Notes

NON-ISOTHERMAL KINETICS

P. D. Garn

The University of Akron, Akron, Ohio, USA

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The flurry of controversy over MacCallum and Tanner's [1] suggestion that only isothermal methods can be used to evaluate the order of reaction, the pre-exponential factor and the activation energy has brought out several deficiencies in our view of both isothermal and non-isothermal kinetics as applied to decompositions of solids.

Hill [2], in his criticism of MacCallum and Tanner's conclusion, appeals to authority (Kissinger [3]) which has been under criticism from several quarters. The statement that "The only effect of an instantaneous change of temperature is in the velocity of thermal motion of the particles", is too specific. Assuming we could perform that instantaneous change, we know only that we have changed the total energy. Whether or not the increment in energy leads to instability and change in direction and/or velocity will depend upon the temperature and, in some cases, other variables.

In citing the authority, Hill failed to note that the expression

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left(\frac{\partial x}{\partial t}\right)_T + \left(\frac{\partial x}{\partial T}\right)_t \frac{\mathrm{d}T}{\mathrm{d}t}$$

was already shown to be incomplete by Kissinger's own data. Both the dilution and the radius of the sample holder influence the rate, so the rate is a function of *at least* three variables. Other work [4] suggests that P_{H_2O}, rather than r, is the appropriate variable.

Kissinger's DTA curve also displays a clear lag in temperature during the decomposition of kaolinite, so $\mathrm{d}T/\mathrm{d}t$ is varying quite markedly during the event. But $\mathrm{d}T/\mathrm{d}t$, rather than T, is used in his calculations of the activation energy. The actual value used, apparently, was the nominal heating rate. By measuring outside the sample, this very real gradient could be shoved under the carpet, but this concealment would not change its reality.

The analogy suggested by Hill is indeed infirm; referring to an arrow in flight he states (Zeno's hypothesis) "although the arrow is in motion, at any moment it is at rest". More accurately, for some purposes it may be *considered* at rest. MacCallum's [5] reply is pertinent; if the arrow were aflame, its condition would depend upon the instant of time chosen. But there are other variables. A particular point in space may be occupied by a point in the arrow at a given instant, but this does not define the orientation of the arrow. It may occupy that point in space from a number of directions or have the same orientation with a number of velocities. The analogy now is more descriptive. The condition of virtually any of the materials under consideration will differ depending upon the path by which it reached that point in time – or even level of decomposition. In any real case, the conditions of the sample at, say, 50% decomposition will depend upon the geometry and/or atmosphere as well as the heating rate [6]. The reaction is by no means homogeneous. Even the atmosphere surrouding a given particle will vary with temperature or time and differently for a surface than for a centrally located particle.

MacCallum and Tanner [1] refer to homogeneous kinetics – but to polymer samples. Except in the case of successive losses of monomer, it is hardly likely that this is a homogeneous decomposition or even the same through the course of the reaction. The arguments of homogeneous kinetics do not apply. For inorganic systems it is well known to solid state kineticists that a single description will not fit the whole course of reaction [6]. Hulbert [7] and Young [8] have shown that at least five distinct regions can be identified in some isothermal decompositions.

The criticism by Gilles and Tompa [9] assumes arbitrarily that T is an explicit function of t, which it is not. While a measureable reaction is taking place, larger temperature gradients will exist in the sample (and possibly the sample holder) compared to the steady state. Further, these gradients will depend upon the heating rate, the nature and condition of the sample, etc.

Felder and Stahel [10] noted that the proposed correction was impossible to calculate because, "contrary to logic", "it implies . . . that the instantaneous reaction rate depends not only on the present state of the system . . . but also . . . on previous . . . states". As pointed out above, the "present state" in a real reaction is very much a result of the path. The "far-reaching implication that . . . the non-isothermal reactor modelling . . . has been fundamentally unsound" is hardly new. The suggestion has been made quite explicitly for solid state kinetics by solid state kineticists several times. This author [6] has discussed the reasons for the success of calculated "activation energies". Felder and Stahel also note that the Arrhenius expression is a frequently erroneous, semi-empirical expression, and cite some of the conditions under which it is not valid. These conditions, plus varying compositions of gaseous products at the reaction interface, are common in solid state decompositions.

The attempt by Simmons and Wendlandt [11] to justify Hill's criticism by an "exercise in fundamental calculus" fails for several of the reasons already advanced. The assumption that T is an explicit function of t fails just when it is needed most; the uniform addition of even an infinitesimal quantity of heat in the absence of a temperature gradient (within the sample) is clearly an impossibility. More important, setting down the claim that a result will necessarily follow "if an expression (the Arrhenius equation) is assumed valid *only* for isothermal reactions" has no meaning when that expression is not valid *even* for isothermal reactions.

MacCallum's [5] defense against Felder and Stahel's [10] emphasis on thermal equilibrium, that "this would seem to be more of a practical than a theoretical problem" is quite intriguing, considering that this controversy arose because of the failure of theory to describe practice.

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