GAS—SOLID INTERACTIONS. GENERAL DERIVATION OF REACTION ENTHALPIES FROM THE DATA OF ISOTHERMAL MICROCALORIMETRY

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(Received 8 April 1980)

ABSTRACT

This paper aims to answer the need for a careful derivation of the thermodynamic quantities from calorimetric experiments carried out on open systems with a gas consumption or evolution. Although the general case of any gas—solid reaction is examined, special attention is paid to the isothermal physisorption (or chemisorption) of a gas (with either discontinuous or continuous introduction) and to the isothermal (or quasi-isothermal) and isobaric evolution of a gas (i.e. in sublimation, vaporization, or thermal decomposition under controlled pressure). Practical conditions to achieve a continuous measurement of the derivative enthalpy of transformation are also given.

INTRODUCTION

A recent paper by Boureau and Kleppa [1] emphasizes the need, in the derivation of thermodynamic quantities from the results of microcalorimetric measurements on gas/solid reactions, to take into account the work done in introducing the gas into the system. As expected, their conclusion is consistent with that previously drawn by Everett [2] and by Letoquart et al. [3] in the case of the calorimetric study of the physical adsorption of gases by solids.

Because of a growing interest in the calorimetric study of gas—solid interactions and because of the special convenience of open reactors (allowing, at will, the introduction or removal of the gas phase), we think it useful to extend our former reasoning to the general case of the microcalorimetric study of gas—solid reactions in an open system, whatever the direction of the reaction (consumption or production of gas) and whatever the nature of the

interactions: weak surface interactions (physisorption), strong surface interactions (chemisorption), bulk interactions (absorption, chemical reaction). Moreover, we will show how, by using special quasi-reversible procedures, it is now possible to take advantage of the high sensitivity and stability of the Tian—Calvet microcalorimeter to follow continuously the enthalpy variation of the system as the reaction progresses.

EXPERIMENTAL CONSIDERATIONS

We focus attention on experiments carried out by means of isothermal microcalorimetry. The word 'isothermal' indicates (in the definition of an 'isothermal calorimeter' previously given [4]) that the temperature of the calorimetric cell (containing the reactants) closely follows that of the surrounding thermostat. In the Tian—Calvet microcalorimeter this is achieved by the high thermal conductance of the thermopiles (made up of several hundred thermocouples) which continuously transmit to (or from) the heat sink (i.e., the thermostat) any heat generated (or absorbed) in the central calorimetric cell. As we shall see, one special feature of this isothermicity, from a thermodynamical point of view, is that it allows under given conditions a reversible exchange of heat between the system under study and the thermostat.

We use the word 'microcalorimetry' to indicate either that the overall amount of heat measured in the experiment does not exceed 0.1 J or that the heat flow recorded never exceeds 10 mW [5]. It is precisely because the heat effects are small that it is necessary to exercise care in the derivation of thermodynamic functions from the raw calorimetric data, and to ensure that, in the case of gas—solid reactions, internal energy changes are not mistaken for enthalpy changes.

One type of experiment examined in this paper is that in which a low-temperature adsorption microcalorimeter is connected with a gas volumetry
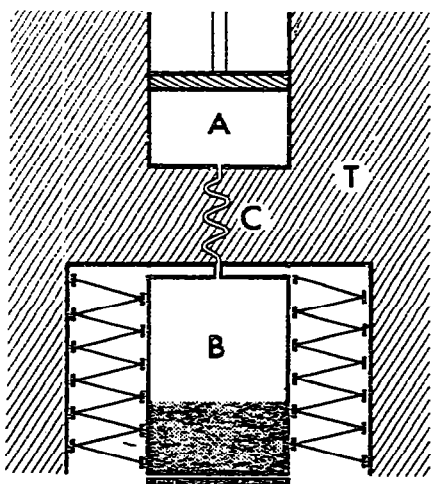

Fig. 1. Schematic arrangement of the apparatus.

apparatus. The experimental device, which is described elsewhere in detail [6—8], is equivalent, from a thermodynamic point of view, to the schematic arrangement of Fig. 1. A cylinder A, closed by a piston, is in contact with a calorimeter cell B containing solid adsorbent through a heat exchanger C of negligible volume. The components A and C are held at a constant temperature by a thermostat T while the temperature constancy of B is maintained by a flow of heat, Q_{ex}, to or from the thermostat through the thermopile which plays the part of a heat flowmeter. The heat flow between A, C and the thermostat need not be known and is not measured. The whole system, ACB, is a closed system; but it may be regarded also as a combination of two open systems (A + C), and B between which gas can be transferred.

There are two ways of carrying out an adsorption experiment with such a calorimeter: either in the conventional way, with discontinuous introduction of the adsorbate, or with continuous introduction of the adsorbate, at a rate which is chosen to be slow compared with the rate of adsorption [9]. With the latter procedure the system is very close, at any time, to true equilibrium, as can be checked experimentally by stopping the gas flow: the pressure then becomes constant and the heat flow recording falls to zero within the time constant of the calorimetric device [10].

Another type of experiment analyzed in this paper is that in which a microcalorimetric study of a thermal decomposition is carried out under a constant residual pressure and with a constant rate of gas evolution. The relevant procedure was described previously [11] under the name of Constant decomposition Rate Thermal Analysis (CRTA).

Both the adsorption and the thermal decomposition experiments considered above provide, at any time, recordings of the gas pressure in the system and of the heat flow produced by the transformation studied.

NOTATION

The notation used here follows in the main the recommendations of the International Union of Pure and Applied Chemistry [12]:

V volume
A_s area
p pressure
T absolute temperature
n amount of substance
Q heat
W work
C heat capacity
U internal energy
H enthaply = $U + pV$
S entropy
R molar gas constant
ν_I stoichiometric coefficient of substance I (negative for reactants, positive for products)

$0 = \Sigma_I \nu_I I$, general equation for a chemical reaction
ξ extent of reaction, $d\xi = dn_I/\nu_I$
$\dot{\xi}$ rate of reaction $= d\xi/dt$

Capital letters are used systematically to represent extensive functions (except for the amount of matter n) while lower case letters represent intensive functions (except for the absolute temperature T and the molar gas constant R).

It follows that for each extensive function X there is a corresponding intensive function x which may be defined by X/n *. We also suggest the use of $\dot{x}$ to represent the partial derivative $(\partial X/\partial n)$ of function X with respect to the amount of matter n **.

A letter used as a superscript, on the right-hand side, indicates the state of the substance: g for the gaseous state, s for the solid state, a for the adsorbed state ***.

Any variation in a state function, resulting from a change of state, is represented by the operator Δ followed by an appropriate subscript on the right-hand side: here we use 'ads' for an adsorption, and 'rct' for a chemical reaction.

ANALYSIS OF EXPERIMENTAL RESULTS

Our practical aim is, starting from the thermal flow $\phi = \partial Q\text{ex}/\partial t$ recorded under given experimental conditions (e.g., T and V constant, but in an open system), to calculate the variation of a state function characterizing the reaction being studied.

The blank experiment

Here the thermal effect is measured in an experiment in which — in the absence of any heterogeneous reaction — a given amount of gas, already at the temperature of the thermostat, is introduced to the calorimetric cell.

To establish a relationship between an increase Δp of the gas pressure (between times 0 and t) and the heat effect $Q\text{ex}$ measured in the calorimeter ($Q\text{ex} = \int_0^t \phi \, dt$), we consider, in Fig. 1, the system filled with a given amount of gas (constant n) but with no reacting solid. The pressure increase Δp is then supposed to be obtained by depressing the piston. When the transformation is carried out in a reversible way, the temperature is uniform in the whole system which receives an amount of work expressed as a function of

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* When we wish to stress that the intensive function is a mean quantity, we represent it by $\bar{x}$.
** The quantity $\dot{x}$ is related to $\bar{x}$ by the relationship: $\dot{x} = \bar{x} + n\partial\bar{x}/\partial n$.
*** In the particular but frequent case of the adsorption of only one gas by a solid adsorbent at sufficiently low pressures, the 'surface excess amount of adsorbed substance', n_i^σ, and the 'amount of adsorbed substance', n_i^s, defined by Everett [13] become equivalent and we represent them, in a simplified notation, by $n^a = n_i^s \simeq n_i^\sigma$.

the pressure p of the gas phase according to

$$W = -\int p \, dV_{AB}$$

which becomes, since T and n remain constant, and we assume the gas to be ideal

$$W = \int V_{AB} \, dp = \int (V_A + V_B) \, dp$$

This work is transformed completely into heat (Q) but part only (Qex) of this is measured by the thermopile.

Provided the compression of the gas is slow enough to be a practically reversible process, we may accept that the ratio of the amounts of heat Qex/Q is equal to the ratio of the volumes $V_B/(V_A + V_B)$. It therefore follows that

$$Q\text{ex} = -V_B \, \Delta p \tag{1}$$

a relationship given previously [3] and which agrees with those of Ward [14], Smith and Ford [15] and Beebe et al. [16].

To establish the experimental conditions under which the assumption of reversibility is acceptable, a set of microcalorimetric experiments were made in which the heat effects corresponding to the introduction or extraction of various amounts of gas were followed as a function of the gas flow rate. For that purpose, a cylindrical glass bulb (of 27 cm³ internal volume) was located in the measuring thermopile of a low-temperature adsorption microcalori-meter [6], itself immersed in liquid nitrogen. The bulb was connected with a volumetric apparatus by means of a 70 cm length of glass capillary (2 mm

TABLE 1

Thermal effect due to the introduction (or extraction) of gas into (or out of) the calorimetric bulb

Vol. gas introduced into (or extracted from) the bulb (cm³ at STP)	Time elapsed during intro-duction or extraction of gas (min)	Mean gas flow rate (μmole) min^{-1})	Pressure (Torr)		Qex (mJ)	Deviation (%)	V_B (cm³)
			p_i	p_f			
+3.0	1	+144	0	25.67	91.2	12.6	26.6
−3.0	1	−144	25.67	0	80.5		23.7
+4.0	2	+100	0	35.52	122.6	9.6	26.6
−4.0	2	−100	35.52	0	111.6		24.2
+1.6	2	+40	0	14.09	48.1	1.2	25.6
−1.6	2	−40	14.09	0	48.7		25.9
+4.0	6	+32	0	33.77	113.2	1.9	25.1
−4.0	6	−32	33.77	0	115.3		25.6
+3.0	6	+24	0	25.67	89.2	0.2	26.1
−3.0	6	−24	25.67	0	89.0		26.0

internal diameter), also immersed in the cryogenic bath, which served as a thermal exchanger. The results are reported in Table 1. The first two columns allow the calculation of the mean flow rate of gas (introduced or extracted), given in column 3. It may be seen that, under our experimental conditions, this flow rate must be reduced to a value of 24 μmole min^{-1} [i.e. 0.5 cm^3 (STP) min^{-1}] in order to give rise to similar thermal effects (within 2%) during the gas introduction and the gas extraction procedures. The last column gives the volume V_B as derived from the heat effect and from eqn. (1), which is to be compared with the volume of 27.13 cm^3 obtained by distilled water weighing.

These results show the importance of a satisfactorily reversible procedure if one is to calculate correctly the thermal effect due to the compression of the gas. The need for such slow gas flow rates is peculiar to calorimetric experiments: it is not necessary in the more common situation in which the solid—gas reaction is followed either by volumetry or by gravimetry.

Physical adsorption of a gas by a solid

The amount of heat measured during an adsorption calorimetric experiment depends critically on the experimental conditions. This was first pointed out by Hill [17] and more recently by Everett [13], who stresses that a very careful analysis of the procedure used is needed to obtain the integral energy of adsorption * $\Delta_{ads}U$: the latter may be defined as the experimental thermal effect when the adsorption is carried out by connecting a constant volume gas reservoir with a constant volume outgassed absorbent reservoir, both vessels being immersed in the same calorimetric cell. It may be expressed in terms of the integral molar energy $\overline{u}^a$ of the adsorbed substance and of the internal molar energy of the gas u^g as follows

$$\Delta_{ads}U = n^a(\overline{u}^a - u^g)$$

The accepted convention is that the adsorbent is inert and therefore does not contribute to the variation of any state function X which is supposed to result only from a change occurring in the adsorbate. In practice, as we now show, the measurement may be carried out in an open system which may be represented by part B of the system of Fig. 1. The initial state consists of the system including the solid adsorbent plus the adsorbable substance (partly in the gas phase and partly in the adsorbed phase).

Discontinuous introduction of gas. We have already shown [3] that in the case of a discontinuous adsorption experiment (provided that at each step the gas is introduced under nearly reversible conditions) the integral energy of adsorption between an initial state I and final state F can be derived from the experimental data according to

$$[\Delta_{ads}U]_i^f = (Q\text{ex})_{T,V} + V_B \Delta p + RT \Delta n^a$$

where $(Q\text{ex})_{T,V}$ is the experimental thermal effect, measured in an open sys-

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* This quantity was, for a long time, called 'integral heat of adsorption' and denoted Q_{int}.

tem, at constant volume and temperature, during the adsorption of Δn^a moles; V_B is the part of the volume of the adsorption bulb which is immersed in the thermopile and corresponds to part B of the cylinder of Fig. 1; Δp is the increase of the equilibrium pressure in the system.

For the first adsorption run, carried out on outgassed adsorbent ($p_i = 0$, $n_i^a = 0$), the above relationship becomes

$$\Delta_{ads}U = (Qex)_{T,V} + V_B p + RTn^a \tag{2}$$

We note that if we employ the Gibbs definition [18] of surface quantities for which $V^a = 0$, the enthalpy of the adsorbed substance defined as

$$H^a = U^a + pV^a$$

coincides with its internal energy. It then follows that

$$\Delta_{ads}U - RTn^a = n^a[\overline{u}^a - (u^g + RT)] = \Delta_{ads}H$$

where

$\Delta_{ads}H = n^a(\overline{u}^a - h^g)$ is the integral enthalpy of adsorption [13]. The above relationship (2) then becomes

$$\Delta_{ads}H = (Qex)_{T,V} + V_B p \tag{3}$$

We thus conclude that both the integral energy and integral enthalpy of adsorption may be correctly calculated from the determination of the thermal effect measured during an isothermal adsorption in an open system of constant volume.

Continuous introduction of gas. In this type of experiment, the gas is introduced at a constant flow rate into B

$$\frac{dn}{dt} = f = \text{const.}$$

Part of the gas is adsorbed. The remainder increases the pressure in the gas phase, which fills the volume $V^g = V_B - V^s$, where V^s is the volume of solid. We may then define a 'flow rate of adsorbed substance' according to

$$\frac{dn^a}{dt} = f^a = f - \frac{V^g}{RT}\frac{dp}{dt}$$

The overall flow rate f of entering gas is slow enough to ensure, at any time, the achievement of an equilibrium pressure in the system. The corresponding thermal flow may be expressed by differentiating eqn. (2)

$$\phi = \left(\frac{\partial Qex}{\partial n^a}\right)_{T,A_s}\left(\frac{\partial n^a}{\partial t}\right)_{T,A_s} = f^a\left[\left(\frac{\partial(\Delta_{ads}U)}{\partial n^a}\right)_{T,A_s} - RT - V_B\left(\frac{\partial p}{\partial n^a}\right)_{T,A_s}\right]$$

The bracketed term on the right-hand side of this equation was called, for a long time, 'isothermal heat of adsorption'; it corresponds to the amount of heat received by a system which reversibly adsorbs, at constant T and A_s, 1 mole of adsorbate.

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It is more useful to obtain a derivative enthalpy of adsorption defined in ref. 13 by

$$\Delta_{ads}\dot{h} = \left[\frac{\partial(\Delta_{ads}H)}{\partial n^a}\right]_{T,A_s} = \left(\frac{\partial U^a}{\partial n^a}\right)_{T,A_s} - h^g$$

and usually called 'isosteric heat of adsorption'. This may be done by differentiating eqn. (3)

$$\Delta_{ads}\dot{h} = \left[\frac{\partial(\Delta_{ads}H)}{\partial n^a}\right]_{T,A_s} = \frac{[\phi + V_B\, dp/dt]}{f^a} \tag{4}$$

Thus from a continuous recording of the equilibrium pressure p and of the thermal flow ϕ, it is possible to follow continuously the derivative enthalpy of adsorption $\Delta_{ads}\dot{h}$ as a function of the coverage. The latter equation may even be simplified, in the special case when the slope dp/dt may be considered as negligible ('vertical' portion of the isotherm), to

$$\Delta_{ads}\dot{h} = \frac{\phi}{f} \tag{5}$$

The above procedure has already been shown to be effective, allowing us to detect two-dimensional phase changes of nitrogen or argon adsorbed on graphite [19,20].

General case

The derivation of thermodynamic quantities from low-temperature adsorption calorimetric experiments may be extended to the case of any solid—gas heterogeneous transformation carried out in an open system, at constant volume. As previously, the system is supposed to be defined as the calorimetric cell B (Fig. 1). Let us assume that, in the initial state, the system contains only the solid reactant R.

We then add to the system an amount Δn_G of gas G (taken at a temperature T with an internal molar energy u_G^g) which reacts with R following the stoichiometric equation (supposed to be the only one possible between R and G)

$$\rho R + \gamma G = \pi P$$

where P is a condensed product.

Part of gas ($\gamma\xi$ if ξ is the extent of reaction) is involved in the reaction. The remainder Δn_G^g increases the pressure in the system by Δp. The work received by this open system, at T and V constant, may then be written

$$W = RT(\Delta n_G^g + \gamma\xi) = V_B\,\Delta p + RT\gamma\xi$$

Now if $(Q ex)_{T,V}$ is the heat measured during this transformation, the internal energy variation of the system is then

$$\Delta U = (Q ex)_{T,V} + W + u_G^g(\Delta n_G^g + \gamma\xi)$$

This variation of internal energy could also have been written

$$\Delta U = (\pi u_P - \rho u_R)\, \xi + u_G^\xi\, \Delta n_G^\xi$$

u_P and u_R being the internal molar energies of substances P and R taken at temperature T.

It then follows that

$$(Q\text{ex})_{T,V} + V_B\, \Delta p + RT\gamma\xi + u_G^\xi\gamma\xi = (\pi u_P - \rho u_R)\, \xi$$

or, since

$$\pi u_P - \rho u_R - \gamma u_G^\xi = \sum_I \nu_I u_I = \Delta_{\text{rct}}u$$

where $\Delta_{\text{rct}}u$ is the molar energy of the single reaction considered

$$(Q\text{ex})_{T,V} + V_B\, \Delta p = (\Delta_{\text{rct}}u - \gamma RT)\, \xi \qquad (6)$$

This very general equation allows one to derive the energy of reaction of a solid—gas system from the thermal effect measured by isothermal calorimetry.

In the gas phase the molar enthalpy h_G^ξ is defined by $h_G^\xi = u_G^\xi + RT$, the gas being assumed ideal, while in the condensed phases R and P, we may assume that internal energy and enthalpy are identical. Therefore,

$$\sum_I \nu_I u_I - \gamma RT = \sum_I \nu_I h_I = \Delta_{\text{rct}}h$$

Equation (6) then becomes

$$(Q\text{ex})_{T,V} + V_B\, \Delta p = (\Delta_{\text{rct}}h)\, \xi \qquad (7)$$

which is equivalent to that given by Boureau and Kleppa [1] in the case of the oxidation or hydrogenation of a metal.

In the special case when the transformation is carried out under constant pressure ($\Delta p = 0$), eqn. (7) simplifies into

$$Q\text{ex} = (\Delta_{\text{rct}}h)\, \xi \qquad (8)$$

Although we have only examined above the case of a solid—gas reaction involving a consumption of gas, the same reasoning holds for the case of an evolution of gas. When the latter takes place under a constant pressure (e.g., in a sublimation, a vaporization or in a thermal decomposition carried out under controlled or atmospheric pressure) then eqn. (8) again applies. The symmetry of the situation goes even further. Indeed, advantages similar to those of a continuous introduction of gas at constant flow rate (which, as we saw, allows one to follow continuously the derivative enthalpy of adsorption $\Delta_{\text{ads}}h$ as a function of the coverage) may be found in a thermal decomposition experiment followed by calorimetry, provided the rate of gas production by the reaction is monitored in a suitable way. In such a case, we may hope to follow continuously the derivative enthalpy of reaction $\Delta_{\text{rct}}h$ as a function of the extent of reaction ξ. As we show hereafter, this is the case with the 'Constant decomposition Rate Thermal Analysis' procedure [11]. Here, the sample under thermal decomposition is heated (by an appropriate control loop) at a temperature just enough to keep the rate of production $f = \mathrm{d}n^\xi/\mathrm{d}t$ of the gas phase at the constant level required. That rate is usually

controlled from the pressure drop through a diaphragm leading to a vacuum line. Since it is kept constant, then the rate $d\xi/dt$ of the reaction producing the gas is also constant. The symmetry towards a constant rate adsorption experiment is not total, since here the experiment is not isothermal (the temperature being allowed to increase in such a way as to keep the reaction rate constant) whereas, instead, the pressure is kept constant. We must then consider that the heat flow received by the system must be expressed in terms of T and ξ according to

$$\phi = \frac{\partial Qex}{\partial t} = \frac{\partial Qex}{d\xi} \frac{\partial \xi}{\partial t} + \frac{\partial Qex}{\partial T} \frac{\partial T}{\partial t} \tag{9}$$

Now

$$\frac{d\xi}{dt} = \dot{\xi} = \frac{f}{\nu_G} \text{ (rate of reaction producing gas G)}$$

and

$$\frac{dQex}{dT} = C \text{ (heat capacity of the calorimetric cell + its contents)},$$

and

$$\frac{dT}{dt} = \beta \text{ (heating rate)}$$

It follows, on combining eqns. (8) and (9), that

$$\phi = \frac{\partial}{\partial \xi} [(\Delta_{rct}h) \xi] \frac{f}{\nu_G} + C\beta \tag{10}$$

The derivative enthalpy of reaction may be defined as

$$\Delta_{rct}\dot{h} = \frac{\partial}{\partial \xi} [(\Delta_{rct}h) \xi]$$

Equation (10) becomes

$$\phi = \Delta_{rct}\dot{h} \frac{f}{\nu_G} + C\beta$$

or

$$\Delta_{rct}\dot{h} = \frac{\nu_G}{f} (\phi - C\beta) \tag{11}$$

Therefore, we have a means of calculating the derivative enthalpy of reaction, from the calorimetric heat flow recording $\phi = f(t)$, at any time of the thermal decomposition. The term $C\beta$ may be calculated but it may often be neglected, either because the use of a 'differential' calorimeter allows most of that term to be cancelled out by the introduction of a compensating heat capacity in the reference cell or because the actual heating rate is small (which happens in the 'vertical' parts of the thermal analysis curve, usually corresponding to the main steps of the thermolysis). When one step of the thermolysis may be

described as a single reaction ($\rho R = \pi P + \gamma G$) then the derivative enthalpy of reaction $\Delta_{rct}\dot{h}$ is constant throughout the step (being equal to the molar enthalpy of reaction $\Delta_{rct}h$) and so is the thermal flow $\phi = (\partial Qex/\partial t)_{T,P}$. This situation was indeed observed in the thermolysis of gibbsite $Al(OH)_3$ [8] where, under the experimental conditions indicated above (constant p and f), we detected two successive plateaux of the heat flow (recorded as a function of t and therefore, here, of ξ). The first one (loss of 0.5 H_2O per $Al(OH)_3$) is ascribed to a partial transformation into boehmite

$$Al(OH)_3 = AlOOH + H_2O \quad (\text{with } \dot{\xi}_1 = f)$$
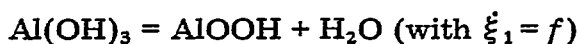
The second (loss of one more H_2O per $Al(OH)_3$) is ascribed to the transformation of the remaining gibbsite into porous and partly hydrated alumina

$$Al(OH)_3 = \tfrac{1}{2}Al_2O_3 + \tfrac{3}{2}H_2O \quad (\text{with } \dot{\xi}_2 = \frac{2f}{3})$$
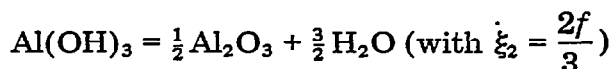
The molar reaction enthalpies (referred to 1 mole of H_2O) corresponding to each step may then be written

$$\Delta_{rct}h_1 = \frac{\phi_1}{f} = 50 \pm 2 \text{ kJ mole}^{-1}$$

$$\Delta_{rct}h_2 = \frac{3}{2}\frac{\phi_2}{f} = 77 \pm 3.5 \text{ kJ mole}^{-1}$$

CONCLUSIONS

The calorimetric study of a heterogeneous solid—gas transformation may be conveniently carried out by the introduction (or extraction) of gas to (or from) a calorimetric cell which plays the part, with its content, of an open system of constant volume. If care is taken to use an isothermal calorimeter, one directly reaches a transformation enthalpy. If, moreover, the apparatus used has the sensitivity of the Tian—Calvet microcalorimeter, it then becomes possible, thanks to an experimental procedure which is both continuous (in order to follow accurately the progress of the reaction) and very slow (in order to ensure continuously satisfactory equilibrium conditions), to derive at any time the derivative enthalpy of transformation. This may be a powerful tool to separate or analyze successive reactions (for instance in a multi-step thermolysis) or to detect weak and short events (for instance a two-dimensional phase change during the course of an adsorption).

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