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OVER-ADIABATIC CALORIMETRY (OAC)

JOSEPH HAKL
Sandoz AG, 4002 Basel (Switzerland)

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ABSTRACT

The method described is suitable for reliable, rapid and accurate determinations of heats of reaction and the rate of the heat production of weak and/or slow exothermic processes. If carried out under plant conformable conditions, the method supplies data directly for the design of chemical production reactors.

INTRODUCTION

With conventional methods the direct determination of the heat of reaction of weak and/or slow exothermic processes runs into insurmountable problems, e.g., the DSC peaks are wide and flat and therefore cannot be meaningfully evaluated, or the heat loss in a Dewar container is so great that the slowly released heat of reaction is lost without causing any significant rise in temperature. The use of complicated methods is usually time-consuming and the necessary instruments are expensive. The method presented here allows the determination of the reaction heat of weak and/or slow exothermic processes with acceptable precision within a reasonably short time with moderately-priced instrumental equipment.

THEORY

The sample is heated in a suitable container by means of an electric heater fed by a constant power source (Fig. 1). The ambient temperature of the sample is kept equal to that of the sample itself (adiabatic conditions). The temperature of the sample is measured and its first derivative with respect to time is formed. If no process with heat effects takes place in the sample, the temperature rises in a linear fashion, i.e., the first derivative remains constant and can be described by a simple differential equation

$$\frac{dT}{dt} = S \tag{1}$$

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where T is the temperature (K), t is the time, and S is the linear rate of heating.

At the point when the reaction starts producing its own heat, the rise in temperature accelerates and can be described by a modified Arrhenius equation. The following equation is valid for the temperature rise under such over-adiabatic conditions for the first-order reaction

$$\frac{dT}{dt} = A(B + St - T)\exp\left(\frac{-C}{T}\right) + S \tag{2}$$

where S is the linear rate of heating from eqn. (1).

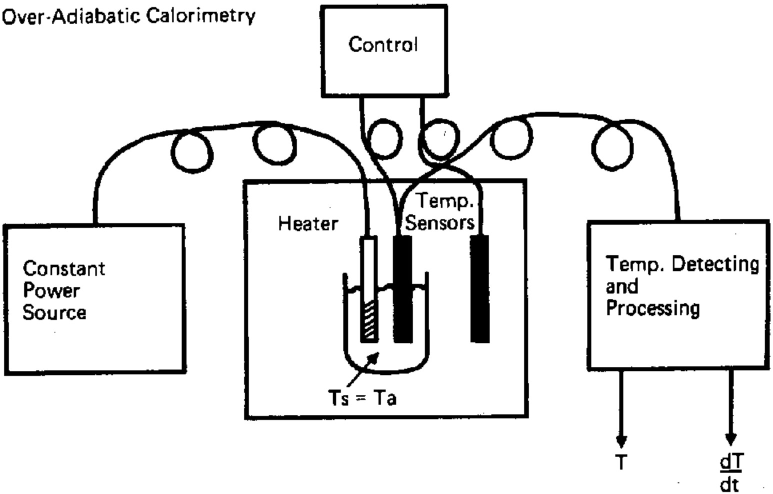


Fig. 1. Scheme of the experimental arrangement.

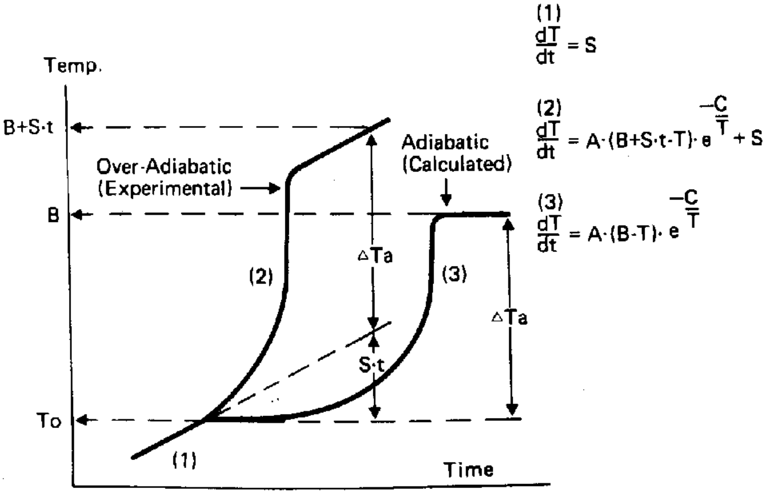


Fig. 2. Over-adiabatic time/temperature curve compared with analogous adiabatic one.

The heat of reaction is determined on the basis of the knowledge of the adiabatic temperature rise (see ΔT_a in Fig. 2) and the heat capacity of the reaction mixture, assuming that the specific heat remains constant during the reaction and does not vary with temperature.

Equation (2) contains three parameters: parameter A comprises the frequency factor, initial concentration, heat capacity of the reaction mixture and coefficients of proportion; parameter B has a physical significance, the final temperature of the reaction mixture after the end of the reaction under adiabatic conditions; and parameter C represents E/R, where E is the activation energy and R is the universal gas constant. These parameters can be estimated as follows.

Parameter B is obtained directly from the course of the temperature (see Fig. 2). Parameters A and C can be calculated from the course of the $\mathrm{d}T/\mathrm{d}t$ curve either graphically or, better, by a regression analysis (Fig. 3). The parameters obtained can than be used in the Arrhenius equations

$$\frac{\mathrm{d}T}{\mathrm{d}t} = A(B - T)\exp\left(\frac{-C}{T}\right) \tag{3}$$

to calculate the course of the temperature of the process under study under ideally adiabatic conditions.

The expression within parentheses $(B + St - T)$ has the dimension of temperature, and it describes the decrease in the educt concentration during the reaction of the first-order kinetics. For a reaction of second (or third) order, eqns. (2) and (3) must be extended accordingly, so that the changing concentration of all the reacting educts can be taken into account.

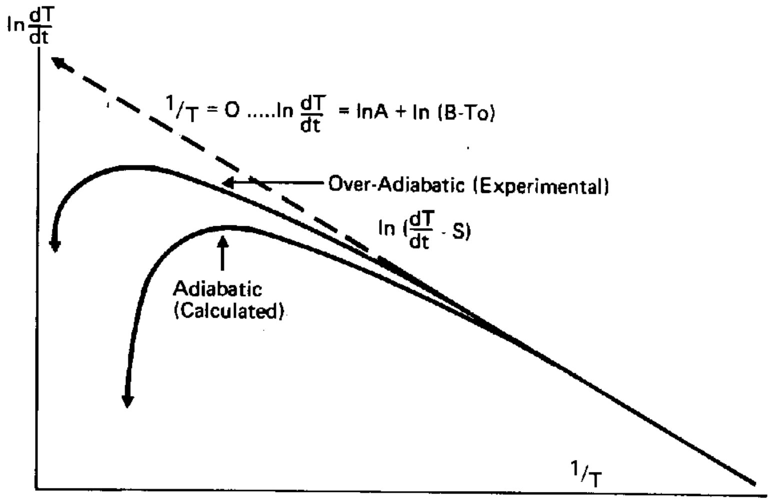
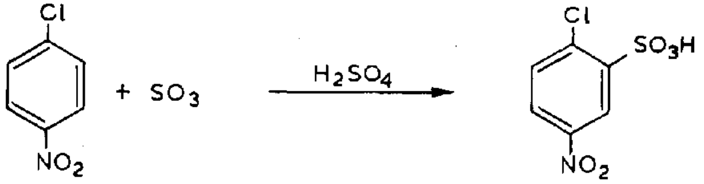


Fig. 3. Over-adiabatic and adiabatic curves in Arrhenius coordinates.

EXPERIMENTAL

The practical application of the OAC method can be demonstrated by the example of the reaction of 1-chloro-4-nitrobenzene with sulfur trioxide in sulfuric acid.



This is a typical second-order reaction and to provide a good reaction of the educts a strong excess of SO_3 was used (ca. 70%). The reaction mixture, consisting of 345.5 g oleum 26% and 101.5 g 1-chloro-4-nitrobenzene, was placed in a Dewar flask. The container was placed in a Sedex oven [1] and the mixture was stirred with a PTFE stirrer at 400 rpm. The temperature was measured by means of a 2 × Pt-100 temperature sensor and a constant heat supply was maintained by a heating element of 240 ohm fed by 7.1 W of electrical power from a constant supply source (Sandoz). To keep the oven temperature equal to that of the sample, the Sedex/ADOPT System [2] was used. An analogue-computation modulus (Sandoz) was developed to generate the first derivative of the temperature with respect to time. The temperature of the reaction mixture and its first derivative (rate of temperature rise) were recorded on a two-channel instrument (Fig. 4). Under the conditions mentioned, the initial heating rate is 37 °C h^{-1}. This rate remains constant up to 62.5 °C; at this point the temperature begins to rise at an accelerated

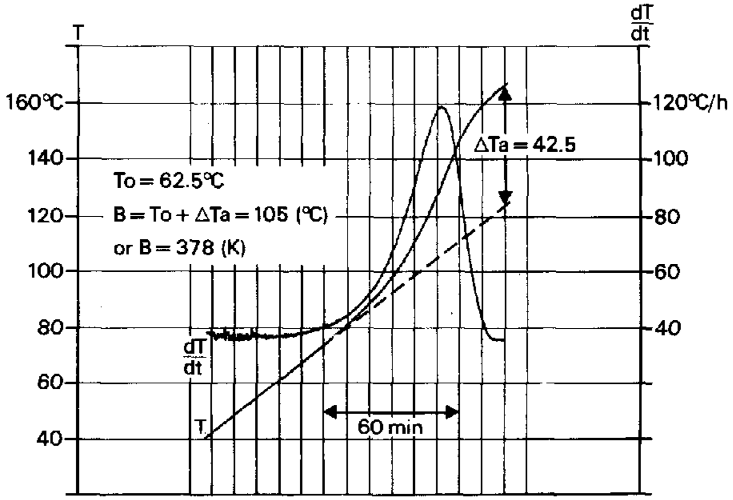


Fig. 4. Over-adiabatic record of the sulfonation of 1-chloro-4-nitrobenzene with sulfur trioxide.

rate as a result of the increasing contribution of the heat of reaction to the overall temperature rise. After reaching the maximum rate at 137 °C, the reaction begins to abate and the rise in temperature rapidly slows down. At about 165 °C the contribution of the heat of reaction to the total rise in temperature sinks to nil—the reaction is over.

RESULTS AND DISCUSSION

From this recording, the value of the adiabatic rise in temperature can be read (42.5 °C) and used to calculate the heat of reaction. In order to obtain the correct value for the heat of reaction, the heat capacity of the container must be taken into account. The specific heat of the reaction mixture in the above experiment was 1.35 J g^{-1} K^{-1}; this gives the heat capacity of the reaction mass as 603 J K^{-1}. With the heat capacity of the container being 88 J K^{-1}, the value of the true adiabatic rise in temperature becomes 48.7 °C; this allows the computation of the released heat: −28.8 kJ/batch, i.e., −64.5 J g^{-1} reaction mixture, or −44.7 kJ mol^{-1}.

From the same recording, the parameter B can be determined. It is in fact the initial temperature of the reaction plus the adiabatic temperature rise: $62.5 + 42.5 = 105$ for the calculations with °C, or 378 for temperature in K.

The estimation of the remaining parameters A and C is carried out by a regression analysis from the experimentally measured dT/dt data given in Table 1 in shortened form. The contribution of the heat of reaction at the respective temperature can easily be determined by subtracting the linear rate from the overall rate of temperature rise (see the 4th column in the table).

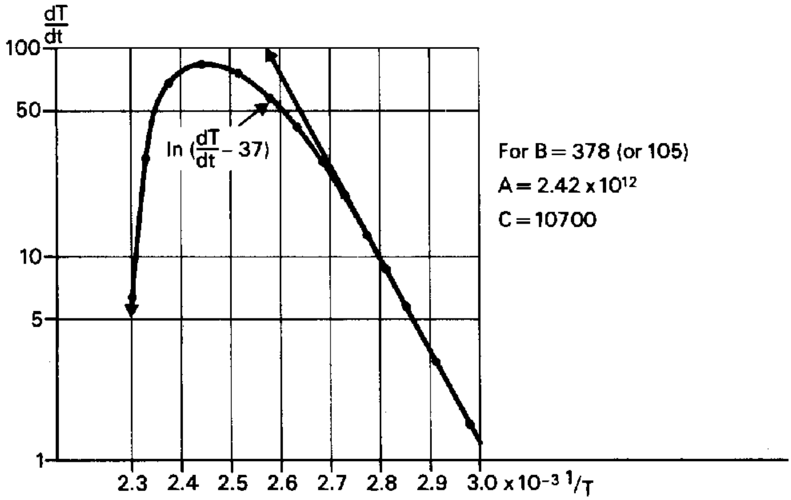


Fig. 5. Over-adiabatic curve of the sulfonation of 1-chloro-4-nitrobenzene with sulfur trioxide in Arrhenius coordinates.

For $S = 37$ and $B = 105$ (or 378) the following values for the parameters were determined: $A = 2.42 \times 10^{12}$ and $C = 10700$ (Fig. 5). To take into account the changes of the concentrations of both the educts (second-order reaction) eqn. (2) has to be modified slightly

$$\frac{\mathrm{d}T}{\mathrm{d}t} = A(B + St - T)\left(\frac{B + X + St - T}{Y}\right)\exp\left(\frac{-C}{T}\right) + S \tag{2'}$$

The new expression in the second pair of parentheses takes into account the changes in the concentration of the second educt (in this case SO_3) and the parameters X and Y depend on the excess of this educt. These parameters can be used to compute the course of the temperature under nearly adiabatic conditions (such as those in a Dewar container) employing a simplified Arrhenius equation for a reaction of second-order kinetics

$$\frac{\mathrm{d}T}{\mathrm{d}t} = A(B - T)\left(\frac{B + X - T}{Y}\right)\exp\left(\frac{-C}{T}\right) \tag{3'}$$

(see Fig. 6, curve "almost adiabatic").

To obtain the true adiabatic temperature course, the parameter B must be rectified taking into consideration the heat capacity of the container: $B' = 111.2\,°\mathrm{C}$ (or 384.2 K) (see Fig. 6, curve "adiabatic").

From the above, it can be seen where the advantages, and also the limits of the method, lie. It is necessary, above all, that the reaction under study is capable of being described by a reasonable equation (not necessary if only the heat of reaction is to be determined). The OAC method mainly allows statements concerning the temperature dependency of the rate of reaction, whereas statements concerning the concentration dependency and thus the kinetics are unobtainable by this method directly. Among the advantages this method offers are, above all, its extreme rapidity (compare Table 1 with Fig. 6), the precise and rapid determination of the onset temperature of the reaction in the same experiment, the possibility of carrying out the measurements under production conditions, and the elimination of the need for costly equipment. The OAC method supplies the value of the heat of

TABLE 1

Experimental $\mathrm{d}T/\mathrm{d}t$ data, sulfonation of 1-chloro-4-nitrobenzene with SO_3

Time (h)	T (°C)	$\frac{\mathrm{d}T}{\mathrm{d}t}$ (°C h^{-1})	$\frac{\mathrm{d}T}{\mathrm{d}t} - 37$
0	62.5	38.5	1.5
0.5	83.2	45.5	8.5
1.0	115.0	93.8	56.8
1.2	136.8	120.0	83.0 (max.)
1.5	161.7	43.2	6.2
1.6	165.8	37.0	0

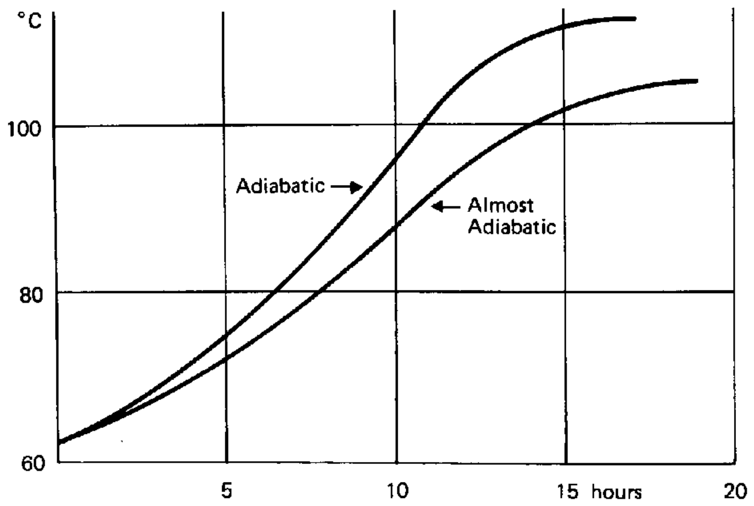


Fig. 6. Nearly adiabatic and ideally adiabatic time/temperature curves during the sulfonation of 1-chloro-4-nitrobenzene with sulfur trioxide.

reaction as well as the data on the rate of heat production at any temperature, and thus it is very suitable for the rapid and simple determination of data for the design of technical reactors.

Various modifications of the method are possible, e.g., if one accepts its less than ideal precision, this method can also be carried out in a Dewar container (without the Sedex oven–poor man's version).

The method is still undergoing further development and continuous improvement. One of the significant projected improvements is that of on-line data processing by a computer.

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