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THE THERMODYNAMIC DRIVING FORCE IN THE KINETIC EVALUATION OF THERMOANALYTICAL CURVES

G. Pokol

Institute of General and Analytical Chemistry, Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Abstract

This paper outlines the different ways of taking the distance from thermodynamic equilibrium into account in kinetic studies based on thermoanalytical experiments. The three main approaches are: (i) avoiding or neglecting the effect of the reverse reaction, (ii) describing the influence of distance from equilibrium on apparent kinetic parameters, and (iii) incorporating a driving force factor in the rate equation. Finally, the contradiction of the microscopic nature of the processes and the macroscopic character of the usual rate equation are briefly discussed.

Keywords: driving force, kinetics, rate equation, reversible reactions

Introduction

Studies on reversible processes have been common since the earliest works with thermal analysis. The fact that the distance from thermodynamic equilibrium influences the reaction rate is well known, too. In the following, a brief outline of the approaches used to handle reversibility in kinetic studies in presented, then some remarks are made about the contradiction between the microscopic nature of the chemical events and the macroscopic rate equation.

The usual approach: transformations assumed to proceed far from equilibrium

When the rate equation generally used in the description of thermoanalytical curves

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

(where α, T and t denote the reacted fraction, absolute temperature and time, respectively, k represents the rate constant and f is an appropriate function) is applied in real kinetic calculations, one of the usual assumptions is that the process takes place far from thermodynamic equilibrium. This assumption is so common that, in the majority of cases, it is not even declared explicitly. Quite characteristically, none of the 12

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articles in the Kinetics section of the proceedings of the 11th ICTAC takes reversibility into account in the analysis [1]. This approach may be correct in the particular cases; then this means that researchers tend to avoid near-equilibrium transformations.

On the other hand, theoretical discussions do not fail to point out that reversible processes are quite frequent among the ones studied with thermoanalytical methods (e.g., [2–6]). Reactions of the type

$$\mathrm{A(solid)=B(solid)+C(gas)} \tag{2}$$

offer a simple model for discussion. It has long been known that, in decompositions of solids, product gas pressure has a strong effect on the temperature range and the rate of the reaction [7]. Provided both solid reactants form pure phases, the equilibrium constant of the reaction, K_p, equals the equilibrium pressure (or partial pressure) of the product gas at the given temperature. The rate equation should include some function of the partial pressure of the product [4]:

$$\mathrm{d}\alpha/\mathrm{d}t=k(T)f(\alpha)h(p) \tag{3}$$

However, as summarised by Brown [4], ‘this complication is usually ignored and this may be justifiable when working in vacuum or with a strong flow of inert gas through the sample’. Discussing the calculation of kinetic data close to the equilibrium, Šesták points out that reversibility often plays a significant role at the beginning of the transformations [2]. This is very important as the initial part of the thermoanalytical curve – depending on the method of calculation – may considerably influence the estimated kinetic parameters. The effect of reversibility at the beginning of the transformation may be one of the reasons for investigating the dependence of apparent kinetic parameters on the reacted fraction.

Reversible reactions: the dependence of formal kinetic parameters on the distance from equilibrium

Even if it is understood that the process to be described takes place near the equilibrium, i.e. the rate of the reverse reaction is not negligible as compared to that of the forward reaction, it is still possible to base kinetic calculations on rate equations like Eq. (1). Because the distance from the equilibrium, or the rate of the reverse reaction, is not reflected explicitly by the rate equation, the apparent parameters will depend on some ‘experimental conditions’. Using quotation marks seems quite justified here since these conditions are actually related to activities of reactants taking part in the (reverse) reaction.

Again, decompositions of solids corresponding to Eq. (2) are the simplest examples for this approach. Using Eq. (1) and the Arrhenius equation for the rate constant,

$$k=A\exp(-E/RT) \tag{4}$$

the estimated values of the activation energy (E) and the preexponential factor (A), as well as the form of the $f(\alpha)$ function, can be studied as functions of product gas pressure. Gallagher and Johnson [8] and Ball and Casson [9] found that both E and A increased with carbon dioxide pressure in the thermal decompositions of calcium carbonate and lead carbonate, respectively. According to Pavlyuchenko and Prodan [10], it is reasonable to calculate E from data obtained either under constant carbon dioxide pressure, or under a constant ratio of actual (p) and equilibrium (p_e) carbon dioxide pressures. In the latter case, the same value was estimated for the activation energy under different p/p_e ratios, and it was equal to the result of experiments carried out in vacuum.

Special experiments in the characterisation of reversible processes near equilibrium: the quasi-isothermal – quasi-isobaric method and constant rate thermal analysis

As has been pointed out earlier, in kinetic studies based on thermoanalytical measurements it is usually assumed that the reaction proceeds far from equilibrium; and in most cases it is possible to set up the experiment so that this assumption is (approximately) valid. However, working far from equilibrium may not be suitable for studying fine details, for describing the mechanism of the process. The two most important experimental techniques designed to keep a selected and, if preferred, a low rate of reaction are the quasi-isothermal – quasi-isobaric thermal analysis developed by the Paulik brothers, and constant rate thermal analysis (CRTA) worked out by Rouquerol. Both methods – though technically different – have solved the maintenance of a selected low transformation rate by controlling the experiment according to actual sample behaviour. In the quasi-isothermal method the DTG (or DTA) signal is kept at the selected level by appropriate control of the temperature program, while in CRTA a pressure signal characterising the flow of the product gas is used for the same purpose. Both techniques fit the term controlled transformation rate (or, simply, controlled rate) thermal analysis (CRTA). The history and technical details of the two methods are not reviewed here, the reader is referred to summarising publications [6, 11]. A new generic term for experiments when the temperature program is controlled according to sample behaviour is sample controlled thermal analysis (SCTA).

Chapter 10 of F. Paulik's monograph is devoted to the kinetics and mechanism of reactions, including the discussion of the effect of product gas pressure on thermal decomposition. The discussion treats the various elements of the mechanism systematically and in detail; at the same time it is qualitative from the aspect of kinetics as F. and J. Paulik 'were sceptical about kinetic parameter calculations' [6]; and other researchers applying the quasi-isothermal method follow this approach, as well. Results from CRTA, on the other hand, have been used in the calculation and modelling of kinetics [12], and it has been pointed out that fine control of the temperature and product gas pressure makes this technique very suitable for the estimation of the (apparent) activation energy, especially when using the 'rate-jump' method [11].

Attempts to incorporate thermodynamic driving force factors in the rate equation

Because the effects of reversibility on the rate of transformations have been well known for a long time, extending the rate equations with terms reflecting the distance from equilibrium seems logical. A discussion of the earlier attempts to do this was included in a review by Pokol and Várhegyi [5].

In the theoretical treatment and mathematical formulation of the relationship between thermodynamics and kinetics, Šesták has played a leading role. Starting from the point that some systems have an equilibrium composition depending on temperature (variant processes), he distinguished an isothermal (α) and a non-isothermal (λ) degree of conversion [13]. The latter has an equilibrium value at every temperature λ_{eq} ($0\leq\lambda_{eq}\leq1$), and the isothermal degree of conversion is

$$\alpha=\lambda/\lambda_{eq} \tag{5}$$

In reactions of solids, the equilibrium conversion can quite often be 1 or 0 (invariant processes as, e.g. decompositions corresponding to Eq. (2) when the solids form pure phases). A continuously changing equilibrium composition occurs when solid or liquid reactants do not form separate phases of defined compositions. Even in those cases, as pointed out by Šesták [2], the distinction between α and λ may not be necessary, due to the fact that, applying the usual heating rates, in the main region of kinetic calculations the equilibrium conversion equals unity. The initial stage of the reaction when this is not valid is quite often omitted from the calculations. However, in order to achieve compatibility of thermodynamic and kinetic data, it is generally necessary to consider the ‘equilibrium background’ of processes [14].

Several theoretical or empirical expressions have been suggested as driving-force factors, i.e., to represent the distance from the state of equilibrium in the rate equation. In thermal decompositions corresponding to Eq. (2), a power function of the product-gas pressure was often applied as a factor in the rate coefficient [2]:

$$k=k(T)p^{m} \tag{6}$$

The power function p^{m} here corresponds to the general expression $h(p)$ in Eq. (3).

A theoretical driving-force factor was introduced by Bradley [15] for solid-solid reactions. Assuming that the forward and the reverse reaction proceed by the same route, starting from thermodynamic and statistical mechanical considerations, he arrived at a factor of $[1-\exp(\Delta G/RT)]$, a function of the Gibbs free energy change and temperature.

Later Šesták and Berggren [16] and Šatava [17] extended the common rate equation (Eq. (1)) using Bradley’s driving force. Thus, for reactions reversible in the thermodynamic sense, the rate of transformation was expressed as

$$\mathrm{d}\alpha/\mathrm{d}t=k(T)f(\alpha)[1-\exp(\Delta G/RT)] \tag{7}$$

The same driving-force factor was applied by Pokol *et al.* [18, 19] in their attempt to construct rate equations for simple heterogeneous reactions in a form resembling the laws of physical fluxes and current densities. The gross transformation rate W (i.e., the macroscopic result of the forward and reverse processes) expressing the time derivative of the amount of a chosen reactant (N, preferably in moles) in the whole system, related to the stoichiometric coefficient (ν) was written as

$$W=-\frac{1}{\nu}\frac{\mathrm{d}N}{\mathrm{d}t}=\int_{\mathrm{Q}} kF\mathrm{d}Q \tag{8}$$

Equation (8) may be discussed using the analogy with the law of heat conduction. Then the rate of transformation W corresponds to heat flux, and the rate constant k is analogous with thermal conductivity. Q, called the reaction cross section, was defined as a measure of the number of situations (sites) suitable for reaction in the whole system. F is the driving-force factor based on Bradley's suggestion [15]. Thus

$$W=\int_{\mathrm{Q}} kF\mathrm{d}Q=\int_{\mathrm{Q}} k\left(1-\exp\frac{\Delta G}{RT}\right)\mathrm{d}Q \tag{9}$$

If reaction sites in the system are equivalent (their temperature, pressure, etc. are uniform) then the integral at the right-hand side of Eq. (9) becomes equal to the kFQ product.

In simple decompositions corresponding to Eq. (2), if the solid reactants are pure, Bradley's driving force can be expressed by the actual (p) and the equilibrium (p_e) pressure of the product gas,

$$[1-\exp(\Delta G/RT)]=1-p/p_e \tag{10}$$

Several authors used the right-hand side of this equation (or p_e-p, which is proportional to it, provided that the temperature is fixed) in the description of reversible reactions, e.g. [20–23]. Even when thermodynamic reversibility is at least questionable, a driving-force factor according to Eq. (9) may be applicable; however in such cases a temperature dependent empirical quantity should be used instead of the equilibrium pressure p_e [24].

Adsorption phenomena may also influence the reaction rate; such processes were described by Criado *et al.* [25] as well as Maciejewski and Baldiga [26]. In those cases the mathematical form representing the effect of product gas pressure was found to be different from Eq. (10).

Reasons for neglecting the driving force in kinetic studies: a summary of the situation and some prospects

As has been presented in the preceding sections, the effect of the distance from equilibrium on the rate of the reaction is discussed (or, at least, mentioned) in theoretical works. On the other hand, it is usually neglected in the evaluation of experimental data, i.e., in the selection of the proper mathematical model and in the estimation of kinetic parameters. Even when the reverse reaction is taken into account in a kinetic study, the effect of reversibility is described by the influence of product gas pressure on the apparent kinetic parameters rather than by using mathematical models containing a thermodynamic driving force.

The first reason is related to the usual experimental conditions (heating rate, an efficient gas purge in the vicinity of the solid sample) [2, 4, 5]. Yet one cannot always be sure which is the cause and which is the result: the process may be carried out far from equilibrium just to avoid the influence of the reverse reaction. It is questionable, however, whether the mechanism of the process is the same near and far from equilibrium. This is a crucial problem because one of the main goals of kinetic studies is drawing conclusions on the character and mechanism of reactions. In this respect, an increase in the application of the quasi-isothermal method and constant rate thermal analysis can be expected.

Another ‘practical’ reason is the lack of meaningful data on the distance from thermodynamic equilibrium. While this distance can be described by the actual and equilibrium pressure of the product gas in simple decompositions, this is certainly not valid if the solid or liquid phases involved are not pure, or if the overall transformation consists of several steps (chemical reactions, structural transitions and transport processes). Because the basic thermoanalytical techniques (TG, DSC, DTA) follow only one physical quantity as a function of time, coupled techniques (like TG-MS, TG-FTIR) as well as other, ex-situ investigations (characterisation of surface and bulk structure) are often needed to characterise the distance from equilibrium – beyond their essential role in elucidating the reaction path and intermediates.

Past and present: a macroscopic rate equation for microscopic events

Let us have a look at our topic from the aspect of basic characteristics of the processes studied, and from the aspect of a general development trend in the chemistry of solids. Thermal analysis is firstly applied to solid samples, and this is the field where its main advantages are obvious. It is well known that all reactions of solids show a topochemical nature: basic chemical events (i.e., scission and formation of bonds) are restricted to certain sites of the solid, and different steps of the overall process (chemical transformation proper, structural rearrangement, diffusion, etc.) take place in different regions of the system.

One of the most important development trends (or maybe the most important one) of the chemistry and physics of solids in the last decade has been the improvement of the spatial resolution of experimental techniques (especially due to the development of scanning probe microscopic techniques). Steps have been taken towards the atomic scale in the description of properties and reactions of solids. In other words: differences among the particles and regions of the solid (surface, interfaces, lattice defects, etc.) can be experimentally characterised and taken into account in the description of the overall process. This approach has a vast practical use in materials engineering, e.g., that of thin solid films, micro- and nanostructures, etc. Techniques capable of microscopic resolution have been worked out in thermal analysis, as well [27–28].

In Eq. (1), the progress of the transformation is represented by the reacted fraction – being an average overall quantity rather than a local variable (for some of the consequences, e.g., [5]). Reacting systems having the same α values and being at the same temperature may show significantly different reaction rates, i.e., the reacted fraction is not suitable for expressing differences in the local, microscopic situations. That is why formal kinetic constants depend on sample and experimental parameters. (In principle, the rational approach to the desription of kinetics reflects these differences by taking into account the total history of the material; however, available experimental data and mathematical means do not seem adequate for practical application [2, 29]).

To summarise the problems and remarks outlined in this section, the well-known contradiction between the macroscopic approach of the usual rate equation (Eq. (1)) and the microscopic nature of the chemical reactions of solids seems to be a major problem of kinetic studies based on thermoanalytical measurements. As there are more experimental techniques and data available on the microscopic events and characteristics of solids, this contradiction may even be a driving force towards new, more adequate (but at the same time, more sophisticated and experimentally more demanding) kinetic models for the reactions of solids.

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