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COMMENTS ON THE "COMPUTER STUDY OF KINETIC PARAMETER VARIATIONS IN DEPOLYMERIZATION BY DIGITAL THERMOGRAVIMETRIC INTERPRETATIONS"

P. D. GARN

The University of Akron Akron, OH 44325 USA

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In their attempt to treat a thermogravimetric curve for the thermal degradation of a partially substituted polyvinylchloride analytically, Liteanu and co-workers [1] assumed an Arrhenius-type model in which the rate of change, with time, of the fraction of the material still unreacted is equal to the product of the frequency factor, the exponential involving an activation energy, and the fraction of the material unreacted to some power that corresponds to an order of reaction. In its simplest form, using twenty values of the remaining weight equally-spaced in time and temperature across the first major weight change, a set of kinetic parameters, A, E, and n, were found as "best values". In plotting a rate curve (DTG *vs.* T) from their computed values, and plotting with it the calculated values, they found a comparison that was obviously not a good fit. From this result, they concluded that the kinetic parameters – rather than the form of the descriptive equation – must be changing during the reaction. To follow these changes, they performed an averaging operation to calculate the parameters over smaller sections. This is a standard technique for smoothing data that is particularly useful when an over-enthusiastic analog-to-digital converter presents us with data with more resolution than our experiments warrant, but it may also be used to smooth out random variations. To use the technique, we simply look at the data within some chosen window as we move that window along our data set, averaging the data points and ascribing that value to the central point. This is an easy operation on a digital computer – at each step the next datum is added to the sum and the earliest datum subtracted to get the next sum. We have used the technique in evaluating another kinetic data set for which we had about one thousand data points. This new curve could be treated as an original data curve and a window of about twenty data points passed along the set.

Liteanu and co-workers used another approach because their sets of five points often included substantial portions of the reaction. They treated each set of five points separately, calculating the kinetic parameters separately for each set. Their results inevitably fit the experimental data curve quite well because the data come from small sections of that curve. But let us look at the variations in A, E, and n that must be accepted if the method is accepted as valid. The frequency factor in the initial process quickly reaches 10^{11}/sec, increases to 10^{21}/sec, drops to less than two hundred per second and climbs again before dropping to one per two hundred million seconds. The calculated activation energy initially reaches 27 kcal/mole or 110 kJ/mole, rises to 54 kcal/mole or 230 kJ/mole, drops to four kcal or seventeen kJ per mole, rises and then drops to -67 kcal/mole or -280 kJ/mole. Meanwhile, the apparent order of reaction was calculated initially as -1.8, rises to 3.7, drops to about 0.6, and rises again before falling to about 0.05 before becoming negative again.

The authors cited the kinetic compensation effect to explain the agreement between the trends of the calculated A and E values but the kinetic compensation effect is simply a fiction arising from use of the Arrhenius equation in describing reactions to which it does not apply [2, 3]. The physical significance of a negative n is not clear.

In this particular case, hydrogen chloride is being evolved. The overall process is clearly irreversible but even so, if an initial step has some degree of reversibility it will be affected by the need for the reaction products to escape. This would introduce a parameter, the HCl pressure at the reaction site, that is not included in these kinetic calculations, and that varies with time and temperature. It is known that the degradation of polyvinylchloride is affected by the HCl evolved [4] and that loss of HCl proceeds rapidly along a chain after degradation has been initiated. That is, the reaction rate depends upon at least one parameter that is not included in the description and the HCl loss is not random anyway [4].

In fact, if the reaction is in any way topotactic, any treatment of the Arrhenius equation that retains the term α fails to be descriptive [5, 6]. Verifying the homogeneity of the process should not be difficult.

Further, the authors do not describe the experiment in sufficient detail to enable evaluation of vitiating factors by the readers. McAdie, speaking for the International Confederation for Thermal Analysis' Committee on Standardization, enumerated the essential information [7]. In this case, we do not even know whether the sample was particulate, a pellet, or a sheet, but this information would help in interpretation.

An important consideration here is the possibility of learning more about the reaction by changing the particle size or sheet thickness drastically. If the simple kinetics is descriptive, the observed rate for the larger sample will at all times be a simple multiple of that for the smaller and the same kinetic parameters will be found [8]. If different parameters are found it is more likely that a variable has been omitted than that the parameters are all changing drastically throughout the course of the reaction.

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