Thermochimica Acta, 33 (1979) 259–265
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DESCRIPTION OF THE RATE OF HETEROGENEOUS CHEMICAL REACTIONS

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(Received 6 December 1978)

ABSTRACT

Theoretical studies using the

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

rate equation for heterogeneous processes — especially those involving at least one solid reactant — are reported. Dependence of k on the sample size is shown in general. Possible rate expressions for reversible systems are discussed.

New forms analogous to physical fluxes and current densities are presented for the kinetic description of the chemical step of the processes concerned.

INTRODUCTION

In practical kinetic investigations of processes involving at least one reactant in the solid state the usual general rate equation is based on the reacted fraction (α) of the sample

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

where f denotes a function, t and k are the time and the rate coefficient (rate constant) which is supposed to be a function of the absolute temperature (T). Equation (1) is applied almost exclusively to the decomposition of solids being studied most frequently by means of thermal analysis methods.

In the following, eqn. (1) will be discussed and a new, more general rate equation will be presented for the chemical step of heterogeneous processes. The basis of this concept was published by the authors as a conclusion of a thermal analysis study on alkaline-earth carbonates [1]. The concrete results of that study [1—3] will not be detailed here, although some characteristics of carbonate decompositions are mentioned to illustrate general considerations.

THE USE OF THE REACTED FRACTION IN THE RATE EQUATION

Equation (1) resembles the rate law of homogeneous reactions, containing the reacted fraction instead of concentrations. Reviews and monographs in this field often contain warnings about the limitations of this analogy [4—8], pointing out that in reactions of solids the f(α) functions express rather the effect of geometry and transport processes (heat conduction, diffusion) than the effect of concentrations. In fact, the concentration itself can be different in various parts of the system, moreover, its change is not continuous at a certain place, if reactants and products form separate phases. Thus, the reacted fraction is an average value for the whole system, which can be very easily calculated from measurable quantities (mass of the sample, evolved or consumed energy), but its relation to local quantities (like concentration) is not simple. Naturally, any quantity having an unambiguous (more practically, linear) relationship with the amount of reactants and products may be used in rate equations, but this may change the characteristics and the meaning of the other variables which in eqn. (1) are summarized in the rate coefficient k. For example, one could use eqn. (1) to describe a homogeneous reaction having the

$$-\frac{dc}{dt} = k_c(T)c^n \tag{2}$$

rate law, where c is the concentration of the reactant with the value c_0 at the beginning of the process and zero at the end, and n is the reaction order. Even in the case of constant volume the rate coefficient in eqn. (1) would become a function of two independent variables, except $n = 1$

$$k = k_c(T)c_0^{n-1} \tag{3}$$

after replacing c with $c_0(1 - \alpha)$.

THE EFFECT OF THE SAMPLE SIZE AND THE REVERSE REACTION ON KINETIC PARAMETERS CALCULATED FROM EQN. (1)

While for homogeneous reactions a law similar to eqn. (2) describes the reaction rate, i.e. the time derivative of the amount of material transformed in the unity of volume, regardless of the entire volume of the system, provided the temperature, the initial concentrations and other intensive quantities are the same, eqn. (1) does not have this invariancy in general if applied to a process with a solid reactant, when the chemical change is going on at a phase boundary of changing configuration and/or size. On this basis, in theoretical considerations starting from some kind of physical model for the mechanism of the process, the rate equations usually contain the number of particles or sites capable of reaction or this number related to the unity of surface [9—11].

However, once turning to expressions applicable in the calculation of kinetic parameters from measurements, α is introduced without real discussion. Other works simply start with eqn. (1) or equivalent [12,13], or use rate equations based on α and the amount of the reactant within one chapter [14].

Although most of the authors cited above do mention that the reaction rate in a heterogeneous process depends on a series of variables beyond those included explicitly in eqn. (1), none of them point out that the rate coefficient will be dependent upon the size of the sample in all but one case. As the most simple example one can take an irreversible decomposition of a solid where the velocity of the advancement of the reacting surface can be assumed to depend on the temperature only. Expressing f(α) in this case for spherical samples yields

$$\frac{d\alpha}{dt} = k(1 - \alpha)^{2/3} \tag{4}$$

Comparing two spheres of different initial radii the rate constant must obviously be inversely proportional to the initial radius.

If the reaction takes place on the changing surface of the solid reactant, the only type of system whose k in eqn. (1) will be independent of sample size, consists of identical particles and involves a process advancing uniformly in each particle (i.e. at any time the reacted fraction of all the particles is the same). This case is quite rare, even powder samples most often behaving similarly to a single piece: there is a reaction zone moving inward, as shown for calcium carbonate by Gallagher and Johnson [15] and our previous work [1].

Using the Arrhenius equation for the rate constant

$$k = A \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) \tag{5}$$

where A and $\Delta H^{\ddagger}$ are the pre-exponential factor and the activation enthalpy, respectively, the particular effect of the sample size discussed above will appear in the A value. Within one study this problem can remain concealed, since most investigators tend to use similar samples in one series of measurements as possible. However, it is certainly one of the causes making the comparison of results from different laboratories difficult and questionable.

A more careful way of kinetic investigation was suggested by Ozawa [16]. He asserted that the rate should be expressed basically in terms of a "structural quantity", x. Assuming the rate constant given by the Arrhenius relation, he wrote similarly to eqn. (1)

$$\frac{dx}{dt} = A \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right) g(x) \tag{6}$$

Here he emphasised that the conversion (being the same as α) calculated from some property of the sample is not necessarily equal to x, rather, in general

$$\alpha = f(x)$$

and that the f(x) function has to be taken into account in practical computations. As an example he showed the actual f(x) for polymer degradation and evaporation with random scission of bonds between the monomer units. However, the structural quantity on Ozawa's work still has characteristics of the reacted fraction (it changes from 1 to 0) that may well be satisfactory in the case of some polymer degradations, but would show the same size effects in heterogeneous chemical reactions as eqn. (1).

It must be emphasized that the size has other, often greater effects on the rate of the overall process, influencing the conditions of the transport processes in the system, as discussed in detail most recently by Garn [8].

Whenever the reverse reaction can take place in a process, the overall rate will depend on the concentrations of the products, which in the decomposition of solids can be characterized by the partial pressure of the evolved gas. Bradley [17], starting from an assumption of Polanyi and Wigner [18], using the terms of the transition state theory, derived a factor to be included in the rate equation for a solid—solid process, which can also complete eqn. (1)

$$\frac{d\alpha}{dt} = k(T)f(\alpha)\left(1 - \exp\frac{\Delta G}{RT}\right) \tag{7}$$

where ΔG is the Gibbs free energy difference in the process. Although (7) had been suggested for general use in the evaluation of thermoanalytical curves by Šesták and Berggren [5] and Šatava [12], it has been usually ignored, assuming the process to be "very far" from equilibrium. One of the few exceptions is Jüntgen and Van Heek's work on calcium carbonate decomposition [19]. In this case the driving force factor equals $(1 - p/p_e)$, p and p_e being the actual and the equilibrium pressure of the product gas.

Rouquerol [13] and Wist [20] without detailed discussion introduced the difference of the equilibrium and the actual pressure as a factor into the right-hand side of eqn. (1). Their factor differs from that mentioned above [19] in a p_e multiplier which is temperature dependent.

Before proceeding to the suggested new form of rate equation, let us briefly mention another way of taking the sample size and product gas pressure into account. It is possible to use eqn. (1) in the investigation calculating the apparent values of kinetic parameters (A, E and the f function) and study the dependence of these parameters on sample size and the pressure as suggested by several authors [4—8]. In a quite detailed study on calcium carbonate thermal decomposition Gallagher and Johnson [15] followed this way, describing the relationship of the initial mass of sample and the Arrhenius parameters with empirical formulae and characterizing the effect of carbon dioxide pressure on the apparent activation enthalpy. Several years before, Berlin and Robinson [21] derived an expression of the relationship between the initial mass and the temperature at which the reaction just terminates in constant heating rate runs.

In spite of the considerations and promising suggestions mentioned above, eqn. (1) is being applied almost exclusively in the kinetic evaluation of thermoanalytical curves.

DISCUSSION OF THE PROPOSED NEW FORM OF RATE EQUATION

When attempting to give a more general expression of the rate of heterogeneous chemical reactions we were looking for a form more or less analogous to other relations describing physical processes in time. For the *i*-th step of a solid—solid reaction Budnikov and Ginstling published a theoretical rate equation [11]

$$\frac{d\alpha_i}{dt} = S_i \frac{\Delta c_i}{R_i} \tag{8}$$

where S_i denotes the contact surface of reactants participating in the i-th step, c_i is a motive force expressed by the concentration drop of one of the reactants, and R_i is the resistance of the step. This form has the advantage that in a strictly consecutive quasi-stationary process the overall rate can be easily expressed. However, the interpretation and calculation of R_i and ΔC_i are generally not simple.

The rate equations suggested by us [1] resemble the form of physical fluxes and current densities (heat, diffusion, etc.) to some extent. The gross rate of the reaction, W, expresses the transformation rate of the chosen reactant related to unit stoichiometric coefficient (ν) for the whole system

$$W = \frac{1}{\nu}\frac{dN}{dt} = \int_Q kF\, dQ\ . \tag{9}$$

Here N denotes the amount of transformed reactant (in molar or mass units). For an explanation of the right-hand side let us use an analogy with heat conduction. Equation (9) contains k, the commonly used rate constant — analogous with thermal conductivity, F, a driving force (a function of chemical potentials, which can be given according to Bradley [17]) which corresponds to the temperature gradient in heat transfer, and Q, called the reaction cross-section, which is defined as proportional to the number of situations geometrically suitable for the reaction. The rate of the reaction (the volume derivative of W) is

$$w = \frac{\partial W}{\partial V} = kF\frac{\partial Q}{\partial V} = kFq \tag{10}$$

where V is the volume and q is the density of the reaction cross-section. Since the latter, in general, is not directly proportional to the volume, the rate of the reaction is not really analogous to a current density (e.g. the density of the heat flux), but such a form can be reached, relating to the unity of the reaction cross-section.

$$w^* = \frac{\partial W}{\partial Q} = kF \tag{11}$$

where w^* can be called the basic rate of reaction. In fact, this quantity is used in catalytic studies, e.g., relating the rate of the reaction to the unity of catalyst surface.

In the simple phase boundary decomposition mentioned before, Q could be related to the free surface of the reactant, while in a nucleation step it would be proportional to the number of existing germ nuclei, or in nuclei growth it would correspond to the surface of active nuclei etc.

Equations (9—11) do not contradict the rate law of homogeneous reactions either. In a simple reversible homogeneous process

$$nA \underset{k^-}{\overset{k^+}{\rightleftharpoons}} mB \tag{12}$$

where A and B are the reactant and the product, n and m are their stoichiometric coefficients, assuming that n and m also express the order of the forward and the reverse reaction, the two partial rates are

$$w^+ = k^+a^n \quad \text{and} \quad w^- = k^-b^m \tag{13}$$

where a and b denote the activities of the components. Expressing the net rate

$$w = k^+a^n \left(1 - \frac{k^-}{k^+} \frac{b^m}{a^n}\right) \tag{14}$$

and taking into account that the chemical potentials are

$$\mu_a = \mu_a^0 + RT \ln a \quad \text{and} \quad \mu_b = \mu_b^0 + RT \ln b \tag{15}$$

we can write

$$\frac{b^m}{a^n} = \frac{\exp(m\mu_b - n\mu_a/RT)}{\exp(m\mu_b^0 - n\mu_a^0/RT)} = K \exp \frac{\Delta G}{RT} \tag{16}$$

Since k^-/k^+ equals K^{-1} (K is the equilibrium constant)

$$w = k^+a^n \left(1 - \exp \frac{\Delta G}{RT}\right) \tag{17}$$

In the last equation the term in parentheses is Bradley's driving force [17] and the density of the reaction cross-section in a^n which is really proportional to the number of collisions necessary for the forward reaction. The reaction cross-section itself equals Va^n in this case.

When recommending eqns. (9—11) for the description of heterogeneous processes, it must be emphasized that they can be valid for one chemical step of the whole process. In the vast majority of the processes involving one or more solid reactants — especially under the conditions of thermal analysis [4—8,12,13] the transport processes cannot be neglected in the description of the rate, moreover, heat transport of diffusion controlled reactions are frequently found rate determining (while in homogeneous systems proper conditions for pure chemical rate control can usually be achieved). Therefore, a detailed and more accurate description of the processes in question has to contain chemical rate equations for each step involving chemical change, and the laws of component and energy transport, together with the necessary balances, initial and limiting conditions. In addition, the suggested relations contain several local quantities being subject to change both in space and time.

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