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POWER SCANNING CALORIMETRY (PSC)

J. Hakl
Sandoz AG, Development Dept. Dyestuffs, 4002 Basel, Switzerland

ABSTRACT

The PSC method is suitable for determination of data on the heat production in reaction mixtures under plant conformable conditions. The method is described and its applicability demonstrated on 2 examples. The reliability of the results obtained is discussed and an isothermal variant submitted.

INTRODUCTION

The heat of reaction and the rate of heat production in a reaction mixture as a function of temperature are important quantities for the design of reactors in chemical industry. At present several methods for the determination of these quantities are available, such as DSC, DTA, Bench Scale Calorimetry (ref. 1) and adiabatic calorimetric methods.

The principal advantage of thermoanalytical micromethods is the prompt availability of the required data and small quantities of the educts necessary for the experiments. The equipment used in these methods, however have many serious limitations and disadvantages: e.g. a strictly limited choice of the receptacles used for the reaction mixture, lack of stirring and the impossibility of addition of chemicals during the measurements.

On the other hand, bench scale calorimetric methods achieve a high level of plant conformability but they have various disadvantages, such as limited flexibility in the choice of reactors and sometimes large volumes; the large volumes comprise, e.g. an increased hazard level with operation under pressure. Moreover, they are usually time consuming and the instruments expensive.

Among the best known disadvantages of the adiabatic methods is the impossibility to control the temperature, resulting sometimes in an uncontrollable run-away reaction and indirect availability of the required data (ref. 2), thus entailing reduced accuracy and rapidity.

The scope of the PSC method is to overcome the disadvantages of the methods listed above, and to provide data on the heat production under plant conformable conditions allowing safe design of production reactors.

PRINCIPLE

The reaction mixture is introduced in a suitable container fitted with a stirrer and an electric heating coil fed by a controlled power source. The surrounding temperature is kept at a selected constant value lower than the temperature of the reaction mixture under investigation. The task of the controller is: a) to keep the first derivative of the reaction mixture temperature with respect to time constant, i.e. to increase the sample temperature in a linear fashion and b) to continue keeping the surrounding temperature at the preselected constant value lower than the temperature of the reaction mixture. If there are no processes with heat effects taking place in this mixture, the electric power to achieve the conditions described above remains constant. (Important condition: The temperature dependence of the

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heat capacity of the reaction fluid is negligible). This electric power is to be measured and recorded on a suitable device.

At the temperature at which the reaction starts producing its own heat, the electric power necessary to control the linear rise of the mixture temperature is reduced, since the reaction contributes to the supply of the necessary energy.

The difference between the original (constant) electric power and the reduced power is the value of the rate of heat production of the investigated reaction measured directly, i.e. obtained instantaneously and therefore exhibiting the least error. The values of the power differences (which equal the rate of heat production of the investigated reaction) plotted logarithmically versus reciprocal temperature in Kelvins, forms the Arrhenius plot, and can be directly used for the design of production reactors. By a simple integration of the power difference curve, the overall heat of the studied reaction can be obtained easily.

EXPERIMENTAL EXAMPLE

The practical applicability and accuracy of the PSC method can be demonstrated by the examples of the thermal decomposition of aromatic diazonium salts in sulfuric acid, (important intermediates for the production of dyestuffs). The diazotation of both amines was carried out by nitrosylsulfuric acid.

Example 1

123.8 g of the reaction mixture after the diazotation were introduced in a beaker and placed in a SEDEX oven (ref. 3). The temperature of this mixture was set at 50°C, the ambient (oven) temperature at 42°C, thus resulting in a temperature difference of 8°C. The stirrer speed was set at 600 RPM and the heating rate selected 20°C/h. Under the conditions described above, the electric power feeding the heating coil levels out at 5.1 W. The temperature increases in a linear fashion with the preset heating rate. Below 115°C, the power of the heating coil remains constant, thus indicating no reaction with heat effects is taking place in the reaction mixture. At 115°C, the electric power starts to decline - the diazonium salt mixture starts to decompose exothermally at a measurable rate. With the increasing temperature, the electric power continues to decrease as a result of the increasing contribution of the heat of decomposition. After reaching a minimum at 150°C, the power starts increasing as the reactions begins to abate. At about 170°C, the heating coil power reaches its original value, as the contribution of the reaction to the energy supply sinks to zero. The reaction is over. The difference between the original electric power and the reduced power at a selected temperature is the experimentally detected value of the rate of heat production of the studied reaction at that temperature (see Table 1, column dQ/dt(exp.)). Considering the decreasing concentration of the educt (see Table 1, column C (norm.)), the true rate of heat production of this reaction can be obtained easily (Table 1, column dQ/dt(corr.)). The values dQ/dt(corr.) plotted logarithmically vs. reciprocal temperature in Kelvins form a straight line as requested by the theory (see Fig. 1). The analogous data obtained by DSC are shown for comparison in the same diagram.

Example 2

121.6 g of another diazonium mixture were investigated under the same conditions as described above. The initial temperature of the scan was selected at 0°C, as this salt starts decomposing at approximately 30°C. The evaluation

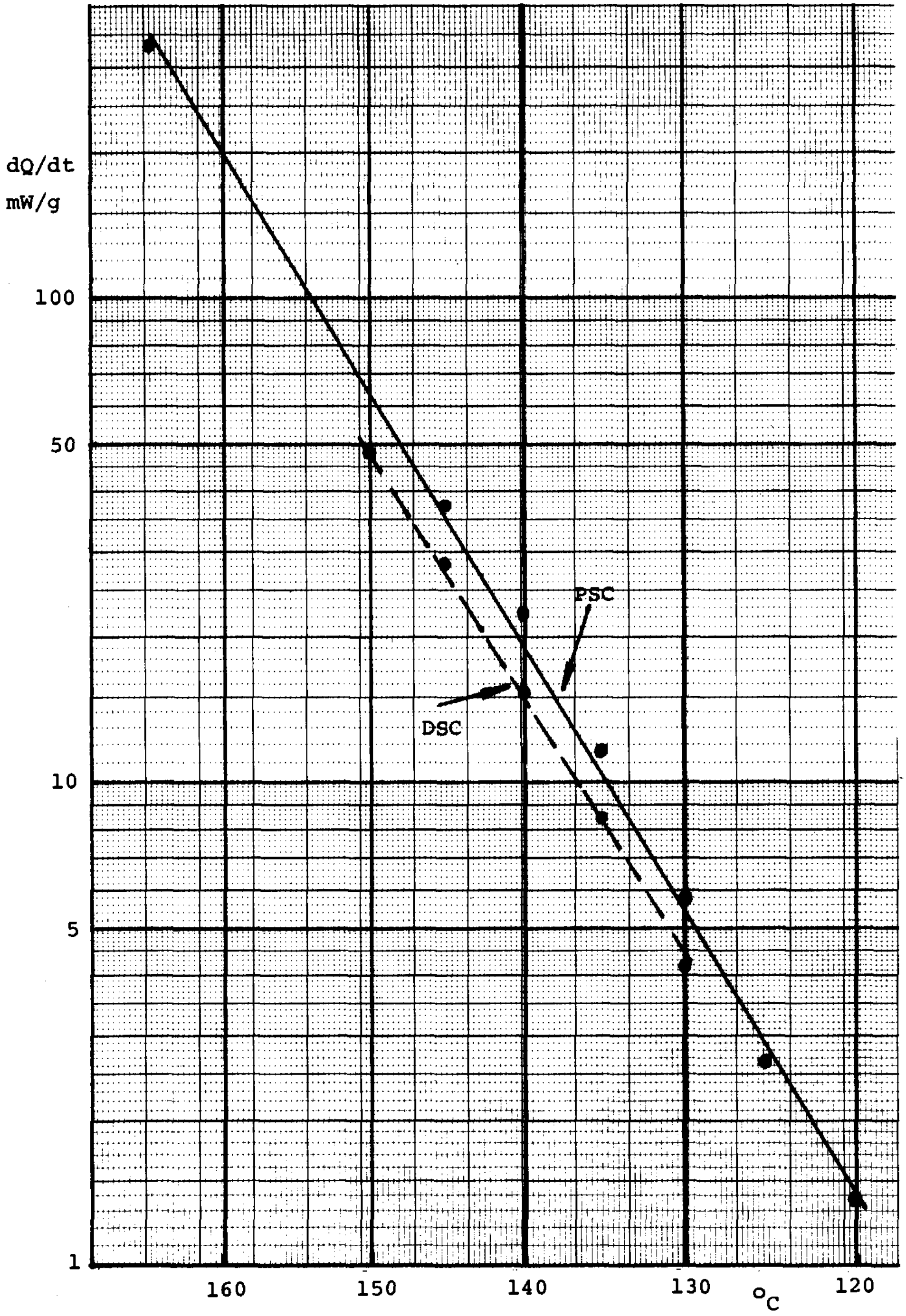

Fig. 1. Arrhenius plot of rate of heat production determined by PSC and comparison with analogous DSC data.

of the PSC curve yielded-74.8 J/g. Considering the specific heat of this mixture (estimated to be 1.46 J/g.K) such heat would inflict, under adiabatic conditions, a temperature increase of 51°C. The adiabatic temperature increase observed with this reaction mixture in a Dewar flask was 53°C.

DISCUSSION

The examples described above are seemingly not ideal to demonstrate the usefulness of the presented method. However, they were chosen intentionally to enable the verification of its accuracy by conventional methods under the conditions at which these methods are supposed to supply reasonably correct results. Both the studied reaction mixtures are homogeneous solutions and as decompositions they may be supposed to obey first order kinetics. The slight difference between the data found by DSC and PSC, as seen in Fig. 1, are evidently due to a higher sensitivity of the PSC, which also allows to detect the onset of exothermic reactions at lower temperatures. Example 2 was chosen to make possible a reasonable comparison with such a simple method as an adiabatic measurement in a Dewar flask in the temperature range where such measurements involve the least error.

An interesting variant of the PSC method is isothermal configuration. In this case, the reaction mixture temperature as well as the ambient temperature, however several degrees lower, are kept constant. One educt is placed in the receptacle and a second one is (possible continuously) added. If the intended reaction is exothermic, the electric power feeding the heating coil starts declining and, again from the power curve the rate of heat production of the studied reaction, can be seen easily (e.g. as a function of educt addition rate at a selected temperature). By integration of the power curve, the heat of this reaction is easily obtained.

TABLE 1

Rate of heat production data

Temperature (°C)	dQ/dt(exp.) (W)	C(norm.)	dQ/dt(corr.) (mW/g)
120	-0.17	0.994	-1.38
125	-0.32	0.983	-2.63
130	-0.64	0.950	-5.82
135	-1.14	0.888	-11.74
140	-1.78	0.784	-22.41
145	-2.12	0.642	-37.59
165	-0.60	0.014	-335.47

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