Advances in hydride phase growth: Automatic high precision calorimeter-volumetric devices, for thermodynamic and kinetics analyses

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A new automatic apparatus has been specifically developed for investigating phase transformations in hydrogen absorbing intermetallic compounds, providing accurate characterizations of the thermodynamic properties as well as of the dynamic aspects of the hydride phase growth over a wide range of pressures 0–4 MPa and temperatures 250–800 K. It consists essentially of a heat flow calorimeter coupled with high precision volumetric devices. The ensemble constitutes of a closed system in which high purity hydrogen gas within the system is transferred between hydrides reservoirs and reactors with high thermal transfer capacity. The excellent stability of the signal of the calorimeter, ±4 nV over a long period of time (>10 days), allows one direct measurement of the heat of H₂ absorption or desorption during a scan of an hysteresis loop with an average accuracy of 1%. To maintain quasi-isothermal conditions during the transformation, a reliable control of the temperature inside the sample is insured by optimizing the hydrogen gas flow rate. Simultaneously the heat flux, pressure, temperature, composition data collected have been used to obtain kinetic parameters through two different and complementary techniques. The first one is based on an analysis of the measured heat flux evolved during the reaction which gives the true rate law at the sample level by deconvolution of the measured signal. It is shown that only overall information can be expected by this method. The results of the numerical treatment raise the problem of the location of the heater used for calibration of the calorimeter. The second technique takes into account the component volumes of the system. Here, the time variation of hydrogen mass flow (excitation of the system) and hydrogen pressure in the reactor (response of the system) is analyzed in the frequency domain which requires knowledge of the experimental transfer function of the volumetric equipment. In the complex plane, the shape of the transfer function appears as a signature of a proposed mechanism. ZrNi–H₂ and LaNi₅–H₂ systems have been used to demonstrate the detailed analysis. © 2000 American Institute of Physics. [S0034-6748(00)05401-0]

I. INTRODUCTION

Intermetallic compounds–H₂ systems (IMC–H₂) have been extensively studied over the past several decades. Today the importance of these systems is found in several applications where a well-defined property of the system satisfies a specific goal, i.e., chemical reactivity for getters, temperature-pressure relationship for fire detectors, or hydrogen storage capacity converted into electrical current in metal hydride batteries. A recent review of hydride applications may be found in Ref. 1. Possible applications cover a wide temperature range, from a few Kelvin up to 500–600 K, and therefore their accurate and extensive thermodynamic characterization is always of paramount importance. IMC–H₂ systems are usually investigated volumetrically using the so-called Sievert’s type apparatus and to a lesser extent using gravimetric analysis or calorimetry. Nevertheless if special precautions are not taken there are difficulties in obtaining reliable thermodynamic data for IMC–H₂ systems, mainly because the dynamic aspects of the hydride phase growth have been overlooked. A new experimental apparatus has been specifically designed for investigating phase transformations in IMC–H₂ systems. The apparatus allows strict control of the variables correlated to the phase growth, leading to precise and complete determination of the thermodynamic properties and simultaneously the kinetics of the reactions.

The paper is organized as follows: the basic problems related to the thermochemical characterisations of IMC–H₂ are discussed, the experimental set-up and several results are presented confirming the potential of the approach.

II. THERMOCHEMICAL PROPERTIES OF IMC–H₂ SYSTEMS

From a technological viewpoint, the thermochemical reactivity concerns the IMC–H₂ system in its fully activated state obtained by repeated hydriding/dehydriding cycles. The activated state is a mechanically disrupted finely divided powder, whose particle sizes are of the order of few dozen of microns or less. One has to characterize the thermodynamic behavior of highly defective materials, where the formation-decomposition of hydride compounds are accompanied by hysteresis as for nearly all first order phase transitions.

Whatever the application, the important property is the “plateau pressure” which corresponds to the coexistence of two condensed phases. Assuming reversible and equilibrium conditions, the Gibbs phase rule gives a variance of one for two components, H and IMC, and three phases, one gas...
phase and two solid phases. For the two coexisting solid phases, the hydride grows according to the reaction:

\[(b-a)^{-1}MH_a + \frac{1}{2}H_2(\text{plat},g) \rightarrow (b-a)^{-1}MH_b,\]  

(1)

where \(a, b\) correspond to the hydrogen contents at the phase boundaries expressed as \(H/M\) and the subscript \(\text{plat}\) indicates that the system is in a two phase region. The following well known relations are deduced:

\[\Delta \mu_{\text{plat}} = \mu_{H,a} - \frac{1}{2} \mu_{H_2} = \mu_{H,b} - \frac{1}{2} \mu_{H_2} = \frac{1}{2}RT \ln(p_{\text{plat}}).\]  

(2)

The relative chemical potential, \(\Delta \mu_{\text{plat}}\), represents the standard Gibbs energy change for reaction (1) while the hydrogen gas is at 1 atm, \(MH_a\) and \(MH_b\) in their standard states. Thus,

\[\Delta H_{\text{plat}} = \frac{d(\Delta G^f/T)}{d(1/T)} \quad \text{or} \quad \frac{[\Delta H_{\text{plat}}]}{R} = \frac{1}{2} \frac{d \ln(p_{\text{plat}})}{d(1/T)}.\]  

(3)

The latter equation is referred to as the van’t Hoff equation and relates the amount of heat evolved (absorbed) during the process of formation (decomposition) of the hydride phase, to the plateau pressure. In a first step, \(\Delta H_{\text{plat}}\) can be taken to be a reasonable approximation of the heat of formation of a hydride, \(\Delta H^f\) as an estimation of the stability of the hydride. The errors introduced are due to the extension of the domains of the solid solution and of the nonstoichiometric hydride, for which the integration of the relative partial heat of solution in each domain is neglected. Recently Luo and Planagan\(^3\) drew a series of correlations for checking the consistency between the thermodynamic data and the phase diagrams for metal hydride systems. Finally Eq. (2) takes the form

\[\frac{1}{2} \ln(p_{\text{plat}}) = \frac{\Delta H^f}{RT} - \frac{\Delta S^f}{R},\]  

(4)

where \(\Delta S^f\) is the entropy of formation. Equation (4) is widely applied to estimate the appropriateness of a given IMC in an application, although its use is restricted to situations where approximate calculations are needed. Due to hysterisis the thermodynamic behavior encountered in real systems is more complex. For example, isothermal hysterisis is illustrated by the fact that thermodynamic paths for the processes of hydride phase growth or hydride phase decomposition are different, leading to pressure and phase boundaries changes such that

\[p_{\text{abs}} > p_{\text{des}}, \quad a_{\text{abs}} > a_{\text{des}}, \quad b_{\text{abs}} > b_{\text{des}}.\]

Equations (1)–(3) should be written for each process, while phases diagrams should be established for absorption and desorption processes. This has been done for the first time for the Pd–H\(_2\) system\(^4\) in 1987, for temperatures higher than 300 K. Only metastable states are reached during phase precipitation because the equilibrium state is unknown. For isothermal conditions, the degree of irreversibility produced per cycle is given by the free energy loss:\(^5\)

\[\Delta G_{\text{loss}} = \frac{1}{2} RT \ln \frac{p_{\text{abs}}}{p_{\text{des}}}.\]  

(5)

This energy is dissipated into the surrounding as heat, and gives the total entropy production per cycle:

\[\int dS = \frac{\Delta G_{\text{loss}}}{T}.\]  

(6)

Equation (6) suggests that stationary metastable states and reproducibility could be satisfied if one is able to find the appropriate parameters which generate a constant minimum entropy production per cycle. Disregarding different values of the ratio \(p_{\text{abs}}/p_{\text{des}}\) due to artefacts\(^6\) or influence of the size of the aliquot of hydrogen\(^7\) in determining isotherms, non reproducibility in the thermodynamic properties results from experiments that are mainly carried out with undefined parameters. These parameters, internal or external to the system, lead to various time-dependent metastable states. Finding the experimental conditions of growth which minimize Eq. (6), will produce the available thermodynamic states characterising a powdered hydride compound. Once these conditions are satisfied, it will then be possible to initiate the kinetic analysis.

III. INSTRUMENTAL

A. General

In order to study IMC–\(H_2\) systems, one should consider the problems created by a powdered activated sample and the presence of hysterisis. Due to the low thermal conductivity of the powder, strong nonisothermal behavior has been observed.\(^8\)–\(^10\) This may lead to drastic temperature gradients within the sample which in turn may induce metallic diffusion and disproportionation of the compound. The thermal ballast technique (mixing the powder with an inert high conductivity material) is not adopted here because it only apparently solves the problem. In fact, the temperature rise at the particle level remains driven by the overpressure over the sample and, of course, by the heat transfer from the mixed powder sample. Assuming that the state of the system is located somewhere on an isothermal hysteresis loop, reversing the hydrogen mass transfer will cause the system to move into the hysteresis loop. As a consequence, signal modulation (pressure, temperature) cannot be achieved because of the nonreversible character of the solid phase transformation. Thus, to fulfill isothermal conditions and to access to the kinetics of the reaction, the main parameter of concern is the dynamic of the flowing gas.

B. Equipment description and principle

A schematic overview of the equipment is shown in Fig. 1. The ensemble is located in a thermostated laboratory whose fluctuations do not exceed 0.2 °C. High purity hydrogen gas is supplied from two hydride reservoirs (HRs), whose gas pressure is set by adjusting the temperature of the reservoirs. With regard to hydrogen transfer, the apparatus operates as a closed system where the same hydrogen gas is recycled. The HRs communicate with either the low pressure or high pressure volumetric devices, which in turn communicate with either of two reactors (in the thermostatic bath or in the calorimeter). In principle, the equipment operates as
follows: for absorption the hydrogen gas pressure is set in one HR, it is transferred from the HR to one reactor via a reference volume chamber. During desorption, hydrogen is transferred backward to one or the other HR, depending on the pressure level requested. The ensemble is controlled by two computers, connected via a serial port. The different studies which can be performed, simultaneously or not, are

(i) pressure, composition, temperature analysis (isotherms),
(ii) direct measurement of the heat evolved (calorimeter)
(iii) kinetic studies,
(iv) dynamic transfers between the two hydride beds.

1. Mechanical assembly

A detailed view of the high pressure gas distribution assembly, together with the reactor used in calorimetric measurements is given in Fig. 2. Aside from the different ranges of the pressure gauges, the low and high pressure gas distribution are identical in terms of conception, management of the valves and thermal isolation. The gas handling system, including hydride reservoirs, reactors, are made of electropolished stainless steel 316L. The different sample holders, inside the reservoirs and reactors are machined with OFC copper. Permanent junctions are welded, while removable elements, such as reactors, supports for thermocouples (case of failure), pressure gauges (for calibration) are connected with VCR-type fittings. Fast response chromel-alumel thermocouples (THERMOCOAX), are mounted in situ at various places of the distribution line, and within the reactors.

The reactors are designed to optimize heat transfer with the surroundings. If space is available, as for the thermostatic bath, a flat type reactor is used. The reactor assigned to the calorimeter is schematically drawn in Fig. 2. It consists of four parts: the head, the inner rod, the sample holder and the chamber body (height=850 mm, o.d.=22 mm, i.d.=20.6 mm). The head supports the thermocouples and the platinum resistor (PtR) used as a heat source for electrical calibration of the calorimeter. After positioning the thermocouples and the PtR, the inner part (o.d.=20.4 mm, i.d.=5 mm) is screwed into the head. Two guides, threaded at both ends, are located at the bottom of the inner rod. These guides serve to hold together the flat disks (mainly to fill up empty space, reinforce gas convection), and the sample holder made of 10 copper plates (o.d.=20.4 mm, i.d.=19.4 mm, h=4 mm). The head, inner rod and sample holder constitute one single rigid piece that fits exactly into the body of the reactor. The mass of the sample loaded in each copper plate is of the order of 100–200 mg, corresponding to a thickness of few tenth of mm for a powdered sample. The superposition of 10 plates makes an exchange surface area of 25.62 cm², providing a sample holder of very high thermal transfer capacity, which is fully embedded within a 92 cm² surface covered by the heat flux sensors.

2. Metrology

a. Pressure measurements. Pressure gauges of high accuracy are used for the volumetric systems, i.e., 0.01% full
scale (MENSOR 0–0.11 MPa), 0.05% (HEISE 0–50 kPa and 0–4 MPa, MKS 0–1.5 MPa). The pressure in hydride reservoirs is controlled by 0.1% transducers (Keller 0–0.2 MPa and 0–4 MPa). Due to the excellent temperature regulation of the laboratory, all the instruments operate with maximum accuracy, fulfilling their specifications, i.e., long term stability, reproducibility, and accuracy.

b. Temperature readings. Fast response thermocouples have been calibrated at three temperatures, (boiling water, melting temperatures of tin and lead). The thermocouples are connected to a module including a cold junction compensation based on a high precision PR100. Their analogue signals are fed into the data acquisition system (MESS MDP82 with GPIB interface). The highest accuracy (±0.1 °C) is obtained with a 24V dc power supply external to the MDP and with integration time of 60 ms for the slowest conversion mode.

c. Calorimeter. Compared with the calorimeter described in Refs. 11 and 12, only the thermopiles have been retained. A new compact furnace has been designed contributing to a better stability of the signal delivered by the thermopiles. Temperature regulation of the furnace has been greatly improved by adjusting the power supply to the control loop in such a way that the regulator (EUROTHERM 900HP) always operates with the highest sensitivity. The signal output of the thermopiles is amplified through a digital nanovoltmeter K182 (KEITHLEY). Fluctuations do not exceed 4 nV. A continuous base line shift of more than 10 nV over two hours can be attributed either to some anomalous behavior or to a true small heat effect. These performances had to be satisfied before undertaking the studies which require permanent operation of the equipment for about ten days in order to complete hysteresis loop.

3. Uncertainties in the measurements

a. Computation of the number of moles. Since the mass balance of hydrogen gas is based on volumetric measurements, there are possible errors associated with the values of the volumes and with the pressure and temperatures measurements. Of course, the system has to be leak free. The ensemble was tested with a helium detector and no leaks were detectable. Finally, the “tightness” of the equipment was checked by loading each component with hydrogen gas, and following pressure changes over a period of one month. No change in the pressure readings were observed.

The number of moles of gas is known at any instant assuming ideal gas law behavior for pressure not exceeding 0.5 MPa. Above that value, compressibility factors are introduced to take into account deviations from the ideal behavior. The volumes were calibrated by the classical gas release method from a known reference volume, \( V_{\text{ref}} = 48466 \text{ mm}^3 \pm 2 \text{ mm}^3 \). During volume calibrations, the pressure scans a 50–100 kPa range with a relative error of \( 2 \times 10^{-4} \) (MENSOR transducer). At room temperature, the relative error introduced by temperature readings amounts to \( 4 \times 10^{-4} \), considering all the chain, calibration of the thermocouple, accuracy of the cold junction compensation and conversion. Thus, the maximum relative error in volume determination is \( 1.25 \times 10^{-3} \). Finally, for perfect isoenthalpic conditions over all the volumes, the expected error in the computation of the number of mole of hydrogen gas will be of the order \( 2 \times 10^{-3} \). Above room temperature, the temperature gradients within the reactors must be taken into account. The reactors have been partitioned in several volumes, \( \Delta V_j \), delimited by thermocouples. According to this partitioning, the number of moles is calculated for a linear temperature gradient along the vertical axis in the considered section, whose temperatures at the extremities are \( T_{j+1} \) and \( T_j \). It can easily be shown that each volume contribution is obtained through:

\[
n_{1m}^j = \frac{P \Delta V_j}{R} \ln \left( \frac{T_{j+1}}{T_j} \right) .
\]

The difference in the computation of the same number of moles enclosed in the reactor at 298.15 and 550 K indicates that the final relative error should not exceed \( 5 \times 10^{-3} \).

b. Calibration of the calorimeter. To evaluate the uncertainties in the heat measurements, it is important for solid-gas reactions to clarify some points of the calibration procedure of the calorimeter. In principle, it should be routine, however, the choice of the method, as well as its validation require careful preliminary studies in order to evaluate the calibration coefficient, \( ke(\text{J nV}^{-1} \text{ s}^{-1}) \). The amount of energy \( Q(J) \) dissipated by the reaction is given by

\[
Q(J) = ke \int_0^t E(t) \, dt, \tag{8}
\]

where \( E(t) \) is the output signal detected by the thermopiles.

With regard to the thermopiles, the reacting chamber is an open system, in which gas flows in or out. Since the thermal conductivity of the gas depends on pressure and temperature, a calibration must be established for the pressure and temperature domains studied. Note, that by construction, the sample holder is in good contact with the bottom of the reactor, while there is only a loose contact with the walls of the reactor because of need for a minimum space for introduction of the inner part of the reactor. This assembly makes the system sensitive to the gas pressure because heat is transmitted through the wall both by the sample holder and the gas. If the thermal conductivity, and thus thermal losses, markedly change during the course of the reaction, then erroneous heats may be obtained despite the accuracy of the calibration coefficient.

To carry out calibrations over a wide range of pressure and temperature and to duplicate as much as possible the experimental conditions without perturbing the system, a platinum resistance (PtR) is used as a heater. It is made of two 100 \( \Omega \) resistances mounted in parallel, covering 35 mm of the 40 mm height of the sample holder. Current is supplied by a laboratory made constant source, which delivers a constant current in a rheostat before switching to the PtR probe, avoiding sharp changes at the closing of the electrical circuit of the PtR probe. The voltage and current are measured through the classical four point method. Typical calibration curves are plotted in Fig. 3 for a heating power of 3.4 mW and 5.4 mW. The correlation between \( ke \) and pressure
dependence of errors into the thermodynamic parameters. The temperature above 100 Pa, while below 100 Pa, measurements indicate a large scattering in the thermograms. The computational heat are negligible in comparison to the errors resulting from the integration of the signal. Although the thermogram, is slightly increased due to the unavoidable baseline shift of the signal. We can expect a minimum error of the order of 1.5%. On the other hand, in the two phase region, a maximum accuracy, 1%, is expected for the heat measurement since no baseline shift occurs.

C. Computer control: Software

The software was written in PASCAL 6.0. Each type of experiment is monitored by a program calling the different subroutines required by the instrumentation in use. A main executable module calls a configuration file which contains all the parameters controlling the experiment. This file is important because it gives access to the experimental conditions of any earlier experiments and to their corresponding data files. The parameters can be modified at the first call of the program, an experiment being fully characterized by the configuration file and the data output files. Management of the experiment is based upon cutting one run into 5 phases, to avoid loss of information in case of accidental, power or other failure. Each phase is characterized by a file which stores the different variables of the previous phase (\( \phi \), \( P \), \( T \), and composition. After a failure, the system is able to restart at the phase (\( \phi \)-1) and only a part of the dynamic information would be lost. Phase 1 is checking the state of the system that must be identical to the state of the system in Phase 5. If \( \Delta T, 0.2^\circ C \) and \( \Delta P \leq 10 \text{ Pa} \) (low pressure system), or \( \Delta P \leq 1 \text{ kPa} \) (high pressure system), the program moves to phase 2, otherwise it stops. Phase 2 corresponds to the filling (withdrawal) of hydrogen gas. This is realised through an algorithm which already acts at the end of phase 3 to anticipate and to adjust the temperature and, as a consequence, the pressure in the selected hydride reservoir. The \( P,T \) data collected at this level characterize the initial state of the experiment. Phase 3 corresponds to the reaction. The counter-timer is reinitialised at the opening of the pneumatic valve to synchronise all the data collection coming out from the different instruments. Phase 4, the pneumatic valve opened, and phase 5, the pneumatic valve closed, characterize the final state. Computation of the mass balance in Phase 4 gives the amount of gas that has been absorbed (desorbed). Phase 5 duplicates the calculation of phase 4, but is necessary to make the correction imposed by the presence of the dead volumes owing to the bellows of the pneumatic valves.

IV. MEASUREMENTS AND SIGNAL PROCESSING

To demonstrate the system for high temperature thermodynamic studies, ZrNi–H\(_2\) system was chosen whose phase diagram indicates the presence of two hydrides,\(^{13}\) a triclinic monohydride phase ZrNiH and an orthorhombic trihydride phase ZrNiH\(_3\). Besides demonstrating the equipment, we proposed to determine the temperature dependence of the enthalpies of formation of the hydrides and to clarify the phase diagram over the 300–500 K temperature domain. This information is needed for this system which is important for its potential applications for hydrogen or tritium storage technology or in closed-cycle hydride cryocoolers.\(^{14}\) A full report of the thermodynamic studies will be published elsewhere,\(^{15}\) and here the presentation is limited to the dual aspect of thermodynamic measurements and to the thermokinetic information which can be derived. Data are collected using the low pressure apparatus coupled to the calorimeter.

FIG. 3. Examples of calibration thermograms of the heat flow calorimeter: a known square heat pulse is produced for 1 h, \( T = 55^\circ C \). The continuous line represents the calculated responses by use of Eq. (18).

FIG. 4. Temperature dependence of the calibration constant showing the sensitivity increase of the signal with increasing temperature.
Next it will be shown that the time evolution of the hydrogen mass flow can be analyzed in the frequency domain, bringing new insight into a complementary kinetic approach. The analysis will be made on the prototype LaNi₅-H₂ system for which isotherms were obtained with the high pressure volumetric equipment.

A. Enthalpy measurements

1. Sample and experiment preparation

The work has been performed with two different batches. The first intentionally contains traces of cerium oxyde (~1%) making the compound more brittle. The second batch is an ingot of very high purity, which needed to be spark machining in order to cut small pieces. Before running the ‘true’ experiments, a series of preliminary tests were carried out to establish the experimental procedures related to the activation process, the sequential loading of hydrogen doses and to the total withdrawal of hydrogen from the sample before starting a new series of measurements. The process of activation concerns the initial uptake of hydrogen by the sample. The first uptake of hydrogen started almost at the same temperature, 81 and 83.4 °C, respectively, for samples 1 and 2.

The setting of the needle valve is optimised for two reasons. The first one is linked to the determination of a maximum acceptable flow rate of hydrogen which will insure quasi-isothermal conditions. The second one concerns the maximum power dissipated during the reaction since the heat flow rate has to remain in the linear regime of response of the calorimeter. A compromise has been found allowing steps in H/M of 0.005 minimum dose for accurate heat detection up to 0.07 H/M with accepted maximum temperature rises at the sample level of 0.5 °C. The flow of gas across the needle valve was found to obey Poiseuille’s law under the experimental conditions which characterises a laminar flow.

2. Results

We restrict the presentation of results to the experiments carried out at 210.6 °C. They represent three series of measurements across the second β⁺γ two phase region, with the formation-decomposition of the nonstoichiometric trihydride, ZrNiH₃₋δ. The raw data from the second absorption (series 3) are plotted in Fig. 5 and the parameters characterizing the thermodynamic states are shown in Fig. 6, for all series.

The superposition of the calorimeter responses for 12 sequential additions of identical doses of hydrogen, series 3, is shown on the top of Fig. 5. Doses of hydrogen are added every 150 minutes, for a step in sample composition of δH/M~0.050. The responses shown in Fig. 5 imply an excellent control of the hydride growth. The accuracy of the measurements allows any small modifications in the shape of a thermogram to be detected, making the method particularly suitable for precise determinations of the phase boundaries of the system. Time variation of the pressure inside the reference volume and inside the reactor, as well as the time variation of the temperature inside the reactor, are reported for the reaction between points a and b in Fig. 6. During the reaction the overpressure on the sample does not exceed 1.5 kPa. 90% of the amount of gas is absorbed within 12 min, indicating the strong reactivity of the activated sample. Despite the high thermal conductivity of the copper sample holder, a temperature increase of 0.5 °C of the sample was recorded by th1 (bottom of Fig. 5) the other thermocouples, e.g., th3+th4

FIG. 5. Top: the observed responses of the calorimeter for twelve sequential additions of identical doses of hydrogen. Below: typical pressure and temperatures variations collected during the reaction. P₁ and P₂ represent pressure variations inside the low pressure gas distribution and the reactor, respectively. Bottom: temperature variation inside the sample. Location of the thermocouples th1 can be seen in Fig. 2.

FIG. 6. Isotherms and enthalpy across the second plateau region, corresponding to the formation (ΔHβ⁺γ), decomposition (ΔHγ⁻β) of the nonstoichiometric γ trihydride, ZnNiH₃₋δ. The vertical lines indicate the phase boundaries. Series 1 corresponds to the initial uptake of hydrogen by the sample. T=210.6 °C.
(see Fig. 2 for location) remain quite stable within $\pm 0.05\, ^\circ C$.

The enthalpy for trihydride formation—decomposition and the isotherms are reported in Fig. 6. Series 1 data represent the system behavior at the end of the activation procedure. The system being already in the two phase region, the quasi-static states have not yet been reached up to H/M = 1.3 for the imposed time duration of the experiment. The transformation being not complete, the pressure remains higher than the plateau value and the enthalpy cannot be taken to characterize trihydride formation. Above that concentration, the activation process seems to be achieved. Next, hydrogen is desorbed with steps of 0.005, series 2, followed by a second set of absorption data, series 3. In the pressure versus composition graph, series 2 and 3 represent a partial loop within the two phase region.

Based on the two absorption plateaux, the free energy dissipation of hysteresis calculated from Eq. (5) is relatively large 2.38 and 1.61 kJ/mol H for the activation and the second absorption, respectively. The corresponding relative enthalpies of transformation are almost equal within the experimental error: $-34.0 \pm 0.35$ and $-34.2 \pm 0.35$ kJ/mol H. Similar behavior was reported by Luo et al.\textsuperscript{16} for the LaNi$_5$–H$_2$ and Pd–H$_2$(D$_2$)\textsuperscript{17} systems. Explanations have been given to justify this result by Flanagan et al.\textsuperscript{17} The decomposition enthalpy values are slightly more scattered, due to the smaller doses of hydrogen withdrawn. Nevertheless, within the experimental error, the hydride decomposition enthalpy, $-34.4 \pm 0.45$ kJ/mol H, is equal to the formation enthalpy, as expected.$^{18}$ The formation enthalpy measured calorimetrically at 50 $^\circ C$ by Luo et al.\textsuperscript{19} amounts to $-34.0 \pm 0.45$ kJ/mol H. Taking into account our results of the 226 $^\circ C$ studies, one can conclude that no significant temperature dependence of the enthalpy is measured over 180 $^\circ C$, implying that over that range, the summation of the heat capacities contributions cancel out. This will be discussed in detail elsewhere.$^{15}$ It has been demonstrated that with a strict control of the growth of the solid hydride phase, it is possible to characterize precisely the thermodynamic states of nonequilibrium systems.

B. Thermokinetics

Thermokinetics is the field which covers the determination of a reaction rate by measuring the course of heat released with time.$^{20}$ In principle, analysis of this heat flux should yield kinetic information, but it is seldom utilized in this way, i.e., information is unutilized. The signal measured being delayed in time, one must reconstruct the digital signal delivered by the nanovoltmeter to obtain the true rate law. It can be done with the knowledge of the dynamic characteristics and the transfer function of the calorimeter.

1. Modeling of the calorimeter

The classical way of modeling linear systems, such as the response of the thermopiles, is to use transfer functions, based on Laplace’s method. The measuring element is conceived as a black box characterized by a function $z(t)$ which transforms the input signal, the rate of heat production $q'(t)$ into the output response, rate of change of the thermopiles signal $u(t)$. The mathematical relation between $q'(t)$ and $z(t)$ is given by the convolution product:

$$u(t) = q'(t) * z(t).$$  \hspace{1cm} (9)

By use of the convolution theorem, it is possible to deconvolute the response of the calorimeter, i.e., to determine $q'(t)$ from the recording of $u(t)$:

$$L[q'(t) * z(t)] = U(s)Z(s)$$

$$= \frac{U(s)}{Z(s)} = L^{-1}\left[Q'(s)\right] = L^{-1}\left[ \frac{U(s)}{Z(s)} \right].$$  \hspace{1cm} (10)

$L$ is the Laplace operator, $s$ the complex variable of the transformed functions, while $Z(s)$ is the transfer function, expressed in V s J$^{-1}$.

To determine the expression of $Z(s)$, a model has to be used. The calorimeter is usually modeled through electric equivalent circuits, where the temperature is equivalent to the voltage and the heat flux to the electric current. Each element of the calorimeter along the thermal path is represented by an electric RC element (parallel connection) and by interconnecting a sufficient number of elements. The resistance $R$ accounts for the thermal resistance and the capacity $C$ accounts for the thermal capacity of the equipment. Two RC elements are used to derive $Z(s)$. The Laplace transform of Eqs. (11), voltage drop across a resistor and a capacitor, provides the individual expression of the transfer function of each element (12), which allows the calculation of the impedance of each RC circuit (13). Finally the global transfer function of the modeled calorimeter is obtained (14)

$$e_R(t) = Ri(t), \quad e_C(t) = \frac{1}{C}q(t) = \frac{1}{C} \int_0^t i(t)dt$$  \hspace{1cm} (11)

$$Z_R(s) = \frac{E_R(s)}{I(s)} = R, \quad Z_C(s) = \frac{E_C(s)}{I(s)} = \frac{1}{sC}$$  \hspace{1cm} (12)

$$Z_1(s) = \frac{R_1}{1 + \tau_1s}, \quad Z_2(s) = \frac{R_2}{1 + \tau_2s}$$  \hspace{1cm} (13)

$$Z(s) = Z_1(s) + Z_2(s)$$

$$= \frac{K(1 + \tau_3s)}{(1 + \tau_1s)(1 + \tau_2s)} \quad \text{with} \quad K = R_1 + R_2,$$

$$\tau_3 = \frac{R_1R_2(C_1 + C_2)}{R_1 + R_2}. \hspace{1cm} (14)$$

The constants $\tau_1 = R_1C_1$ and $\tau_2 = R_2C_2$ have units of time, while $\tau_3$ represents an interaction time constant between the two RC circuits. The constant $K$ has the same units as $Z(s)$, V s J$^{-1}$. This is the ratio of the steady state response of the system $u_0$ to the steady state heat flux perturbation $q_0'$. Knowing the transfer function, and the input signal, an analytical expression of the response signal $u(t)$ can be obtained through the calibration measurements, which are also used to determine the parameters $K$, $\tau_1$, $\tau_2$, and $\tau_3$. Figure 3 shows typical responses of the calorimeter to a known square heat pulse generated by Joule heating. In the time domain, the heat pulse can be written as:

$$q'(t) = q_0'[y(t-t_0) - y(t-t_1)]. \hspace{1cm} (15)$$
where \( y(t-t_1)=0 \) for \( t<t_1 \) and \( y(t-t_1)=1 \) for \( t\geq t_1 \). Laplace transformation of Eq. (15) gives:

\[
Q'(s) = \frac{q'_0}{s} [e^{-t_0 s} - e^{-t_1 s}].
\]  

(16)

Therefore, the response of the electrical equivalent circuit to a heat pulse is obtained in the transformed domain from Eqs. (10), (14), and (16):

\[
U(s) = \frac{Q'(s)}{Z(s)} = \frac{u_0}{s} \left[ e^{-t_0 s} - e^{-t_1 s} \right] \times \frac{(1 + \tau_2 s)}{(1 + \tau_1 s)(1 + \tau_2 s)}.
\]  

(17)

Inverse Laplace transformation of Eq. (17) gives the response \( u(t) \) of the equivalent circuit:

\[
\begin{align*}
\frac{u(t)}{u_0} &= y(t-t_0) \left[ 1 - \frac{\tau_1 - \tau_3}{\tau_1 - \tau_2} e^{-(t-t_0)/\tau_1} + \frac{\tau_2 - \tau_3}{\tau_1 - \tau_2} e^{-(t-t_1)/\tau_1} \right. \\
&\left. \times e^{-(t-t_0)/\tau_2} - y(t-t_1) \right] 1 - \frac{\tau_1 - \tau_3}{\tau_1 - \tau_2} e^{-(t-t_1)/\tau_1} \\
&+ \frac{\tau_2 - \tau_3}{\tau_1 - \tau_2} e^{-(t-t_1)/\tau_2}. 
\end{align*}
\]  

(18)

The graph of \( u(t) \), expressed in J s\(^{-1}\) as given by Eq. (18), is plotted in Fig. 3 after adjusting it to the experimental data. The fit is obtained by using a non-linear least-square routine, the Levenberg–Marquardt method, allowing calculation of the parameters for each temperature studied. The values are used to deconvolute the responses of the calorimeter measured during the \( \beta+\gamma \) phase transformation of the ZrNi–H\(_2\) system.

2. Deconvolution

Deconvolution of the response of the calorimeter measured during hydrogen absorption is achieved by use of Eq. (10). In the particular case where \( \sigma=0 \), \( s=\sigma + j \omega \), the Laplace transformation is equivalent to the Fourier transformation which is more convenient to use. The response signal of the calorimeter is sampled at constant time intervals \( \Delta t = 4 s \). The discrete time dependent signal is then numerically Fourier transformed. The Fourier transform of the deconvoluted signal \( Q'(s) \) is calculated for each frequency component. Finally, the inverse Fourier transformation of \( Q'(s) \) yields the desired deconvoluted signal \( q'(t) \).

Results of the numerical treatments are plotted in Fig. 7 altogether with the recorded signals. The curves clearly show the smearing effect of the calorimeter which spreads out the heat flux in time. The desmeared curves should correspond to the true rate law for phase transformation at the sample level for the given needle valve position. The treatment has also been applied to demonstrate the effect of the operating temperature on the kinetics of trihydride formation. The results are shown in Fig. 8 for the same mass of hydrogen absorbed. A clear increase of the transformation rate is evidenced upon increasing the operating temperature, the heat generated by the reaction becoming negligible after 25 min. and 15 min. at 191.2 and 226 °C, respectively.

![Image](image-url)
ated by the reaction. The numerical treatments are correct, but the parameters derived from the calibration do not corre-
respond to those which would be expected if the heat had been released directly within the sample. It is particularly true for the highest value of the parameter $\tau_1$ which contributes to the sharp increase at the short time scale. These remarks are important because the results are not restricted to our equipment, but to any equipment with built-in electrical calibration whose the heat is not released directly within the sample. In that case thermokinetics analysis is restricted to give important, but overall information as seen above, or useful to establish relative comparisons between the absorption and desorption processes. Kinetics analysis can still be attempted as it is shown in the following.

C. Kinetics studies in the frequency domain

The problems encountered in the studies of the kinetics and mechanisms of hydriding reactions have been examined by Minz and Zeiri,\textsuperscript{22} complemented recently by Bloch.\textsuperscript{23} Concerning IMC–H\textsubscript{2} systems, most of the earlier experimental studies have produced empirical rate laws which are valid for the specific equipment and sample morphologies used by the authors. There generally have been difficulties in maintaining isothermal conditions. In order to eliminate the temperature increases, Gray\textsuperscript{24} applied a small sinusoidal modulation of the hydrogen gas pressure in a high pressure microbalance. Unfortunately, due to the sinusoidal modulation, this technique is restricted to the studies of reversible reactions. Kinetic studies utilizing the frequency response method have appeared in solid-gas reactions around the 1960s for sorption measurements, permeation through membrane, and gas diffusion in catalyst.\textsuperscript{25}

1. Frequency analysis developed for a volumetric device

If the isothermal character of the reaction is maintained, the kinetic information included in the time-dependent hydrogen pressure is correlated to the mechanisms involved during the hydrogenation of the compound. Consider a volumetric system in which the reaction occurs in several steps. In a stationary regime of perturbation, the slowest step will control the overall kinetics. In the time domain, no distinction between mechanisms will be possible. On the other hand, if the transfer function of the equipment is known, we can move into the frequency domain where the analysis of a transient signal allows, in principle, to distinguish the different steps according to their frequency. In the experiments, the applied perturbation is the flow rate of hydrogen gas, $dn/dt$ and the response is the overpressure over the sample, $P_{H_2}(t)$. As in the previous section, modeling of the transfer function is based on an electrical analogy. Here the pressure (or chemical potential) is equivalent to the voltage, the mass flow of gas to the electrical current. Finally, from comparison between the model and the experimental transfer function it should be possible to identify the different kinetic parameters characterizing the reaction.

2. Transfer function of the sample free system

The gas distribution of the experimental set up is described schematically in Fig. 10. We have seen that due to the presence of hysteresis, a periodic excitation was not suitable and as a consequence a nonperiodic perturbation of a small amplitude was applied. Thus, by imposing a constraint on the direction of the perturbation, $dn/dt>0$ for absorption and $dn/dt<0$ for desorption, the system can now be qualified as linear over a definite domain. We introduce a system which obeys a piecewise linear behavior. According to these assumptions, which are satisfied in these experiments the impedances of the needle valve, $Z_1$, and of the reactor, $Z_2$, must be known before introducing the contribution of the sample. $Z_1$ and $Z_2$ are given by

$$Z_1(s) = \frac{L[P_1(t) - P_2(t)]}{L[dn/dt]}, \quad Z_2(s) = \frac{L[P_2(t)]}{L[dn/dt]}.$$  

(19)

$Z_1(s)$ and $Z_2(s)$ can be obtained numerically by expanding a known amount of gas from $V_1$ into the empty reactor through the needle valve (Fig. 10). Using the property of laminar flow, it is possible to derive an analytical expression for $dn/dt$ by solving Poiseuille’s law (20a). $P_1(t)$ and $P_2(t)$ are solutions of the nonlinear ordinary differential equation of the Ricatti type (20b).

$$\frac{dn}{dt} = \frac{K \cdot V}{RT} [P_1(t) - P_2(t)],$$  

(20a)

$$\left\{ \begin{array}{l} \frac{dP_1}{dt} = - \frac{K \cdot V}{V_1} [P_1(t) - P_2(t)] \\ \frac{dP_2}{dt} = \frac{K \cdot V}{V_2} [P_1(t) - P_2(t)] \end{array} \right.$$  

(20b)
with $K_V$, a constant characterising the needle valve. For the sake of simplicity, the solution is written for the particular case, where $V_1 = V_2$ with the initial conditions $P_1 = P_1^0$ and $P_2 = 0$.

$$\frac{dn}{dt} = \frac{K_V}{RT} (P_1^0)^2 e^{bt}.$$  \hspace{1cm} (21)

with $b = 2(P_1^0/V_1) K_V$. After Laplace transformation of $P_2(t) - P_1(t)$, and substitution into Eq. (19), with $s = j \omega$, the transfer functions are obtained for each element:

$$Z_1(\omega) = \frac{RT}{K_V P_1^0}.$$  \hspace{1cm} (22)

The total transfer function of the equipment is given by

$$Z(\omega) = + R_N + \frac{1}{\omega C}$$

with

$$R_N = \frac{RT}{K_V P_1^0} \text{ Pa s mol}^{-1}, \quad C = \frac{V_2}{RT} \text{ mol Pa}^{-1}. \hspace{1cm} (23)$$

$R_N$ represents the mass resistance of the needle valve which is similar to an electrical resistance and $C$ represents the mass capacitance of the reactor, similar to an electrical capacitance. In Fig. 11(a) the transfer function is represented in the complex plane. The graph of $Z(\omega)$ is a segment parallel to the imaginary axis whose the high frequency limit is on the real axis and has the value $R_N$. The equivalent electric circuit of the device being a resistance connected in series with a capacitance, the reaction can now be treated by this analogy as an alternative to gas accumulation inside the reactor. Therefore the transfer function associated to the reaction, $Z_{\text{sample}}$, either in the solid solution or in the two phase region, is represented as an electric module in parallel to the capacitance of the reactor, Fig. 11(b). Any volumetric equipment will have such an equivalent circuit, if the conditions of transfer are comparable with the above assumptions. It becomes possible to compare the dynamics of the reactions from different equipments.

### 3. Parametric analysis of the model transfer function

The method will be applied to the kinetic analysis of the solid solution domain. To interpret the experimental transfer function, one needs a diffusion model which assumes the existence of two steps mechanisms occurring in series. The first one includes all the surface phenomena. They are introduced by a linear flux-force relation equivalent to a resistor, $R_S$. The second one corresponds to the diffusion process into the bulk, $Z_D$, giving the total sample impedance $Z_{\text{sample}} = R_S + Z_D$. Finally, applying the elementary rules of combination of electric dipoles to the equivalent circuit of Fig. 11(b), the global transfer function is given by

$$Z_T(\omega) = R_N + \left[ \frac{1}{j \omega C_{\text{reactor}}} + \frac{1}{R_S + Z_D} \right].$$  \hspace{1cm} (24)

The expected form of $Z_T(\omega)$ from Eq. (24) can be anticipated with regard to the geometrical parameter of the sample and to the capacitance effect of the reactor. To compensate for the fact that morphology of the powder is unknown, it is assumed that the three cases of diffusion in a plane, a sphere or a cylinder. $Z_D$ has been calculated assuming that Fick’s law of diffusion is obeyed. The details of the calculations are found elsewhere. The graph of $Z_T$, Fig. 12, is for the three different geometries of the grains. Each point is calculated for a different frequency. In the most favorable case, the graph will present three distinct regions. The high frequency domain is characterized by a semicircle along the real axis. This contribution is independent of the shape of the particles in which diffusion occurs. The intercept at the highest frequency gives the resistance to flow, $R_N$, while the diameter represents $R_S$, the resistance related to surface mechanisms. Oxidation of the sample surface should cause an increase of this value, and this will decrease if the size of the grains decrease with a concomitant increase of the specific area of the sample. The medium linear segment and the vertical line represent the contribution of the mechanism of diffusion. In the low frequency domain, $Z_D$ takes the form:

$$Z_D(\omega \rightarrow 0) = R_d + \frac{1}{j \omega C_d} \text{ with } \tau_d = R_d C_d = \frac{\delta^2}{x D_H}.$$

where $R_d$ and $C_d$ are respectively the resistance and the capacitance related to the diffusion of $H$ in the compound, the
product $R_SC_d$ being related to the $H$ diffusion coefficient in the bulk sample. The sensitivity of the model to the impact of the dead volume of the reactor, $C_{\text{reactor}}$, can be tested by varying the ratio $C_{\text{reactor}}/C_d$, Fig. 13. This graph shows clearly that the different reaction steps are well separated in the frequency domain if the dead volume is minimized, allowing a quantitative determination of the parameters.

4. Experimental transfer function

The method is applied to the $\alpha$ solid solution of the LaNi$_5$–H$_2$ systems. The isotherm determinations were carried out with the high pressure equipment coupled with the thermostatic bath (Fig. 1). The measured temperatures inside the sample remained within ±0.15°C. To observe relaxation phenomena, data were collected over 10 h, making the measurements appropriate to the studies of diffusion within the sample. The transfer function has been obtained numerically. The results are plotted in Fig. 14. The similarities between experimental and ideal behavior, Figs. 12 and 13, support the validity of the modeling. With regard to the range of frequency over which the transfer function is obtained, the minimum and maximum values depend only on the experimental conditions. The minimum values depend on the time required to reach equilibrium, while maximum values are directly related to the sampling frequency. According to the experiments, the analysis is spread out over a rather narrow range, from $10^{-2}$ mHz up to few mHz, as compared with electrochemical processes whose bandwidth extends from 1 mHz up to few hundreds of kHz. Nevertheless, the semicircle is present as for the ideal case, but the medium region does not show a real marked segment. According to Fig. 12, this might be due to the random distribution in the particle size as well as to the undefined shape of the particles; according to Fig. 13 it would suggest that the contribution of the dead volume is relatively important. This can be solved by increasing the mass of the sample.

As for the numerical treatment of the signal of the calorimeter, the precision of the method is weighted by the same numerical problems. Here the digital raw pressure data show fluctuations of small amplitude (precision of the sensor) which now will be present in the high frequency range of $Z_T$. The validity of the analysis may be tested directly from information derived from the plot. Thus, the high frequency semi circle, the characteristic frequency at the top of the circle ($0.63$ mHz) can be determined, as well as the value of $R_S$, diameter of the circle ($1 \times 10^{10}$ Pa mol$^{-1}$ s). Since $\tau_c = R_SC_{\text{reactor}}$, the capacitance contribution $C_{\text{reactor}}$, can be obtained. When this value is substituted into Eq. (23), with $T = 278$ K, $V_2$ amounts to $59 \pm 3$ cm$^3$, compared with $60.012$ for the true value. The large uncertainty in $V_2$ is largely due to the uncertainties in determining precisely the characteristic frequency. Making use of Eq. (25) in the low frequency region, a value for the global hydrogen diffusion coefficient has been estimated knowing that the grain size distribution of the sample was centered around 100 $\mu$m. Taking this value for $\delta$, $D_H$ was found to be of the order of $1 \rightarrow 3.5 \times 10^{-5}$ cm$^2$ s$^{-1}$, consistent with other values reported in the literature.

These first results demonstrate the interest of this novel approach for solid gas reactions. Improvements can be made to extend the frequency range over which the signal can be analyzed. The shape of the excitation signal has to be optimised and observations must be extended into the high frequency region to access more fully the surface phenomena. We are currently developing this type of analysis for the phase transformation.

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