Determination of the enthalpy of phase change materials by inverse method from calorimetric experiments. Applications to pure substances or binary solutions.

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Abstract. The aim of this paper is to present an inverse identification method to determine specific enthalpy of PCM from calorimetry experiments. We will focus on the cases of pure substances and ideal binary solutions including the eutectic equilibrium. The corresponding direct model, based on energy balance, is first presented. A classical enthalpy method is then used, which presents the advantage of easily decoupling the thermal transfers from the specific energetic behavior of the material (i.e. thermodynamical phenomenon). In the second part of the paper, we will present the used inverse method (genetic algorithms). The sensibilities of the different parameters for the identification are analyzed. Finally, we will present the identification from DSC experiments (1) at different rates of heating for pure substances and (2) at different concentrations of aqueous solutions of NH₄Cl. In each case, we identify the thermodynamical parameters of the model and compare the corresponding thermograms with the experimental ones. A good agreement is obtained for both cases.

1. Introduction
Among the possible methods to store strong densities of thermal energy in a reduced volume, the use of phase change materials (PCM) is largely recommended. It is particularly the case in thermal improving of buildings integrating PCMs. The modeling of the energetic and thermal behavior of such buildings requires a fine knowledge of the phase transition processes. The commercial computer codes often use apparent characteristics. The use of differential scanning calorimetry (DSC), which is the most currently experimental method encountered [1, 2], to evaluated these works ones leads to wrong estimations as we will show hereafter.

Generally, the enthalpy is given by a simple integration of the DSC thermogram [3]. In essence, the power-compensated DSC measures the power difference between a sample cell containing the material to characterize and an empty reference cell. These two cells are maintained at the same plate temperature $T_p(t)$, which is generally a linear function of time $T_p(t) = T_{init} + \beta \cdot t$ where $\beta$ is the heating rate.

This historical approach is not correct for two main reasons. First, the thermogram, which is a measure of the heat flow rate transferred from the sample to the plate of the calorimeter,
Figure 1. Experimental thermogram for water at 5 K min\(^{-1}\).

Figure 2. Erroneous (dashed) and exact (line) enthalpy curve for pure water.

not only depends on the thermodynamical properties but also of the thermal transfers inside the sample. Secondly, the thermogram is a function of time even if it is often presented as a function of \(T_p\) (since this one depends on time). Furthermore, the error is that the temperature of the sample is neither uniform nor equal to the temperature of the plate.

We can summarized this as following [4]:

\[
\phi(t) \text{ is not proportional to } \frac{\partial h}{\partial T} \quad (1)
\]

A good example is the fusion of pure water. Fig. 1 shows the experimental thermogram of a 7.8 mg pure water sample heated at a rate of \(\beta = 5 \text{ K min}^{-1}\) (Pyris Diamond Perkin-Elmer DSC). If we consider that this thermogram represents the derivative of the enthalpy over temperature, we obtain the dashed curved enthalpy profile shown in Fig 2. The raw analysis leads to consider that water melts over 0\(^\circ\)C and 7\(^\circ\)C, which should logically shock all readers.

However, if the same analysis is performed for a non pure substance, the mistake may go unnoticed. Indeed, since we do not attempt an Heaviside form of the enthalpy, one may be mistaken when directly integrating the thermogram. To highlight this, let us present the experimental thermogram of a 9.02% \(H_2O/NH_4Cl\) binary solution depicted in Fig. 3. Here again, the enthalpy profile obtained with a raw analysis, presented in dashed curve, is clearly different from the exact solution (Fig. 4).

2. Method
Following the previous discussion, the approach we present here can evaluate the thermodynamical properties of a sample, in particular the specific enthalpy in function of it’s temperature, by an inverse method. The principle of these methods is to compare the experimental thermogram with the calculated one supposing an \textit{a priori} value for each estimated parameters, and a specific enthalpy function consistent with the laws of thermodynamics. The inversion algorithm has to iteratively modify these parameters in order to minimize the quadratic error (i.e. the ”distance” between the two curves).
2.1. **Inverse method**
Genetic algorithm (GA) is a stochastic optimization method inspired by the biological evolution [5, 6]. Contrary to classical gradient-based methods, the GA method works on a set of potential solutions (a population of individuals) which evolve through iterations (i.e. generations). Further description of the algorithm can be found on [7]. One of the main advantages of this approach is to avoid the necessity of calculating gradients with respect to all estimated parameters, leading to more robust heuristic which easily converges toward a global solution over the search space.

2.2. **Direct model**
It is based on an energy balance of the sample written in its enthalpic form [8]. We take into account both thermodynamical behavior (modeled by the \( h(T) \) function) and thermal effects inside and at the boundaries of the sample. Considering a cylindrical geometry (see Fig. 5) with radius \( r \) and height \( z \), we have:

\[
\frac{\partial \rho h(T)}{\partial t} = \nabla \cdot (k \nabla T) \tag{2}
\]

The associated boundary conditions involve the thermal resistance between the plate and the sample. For convenience, it is usual to treat them as equivalent heat transfer coefficients [9]:

\[
-k \nabla T \cdot \hat{n} = \alpha_i \cdot (T - T_p) \text{ over } \partial \Omega_i \tag{3}
\]

where \( \partial \Omega = \cap_i \partial \Omega_i \), is the frontier of the sample.

Let us now present the different enthalpy profiles that we consider in this study.

2.2.1. **Pure substance** Supposing that the specific heat capacities are constant over temperature, the specific enthalpy function can be written:

\[
h = \begin{cases} 
    c_s \cdot (T - T_{ref}) & \text{if } T < T_M \\
    c_s \cdot (T - T_{ref}) + f \cdot L_M & \text{if } T = T_M \\
    c_s \cdot (T - T_{ref}) + L_M + c_l \cdot (T - T_M) & \text{if } T > T_M
\end{cases}
\tag{4}
\]
where $f$ is the molten fraction.

### 2.2.2. Ideal binary solution

For this study, the phase diagram is supposed to have a vertical solidus curve and a straight liquidus (cf. Fig. 10). Under these hypothesis, $h(T)$ is as a piecewise function of $T$ and expresses:

- $T < T_E$
  \[
  \frac{dh}{dT} = \frac{d}{dT} \left( \frac{H}{m_w^0 + m_a^0} \right) = (1 - x_0)c_w^S + x_0 c_a^S
  \]  \hspace{1cm} (5)

- $T = T_E$
  \[
  \frac{dh}{d\chi} = - \left( L_w(T_E) + \frac{x_E}{1 - x_E} \Delta h_a^{\text{diss}} \right)
  \]  \hspace{1cm} (6)

- $T_E < T \leq T_M$ and $0 \leq \chi \leq 1 - \frac{x_0}{x_E}$
  \[
  \frac{dh}{dT} = \frac{T_{M,w} - T}{(T_{M,w} - T)^2} \left( L_w(T) + c_w^{\text{SS}} \left( 1 - \frac{T_{M,w} - T_M}{(T_{M,w} - T)} \right) + c_L \frac{T_{M,w} - T}{(T_{M,w} - T)} \right)
  \]  \hspace{1cm} (7)

- $T > T_M$
  \[
  \frac{dh}{dT} = (1 - x_0)c_w^L + x_0 c_a^L = c_w^L(x_0)
  \]  \hspace{1cm} (8)

where $\chi$ is the solid fraction, $T_{M,w}$ the melting temperature of the solvent, $T_M$ the liquidus temperature.

### 3. Sensitivity analysis

The sensitivities analysis is the first step to be performed in order to determine parameters which can or cannot be easily and accurately estimated. Indeed, as the only information available to adjust parameters is the thermogram, a parameter is estimable only if its variation has a significative impact over the thermogram. On the other hand, this parameter is not relevant and we may take any approximated value because of its small influence on the final computation.

We present here some results obtained with numerical experiments by changing parameters one by one around a nominal case. The dimension of the sample is $r = 1.125$ mm and height $z = 1.10$ mm and several heating rates are performed ($\beta = 1, 2, 5$ and $10$ K min$^{-1}$).
Table 1. Basic parameters of pure substances.

| Material       | $k_S$  | $k_L$  | $c_S$  | $c_L$  | $T_M$  | $L_M$  |
|----------------|--------|--------|--------|--------|--------|--------|
| Water          | 2.6    | 0.5    | 2000   | 4180   | 0.0    | 3.33 $10^5$ |
| Hexadecane     | 0.4    | 0.21   | 1753   | 2000   | 18.0   | 2.30 $10^5$ |
| Mercury        | 29     | 8      | 140    | 140    | -38.8  | 1.14 $10^4$  |
| Palmitic acid  | 0.5    | 0.162  | 1900   | 2800   | 64.0   | 1.85 $10^5$  |

3.1. Pure substance

Analysis was made for four pure substances in order to cover a large range of thermophysical properties (cf. Tab. 1).

Solid thermal conductivities have a very small influence over the thermogram. On the other hand, the effect of liquid thermal conductivity is small for low heating rate but increases with $\beta$. So, in order to estimate the specific enthalpy, the influence of inaccurate value of thermal conductivities may be minimized by using a low heating rate.

Specific heat capacities also have little influence on the thermogram, the only part impacted are the levels of the solid and liquid plateau before and after the main peak. Again using a weak heating rate diminishes the influence of these parameters.

As expected, the value of the melting temperature greatly influences the thermogram, as a little variation induces an offset, easily observed, of the onset point. In the same manner, the latent heat is directly correlated to the peak area. These two parameters, which are certainly the most important in the enthalpy model, are consequently easy to identify.

3.2. Ideal binary solution

The analysis was performed using $H_2O/N\text{H}_4Cl$ binary solutions at three different mass fractions for the solute: $x = 2.5, 5.0$ and $10.0\%$ ($x_E \approx 19.5\%$).

The conclusions for thermal conductivities are same as for pure substance. However, the influence of solid one is slightly higher.

The concentration has no effect on the influence of the specific heat capacities and we can drawn the same conclusions than for pure substances.

The eutectic and liquidus temperatures have a deep effect on the thermogram shape. For low concentrations, the two peaks remain separated and each parameter affects its own peak. For higher concentrations, the peaks merge and the influence of these temperatures becomes global. The same behavior exists for the two latent heats.

4. Results

We present here the results of estimations carried out using experimental thermogram for pure substances and ideal binary solutions.

For pure substances, Fig. 6 and 7 present the comparisons of experimental thermograms with those calculated with the estimated parameters, for several heating rate. We have used here a 11.4 mg water and a 3.7 mg benzoic acid samples. We may note without ambiguity the good agreement with the experimental data.

For a binary solution ($H_2O/N\text{H}_4Cl$ at several concentrations), we show on Fig. 8 and 9 the same kind of results. Here again, we can note the good agreement between experimental measurements and the reconstructed thermograms.
As the eutectic temperature $T_E$ and the melting temperature $T_M$ are among the estimated parameters, it is possible to partially reconstruct the phase diagram of the solution (Fig. 10). We note once again a very good agreement with literature data [10].

5. Conclusion
We have presented in this paper a new method of identification of the enthalpy of phase change materials by an inverse method from calorimetry experiments. The modeling is thermodynamically consistent, contrary to many others available methods, and allows the correct determination of the enthalpy in function of the temperature for any sample, be it a pure substance or a binary solution and even when heat flow peaks are not distinguishable from each other. We have briefly summarised sensitivity analysis studies, so as to control which parameters may be identified through an inverse method. Then, we show many comparisons of the identified thermograms with experimental ones, considering still pure substances and a binary solution. The method has been shown to be very efficient and to lead to quantitatively good estimations. Finally mention that we have done the same work using the Simplex method for identification and that the results are identical.

Acknowledgments
This work was performed under the auspices of the French National Agency for Research (ANR), under the reference Stock-E 2010 MICMCP

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Figure 9. Comparisons of the experimental and numerical thermograms after identification ($H_2O/NH_4Cl$ solution) with a heating rate of 2 K min$^{-1}$.

Figure 10. Comparisons between identified and exact phase diagram for the $H_2O/NH_4Cl$. 