-ISOTHERMAL PROCEDURES

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(Received October 10th, 1971)

ABSTRACT

During the past decade a large number of methods have been suggested for the kinetic treatment of data obtained from the thermal traces of differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), in addition to a variety of other thermal methods[1]. The temperature of the sample in these systems is usually advanced at a constant linear rate. This paper attempts to describe the treatment of experimental data under non-isothermal conditions in order to obtain the kinetic parameters of chemical reactions.

INTRODUCTION

The advent of commercially available instruments for various types of thermal analysis has been responsible in part for the fast growing use of this technique. As yet the significance of non-isothermal procedures in the general picture of kinetics appear to have been overlooked in the many excellent books on chemical kinetics[2]. Perhaps this situation is due to the fact that thermal methods have been applied to reactions mainly in the solid state although the historically important paper in this field dealt with the kinetics of a homogeneous reaction in solution using a DTA technique[3].

The significance of thermal methods for kinetics may be seen from the thermogravimetric trace of calcium oxalate monohydrate as shown in Fig. 1. Here, in a single run, the three sequential reactions may be observed; the first reaction being

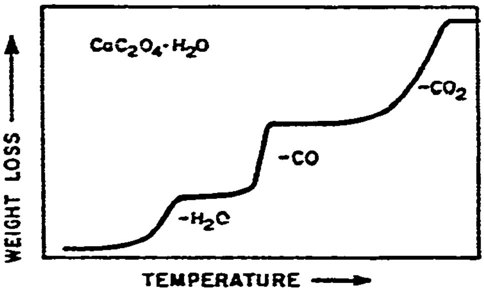

Fig. 1. Thermogram for decomposition of calcium oxalate monohydrate.

dehydration, the second the loss of carbon monoxide to yield calcium carbonate and finally, the third reaction being the conversion of the carbonate to the oxide with the loss of carbon dioxide. Whereas books on thermogravimetry[5] have been concerned with the values of the plateaus, in order to assay the purity of the initial sample, and have discarded the trace between plateaus, in kinetic analysis one studies the previously discarded trace and, in the main, discards the plateaus. The kinetic analysis of the trace in Fig. 1 can lead to the plots shown in Fig. 2 yielding values for the activation energy and order of reaction. The calculation of the specific rate and frequency factor can be readily obtained for simple reactions from a knowledge of the former parameters.

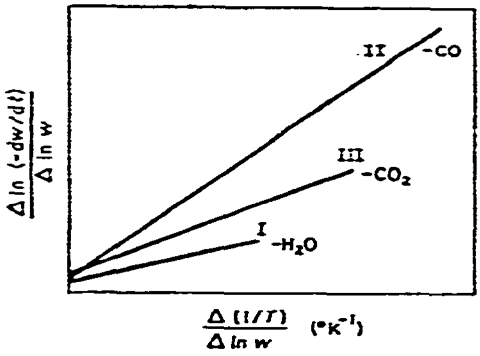

Fig. 2. Schematic showing how the kinetics for the decomposition of calcium oxalate monohydrate is obtained. The values of order of reaction and energy of activation for dehydration, decomposition of CaC_2O_4, and $CaCO_3$ were found to be 1.0, 0.7, 0.4 and 22, 74, 39 kcal/mole, respectively[4].

The general significance of non-isothermal procedures as compared to isothermal ones can be appreciated by considering the derivative curve of the thermogravimetric trace as shown in Fig. 3. This shows three widely separated peaks indicating clearly that three reactions in the thermal decomposition of $Ca_2C_2O_4 \cdot H_2O$ completely resolved along the temperature coordinate. There are systems that may exhibit parallel reactions. Because of the difference in kinetic parameters of the

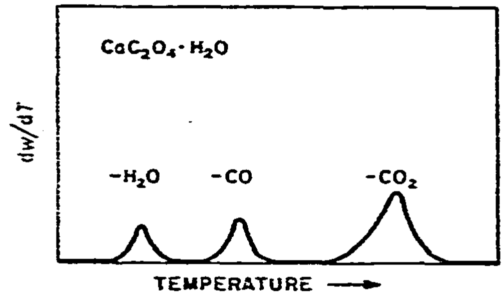

Fig. 3. Schematic representation of the derivative curve for the thermogravimetric decomposition of $CaC_2O_4 \cdot H_2O$.

parallel reactions however, the use of a non-isothermal procedure will probably yield a derivative curve where the peaks may be resolved, though there may be considerable overlapping of the curves. Here then we come to an important advantage of non-isothermal kinetics. The continuous temperature changes may reveal the existence of a temperature range of special interest. This could be overlooked with the conventional isothermal procedures used initially. The temperature scan can then be followed by the more precise isothermal procedures at temperatures that are most meaningful. It should be noted that given a set of parallel reactions exhibiting overlap, the initial part of the derivative curve may frequently yield sufficient information for the accurate determination of the kinetic parameters for the first reaction, whereas the tail end of the overlap may be used for the second reaction of the parallel set.

EXPERIMENTAL

This paper will be restricted to some of the procedures for DTA, DSC, and TGA. With minor modifications the kinetic analysis for these methods may usually be adapted to other thermal methods. We may write that the time rate of conversion, $d\alpha/dt$ is given as

$$d\alpha/dt = kf(\alpha) \tag{1}$$

where α is the degree of completion of the reaction with respect to the initial sample. It should be noted that the specific rate constant, k, as defined in Eqn. 1 has the physical dimensions of a first order rate constant, *i.e.* reciprocal time, regardless of the order or type of reaction. We consider DTA first.

Differential thermal analysis (DTA)

A number of DTA methods stem from the original treatment of Borchardt and Daniels[3,6]. Based on their assumptions it can be shown that

$$d\alpha/dt \approx \Delta T/A \tag{2}$$

where ΔT is the observed temperature difference between the sample and reference substance and A is the area under the thermal trace. Here ΔT is plotted *versus* time. With a constant linear heating rate,

$$\Phi = dT/dt \tag{3}$$

(which is usually about 10°C per min), Eqn. 2 may be rewritten as

$$d\alpha/dT \approx \Delta T/A \tag{4}$$

provided temperature is plotted as the abscissa of the DTA curve. Integration of Eqn. 4 yields the plausible relation that the degree of conversion, α, at temperature T, is equal to a, the area under the thermal trace up to T, divided by A, the total area under the thermal trace, *i.e.*,

$$\alpha = a/A \tag{5}$$

Freeman and Carroll[4] considered simple reactions where the form of $f(\alpha)$ was given by the equation

$$d\alpha/dt = k(1-\alpha)^n \qquad (6)$$

Substitution of the Arrhenius equation for the specific rate constant

$$k = Z\exp(-E/RT) \qquad (7)$$

yields

$$d\alpha/dT = (Z/\Phi)\exp(-E/RT)(1-\alpha)^n \qquad (8)$$

Again the variable t has been replaced by T as indicated in Eqn. 3. Taking the logarithm of both sides of Eqn. 4, differentiating and then integrating, one obtains

$$\Delta\ln(d\alpha/dT) = n\Delta\ln(1-\alpha) - (E/R)\Delta(1/T) \qquad (9)$$

provided one assumes the frequency factor, Z, is temperature independent. In terms of the DTA trace as indicated by Eqn. 5, Eqn. 9 may be expressed as

$$\Delta\ln(\Delta T) = n\Delta\ln(A-a) - (E/R)\Delta(1/T) \qquad (10)^*$$

A plot of

$$\Delta\ln(\Delta T)/\Delta\ln(A-a)\ vs.\ \Delta(1/T)/\Delta\ln(A-a) \qquad (11)$$

will lead to an intercept value for n, the order of the reaction; the slope will yield a value for E/R. Knowing E and n it is a simple matter to obtain values for the specific rate constant, k, and the frequency factor, Z.

The above treatment depends upon an assumed analytical form for $f(\alpha)$ as defined in Eqns. 1 and 6. Piloyan and co-workers[7] circumvented this problem in the following way. Consider the general expression for a reaction rate

$$d\alpha/dT = (Z/\Phi)f(\alpha)\exp(-E/RT) \qquad (12)$$

where $f(\alpha)$ is a function of extent of the reaction. Substituting Eqn. 4 in Eqn. 12 and taking logarithms, the following equation is obtained

$$\ln(\Delta T) = c + \ln f(\alpha) - E/RT \qquad (13)$$

where $c = \ln A + \ln(Z/\Phi)$. On the assumption that under usual laboratory conditions, particularly at the early stage of reaction, ΔT changes more rapidly than α, one may write

$$\ln(\Delta T) = c - E/RT \qquad (14)$$

A plot of $\ln(\Delta T)$ *versus* $1/T$ from approximately the point of maximum curvature to about the peak of the trace, should provide the information required for the determination of activation energy. Comparison of data for several inorganic compounds with data from other sources indicates that this simple procedure of data handling yields fair results. In this method the order of reaction is lost. Reich[8] has suggested a

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[*] It is to be noted that (ΔT) is an observable at various values of T of the sample, represented as $\Delta(1/T)$.

modification of the Piloyan procedure in order to obtain the order of the reaction. However, an analytical form for a simple reaction is assumed in the latter treatment.

*Differential scanning calorimetry (DSC)**

Whereas in DTA a temperature change is measured between base-line and trace as the sample is being heated or cooled, in DSC, the power required to prevent such temperature change is measured. Thus dH/dt, the time rate of change of the enthalpy of the reaction, is a measure of the rate of the reaction and is a direct observable. The simplicity and exactness of recently developed instruments should make DSC a widely used technique for kinetic analysis.

On the basis that the area under the thermal trace is a measure of the enthalpy of the reaction, it can be shown that, for a simple reaction at a given temperature,

$$k = (AV/N_0)^{n-1}\,(\mathrm{d}H/\mathrm{d}t)/(A-a)^n \tag{15}$$

This relation was first given by Barret[9] in 1967. It contains the assumption that the reaction is of the simple type, *i.e.*, $f(\alpha) = (1-\alpha)^n$. In the above expression, V is the volume of the system containing initially N_0 moles of reactant. Barret plotted the logarithm of k *vs.* $1/T$ to obtain the activation energy. An order for the reaction was assumed.

The alternative procedure is to use a linear heating rate. The Freeman and Carroll method may be applied to Eqn. 15 as follows. The Arrhenius equation is substituted in Eqn. 15 so that

$$(Z/\Phi)\exp(-E/RT) = (AV/N_0)^{n-1}\,(A-a)^n\,(\mathrm{d}H/\mathrm{d}T) \tag{16}$$

where Φ is the linear heating rate, and the abscissa of the trace is on a temperature basis. Taking logarithms of both sides of Eqn. 16, differentiating and then integrating, one obtains

$$\Delta\ln(\mathrm{d}H/\mathrm{d}T) = -(E/R)\,\Delta(1/T) + n\ln(A-a) \tag{17}$$

provided that it is assumed that the volume change is not appreciable. Thus, a plot of Eqn. 17, such as

$$\Delta\ln(\mathrm{d}H/\mathrm{d}T)/\Delta\ln(A-a)\ \textit{vs.}\ \Delta(1/T)/\Delta\ln(A-a) \tag{18}$$

will lead to an intercept for n, and the slope will yield a value of $-E/R$. The above procedure was recently suggested and used by Ellerstein[10] in an investigation of the kinetics of the thermal degradation of several synthetic polymers.

Other procedures have been suggested for DSC[11]. Also, the treatment of base-line deviations, particularly for the case of fast scanning rates, has been considered in detail by Heuvel and Lind[12].

Thermogravimetric analysis (TGA)

Clearly, the analytical balance is capable of enormous accuracy and precision. Unfortunately, many reactions are unaccompanied by weight changes. However,

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*Sometimes referred to as differential enthalpic analysis (DEA).

when they do occur, thermogravimetry is most reliable. A wide variety of methods have been developed, assessed, and reassessed for this technique. Some excellent reviews in this field, as applied especially to the thermal degradation of polymers, have appeared[13,14]. Most kinetic methods may be classified as derivative or integral. We shall consider the derivative methods first.

Derivative methods. — It should be evident that unlike DTA or DSC, the read-out of the thermal balance does not yield a differential signal directly. To obtain the instantaneous rates of reaction the slope of the weight loss *versus* temperature must be obtained. This is usually done manually*. As a result, the derivative methods may lack the desired precision[15]. However, it will be seen that for systems whose kinetic parameters keep changing during the progress of a reaction, the derivative methods may have a decided advantage.

Since the observable is weight w as a function of the linear advancing temperature, we write**

$$-\mathrm{d}w/\mathrm{d}T = (Z/\Phi)\exp(-E/RT)\,\mathrm{f}(w) \tag{20}$$

With the exception of rates of vaporization of liquids, kinetic analysis in thermogravimetry is almost entirely restricted to reactions in the solid state. Empirically, it seems that for these reactions, which are essentially heterogeneous, reasonably good results are usually obtained by setting

$$\mathrm{f}(w) = w^n \tag{21}$$

or $f(x) = (1-x)^n$. It should be noted that w refers to the weight of the reactive portion of the sample, *i.e.*, the actual weight of the sample minus the weight when the reaction has gone to completion. Combining Eqns. 20 and 21, and using the procedures as described for DTA and DSC, it can readily be shown that

$$\Delta\ln(-\mathrm{d}w/\mathrm{d}T) = -(E/R)\Delta(1/T) + n\ln w \tag{22}$$

Thus, a plot of $\Delta\ln(-\mathrm{d}w/\mathrm{d}T)/\Delta\ln w$ *versus* $\Delta(1/T)/\Delta\ln w$ will lead to analytical values for E and n. Such a plot is illustrated in Fig. 2.

It has been found desirable in some cases to have the logarithm of the experimental rates plotted initially against $1/T$ so that one may use the smoothed-out curve to obtain a set of values for constant increments in $1/T$. Keeping $\Delta(1/T)$ constant, a subsequent plot of $\Delta\ln(-\mathrm{d}w/\mathrm{d}T)$ *versus* $1/\Delta\ln w$ leads to a value of n as the intercept. The activation energy is obtained from the slope. The reliability of this procedure has been illustrated for the case of the vaporization of octamethylcyclotetrasiloxane[16]. Here it is known that the vaporization is zero order rate process, and that the activation energy should be equal to the thermodynamic latent heat of vaporization (10.9 kcal.mole^{-1}). Identical values are obtained from the analysis of the thermal trace.

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*An electromechanical differentiator with digital readout has been recently described. See E. P. Manche, *Rev. Sci. Instrum.*, 42 (1971) 269.

**These equations may also be written in terms of degree of conversion, α.

A basic assumption in the above treatment is that an analytical form for f(w) or f(α) is assumed. It is possible to obtain the activation energy of a reaction without this assumption by using different heating rates[14,17]. Eqn. 20 may be rewritten as

$$\ln[\Phi(-\mathrm{d}w/\mathrm{d}T)] = \ln[Z\mathrm{f}(w)] - E/RT \qquad (23)$$

A plot of $\ln[\Phi(-\mathrm{d}w/\mathrm{d}T)]$ *versus* $1/T$ for a given value of w obtained at different heating rates, will lead to a value for E. Several thermal traces at the various values of Φ are required (see Fig. 4). Also it is assumed, as in the Freeman–Carroll treatment, that f(w) is a unique function of w and is independent of the temperature. The method of multiple heating rates, in general, may be considered the basis for the most powerful methods for the determination of kinetic parameters[13]. In this particular procedure, changes in the activation energy may be determined as a function of the progress of the reaction. The value for n may be obtained by setting the intercepts of the above plots, *i.e.* $\ln[Z\mathrm{f}(w)]$, equal to $\ln Z + n\ln w$. A plot of the values of the intercepts *versus* $\ln w$ will then yield values of n and Z.

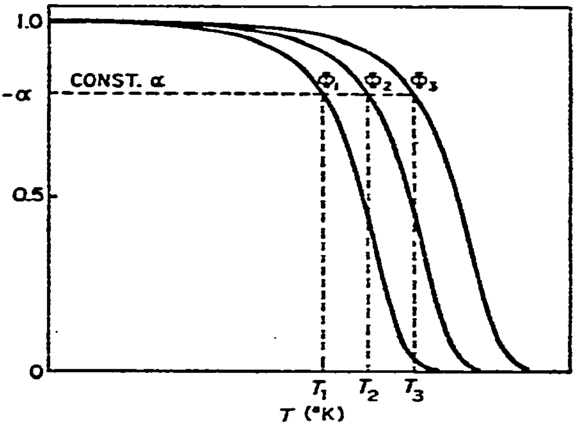

Fig. 4. Schematic representation of effect of heating rates ($\Phi_3 > \Phi_2 > \Phi_1$) upon thermogravimetric traces; α is the fraction of conversion and is a measure of the progress of the reaction[23]. Data taken from such a figure are used in Eqn. 23.

More recently[15], the terms in Eqn. 21 have been rearranged. Given in terms of α

$$\ln[(1/\mathrm{f}(\alpha)(\mathrm{d}\alpha/\mathrm{d}T)] = \ln(Z/\Phi) - (E/RT) \qquad (24)$$

In this procedure only a single thermogram is required. Chemical intuition guides the selection of f(α) with trial-and-error modifications of n, so that a linear plot may be achieved when the left hand side of Eqn. 24 is plotted against $(1/T)$. With a known value of Φ the intercept leads to a value for Z, and the slope will yield a value for E.

Integral methods. — Under this general heading are those methods based on the exponential integral

$$\int_0^T \exp(-E/RT)\,\mathrm{d}T$$

This may be seen as follows. The separation of the variables in Eqn. 24 yields

$$d\alpha/f(\alpha) = (Z/\Phi)\exp(-E/RT)\,dT \tag{25}$$

We define

$$F(\alpha) \equiv \int_0^\alpha d\alpha/f(\alpha) \tag{26}$$

so that

$$F(\alpha) = (Z/\Phi)\int_{T_0}^{T} \exp(-E/RT)\,dT \tag{27}$$

where T_0 is the value of T at the beginning of the reaction. Ordinarily, the reaction rate is neligible at low temperatures, so that

$$\int_{T_0}^{T} \exp(-E/RT)\,dT = \int_0^T \exp(-E/RT)$$

The many techniques used for evaluating the exponential integral fall into three groups[18]: (a) using a simple approximation, (b) using a series expansion, and (c) using tabulated values.

In group (a) may be added the recent method of MacCallum and Tanner[19]. This will be discussed at the end of this section.

Integration of Eqn. 27 yields

$$F(\alpha) = (ZE/\Phi R)\left[-e^x/x + \int_{-\infty}^{x} (e^x/x)\,dx\right] = (ZE/\Phi R)\,p(x) \tag{28}$$

where $x \equiv -E/RT$.

The function $p(x)$ may be expanded[13] as

$$p(x) = (e^x/x^2)[1 + (2!/x) + (3!/x^2 + \ldots)] \tag{29}$$

Values for $p(x)$ have been tabulated for limited ranges[20,21]. One of the difficulties in using Eqn. 28 is that $p(x)$ depends on both temperature and the activation energy. Thus the methods based on Eqn. 28 are generally of the trial-and-error type involving iteration.

In 1961, Doyle[20] presented an approximation procedure to reduce the tediousness of the trial-and-error method. This was modified rather successfully by Zsakó[21] in 1968 by re-writing Eqn. 28 as follows

$$\log(ZE/R\Phi) = \log F(\alpha) - \log p(x) = B \tag{30}$$

It will be seen that B depends only upon the heating rate, Φ, for a given chemical reaction. From the thermal trace the value for $F(\alpha)$ at a given temperature can be calculated if an expression for $f(\alpha)$ is assumed. Similarly, $p(x)$ for the same temperature can be found from the tables for $p(x)$ (see Refs. 20 and 21) for assumed values of E. The constancy of B for a given run permits a quantitative method for testing the apparent activation energy consistent with a given analytical form for f(α). A comparison of data for this modified Doyle method and the Freeman–Carroll method was published by Zsakó and is shown in Table I.

TABLE I

A COMPARISON OF RESULTS FOR INTEGRAL AND DERIVATIVE METHOD IN THE THERMAL DECOMPOSITION OF A COMPLEX SALT[21]

Method	*Complex I*[a]		*Complex II*[b]	
	n	*E (kcal/mole)*	*n*	*E (kcal/mole)*
Doyle–Zsakó	1	28.9	1	28.3
Freeman–Carroll	1.16	29.2	0.82	28.7

[a] Complex I, [Co(dimethylglyoxime)$_2$(p-ethylamine)$_2$]NCS. [b] Complex II, [Co(dimethylglyoxime)$_2$ (γ-picoline)$_2$]NCS. The value for n is assumed to be unity for the Doyle–Zsakó method.

A number of investigators have used the method of Coats and Redfern[22]. This is based on the first three terms of the asymptotic approximation for p(x). If f(α) = $(1-\alpha)^n$ then it can be shown that

$$[1-(1-\alpha)^{1-n}](1-n) = (ZRT^2/\Phi E)[1-(2RT/E)] \exp(-E/RT) \tag{31}$$

or

$$\log\{[1-(1-\alpha)^{1-n}]/T^2(1-n)\} = \log\{(ZR/\Phi E)[1-(2RT/E)]\} - (E/2.3RT) \tag{32}$$

for all values of n except $n = 1$. In the latter case,

$$\log\{-\log[(1-\alpha)/T^2]\} = \log(ZR/\Phi E) - (E/2.3RT) \tag{33}$$

A plot of the left hand side of Eqns. 32 and 33 *versus* $1/T$ should result in a straight line of slope $-E/2.3R$ for the correct value of n. The linear relation is due to the almost constant value for log $\{(ZR/\Phi E)[1-(2RT/E)]\}$, for most values of E and T over which many reactions occur.

Most recently (1970), MacCallum and Tanner upon examining Zsakó's table of values for log p(x) came up with an empirical approximation

$$-\log p(x) = 0.4828E^{0.4351} + (0.449+0.217E)/T \times 10^{-3} \tag{34}$$

where E is given here in units of kcal.mole^{-1}. These authors found that the above values for log p(x) agree with Zsakó's table values to about one percent or better. In the latter tables, $-$log p(x) ranges from about 8 to 24. Thus, the complete integrated rate equation may be approximated by the expression

$$\log F(\alpha) = \log(ZE/\Phi R) - 0.48E^{0.44} - (0.45+0.22E)/T \times 10^{-3} \tag{35}$$

A plot of log F(α) against $1/T$ should lead to values for E and Z.

Eqn. 35 affords an additional method, that of varied heating rates. If a series of runs is made at different heating rates, then a plot of logΦ *versus* 1/T should yield a straight line for constant values of α. This procedure is somewhat similar to the derivative method using varied heating rates, except that the experimental scatter of slope measurements may now be avoided. The linear relationship between $\log\Phi$ and $1/T$ at constant α may be seen from the following. Rewriting Eqn. 35,

$$\log F(\alpha) - \log(ZE/\Phi R) + \log 0.48E^{0.44} + (0.45 + 0.22E)/T \times 10^{-3} = 0 \qquad (36)$$

This yields

$$\{\partial \log\Phi/\partial(1/T)\}_{\alpha} = -(0.45 + 0.22E) \times 10^{3} \qquad (37)$$

where E is given in kcal.mole^{-1}.

The above equation compares favorably with the approximation given in 1966 by Flynn and Wall[23], *viz.*,

$$[\partial \ln\Phi/\partial(1/T)]_{\alpha} = -0.228E \qquad (38)$$

Here E is given in cal.mole^{-1} and is based on Doyle's table of values for $p(x)$ where $-x$ or E/RT exceeds 20.

CONCLUSION

The question has been raised whether kinetic parameters obtained in non-isothermal procedures are the same as those obtained by conventional isothermal methods[24]. It has been suggested that it would be more accurate to write

$$d\alpha/dt = (\partial\alpha/\partial t)_T + (\partial\alpha/\partial T)_t\Phi \qquad (39)$$

Clearly, if for example, $f(\alpha)$ or $F(\alpha)$ were not uniquely defined for a given value of α, but was also a function of the temperature, then isothermal and non-isothermal procedures could lead to differing results. Recently, Audebert and Aubineau[25] have examined the activation energy for the thermal decomposition of several high polymers and obtained, within experimental error, the same values for both the isothermal and non-isothermal procedures. Our own experience with the thermal decomposition of inorganic solids[26] indicates that both procedures yield the same results.

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