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Reply to "What is meant by the term 'variable activation energy' when applied in the kinetics analyses of solid state decompositions (crystolysis reactions)?"

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Abstract

Galwey, in his recent paper [Thermochim. Acta 397 (2003) 249] critically discusses the problems associated with the concept of variable activation energy that was proposed in my earlier publication. Although the concept was put forward for the effective activation energy, Galwey tends to interpret it as applied to the energy barrier. As a result, Galwey criticizes the fruits of his own overinterpretation rather than the concept as it was proposed by me.

Keywords: Activation energy; Kinetics; Solid state; Condensed phase; Thermal analysis

Some time ago I wrote what Galwey [1] calls "a thought-provoking review" in which I proposed the concept of variable activation energy as a compromise between the actual complexity of solid state reactions and oversimplified methods of describing their kinetics [2]. I am really glad to see that my review seems to be accomplishing its provoking goal because Galwey takes the concept seriously, although he strongly disagrees with it. Regrettably, he takes it so seriously that sees in it "reappraisal of this essential theoretical concept" (i.e., activation energy) and a threat to "the accepted meaning" of activation energy [1].

I would like to start by briefly addressing "the accepted meaning" of the activation energy. By that Galwey means that the value must be constant [1]. This meaning appears to exist only within undergraduate courses of physical chemistry that almost exclusively and, by no means, comprehensively treat gas phase reactions. Although thermal analysis is not really concerned with the kinetics of gas phase reactions, it is worthy of note that even for these reactions the activation energy should show a temperature dependence because of the temperature dependence of the heat capacity of activation [3]. As soon as the theory moves from vacuum to the condensed phase (cf., Glasstone et al. [4], Marcus [5], etc.) the free energy of activation becomes a function of temperature dependent properties of the reaction medium. A brief discussion of this issue has been presented in my paper [6]. In the light of these facts, it is hard to say what is "the accepted meaning" [1] of the activation energy. Nevertheless, it appears to be somewhat more complicated than meant by Galwey, especially for the condensed phase reactions, whose rate cannot in principle be separated from the properties of the reaction medium.

Galwey states that my paper "does not define this revised term, explain the advantages of the new

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concept, or indicate how this modification to theory will contribute towards the advance of the subject" [1]. Let us start from the definition. In my paper [2] I repeatedly use the term "effective activation energy". I did not feel that an additional definition might be needed because, say, Webster's Dictionary clearly defines the word "effective" as "actual, not merely theoretical". If further explanation is still needed, I mean by my effective activation energy, a parameter measured from a temperature dependence of the overall reaction rate. Despite the absence of the exact definition, Galwey understands the meaning correctly calling this activation energy "a compound and empirical parameter" [1]. It seems unfortunate that this experimentally measured parameter is traditionally termed "activation energy", because this term appears to be mentally tied up with the free energy barrier graph that is found in every physical chemistry textbook. No, the effective activation energy does not have to be the free energy or enthalpy of activation. The relation of the effective value to the energy barrier may be quite straightforward for gas phase reactions, but it certainly gets increasingly complex when we move to liquid and to solid state reactions. If one must think of complex reactions in terms of that ever-present free energy graph, I suggest visualizing a cascade of these graphs. By the way, this image would be much more consistent with the modern modifications of the transition state theory for complex systems whose kinetics is determined by an ensemble of numerous transition states [7] (so much for "the accepted meaning" [1] of the activation energy).

As Galwey fairly mentions [1], for the condensed phase reactions, variations of the effective activation energy may be caused by many reasons. I believe that most of the time the variation is caused by the fact that the overall rate measured by a thermal analysis method is a function of the rates of several simultaneously occurring single step reactions, each of which has its own energy barrier. Therefore the effective activation energy derived from these overall measurements becomes a function of the individual energy barriers and, as such, it varies with the temperature and/or reaction progress. In this situation, Galwey advocates experimentally measuring the absolute rate of a single step by isolating it from "controlling factors" [1]. This idea is vintage (recall "*dīvide et imperā*") and is traditionally offered as a universal method of dealing with complex reactions. However, it is not clear how to measure the absolute rate of, say, a solid decomposition whose actual rate is controlled by diffusion of a product or a reactant through a solid. If one decides to measure the rate of diffusion, how then to eliminate, e.g., the effect of thermal expansion that, as shown by Jost [8], may cause a variation in the activation energy of diffusion. It is also not clear how far Galwey wants to go in isolating the single steps. In any event, there is a natural limitation for breaking a chemical process down to elementary steps; it is electron transfer. However, the temperature dependence of the free energy of activation for this process has already been reported (cf., references in my paper [6]). And it is totally unclear what one would need to isolate for a liquid phase (e.g., melted solid) reaction whose free energy barrier is partially determined by physical properties of the medium [6].

What are the advantages of the variable energy concept? There is a strong but rather unjustified tendency in the thermal analysis community to directly interpret the effective activation energy in terms of a free energy barrier. Also, there are many flawed methods (the Coats-Redfern method definitely being the champion in popularity) that use a single heating rate and directly deliver a single and constant value of the activation energy as well as a preexponential factor for any reaction, no matter how complex it might be. For details, the reader is forwarded to the discussions of the results of the recent ICTAC Kinetics Project [9–11]. The more than questionable resulting values are then frequently converted to the free energy, enthalpy, and entropy of activation by using the transition state theory equations! Frustratingly, this dreadful scenario presents a very unfortunate but a quite common real life example of the concept of a constant activation energy at work. I hope that by accepting the concept of variable activation energy as a practical compromise, people abandon the methods that invariably produce a single value of the activation energy and start using multiple run (isothermal and/or nonisothermal) methods that allow for detecting reaction complexity [9–11]. The complexity can be detected in various interrelated forms such as multiple steps with respective values of E [9], a variable value of E [2], or a distribution of the E values [6], E being the effective activation energy. It occurs to me that if one chooses to use, for instance, an isoconversional method (one of the simplest ways of detecting the complexity) and determines a variable activation energy, the natural question would pop up: Why does it vary? And this would be the point to start looking for mechanistic interpretations of the phenomenon, and ultimately for the link with the free energy barriers of individual steps. Therefore the advantage would be in changing mentality and broadening the horizons. Not speaking of the very practical problem of predicting the reaction rates that is efficiently solved by using the variable activation energy.

Galwey inquires "... how this modification to theory will contribute towards the advance of the subject" [1]. First of, there is no modification to theory because there is no adequate theory of solid state kinetics, as rightly mentioned by Galwey [1]. Secondly, the concept was not proposed as a modification to any theory but as a practical compromise within the widely used the Arrhenius–Eyring theoretical treatment. Can the acceptance of the variable energy concept contribute to the advance of solid state kinetics? I would hope so. If people stop being afraid of variable effective activation energy as being "inherently unreliable" [1] and contradictory to the nonexistent theory of solid state kinetics, and start exploring the phenomenon, they will definitely contribute much more to the understanding of solid state kinetics than by simply converting a single thermal analysis curve into a single pair of more than questionable Arrhenius parameters.

I hope this clarifies my position concerning the concept of variable activation energy. I feel that Galwey tends to overinterpret my concept and, as a result, he criticizes the fruits of his own overinterpretation rather than the concept as it was put forward by me. Perhaps Galwey's paper will inspire some of the mysterious "crystolysis chemists" [1] on a crusade to deliver that highly desirable but elusive single value of the activation energy from the "evil" variations. Although I greatly doubt it, but maybe they will come back from that crusade with a new theory of a single activation energy for solid state reactions and the ways of determining it. But until that glorious moment has come true, I stand by my provoking concept of variable effective activation energy as "a reasonable compromise between the actual complexity of solid state reactions and oversimplified methods of describing their kinetics" [2].

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