Thermochimica Acta, 130 (1988) 269–279
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ILLUSTRATION OF THE AMBIGUITY IN SOLVING INVERSE KINETIC PROBLEMS

S.V. VYAZOVKIN, A.I. LESNIKOVICH, E.A. GUNIN and V.G. GUSLEV

Institute for Physico-Chemical Problems, Byelorussian State University, Minsk (U.S.S.R.)

(Received 4 November 1987)

ABSTRACT

Different aspects of the ambiguity in solving the inverse kinetic problems both under isothermal and non-isothermal conditions are considered for particular examples. It is emphasized that discrimination is inadmissible when a real process does not consist of any of the elementary formal models. An alternative use of the generalized description based on the complementary principle is advisable. Possible application of the results of isothermal experiments for processing non-isothermal data is discussed.

INTRODUCTION

It is well known that the solution of a particular inverse kinetic problem which consists of finding a formal model and kinetic parameters of a process is ambiguous. Such an ambiguity shows itself in the existence of several formal models for a process all of which equally well describe the experimental data [1]. The relevant values of the kinetic parameters (E for the activation energy and A for the pre-exponential factor) calculated from the equation

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \tag{1}$$

for different formal models $f(\alpha)$ slightly depend on $f(\alpha)$ under isothermal experimental conditions. In the case where non-isothermal methods are used, however, an error in the choice may drastically affect the parameters A and E [2], which is why isothermal experimental data are preferred in solving inverse problems as more unambiguous and are often used as reference data. Nevertheless, it should be remembered that ambiguity is a common property [3] and is a shortcoming of any inverse problem regardless of the method used to obtain the experimental data. In view of this, the confrontation of the isothermal and non-isothermal methods is only quantitatively reasonable as the former provide more definite rather than unambiguous information on the process kinetics. In this paper, specific examples

TABLE 1

Formal models used for calculation

No.	$g(\alpha)$	Kinetic law
1	$\alpha^{1/4}$	Power law
2	$\alpha^{1/3}$	
3	$\alpha^{1/2}$	
4	α	
5	$\alpha^{3/2}$	
6	α^2	
7	$-\ln(1-\alpha)$	Mampel
8	$[-\ln(1-\alpha)]^{1/4}$	Avrami–Erofeev
9	$[-\ln(1-\alpha)]^{1/3}$	
10	$[-\ln(1-\alpha)]^{1/2}$	
11	$[-\ln(1-\alpha)]^{1/1.5}$	
12	$\frac{3}{2}[1-(1-\alpha)^{1/3}]^2$	Jander
13	$\frac{3}{2}[(1+\alpha)^{1/3}-1]^2$	Anti-Jander
14	$3[1-(1-\alpha)^{1/3}]$	Contracting sphere
15	$2[1-(1-\alpha)^{1/2}]$	Contracting cylinder
16	$(1-\alpha)^{-1}-1$	Second order
17	$\frac{1}{2}[(1-\alpha)^{-1/2}-1]$	One and a half order

demonstrate ambiguity in solving inverse problems under isothermal and non-isothermal conditions, thus confirming the above statements. Ways of overcoming it are discussed.

For clear representation, the graphical affinitive transformation of kinetic curves is used. The affinitive transformation is most widely used to solve inverse kinetic problems based on isothermal experimental data. Its fundamentals are cited in ref. 4. The affinitive transformation of non-isothermal experimental data is considered in ref. 5.

All the plots were obtained for 17 formal models presented in an integral form in Table 1 using the "intellectual" plotter EM-7042 AM on-line with the computer Elektronika-100/25 (PDP-11 analog) and program package GRAFOR [6].

AMBIGUITY IN THE CASE OF ISOTHERMAL EXPERIMENTAL DATA

The affinitive transformation of isothermal experimental data implies going from the transformation degree α vs. time to the transformation degree versus reduced time: α_i vs. t_i/t_α where α_i, t_i are the coordinates of

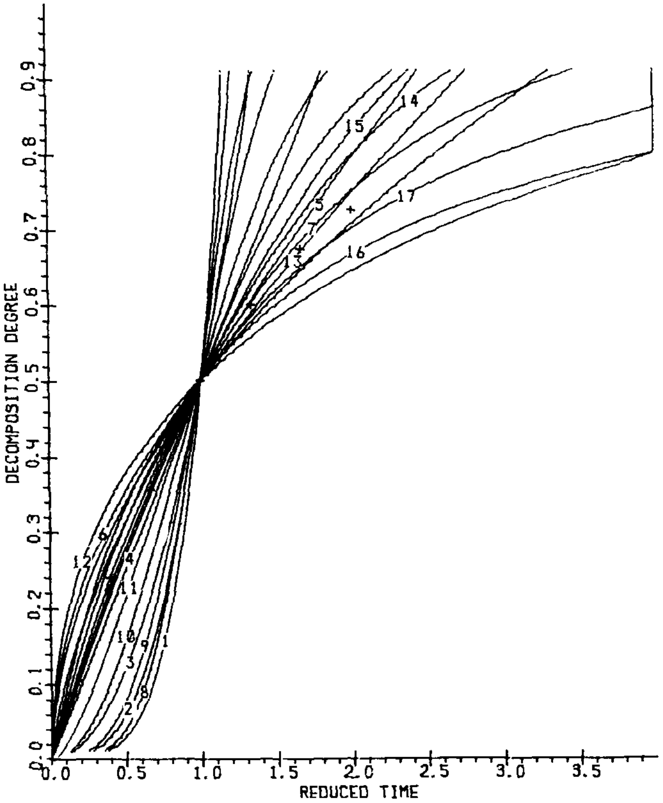

Fig. 1. Reduction of ZnO in reduced coordinates ($t_\alpha = t_{0.5}$) (numbers correspond to the models from Table 1).

an ith point on the kinetic curve and t_α is the time consistent with a certain transformation degree (as a rule, $\alpha = 0.5$ or 0.9 [7]). It can be shown easily that in the reduced coordinates a certain curve invariant to kinetic parameters and temperature conforms to each formal model. For the formal models of Table 1 these curves are plotted in Figs. 1 ($t_\alpha = t_{0.5}$) and 2 ($t_\alpha = t_{0.9}$).

Comparison of Figs. 1 and 2 shows that the affinitive transformation at $t_\alpha = t_{0.9}$ yields a set of curves for which it is more appropriate to choose a formal model than for those obtained at $t_\alpha = t_{0.5}$. In the latter case many of the curves almost merge, particularly in the vicinity of the intersection point. Some examples of using the affinitive transformation to determine a formal mechanism of a process are considered below.

Experimental data from ref. 7 on hydrogen reduction of zinc oxide are plotted in Fig. 1 in the reduced coordinates ($t_\alpha = t_{0.5}$). The process in ref. 7 exemplifies the interface reaction in accordance with the equation $1 - (1 - \alpha)^{1/3}$. However it is seen from Fig. 1 that the first point corresponds to eqn. (7) (Table 1), the second one lies between the curves for eqns. (7) and (14), the third is between eqn. (14) and eqn. (15), the fourth is the intersection

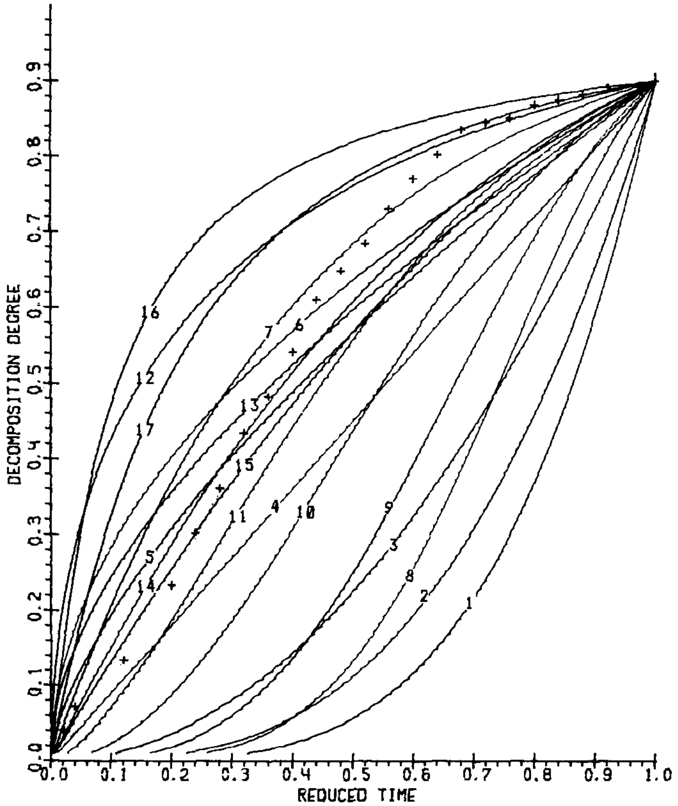

Fig. 2. Dehydrotation of $Na_5P_3O_{10}\cdot 6H_2O$ in reduced coordinates ($t_\alpha = t_{0.9}$) (numbers correspond to the models from Table 1).

point, the fifth and the sixth are between eqns. (7) and (13) and the seventh point lies between eqns. (13) and (6). So, no certain conclusions on the formal mechanism of the reduction process for zinc oxide can be drawn from the affinitive transformation.

In Fig. 2 is illustrated the reduced coordinate ($t_\alpha = t_{0.9}$) plot of the experimental data on the dehydration of $Na_5P_3O_{10}\cdot 6H_2O$ ($T = 393$ K at water vapor atmosphere pressure). It can be seen easily that only the last eight points are consistent with a certain model (eqn. (17)) while all the remaining ones are intermediate between different reduced curves. Thus, in this case none of the 17 formal models of Table 1 can describe dehydration to the transformation degree $\alpha = 0.8$ unambiguously.

Figure 3 presents data [8] on decomposition of $CaCO_3$ ($T = 983$ K). In contrast to other cases, here experimental points tend to coincide with the curve for model (4) (Table 1). The first two and the last three points, however, can be said to lie on curve (4) while the intermediate eight are systematically shifted to the left. In addition, the last three points lying on curve (4) are no less successfully described by curve (9). As the dependence

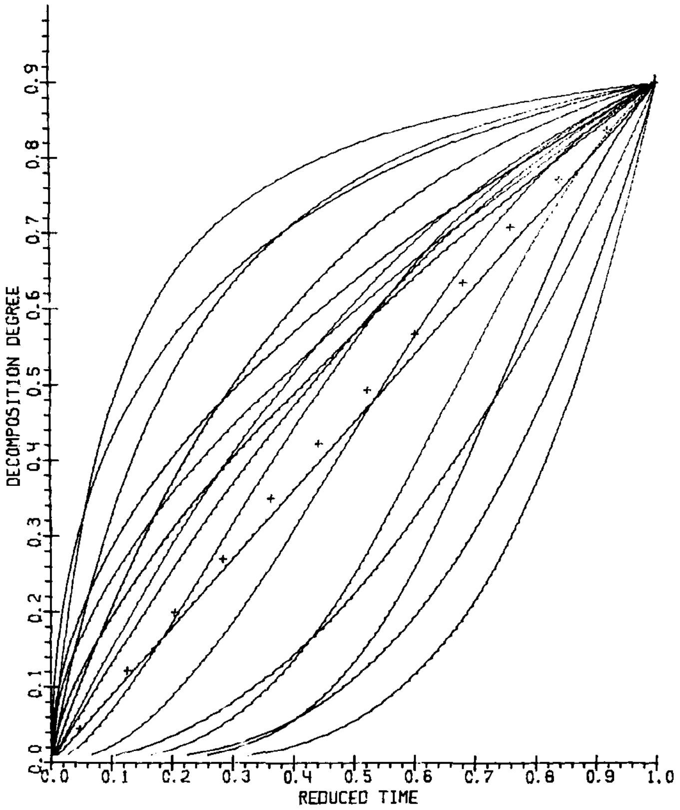

Fig. 3. Decomposition of $CaCO_3$ in reduced coordinates ($t_\alpha = t_{0.9}$).

(4) is a line and the experimental points lie along some convex curve, the process, as a whole can be characterized as an intermediate one between models (4) and (15) (the convex curve most proximate to the experimental points).

Though more examples can be given, these are sufficient to state that real solid phase processes can satisfy none of the elementary formal models. It is clear that in this case any attempts to discriminate the competing models are ineffectual.

AMBIGUITY IN THE CASE OF NON-ISOTHERMAL EXPERIMENTAL DATA

The affinitive transformation of non-isothermal experimental data implies going from the transformation degree vs. temperature to the transformation degree vs. reduced temperature, i.e. α_i vs. $(T_i - T_0)/(T_\alpha - T_0)$ [5] where α_i, T_i are the coordinates of the ith point on the kinetic curve, T_α is the temperature corresponding to a certain transformation degree, and T_0 is the incipient transformation temperature. Note that the necessity for using T_0

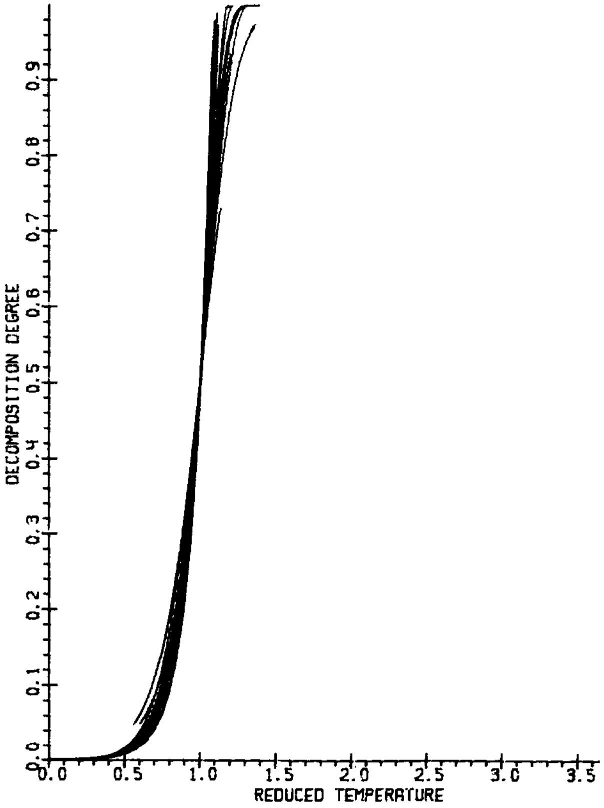

Fig. 4. Reduced curves in the non-isothermal case ($T_\alpha = T_{0.5}$).

which is always difficult to determine [9] hinders the affinitive transformation in the case of non-isothermal data. For T_0, we have used $T_{0.0001}$ found for each individual formal model (Table 1). The relevant reduced curves are given in Fig. 4 ($T_\alpha = T_{0.5}$) and Fig. 5 ($T_\alpha = T_{0.9}$). Both are plotted using the scale of analogical dependence for isothermal conditions (Figs. 1, 2).

Comparison of Figs. 4, 5 and 1, 2 demonstrates much more ambiguity in processing the non-isothermal data. Almost all the kinetic curves reduced to $T_{0.5}$ coincide. At $T_\alpha = T_{0.9}$ it is only possible to identify some formal models within individual sections. As the accuracy of non-isothermal experimental methods does not exceed that of isothermal ones, it is possible to state that it is hardly possible to choose reasonably a formal mechanism of a process using the affinitive transformation of non-isothermal data.

DISCUSSION

Let us analyse the problem of ambiguous solution to the inverse kinetic problem based on these examples (Fig. 1–3). Two reasons responsible for

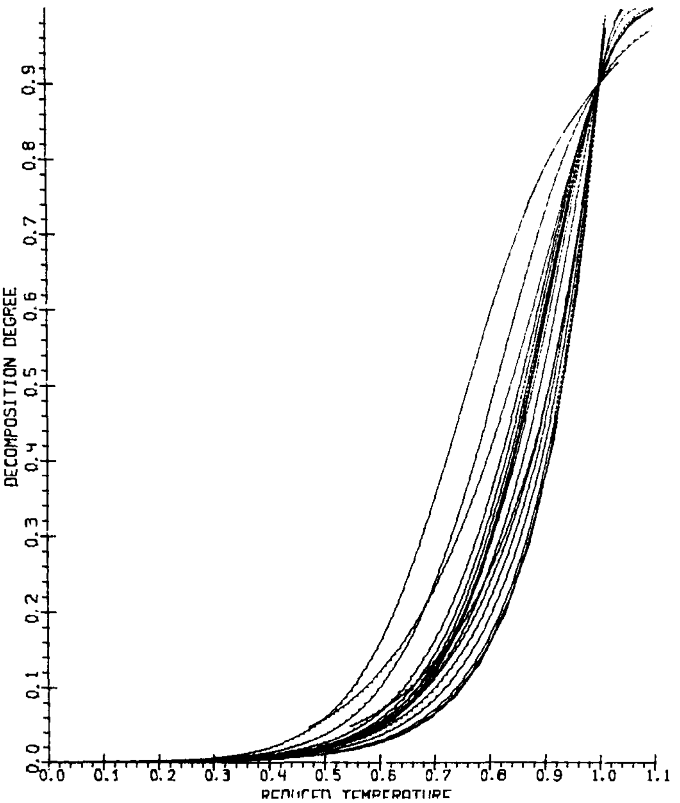

Fig. 5. Reduced curves in the non-isothermal case ($T_\alpha = T_{0.9}$).

ambiguity should be identified. First, ambiguity may stem from the fact that it is impossible to distinguish between individual formal models of a process within some experimental error. Ambiguity is generally attributed just to random experimental errors. Let us emphasize that various methods of discrimination of formal models are only legitimate when ambiguity is due to random experimental errors.

Secondly, ambiguity may appear when the real process, on the whole, is not consistent with any of the models applied by the researcher (see Figs. 1–3). The systematic displacement of experimental points relative to any of the theoretical kinetic curves may be interpreted as a systematic error. Any discrimination of formal models seems to be useless in the case of systematic errors. Also in such a situation statistical data processing which assumes random errors is no longer useful. In particular, in the case of systematic errors the confidence limits for kinetic parameters determined, for example, using the least-squares method fail to be interpreted as the errors due to inaccuracy of experimental methods.

In view of these two sources of ambiguity, two different strategies for solving the inverse kinetic problem can be identified. If ambiguity is due to random errors, it can be reduced by increasing the accuracy of experimental data. To do this, various methods [7] can be used such as treatment of the subject of inquiry, selection of experimental conditions and so on. However, when ambiguity is due to systematic errors, no increase in the accuracy of experimental data will reduce the error until the real model of the process is found. As it is impossible, in principle, to list all possible formal models, these approaches should be used to calculate kinetic parameters which do not require an explicit elementary formal model. It is worth noting that such methods are universal since they allow the estimation of the reliable values of effective kinetic parameters irrespective of the source of the ambiguity. Those include, for example, non-traditional methodology [3] of solving the inverse kinetic problem and isoconversion methods [10].

The non-traditional methodology approaches are based on the complementarity principle permitting the consideration of the competing models as complementing one another. Such an approach provides a generalized description, based on a set of competing models, to substitute in individual models. The generalized descriptions are represented, for example, by the apparent compensation relations used in the method of invariant kinetic parameters [11], classes of formal models [12] and their linear combinations [13] and probability distribution spectra [14]. The model suggested by Šestak–Berggren [15] as well as various approximations [16] neglecting elementary formal models can also be used appropriately for generalized description.

The isoconversion methods of calculating kinetic parameters admit estimation of the effective activation energy by the temperature at which one and the same transformation degree is achieved for different heating rates. For the pre-exponent, the isoconversion methods only allow its unambiguous estimation in combination (product or ratio) with a formal model. The pre-exponential factor itself can be determined by a particular formal model and its value varies with the form of the model. The numerical value for their combination is a constant. The form of such a relationship between the pre-exponential factor and formal model in the isoconversion methods is equivalent to the well-known uncertainty relation. This situation, in particular, shows that the pre-exponential factor and formal models are complementary descriptions.

Hence, the complementarity concept [3] we have applied to overcome ambiguity is beneficial not only when the generalized description is based on a set of complementary formal models (non-traditional methodology) but also when the generalized description is a combination of the formal model and pre-exponent (isoconversion methods). In both cases, the generalized descriptions are advantageous for possible single-valued estimation of effective kinetic parameters. In addition, in the isoconversion methods the pre-exponential factor can be determined without choosing a formal model of a process [17]. It requires additional information, neglected by the isoconversion methods, i.e. information about the correlation between the activation energy and pre-exponent in the form of compensation effect.

The common methodological basis (complementarity principle) of the isoconversion and non-traditional methodology approaches results in the coincidence of the kinetic parameter values they determine for the same process. The coincidence of effective activation energy values calculated by the isoconversion methods and the method of invariant kinetic parameters (non-traditional methodology) is described elsewhere [18]. The calculations of both kinetic parameters for a model process with their definite values using the method of invariant kinetic parameters in ref. 19 and isoconversion technique in ref 17 point both to the adequacy of each method and their mutual equivalence.

Hence, our understanding of ambiguity and the way it is overcome by solution of the inverse kinetic problem can be presented as the following chain of cause and consequence relations. The complexity of solid-phase processes results in incomplete (imperfect) models. The incomplete models, in their turn, generate ambiguous description of a process. The ambiguity can be overcome with the aid of the complementarity principle. In this case, every element link of this chain is well known. Thus, the incompleteness of formal models was mentioned in ref. 6, the relationship between incomplete models and ambiguous descriptions was discussed in ref. 20 and, finally, it was shown in ref. 21 that ambiguity in different fields of knowledge can only be overcome with the complementarity principle. By combining these links into a single chain we have for the first time extended the complementarity concept to the solution of the inverse kinetic problem [3].

On the application of the isothermal experimental data for interpretation of non-isothermal data

With our understanding of ambiguity we shall consider the approach to the solution of the inverse kinetic problem by the non-isothermal kinetic data proposed by Tang [22]. It implies that the choice of a model of a process is based on isothermal experimental data to calculate kinetic parameters for non-isothermal experimental data. Certainly, it is easier to choose the formal model in terms of isothermal rather than non-isothermal data as the number of competing models in the former case will always be less than in the latter. However, the situation with no competing models is hardly possible since, in fact, it can be implemented in two hypothetic cases: when the real process follows some formal model or when such a formal model exists which can exactly describe a particular process. It is unnecessary to say that none of the cases is realized in practice as real processes are extremely intricate. Here, the former case is not realized because all the experimental methods fail to simplify the real process to formal models level. Thus, even vacuum dehydration of a monocrystal is a macrokinetic process [23]. The latter case cannot be realized because formal models are extremely imperfect [7]. The attempts to make them complex yield a great number of empirical parameters whose appropriate numerical values allow description of any experimental relation.

The main shortcoming of the proposed approach stems exactly from the ambiguous choice of the formal model based on isothermal data. This shortcoming manifests itself in the fact that even insignificant error in choosing the process model by isothermal experimental data may result in an essential error in the kinetic parameters calculated by this model in terms of non-isothermal data. It is worth noting here that in contrast to isothermal data, for which the kinetic parameters slightly depend on the model form [24,25] and can, therefore, be determined exactly even if it is incorrectly chosen, in the case of non-isothermal data the kinetic parameters may vary by several orders depending on the form of the model [2]. Hence, the application of the approach [22], as well as of any other based on the discrimination of formal models, always involves a certain risk.

In principle, we think it more reliable to calculate the kinetic parameters by isothermal data with subsequent choice of a formal model based on non-isothermal findings to obtain the values of kinetic parameters as close as possible to isothermal ones. Such an approach is used, for example, in ref. 26. It allows exploitation of the main advantage of the isothermal experiment in solution of the inverse kinetic problem which is slight dependence of kinetic parameters on the form of the formal model. The process model so chosen can by no means be interpreted as some real process mechanism. However, this model can serve as a rather reliable (depending on how close are the values of kinetic parameters obtained with the model by non-isothermal data to isothermal ones) approximation which allows various extrapolations of kinetic data from one temperature condition to another.

CONCLUSIONS

The choice of the solution method for the inverse kinetic problem, as noted in ref. 3, always reduces to the choice of one of the two methodologies: unambiguous description (discrimination of models) or complementarity (generalized descriptions). In non-isothermal kinetics with extremely pronounced ambiguity, the methodology of unambiguous description, we think, cannot be applied in the general case and the complementarity has, therefore, no alternative. The complementarity methodology is also fully admissible for isothermal kinetics. However, in isothermal kinetics, in view of the above dependence of kinetic parameters on the form of a model the generally accepted unambiguous description methodology can also be used.

ACKNOWLEDGEMENTS

The authors are grateful to Professor V.V. Sviridov for useful discussion and permanent interest to our researches in the field of solid phase reaction kinetics. We also thank L.A. Lesnikovich for the data on sodium tripolyphosphate dehydration.

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