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ON THE USE OF THE CLASSICAL RATE EQUATION IN NON-ISOTHERMAL HETEROGENEOUS KINETICS

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In a recent note to the Editorial Board of this journal [1], Dr. Shlensky recommends the rejection from now on of articles dealing with kinetics of non-isothermal decomposition of substances, where experimental data are processed using the rate equation:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}(1-\alpha)^n \tag{1}$$

all the symbols having known meanings. To vindicate this drastic request, Dr. Shlensky mentions two previous articles published by him and his coworkers [2, 3]. After a careful reading of these articles we found that they actually refer to the thermal destruction of some polymeric materials, so from the very beginning the possible inapplicability of Eq. (1) should be restricted to this group of compounds. However, as Dr. Shlensky and his coworkers show in these articles, Eq. (1) correctly describes even the thermal destruction of polymers at low heating rates (below 10°/min). We consider these results as normal, because it is very well known that, in order to remove the disturbing effects of the heat transfer on the kinetic data, one has to work at various heating rates and to extrapolate the values of the kinetic parameters to zero heating rate. Equally, one can use such low heating rates that their further decrease no longer influences the values of the kinetic parameters. Actually, these heating rates should be low enough to ensure a kinetic regime, and high enough to ensure conditions far from equilibrium for the reaction. As shown by widespread experience, the heating rate values which fulfil these requirements should be below 10°/min, in agreement with the findings of Dr. Shlensky and his coworkers. It has to be pointed out that this is the field of heating rates used in non-isothermal heterogeneous kinetics. At higher heating rates, over 70°/min, it is normal that one can not describe the decomposition kinetics by using Eq. (1).

The possibilities of using Eq. (1) to describe the thermal destruction of polymers have been critically analyzed with special emphasis on the disturbing effects generated by the changes of mechanism during heating of the sample [4]. It is noteworthy that some of the methods used in non-isothermal kinetics, based on Eq. (1), such as those given by Flynn and Wall [5] or Ozawa [6], provide evidence of the above-mentioned changes of mechanism and, moreover, permit determination of the kinetic parameters corresponding to the different regimes of the destruction.

The validity of Eq. (1) has been discussed in connection with its applicability to the non-isothermal decomposition of solids [7, 8]. As this problem falls beyond the framework of our discussion, we will mention only that Eq. (1) should not be considered as coming from homogeneous kinetics, but as a particular case for $m = 0$, of the general equation [9]:

$$\frac{d\alpha}{dt} = k\alpha^{m}(1-\alpha)^{n} \quad (2)$$

which adequately describes the decomposition kinetics of solids.

To conclude, we consider Dr. Shlensky's request as being too restrictive and quite inconsistent. Equation (1), carefully applied, correctly describes some cases of solid-gas decomposition (the value $n = \frac{2}{3}$ corresponds to the contracting sphere model and has a clear meaning [10]).

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