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QUALITY AND LIMITS OF A THERMOKINETIC METHOD TO STUDY GAS—SOLID INTERACTIONS

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ABSTRACT

In order to test the qualities and limits of a thermokinetic method for the determination of adsorption rates, the adsorption of separate doses of oxygen on an initially nearly stoichiometric nickel oxide was studied at 473 K by two independent methods: calorimetry and pressure measurements.

The calorimetric curves were corrected for instrumental distortion and compared with the results based on pressure curves. The following aspects of the correction procedure are discussed: determination of the instrument response function, smoothing procedure, influence of the ratio of the velocities of the instrument response and of the reaction under study.

INTRODUCTION

In attempting to apply heat-flow calorimetry to the determination of thermokinetics (i.e. heat development as a function of time), one is inevitably confronted with the notorious problem of line-shape broadening, which is essentially expressed by the convolution integral

$$h(t) = \int_{-\infty}^{\infty} f(x)g(t-x)\,\mathrm{d}x \tag{1}$$

where h is the experimental function (the calorimetric curve), f the (wanted) thermogenesis and g the response function of the instrument (g is the response of the instrument if the input is a Dirac function). A number of mathematical techniques are known to solve eqn. (1) with respect to f when h and g are known and, in the field of calorimetry, various methods are in use, see, e.g., refs. 1 and 2. Although it is a difficult task to obtain optimal results with any of these methods, the mathematical aspect of deconvolution has been reasonably well mastered. However, before any practical application of deconvolution, the response function of the instrument must be determined and this may be a severe problem. For gas—solid interaction,

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attempts have been made to solve this problem [3]; however, the accuracy of a given response function can be estimated only in those cases where thermokinetics can be verified by other kinetic methods. In the study described in the present article, information on kinetics was simultaneously obtained from both volumetric and calorimetric measurements.

Following and extending our previous work on the surface activity of the oxidation catalyst NiO, the adsorption of oxygen on nickel oxide at 473 K has been selected for the present investigation and an incremental procedure has been used. In this procedure, the surface is arbitrarily divided into a number of patches, the reactivity of which is separately tested by the introduction of successive doses of oxygen.

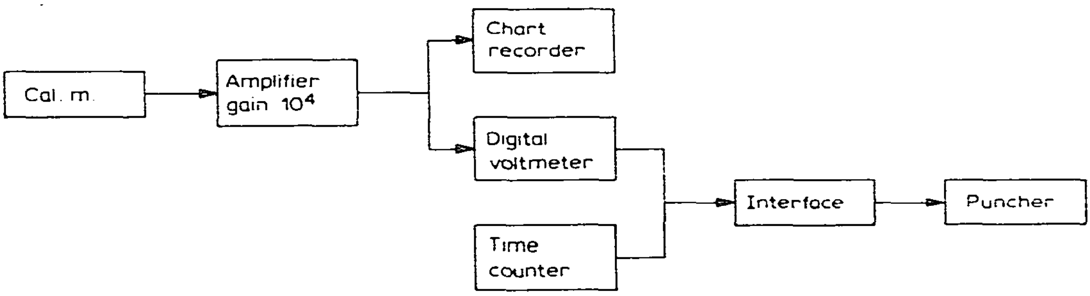
In principle, more detailed information about the adsorption process may thus become available. In particular, if during the adsorption of each dose both the oxygen pressure changes and heat production are measured as a function of time, one might be in a position to directly establish a relation between the rate and the heat of adsorption.

The purpose of the present article is to discuss some of the problems one encounters when using heat-flow calorimetry for kinetic purposes in gas—solid reactions. The physicochemical results obtained with the present method will be presented in a forthcoming article.

EXPERIMENTAL

Apparatus

A scheme of the calorimetric and volumetric apparatus is shown in Fig. 1. Except for the pressure difference gauge (MKS Baratron type 90; measuring range 10^{-5}—1 torr) its use has been described earlier [1]. Chemisorption was achieved by admitting successive doses of oxygen via stopcock K_1. The resulting heat flows were registered by a strip chart recorder and by a paper tape puncher according to the following data acquisition system



Sampling frequency of the puncher was 0.25 s^{-1}. The pressure drop during the chemisorption of each O_2 dose was registered on a second strip chart recorder.

A total of 45 doses of oxygen were successively admitted to 45 mg of NiO up to an amount of 0.043 mmole O_2. The NiO was prepared from $Ni(OH)_2$ according to the procedure described in ref. 4 and had a specific surface area of about 160 m^2 g^{-1}.

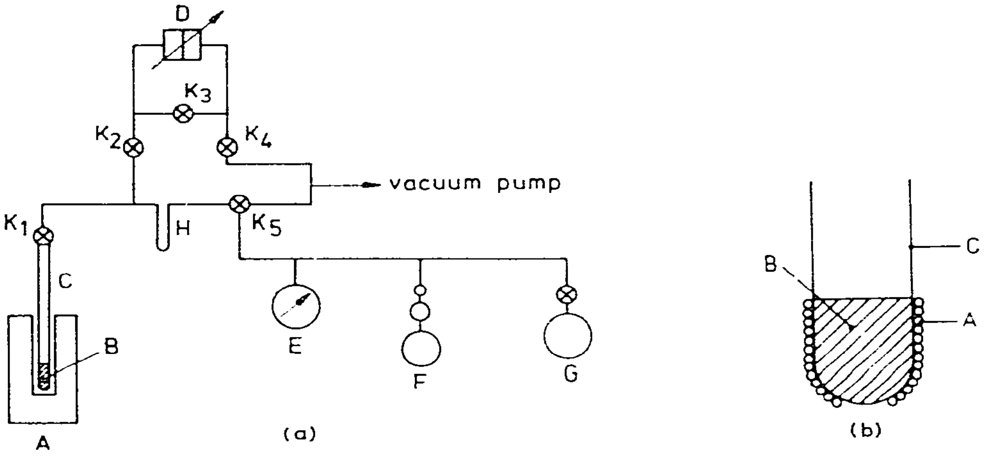


Fig. 1. (a) Schematic picture of the volumetric apparatus connected with the calorimeter. A, Heat flow calorimeter; B, NiO sample; C, reaction tube; D, pressure difference gauge; E, pressure gauge (MacLeod); F, volume calibration burette; G, bulb for oxygen stock; H, liquid nitrogen trap; K_1—K_5 stopcocks. (b) Relative position of resistor and adsorbent sample. A, Electrical resistance wire; B, sample; C, glass tube. The electrically isolated wire is held tightly against the glass wall by means of a temperature-resistant lute.

Calibration

The calorimeter sensitivity was calibrated by evolving a known heat flow by means of the Joule effect in a resistance wire that was wound directly round that part of the glass cell [see Fig. 1(b)] that adjoined the NiO sample. The signal appeared to be proportional to the input at least up to a heat flow of about 1 mW which is more than the values occurring in the adsorption experiments.

Data processing

Deconvolution calculations were performed with the Fourier transform method. Preliminary runs were made on the Télémécanique 2000 computer of the Institut National des Sciences Appliquées at Villeurbanne; eventual runs were made on the PDP-11/45 of the Prins Maurits Laboratorium TNO at Rijswijk. The calculation procedure was the same as mentioned in ref. 5, except for the algorithm of the transformation; presently the procedure proposed by Polge and Bhagavan [6] was followed. This method requires 12 s CPU time for a 512 points transformation.

General discussion on thermogram correction

The solution of the convolution integral (1) constitutes one of the facets of the entire problem of line-shape correction. In the field of calorimetry various mathematically different methods have been successfully applied; some methods may even be transposed into electronic devices (analogous or digital) that operate on line [7—9]. The value of the merely mathematical aspect may be estimated by means of simulated experiments as described e.g. in ref. 10. The practical value of a calculation procedure must be estimated by means of real experiments as performed in ref. 5; then the influence of noise, that may be formidable, is incorporated into the evaluation. In real test experiments both *h* and *f* have to be known, while *g* must be determined independently. A thermal system where heat is generated by means of the Joule effect may be utilized for these test experiments. It is much more difficult to estimate the value of a correction procedure for a chemical reaction system, since the response function of a calorimeter loaded with reagents can be known only approximately; the exact response is hidden in the very experiment. This does not preclude that very useful information on the kinetics of relatively fast chemical reactions may be obtained.

It seems impossible to calculate the response curve of a calorimeter loaded with a chemical system by means of the relevant heat transfer equations even in the highly unlikely situation where the thermal parameters of the system are known; the solution of the differential equations involved would be too complicated on account of the geometry of the materials participating in the heat conduction. For this reason one has to find an experimental method that allows the creation of an arbitrary but well-known input (*f*) and the measurement of the resulting output (*h*).

By means of eqn. (1) the response function *g* may be then calculated, for example, by means of Laplace or Fourier transforms. The experiment has in principle to meet two requirements: (i) the spatial distribution of the heat source must be equal to that during reaction (in practice this usually means that the distribution has to be even over the reagents); (ii) determination must be performed on the very reagents of the reaction of interest (this seems the only warrant that heat flow patterns are not different). The closer the experiment comes up to these conditions, the more true the thermogenesis *f* is reconstructed. It is extremely difficult to estimate how a deviation in the response function affects the accuracy of *f*. Empirical tests again may provide a useful answer.

A universal experimental determination of the response function does not seem possible. Dependent upon the nature of the system one has to choose in each case the conditions that lead to the best approximation of the basic requirements. For gas—solid systems one may create a short-lived adsorption process in the very adsorbent bed to be used during reaction [3]; then the thermal patterns during the response function determination on the one hand, and the experiment proper on the other, are presumably identical. The shape of such a thermogenesis is a truncated exponential; if the period is short enough, this function may be readily described as a block-shaped function having the same total amount of heat. Experiments described in ref. 3 proved that the amount of adsorbate used in the response function measurement had a negligible influence on the reconstruction of the thermogenesis. However, it seems possible that in unfavourable cases gas phase heat conduction may have some influence. This method has been tested again during the present study.

RESULTS AND DISCUSSION

The extent of line-shape deformation is primarily dependent on the relation between two quantities: the response velocity of the instrument and the rate of the phenomenon to be studied. Accordingly, the reconstruction of the thermogenesis requires more precise treatment as the rate is higher.

The adsorption of successive doses of oxygen on a nickel oxide surface at 473 K is a convenient system with which to study the influence of the reaction rate upon the quality of the reconstruction since the overall rate of adsorption of the successive doses decreases as the surface becomes progressively covered by adsorbed oxygen. If, moreover, it is assumed that the primary adsorption step, which causes the oxygen-pressure drop, is rate determining, then a record of the pressure changes will give another measure of the adsorption rate, independent of the calorimetric signal. Under these conditions and by making use of the known physical properties of the chemisorption system, we may therefore check the entire correction procedure in a wide range of velocities.

Determination of the response function

Approximations of the response function were made in two ways. Firstly, by means of the Joule effect, heat was developed in the resistance wire wound round the reaction cell [see Fig. 1(b)]: the heat flux pulse lasted 4 s. Secondly, a first dose of oxygen was admitted to the fresh sample by opening stopcock K_1 in Fig. 1 for 14 s; from previous experiments it was known that the freshly prepared nickel oxide adsorbs oxygen at a very high rate. Both response curves are shown in Fig. 2. The response to the Joule effect is faster than that to the adsorption process; this is logical as the heat source is situated closer to the thermopiles in the former case.

The duration of the applied heat flux pulse is easily accounted for by

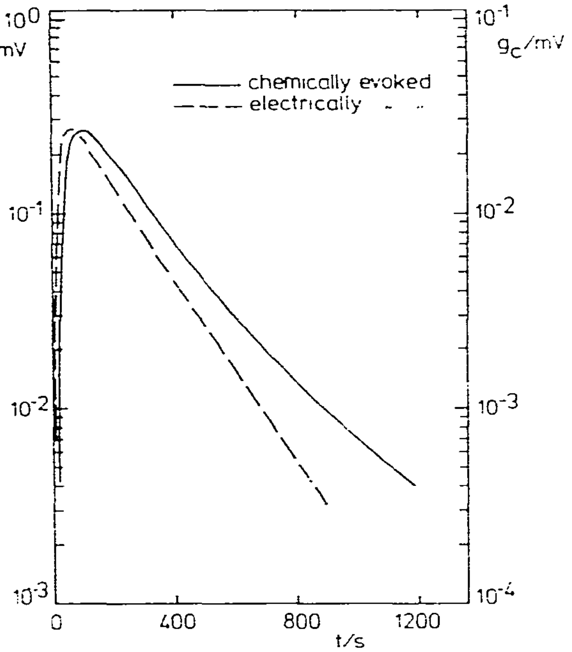


Fig. 2. Two approximations of the response function of the calorimeter loaded with the sample of NiO to be studied. (The curves are not standardized to unit area.)

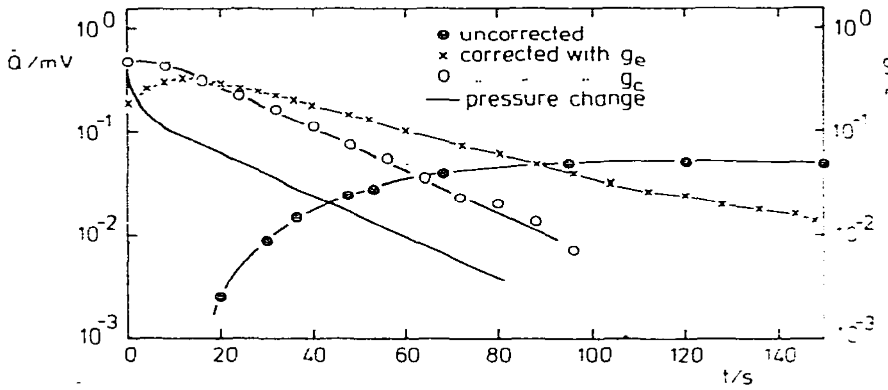


Fig. 3. Reconstructions of the heat flow signal of Dose No. 18 based on the two *g* curves from Fig. 2; the rate curve based on pressure change is also shown. The uncorrected curve has been added as an illustration.

means of eqn. (1). If this equation is applied to one of the two experiments f represents the known input (viz. a block pulse of either 4 or 14 sec) and h is the corresponding output. After transformation of the two members, the transform (G) of the response function (i.e. the transfer function) is found directly

$$G = H_b/F_b$$

where H_b and F_b represent the transforms of the experimentally measured signal and the (known) input, respectively.

If now the corresponding functions of an arbitrary experiment are designated by F and H, it follows easily that

$$F = \frac{H \times F_b}{H_b}$$

Inverse transformation of F now delivers the wanted thermogenesis. The influence of the choice of the response curve appears from the smoothed corrected curves shown in Fig. 3. Oxygen dose number 18 causes a chemisorption which, after about the 10th second, is very well described by a first-order rate equation with a time constant of 22 s, as follows from the pressure drop rate. This curve may serve as a standard. It is clear from comparison with this standard that the correction based on the Joule effect response curve is not satisfactory: the reconstructed calorimetric curve has a time constant that is too long. The response to the electrical block pulse is apparently too fast. The response function calculated from the adsorption block pulse gives a correct reconstruction of the calorimetric curve, both rate curves dp/dt and dq/dt being parallel.

Smoothing

Data-smoothing is necessary, because the reconstructed calorimetric curves are marked by excessive fluctuations. The origin of these fluctuations is found in the background noise, which is, as well as the relevant signal, deconvoluted. Smoothing may be achieved either by convolution with an

TABLE 1

Comparison of O_2 adsorption rate curves with pure exponentials

Formula	O_2 dose No.	Line-shape undistorted after (s)	Shift (s)
$100\exp(-t/10)$	6	35	6
$100\exp(-t/20)$	18	30	3
$100\exp(-t/30)$	30	25	2

appropriate function or by filtering in the Fourier spectrum; essentially these two operations are equivalent [11]. Although it is possible to define severely smoothing procedures with respect to maximization of signal-to-noise ratio, or to optimization of line-shape conservation [12], a more direct method has been found in empirical tests. Smoothing of thermogenesis curves by convolution with the function $(\frac{1}{4}, \frac{1}{2}, \frac{1}{4})$ has been successful in the past [5]; the procedure consists in assigning a new value f_i' to every f_i according to

$$f_i' = \tfrac{1}{4}(f_{i-1} + 2f_i + f_{i+1}) \qquad (2)$$

For the first and last point the total interval is considered to be periodic. A single application of eqn. (2) is a very mild intervention. The optimal number of convolutions is dependent on the specific curves and the nature of the noise.

To establish the influence of $(\frac{1}{4}, \frac{1}{2}, \frac{1}{4})$ convolution on the line shape, calculations have been performed with exponential functions that are reasonably good approximations of experimental rate curves or parts of them. After it had been established that about 15 convolutions sufficiently smoothed the experimental curves, the simulated curves were also subjected to this number of convolutions; the results are shown in Fig. 5. It is seen that line shape is seriously distorted in the starting period. This is to be ascribed to the discontinuity at $t = 0$. Table 1 summarizes the times after which the corrected line shapes are no longer affected by a smoothing procedure of 15 convolutions.

Figure 5 also shows a constant shift in a large interval for exponential line shapes. This shift is characteristic for those intervals where the derivative is monotonously increasing or decreasing. Apparently it has some weight for fast first-order reactions, but is negligible at lower rates. If necessary, due corrections can be made.

Authenticity of the chemically determined response function

The extent of authenticity of the response function is the last factor to be considered. To this end a comparison was made with rate data that were obtained from the pressure changes. Clearly this comparison is only valid for times exceeding those mentioned in Table 1. Figure 4 shows for O_2 dose No. 30 the rates measured both by calorimetry, after reconstruction, and by volumetry. The close resemblance suggests that the same quantity is measured; this holds also for dose No. 18 in Fig. 3. The ratio of $\dot{Q}$ and r_p for

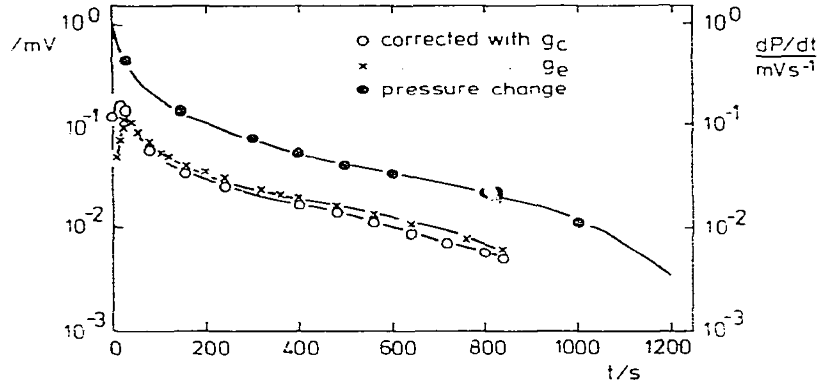
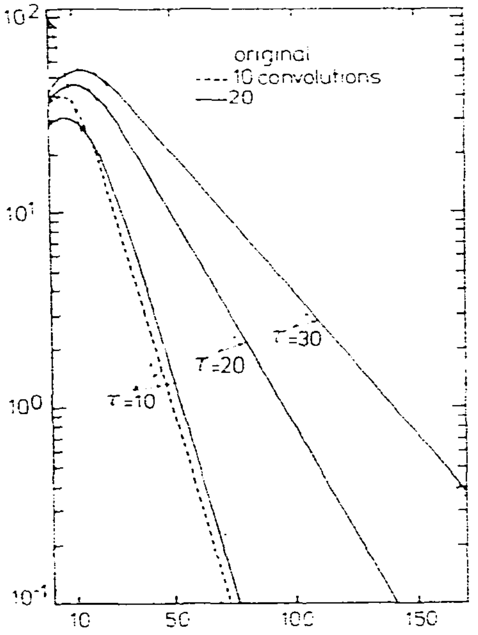


Fig. 4. Reconstructions of the heat flow of dose No. 30 based upon the two *g* curves from Fig. 2 and the rate function based on pressure change.

these experiments is plotted in Fig. 6 as a function of the relative amount already adsorbed as this is given by the pressure change; for slower rates this ratio can be traced to lower conversions. The slight decrease at the end of the conversion for dose No. 30 may be ascribed to a lack of accuracy, as both rate of pressure change and heat flow were then measured near their detection limits. Both curves show little variation in adsorption enthalpy.



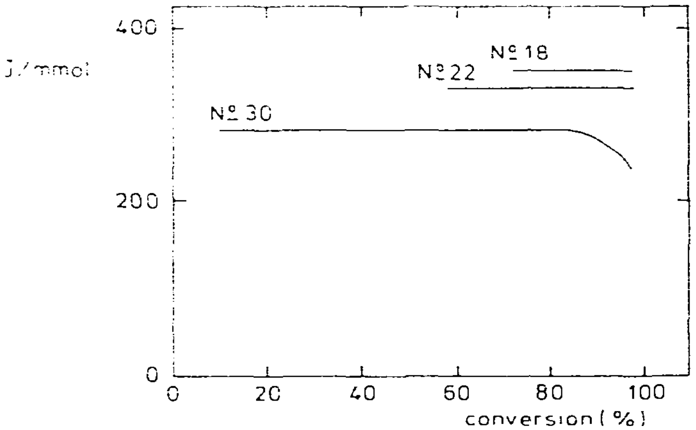


Fig. 5. Exponential functions of the form 100 exp $(-t/\tau)$ after a number of successive convolutions with the function $(\frac{1}{4}, \frac{1}{2}, \frac{1}{4})$.

Fig. 6. Ratio of the corrected heat flow (J s^{-1}) to the adsorption rate (mmole s^{-1}) derived from pressure drop, as a function of degree of conversion. The resulting heat of adsorption is given for three doses of O_2 insofar the heat flow was reliably corrected.

The determination of the mean heat of adsorption for dose Nos. 18 and 30, by integration of the calorimetric curve, allows further argument.

For dose No. 30 the average value 287 kJ mole^{-1} does not differ from the dynamic value (Fig. 6); this means that the heat of adsorption has the same value for the first 10% also (perhaps slightly more if the decrease at the end (see Fig. 6) is real). It also means that at this coverage, there is a perfect parallel between rates of pressure change and heat production.

This proves that the entire correction procedure for the rate of dose 30 operates satisfactorily. On the basis of this conclusion it seems allowed to consider the chemical response curve to be appropriate for the other doses as well. For dose No. 18 the average heat of adsorption (400 kJ mole^{-1}) is considerably higher than the dynamic heat of adsorption of 356 kJ mole^{-1} calculated for the last 25% oxygen that is adsorbed (Fig. 6). This means that there must be a fraction of O_2 that is chemisorbed with higher changes in enthalpy. This result will be more thoroughly discussed in a following article.

CONCLUSION

The procedure presently used to obtain kinetic information from heat flow calorimetry has been proved to be reliable in a wide range of reaction rates. Due to the discontinuity at $t = 0$ the initial part of each reaction rate curve is not well reconstructed; the faster the reaction, the longer this part. A gas—solid reaction with a first-order rate constant of about 0.05 s^{-1} (dose 18) can be followed for its last 28% conversion. A reaction with a first order rate constant of about 0.01 s^{-1} (dose 30) can be followed for its last 90% conversion. The most important points for a reliable correction for line shape broadening are:

(1) the spatial distribution of the heat source during measurement of the response function must be identical to the one during the experiment. Application of a separate adsorption process may be useful in gas—solid reaction systems;

(2) background noise in the experimental curve is greatly magnified by the deconvolution procedure as applied here; it may be abated by filtering the experimental or the corrected curve appropriately;

(3) the experimental curve must often be truncated before the signal has fallen to zero. This causes additional fluctuations in the corrected curve; accordingly, more smoothing may be required;

(4) the necessity to filter the high frequency background noise has a direct consequence for the sampling frequency. It is no use to trace those frequency components that are precluded later on because of noise content.

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