

The influence of errors of Arrhenius parameter calculation on the exactness of the solution of the direct kinetic problem

S.V. Vyazovkin and A.I. Lesnikovich

Institute for Physico-Chemical Problems, Byelorussian State University, 220080 Minsk (U.S.S.R.)

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Abstract

The influence of errors arising in calculating the Arrhenius parameters (AP), with and without discrimination to solve the inverse kinetic problem, on the exactness of the solution of the direct kinetic problem (DKP) has been studied. As an example of solving a DKP, the time of reaching a given transformation degree at a known temperature is calculated. The relative error in calculating this time from the AP values found by the discrimination methods is shown to be always higher than that for the non-discrimination methods, and in many cases it exceeds 100%. The conclusion is that solely non-discrimination methods should be used in solving applied kinetic problems.

INTRODUCTION

The calculation of Arrhenius parameters (AP) (activation energy and pre-exponent) pursues, as a rule, two main objectives. The first objective, obtaining the characteristics associated with the substance reactivity, is conditioned mainly by the necessity of solving theoretical problems. Of prime importance [1] is the interpretation of AP as parameters really involved in the reaction system of processes such as the formation and growth of nuclei in a solid, i.e. a knowledge of the mechanism of the reaction being investigated is required. The second objective — the estimation of the values of the parameters which make it possible to solve the direct kinetic problem (DKP), i.e. to model the kinetic curve corresponding to the process being investigated when changing the regime of the experiment (from non-isothermal to isothermal conditions) or the parameter of the state of the system (temperature in the isothermal or heating rate in non-isothermal kinetics) — has been determined mainly by practical requirements. To reach this goal, it is not necessary to know the mechanism of the process proceeding in the sample of the substance being investigated if we have every reason to suppose that, beyond the experimental temperature range, it will remain the same as it is within this range. In this case, the main requirement of the AP values is reliability by which we mean primarily the ability of AP to

describe the temperature dependence of the rate in a temperature range wider than the experimental one.

It has been noted [2] that a change in the mechanism of the process outside the experimental temperature range could lead to a wrong prediction of the behaviour of the material involved. In this connection, it should be noted that a similar result is also obtained in cases where the mechanism of the process is not changed but its AP have been calculated incorrectly owing to the use of an inadequate method. The adequacy of the calculation method is determined by the methodological principle [3] which forms the basis for solving the inverse kinetic problem (IKP). In turn, the adequacy of the calculation method provides reliability of the AP values. We have substantiated [3] the postulate that the non-discrimination methods, which rely on the principle of complementarity, always give more reliable solutions of IKP than the methods which use discrimination of the formal models of the process. This statement was confirmed in ref. 4 where it was proved that the reliability of the IKP solution obtained by non-discrimination methods is the result of the higher information content of the latter. Additionally, in ref. 5, examples are given of cases where the real process does not correspond to any of the formal models used, which obviously makes any discrimination senseless and makes the calculation of AP inadequate. The quantitative relationship between the error in determining the activation energy and the error caused by incorrect discrimination of the formal model has been established [6].

It is obvious that AP calculated for the process as a whole are gross values. However, adequately calculated gross AP, like the parameters of elementary processes, contain information about the reactivity of a concrete sample of the substance being investigated, which appears as different values of AP for samples with different prehistories. Thus, the gross AP implicitly take into account the specific features of the object under study. It should be noted that theoretically it is possible to take into account explicitly some of the specific features of the sample, i.e. by introducing corresponding characteristics into the equation

$$d\alpha/dt = k(T)f(\alpha)$$

It should be remembered that any complication of the form of this equation will, of course, lead to the strengthening of the ambiguous solution of IKP and consequently to a decrease in the reliability of the AP calculation. Therefore the implicit account of the specific features of a concrete sample by means of gross AP is most likely to be the only appropriate one for solving practical problems.

The aim of the present paper is to evaluate the influence of errors in AP determination arising within the framework of two different approaches to the IKP solution (with or without the use of discrimination) on the exactness of the DKP solution. To evaluate the exactness of the DKP solution, we

shall use the relative error in determining the time of reaching a given transformation degree at a definite temperature.

DISCUSSION

Exactness of the DKP solution in solving IKP by the non-discrimination method

Previously [7] we proposed a method of non-isothermal kinetic curve transformation to an adequate isothermal form. Assuming that the AP and the process model remain unaltered on going from the non-isothermal to the isothermal regime of experiment, we can obtain [7] a simple relation

$$t = \int_0^T \exp(-E/RT) dT/q \exp(-E/RT_{\text{iso}}) \quad (1)$$

which makes it possible to find the time in which, at a constant temperature T_{iso} , the transformation degree corresponding to temperature T on the non-isothermal kinetic curve obtained at heating rate q , will be reached. Expression (1) can be significantly simplified by replacing the integral by an approximation so that

$$t = RT^2 \exp(-E/RT)/qE \exp(-E/RT_{\text{iso}}) \quad (2)$$

The relation between the relative error in determining the activation energy and the limiting relative error in calculating t by eqn. (2) is given by

$$|\Delta t/t| \approx |d \ln t| = |(1/T_{\text{iso}} - 1/T)E/R - 1| \Delta E/E \quad (3)$$

In the cases where the accuracy of the activation energy calculation cannot be increased to a sufficient extent by increasing the accuracy of the experimental data, the necessary accuracy in determining the time of reaching a given transformation degree can be obtained by choosing T close to T_{iso} , i.e. by changing the heating rate. The temperature T at which the time of reaching a given transformation degree at temperature T_{iso} can be estimated to the required accuracy, can then be found. Let us introduce a quantity z which is the ratio of the relative errors in calculating the time and the activation energy and let us find the relation between z and the temperature range within which extrapolation is realized. According to eqn. (3),

$$T = T_{\text{iso}} E / |E - RT_{\text{iso}}(1 + z)| \quad (4)$$

Equation (4) gives the required temperature value at which the time of reaching a given transformation degree can be estimated with a relative error differing from the relative error in determining the activation energy z times.

The heating rate at which *this* transformation degree is reached at the temperature given in eqn. (4) can easily be estimated by the equation

$$\ln q = C + 2 \ln T - E/RT$$

where C is the free term of the equation of a straight line in coordinates $(\ln q/T^2 - 1/T)$ used in the isoconversion method [8] for calculating AP.

Exactness of the DKP solution in solving IKP by the discrimination method

In solving the IKP by the method of discrimination the formal models of the processes $g(\alpha)$, the time of reaching a given transformation degree α at temperature T_{iso} can be calculated using the equation

$$t = g(\alpha)/A \exp(-E/RT_{\text{iso}}) \quad (5)$$

Obviously, in this case the assumption about invariability of the formal model and AP values on going from the non-isothermal to the isothermal regime of an experiment must be realized. The limiting relative error of determining t by eqn. (5) will be

$$|\Delta t/t| \approx |\Delta g(\alpha)/g(\alpha)| + |\Delta A/A| + |\Delta E/RT_{\text{iso}}| \quad (6)$$

Comparison of the exactness of the DKP solution in solving IKP by the non-discrimination and discrimination methods

Let us find under what conditions the relative error in determining the time of reaching a given transformation degree, which arises in calculations by the non-discrimination methods, will be smaller than the error caused by the application of methods using discrimination in solving IKP. To begin with, we shall restrict ourselves to a comparison of the terms of eqns. (3) and (6) which contain an error in activation energy calculation

$$|(1/T_{\text{iso}} - 1/T)E/R - 1| |\Delta E/E| < |\Delta E/RT_{\text{iso}}| \quad (7)$$

Assuming equality of the activation energy values and the errors in their calculation, this inequality can be reduced to the form

$$|(1/T_{\text{iso}} - 1/T)E/R - 1| < E/RT_{\text{iso}}$$

If the activation energy of the process is a few dozen kcal mol⁻¹, this inequality holds in two cases. Firstly, at extrapolation to the low temperature region when $T_{\text{iso}} < T - 10$ K. Secondly, at extrapolations to the high temperature region when $T_{\text{iso}} > 2T$.

Consequently, the relative error in determining the time of reaching a given transformation degree, which arises in calculations by the non-discrimination methods, will be smaller than that caused by the use of discrimination methods in almost all the cases of low temperature extrapolations, as well as when the high temperature extrapolation is carried out to a

temperature twice as high as the experimental temperature. It should also be remembered that we have made an assumption about the equality of the absolute errors in activation energy calculation by non-discrimination and discrimination methods. However, we have previously shown [6] that the discrimination methods always lead to considerable errors. This fact indicates that inequality (7) holds over a wider temperature range than that mentioned above. Moreover, we have taken into account only one term of eqn. (6) which introduces an error into the calculation of the time of reaching a given transformation degree. The real error arising when the discrimination methods are used will be much higher, especially if the error in the pre-exponent determination is taken into account. By virtue of the approximate equality $|\Delta A/A| \approx |\Delta \ln A|$, it is clear that when the value of the absolute error in $\ln A$ is greater than 0.5, eqn. (5) will not permit estimating the time of reaching a given transformation degree, not even its order of magnitude. It is needless to say that in practice, as a rule, we have to deal exactly with such errors. We therefore do not recommend using AP calculated by the discrimination methods for solving any DKP. The concrete example given below not only confirms the validity of our theoretical conclusions, but also visually demonstrates the quantitative level of errors in DKP solution to which each of the two methods of solving IKP leads.

Practical example

As a concrete example of DKP, let us consider the calculation of the time to reach a given transformation degree at a given temperature using non-isothermal data. Such calculations are needed for solving such practically important problems as the estimation, at a known temperature, of the time required for completing a process, of the useful life of a material or its possible storage time. We shall dwell upon the last problem, for solving which a method relying on performing two isothermal experiments is proposed in ref. 9. Our approach permits obtaining such information from a single non-isothermal experiment.

Let us suppose that there is a particular substance whose limiting process of transformation is a reaction which obeys the contracting sphere equation and is characterized by the following AP values: activation energy, $E = 125.4$ kJ mol⁻¹; pre-exponent, $A = 10^{12}$ min⁻¹. Proceeding from the non-isothermal data (the kinetic curve obtained at the heating rate $q = 10^\circ$ min⁻¹), we can estimate the potential storage time of this substance, using as the estimate the time of reaching the 1% transformation degree at $T_{\text{iso}} = 300$ K. The precise calculated time of reaching the given transformation degree is 137.3 years.

Let us estimate the error in calculating the time of reaching the 1% transformation degree at $T_{\text{iso}} = 300$ K from eqn. (2). In the case of a simple (gross single-stage) process, the required activation energy value can be

calculated from one non-isothermal curve by the Piloyan method [10] if only the initial portion of the curve is used for the calculation [11]. For complex processes the activation energy should be calculated by isoconversion methods [12]. The activation energy calculated by the Piloyan method for the 0–5% range of transformation degrees is $124.4 \text{ kJ mol}^{-1}$ and differs from the true value by 0.76%. The limiting relative error estimated by eqn. (3) is 12.8% or 17.5 years. Thus the time of reaching the 1% transformation degree at $T_{\text{iso}} = 300 \text{ K}$, calculated according to eqn. (2), is 136.6 ± 17.5 years.

Obviously, the change from model to real data will lead to an increase in the relative error in determining the activation energy. However, to solve many of the practical problems, it is sufficient to estimate only the order of magnitude of the time of reaching the given transformation degree, i.e. the limiting relative error can amount to 50%. Such an accuracy in determining the time can be obtained in our case with a fairly small relative error in activation energy calculation—about 3%.

Consequently, the use of AP calculated by the non-discrimination method of IKP solution makes it possible to estimate the time of reaching a given transformation degree at a given temperature with an accuracy required for solving practical problems. This is an additional argument for the results of refs. 3–7, 12 and 13, confirming the adequacy of the non-discrimination methods and the reliability of AP calculated by them.

Now let us estimate the error in calculating the time of reaching a given transformation degree, assuming that in calculating AP, we have erroneously chosen, due to inappropriate discrimination, the equation of a contracting cylinder instead of that of a contracting sphere. The indistinguishability of these models within the ordinary experimental accuracy has been proved [13]. The AP calculated from the equation

$$\ln \left[q(1 - \alpha)^{-0.5} \frac{d\alpha}{dT} \right] = \ln A - E/RT$$

are $E = 118.1 \text{ kJ mol}^{-1}$ and $\ln A = 25.75$. Substitution of these values of AP into eqn. (5) gives a time of 48.6 years to the 1% transformation degree at $T_{\text{iso}} = 300 \text{ K}$, which is 2.8 times smaller than the true value.

Let us now assess the contribution of errors in determining AP to the value of the limiting relative error in determining t (eqn. (5)). The relative error in pre-exponent determination (the second term in eqn. (6)), estimated according to the approximate equality $|\Delta A/A| \approx |\Delta \ln A|$, is 1.9, i.e. 190%. The contribution of the error in the activation energy determination (the third term in eqn. (6)) to the relative error in the determination of t is equal to 2.9 or 290%. Obviously, the contributions of the errors in determining AP caused by poor choice of the formal model of the process are such that the relative error in calculating the time of reaching the given transformation degree of eqn. (5) exceeds 100%. Thus even a minimal error made in solving IKP by the discrimination method makes the DKP solution senseless. Also it should be noted that the relative error in the activation energy determina-

tion arising from the wrong choice of the process model is at first sight small, 5.8%. However, substitution of this activation energy value into eqn. (2), which we recommend [7] for non-discrimination methods of calculating AP, gives $t = 58.5$ years and a very large value of the relative error (eqn. (3)) in its determination, 97.4%. Thus even small errors in AP determination, which are due to the poor discrimination of the formal models of the process, make it impossible to estimate the time of reaching a given transformation degree at a given temperature even to an order of magnitude, since the limiting relative error is 100% and higher.

Obviously, on going to real data, the deviations of the calculated AP values from the true ones will be much greater than for the above model example. From this point of view, a vivid example is the result of ref. 14, which shows that a wide set of formal models of the process and their corresponding essentially different values of AP obtained in solving IKP by the discrimination method, permit description, to an almost equal degree of accuracy, of the kinetic curve for which they have been calculated. Of course, this does not mean that the above set of AP and models of the process can be used for solving DKP when it is necessary to model the kinetic curve in a temperature range other than the experimental one. In particular, substitution into eqn. (5) of the AP values and the order of reaction for calcium oxalate monohydrate dehydration [14] gives values of the time, varying from 0.1 to 18.3 days, during which, at a temperature of 300 K, 1% of water is lost. Consequently, the accuracy in describing the kinetic curve by means of different models of the process and their corresponding AP values does not suggest the possibility of using a given set (AP and models) for obtaining information about the progress of the process beyond the range of experimental temperatures. As mentioned above, in this case we need AP values describing sufficiently accurately the temperature dependence of the gross-process rate, since it is exactly these values that determine changes in the position of the kinetic curve with temperature. Therefore the methods of calculating AP, which rely on discrimination, cannot be used for solving DKP associated with extrapolation of experimental kinetic curves beyond the region of experimental temperatures.

CONCLUSION

It seems to us that the results of this and previous work [3-7,11,12] indicate convincingly that the discrimination methods are inapplicable and the non-discrimination methods are suitable for solving practical IKP. In a review [15], based on comprehensive literature data, we attempted to analyse, in different aspects, the potentialities of the above-mentioned methods and came to the conclusion that the non-discrimination methods are always preferable, and for non-isothermal kinetics they have no alternative.

It was shown previously [7] that the solution of a DKP associated with modelling of the isothermal kinetic curve by non-isothermal data does not require a knowledge of the formal model of the process—it is sufficient to have reliable estimates of the effective activation energy. This value also suffices for modelling curves corresponding to other heating rates, using the non-isothermal curve obtained at one heating rate. Thus the non-discrimination methods of solving IKP make it possible to solve a wide range of practical problems without using the formal models of the process in explicit form. As to the problem of elucidating the gross mechanism (kinetic scheme) of the process, it can also be solved without discrimination of the formal models which are not directly associated [5] with the real mechanism. In particular, we have proposed [12] an approach based on investigating the form of the dependence of the activation energy calculated by the isoconversion method, on the transformation degree, which makes it possible to establish whether the process being investigated is simple or complex and to suggest the kinetic scheme of the latter. This approach has made it possible to obtain interpretable kinetic schemes for the thermolysis of tetrazole [16] and its polymeric derivatives [17]. Vaganova et al. [18,19] proposed variants of calculating AP by the isoconversion method for complex processes of different types. Attempts were made [11,20] to calculate AP of complex processes by quasi-isoconversion [11] methods, using one non-isothermal kinetic curve in the calculation. Thus the use of non-discrimination methods for solving IKP makes it possible to establish the kinetic scheme of the process involved.

In the Introduction, we noted that the calculation of AP can pursue two different objectives: first, to obtain the characteristics of substance reactivity, and secondly to obtain the parameters of the temperature dependence of the process rate. Taking into account these goals as well as the results of this work, we deem it is necessary to distinguish between two different types of kinetics.

One type, the kinetics associated with the study of the reactivity of a substance, is impossible without studying the mechanism of the processes proceeding in it as a total combination of elementary stages and determining their kinetic constants. The ultimate goal of this kinetics is the establishment of the general principles of the character of the processes being investigated, i.e. the creation of their theory. Therefore, such kinetics can conditionally be called theoretical kinetics. It always suggests a thorny path for a researcher, following which one cannot expect fast practical results. Without this path, however, there can be no scientifically substantiated creation of quantitatively new materials and technologies.

The second type of kinetics can be called applied kinetics. It is fully aimed at solving such practical problems as prediction of the behaviour of a substance when the temperature (or other parameters) is changed, optimization of technological processes, regulation of the properties of products by

changing the reaction conditions etc. The solution of such problems has been the subject of the overwhelming majority of the kinetic works published in the thermochemical periodicals. It should be emphasized that not only our own experience, but the experience of other workers [21–23] too, proves convincingly that the only reliable basis for solving practical problems, and consequently, problems of applied kinetics, can only be the non-discrimination methods of solving IKP. The use of applied kinetics based on non-discrimination methods not only gives reliable information about the kinetic scheme and AP of the process, but also makes it possible to avoid, in good time, senseless attempts to interpret the formal model of the process chosen as the result of discrimination in terms of the real mechanism and vain research for the physical meaning of AP calculated in accordance with this model.

We believe that the division of kinetics into theoretical and applied branches will make it possible to order kinetic studies, since to choose the kinetics required for solving the problem raised the researcher must clearly realize what information he needs: information about the progress of the reaction as a whole or about its elementary stages. In turn, the choice of a particular kinetics determines the field of application of the information obtained and possible ways for its interpretation.

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