SUPERPOSITION OF TEMPERATURE AND
KINETIC CONSTANTS FOR A CHEMICAL REACTION

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It is shown in this work that the effect of changes in the temperature field may be replaced at certain conditions by a change in the coefficient a_1 in the relation for the rate constant $\ln k = a_1 - a_2/T$. This fact is of great importance, *e.g.* for modelling the course of an nonisothermal reaction, as it decreases considerably the extent of necessary experiments or calculations.

Let us follow the course of a chemical reaction proceeding nonisothermally in the solid phase. The temperature field in the region considered is determined completely or largely by heat transfer at the boundary of this region and it is of an unsteady type. First we will show conclusions which we want to arrive at on a simple case of a chemical reaction of the first order $A \rightarrow B$ proceeding in an infinite slab heated or cooled at its both ends. Let the initial concentration of component A be

$$c = c_0 \quad \text{in time} \quad \vartheta = 0 \qquad (1)$$

and let the reaction proceed according to the well-known differential equation

$$\mathrm{d}c/\mathrm{d}\vartheta = - k \cdot c \,, \qquad (2)$$

where c is the concentration of component A in time ϑ, k is the rate constant with the temperature dependence given by the relation

$$\ln k = a_1 - a_2/T \,, \qquad (3)$$

T is absolute temperature, a_1 and a_2 constants. Let the temperature in the slab obey the equation for heat conduction

$$\partial t/\partial \vartheta = a(\partial^2 t/\partial x^2) \,, \qquad (4)$$

where x is the distance from the central plane of the slab with a half-width r. The quantity a is the thermal diffusivity of the solid phase. Heat transfer at the system boundary is described by the coefficient of heat transfer α and by the heat conductivity coefficient of the system λ; the external temperature field is characterized by two constant temperatures, *e.g.* a maximum temperature (heating temperature) t_2 and a minimum temperature (cooling temperature) t_1.

Concentration c is according to the description of the process a function of 12 quantities on the whole. Three of them are variables: time ϑ, temperature $t(T)$ and local coordinate x. The rest of them are parameters: the initial concentration c_0, constants a_1 and a_2 in Eq. (3) expressing the temperature dependence of the rate constant, heat conductivity λ, thermal diffusivity a, heat transfer coefficient α, characteristic parameters of the external temperature field t_1 and t_2 and the half-width of the slab r. So we have

$$c = c(t, x, \vartheta; c_0, a_1, a_2, \lambda, a, \alpha, t_1, t_2, r) \,. \tag{5}$$

A considerable simplification of the problem may be achieved by arranging all equations into a dimensionless form. Currently we use the dimensionless time $\Theta = a\vartheta/r^2$, the dimensionless longitudinal coordinate $X = x/r$, the dimensionless heat transfer coefficient $\mathrm{Nu} = \alpha r/\lambda$, the dimensionless coefficient of reaction rate $K = ak/r^2$ and the dimensionless concentration $C = c/c_0$. The dimensionless temperature $S = (t - t_1)/\Delta t$, where $\Delta t = t_2 - t_1$, is used less usually.

Original Eqs (1)—(4), which describe the problem, assume the following dimensionless form

$$\mathrm{d}C/\mathrm{d}\Theta = - K \,.\, C \,, \tag{6}$$

with the initial condition

$$C = 1 \quad \text{for} \quad \Theta = 0 \,, \tag{7}$$

$$\ln K = a_3 - a_4/(a_5 + S) \,, \tag{8}$$

where

$$a_3 = a_1 + \ln (r^2/a) \,, \qquad a_4 = a_2/\Delta t \,,$$

$$a_5 = (273 \deg + t_1)/\Delta t \,, \tag{9}$$

and finally

$$\partial S/\partial \Theta = \partial^2 S/\partial X^2 \,, \tag{10}$$

with the field boundary at $X = \pm 1$.

As a result of this transformation into the dimensionless form, five from original nine parameters have been removed: the dimensionless concentration C is now a function of only four dimensionless parameters, namely of the Nusselt number Nu and of the coefficients a_3, a_4 and a_5 in Eq. (8) for the rate constant; three variables X, Θ and S remain

$$C = C(X, \Theta, S; \mathrm{Nu}, a_3, a_4, a_5) \,. \tag{11}$$

Coefficients a_4 and a_5 are of course according to Eq. (9) connected with both the rate of the chemical reaction and the temperature field in the system:

$$a_4 = a_2/\Delta t \,, \qquad a_5 = (273 + t_1)/\Delta t \,, \qquad \Delta t = t_2 - t_1 \,.$$

This fact, besides the more complicated form of dependence (8), constitutes a probable reason for the rare usage of the dimensionless temperature S. Despite this, it is very useful in our case as it "absorbs" one parameter of the original system.

A further important aspect refers to the mutual interchangeability of the effects of temperature and the reaction rate. Therefrom it follows that during a mathematical modelling (or an experimental investigation) of a nonisothermal chemical reaction we can study with the single parameter a_3 the effects of changes in both the temperature field and the rate constant, in every case at least approximately.

Let us investigate for example the effect of "shifting" the temperature field so that the original temperature parameters t_1, t_2 change to t_1^*, t_2^*. This change does not affect at all the dimensionless temperature field, which, according to its definition, remains unchanged. It will, however, manifest itself in changes of constants a_4, a_5 which depend on t_1, t_2. Let the new values of these constants be a_4^*, a_5^*. The second term of the rhs of Eq. (8) may be rewritten as:

$$\frac{a_4^*}{a_5^* + S} = \frac{a_4}{a_5 + S} - m \,, \tag{12}$$

where
$$m = \frac{a_2[t_1^* - t_1 + S(\Delta t^* - \Delta t)]}{(273 + t_1^* + S\Delta t^*)(273 + t_1 + S\Delta t)}. \qquad (13)$$

The quantity m is indeed a function of the temperature variable S, nevertheless the value of m may be practically both considerably low and sufficiently constant in a wide range of the temperature S. Let us admit that this is the case and that we can assume m = constant. Eq. (8) can be then written in the form

$$\ln K = a_3 - m + a_4/(a_5 + S). \qquad (14)$$

A shift (linear transformation) of the temperature field does not manifest itself in the dimensionless temperature field, but only in a change in the coefficient a_3 in the expression for the reaction rate constant; the coefficients a_4, a_5 remain unchanged. At modelling the process we need not thus distinguish between the effects of changes in the temperature field and in the coefficient a_3 and we can model both effects only by changes in a_3. This decreases in fact the number of modelled parameters by one, which might save considerably the computer time or experimental expenses.

Example: Let the original temperature field be determined by external temperatures $t_1 = 27°C$, $t_2 = 167°C$, or $\Delta t = 140°C$. We increase the temperature t_1 by 10°C, t_2 by 20°C, so that $t_1^* = 37°C$, $t_2^* = 187°C$, $\Delta t^* = 150°C$, and the values of m/a_2 according to relation (13) for different dimensionless temperatures S are in Table I:

TABLE I

Dependence of m/a_2 on the Dimensionless Temperature

S	0	0·2	0·4	0·6	0·8	1
$10^4 . m/a_2$	1·11	1·10	1·08	1·05	1·02	0·99

The proposed arrangement is very useful and practically it is quite sufficient even for considerable changes in m (ref.[1]).

Before all, the form of the reaction field is not substantial for our formulation. For a more complicated shape of the system than that of an infinite slab (or a similar onedimensional field), further longitudinal simplexes L_1, L_2 ... appear which characterize the shape of the system. Even a more complicated reaction course does not change anything in our considerations. It is only the form of the dependence of the reaction rate constant on temperature as expressed by Eq. (3) or dimensionlessly by Eq. (8) that is substantial. Another form of this equation has not been investigated. The external temperature field need not be characterized by only two fixed temperatures (this case occurs of course very often). If there are more fixed temperatures, other dimensionless parameters derived from them appear in the formulation and their influence must be examined.

REFERENCES

1. Slavíček E.: Plaste u. Kautschuk *16*, 275 (1969).

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