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HOW IMPORTED IS IT TO KNOW THE EXACT PATH OF THE BASE LINE ?

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ABSTRACT

Calorimetric measurements were carried out on mainly liquid reaction mixtures, using a new reactor-calorimeter in the 100 ml range. In contrast to conventional instruments it makes it possible to record simultaneously the practically undistorted gross curve and the corresponding reference curve for thermal events with half life in excess of three minutes under isothermal condition. Results show that the base line very often follows an unexpectedly complicated path. This suggests that, unless the exact path of the base line is known, an absolute, conclusive calorimetric analysis (particularly a refined thermokinetic one) is not possible.

Generally speaking, conventional calorimeters are characterized by the more or less distinct feature that the signal actually wanted - that is the immediate calorific sign of life from the test sample - is integrated in a more or less temporarily distorted measured gross signal. The profile of the wanted signal - the net curve - can only be obtained by taking the difference between the gross curve and a reference curve (base line) which indicates the proportion of the gross curve accounted only for the changes in physical properties during the measurement, for instance heat transmittance, viscosity, surface tension, specific heat e. c., fig. 1. The distortion of the difference curve obtained must generally still be corrected. The base line cannot be measured with conventional calorimeters. To make a virtue of necessity, the profile of the base line is approximated on the basis of theory or let's better say on the basis of a plausibility consideration which may or may not be supplemented by measuring techniques. This procedure yields preferably simple monotonic profiles (1), (2), (3). (Plausibility lulls into security, measurement gives security!)

Such an approximated profile of the base line is fundamentally inadequate for accurate thermal analysis, at least such as a thermokinetic one, because it stands to reason that the thermokinetic analysis of a complex reaction system is only feasible if its conglomerated caloric sign of live can be measured exactly, practically during the whole run of the process. That is even necessary with simple reactions like elementary reactions as is outlined by means fig. 2.

Fig. 2 illustrates - represented by symbols - the logarithmic plot versus time of the theoretical profiles of the rate r of elementary reactions of order one, two and three for isothermal conditions. Everybody knows that a straight line is valid for first order reaction. It can be seen that there is only a small curvature in the profiles of second and third order reaction up to relatively high conversion. Considering that experimental data are usually loaded with imperfection, a straight line may also be

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drawn to the best knowledge and belief through experimental data of reactions with an order greater than one, for instance up to a conversion of 45 % for third order reaction and 60 % for second order reaction. The situation is the same if $\sqrt{\frac{1}{r}}$ is plotted versus time, in that case a straight line being theoretically valid for second order reaction, fig. 3. This means, in practice it cannot be distinguished up to relatively high conversions undoubtedly between reactions of order one, two or three. The difference becomes evident without doubt only by means of data measured during the final stage of reaction. The calorific effect during this stage of the reaction is, however, usually rather small, and, consequently, the accuracy of the desired net curve is very closely associated with the accurate knowledge of the profile of the base line.

For this reason, we have designed a reactor-calorimeter for essentially liquid reaction mix which permits under isothermal conditions the synchronous measurement of both the practically undistorted gross curve and the corresponding base line for reaction with half-life values in excess of three minutes (4). Numerous measurements were made on reaction systems of widely varying physicochemical composition such as occur in industrial practice, fig. 4, 5 und fig. 4 a, 5 a, 6 a, 7 a, 8 a, 9 a in (4).

The examples show that the base line often display an unexpectedly complicated profile. It can be assumed that this is not primarily due to the type of calorimeter used. Rather, it may be suspected that the complex changes in the physical conditions which occur during any physicochemical conversion also have unexpectedly manifold and more or less significant effects on the profile of the reference curves when using calorimeters of different design.

Basic relation between gross curve, net curve and reference curve

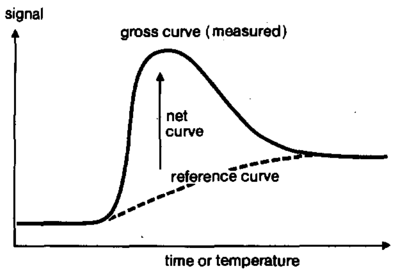

Fig.1

Log. r versus time for reactions of order n

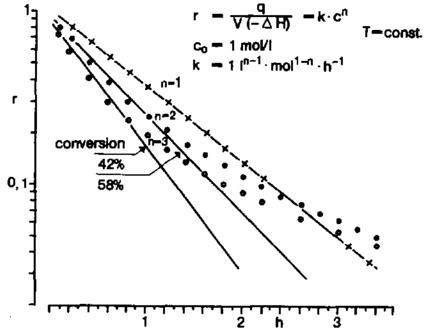

Fig.2

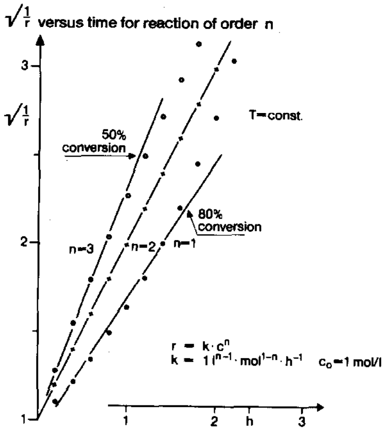

Fig.3

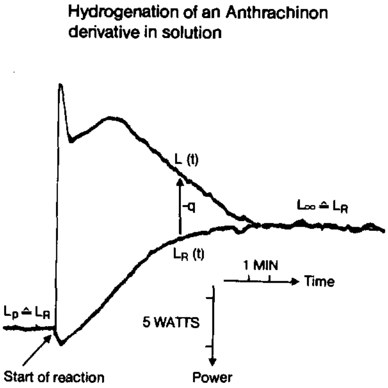

Fig.4

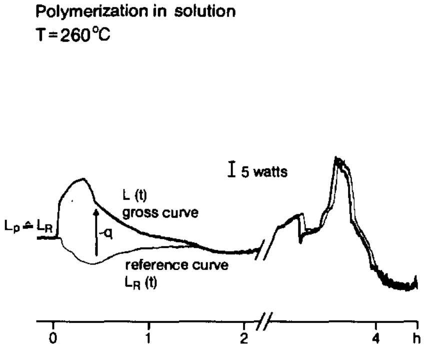

Fig.5

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