Modelling of hydrogen thermal desorption spectrum in nonlinear dynamical boundary-value problem

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Abstract. One of the technological challenges for hydrogen materials science (including the ITER project) is the currently active search for structural materials with various potential applications that will have predetermined limits of hydrogen permeability. One of the experimental methods is thermal desorption spectrometry (TDS). A hydrogen-saturated sample is degassed under vacuum and monotone heating. The desorption flux is measured by mass spectrometer to determine the character of interactions of hydrogen isotopes with the solid. We are interested in such transfer parameters as the coefficients of diffusion, dissolution, desorption. The paper presents a distributed boundary-value problem of thermal desorption and a numerical method for TDS spectrum simulation, where only integration of a nonlinear system of low order (compared with, e.g., the method of lines) ordinary differential equations (ODE) is required.

1. Introduction

Interaction of hydrogen and its isotopes with solids has many applications [1–7]. It is sufficient to mention power engineering, protection of metals from hydrogen corrosion, design of chemical reactors, rocket and missile engineering. Hydrides help to retain substantial amounts of hydrogen: environmental-friendly energy source. Hence high expectations are attached to hydrogen batteries and motors that avoid using high pressures or low temperatures. Some special topics are considered in [8, 9]. Enthusiasts speak not only of hydrogen energy but also of hydrogen economy [5]. Transfer parameters depend on the process characteristics of producing the material batch, and one needs effective algorithms for processing measured curve instead of focusing on ‘tabular data’. We focus on the thermal desorption method and take into account only the limiting factors and the information capacities of the TDS experiment explicated below.

2. Mathematical model of TDS-experiment

We consider hydrogen transfer through a test metal sample (plate of thickness \( \ell \)). For brevity we speak of a metal plate, although it may be a multialloy. Suppose heating is relatively slow and uniform so that the diffusion flow can be assumed to be proportional to the concentration gradient. The material is sufficiently homogeneous to neglect interaction of \( H \) with traps (microdefects of the crystal structure). Let us assume a standard model for diffusion:

\[
c_t(t, x) = D(T)c_{xx}(t, x), \quad (t, x) \in Q_{\ell},
\]
where \( t \) is time, \( Q_{\ell,\ell} = (0, t_{\ell}) \times (0, \ell) \); \( c(t, x) \) is concentration of dissolved atomic hydrogen. Diffusion coefficient \( D \) is an Arrhenius function of temperature \( T(t) \): 

\[
D = D_0 \exp \left\{ -E_D / [RT(t)] \right\},
\]

\( D_0 \) and \( E_D \) are the preexponential factor and activation energy.

More detailed transfer models are known. For example, different diffusion channels can be considered: transcrystalline, the grain boundary diffusion, along the defects, with interchange between them. However, a significant increase of number of unknown a priori coefficients leads to the complex problem of parameter estimation. TDS-experiment provides limited amount of information. Transfer by different diffusion channels is impossible to distinguish; therefore we use integral parameters (effective coefficients). The main difficulty of computations is due to dynamic boundary conditions (not the diffusion equation). Suppose the plate contacts with gas \( H_2 \) and external surface is potential barrier (see [2, pp.177–206]). Taking into account (de) sorption processes, we obtain the following boundary conditions:

\[
\begin{align*}
    c(0, x) &= c(x), \quad x \in [0, \ell], \quad t \in [0, t_{\ell}], \\
    c_0(t) &= g(T)q_0(t), \quad c_\ell(t) = g(T)q_\ell(t), \\
    \dot{q}_0(t) &= \mu s(T)p_0(t) - b(T)q_0^2(t) + Dc_x(t, 0), \\
    \dot{q}_\ell(t) &= \mu s(T)p_\ell(t) - b(T)q_\ell^2(t) - Dc_x(t, \ell),
\end{align*}
\]

\( b(T) = b_0 \exp \left\{ -E_0 / [RT] \right\}, \quad s(T) = s_0 \exp \left\{ -E_s / [RT] \right\} \). Here \( c_0(t) \equiv c(0, t), \quad c_\ell(t) \equiv c(\ell, t) \) are boundary bulk concentrations of diffusing atomic hydrogen; \( q_0(t), \ q_\ell(t) \) are concentrations on the surfaces \( (x = 0, \ell) \); \( g(T) \) is the coefficent of local equilibrium between concentrations on the surface and near-surface bulk; \( \mu \) is the kinetic coefficient; \( s(T) \) is the parameter indicating that only a small part of incident hydrogen find its way on the surface (for brevity, we call \( s \) the adhesion coefficient and keep in mind that this coefficient describes the result of concurrent physisorption, dissociation, and chemisorption of molecular gas on the surface); \( p_0(t), \ p_\ell(t) \) are pressures of molecular gas. Although hydrogen can be both in atomic and molecular forms, we use atoms as the unit of amount: \([c] = 1/\text{cm}^3, \ [q] = 1/\text{cm}^2, \ [Dc_x] = [J] = 1/\text{cm}^2s \quad (J = bq^2)\). According to the kinetic gas theory, \( \mu p \) is the number of \( H_2 \) particles colliding with unit area per unit time; then \( \mu s p \) is the flux density of atoms precipitating on the surface. This quantity is a general parameter, applicable without distinguishing the processes. The quick dissolution model (3) is obtained from the more universal formulas

\[
\begin{align*}
    k^-(T)q_0(t) - k^+(T)c_0(t) &= -D(T)c_x(t, 0), \\
    k^-(T)q_\ell(t) - k^+(T)c_\ell(t) &= D(T)c_x(t, \ell).
\end{align*}
\]

Coefficients \( k^-, \ k^+ \) describe the intensity of the dissolution processes in the bulk and transfer to surface. If these processes are significantly faster than diffusion (for considered temperature range) then it is assumed that \( Dc_x \approx 0 \). Hence we obtain (3), where \( g = k^- / k^+ \). If the surface is isotropic (in terms of \( E_{k-} \approx E_{k+} \) ) then the coefficient \( g(T) \) has weak temperature dependence.

We can formally use the Arrhenius equation \( g(T) = g_0 \exp \left\{ -E_g / [RT] \right\}, \quad E_g = E_{k-} - E_{k+} \). Here activation energy \( E_g \) is not necessarily positive. In addition, we can take into account degree of the surface covering and near-surface bulk saturation:

\[
k^-(T)\left[1 - c_{\ell,\ell}(t)c_{\text{max}}^{-1}\right]q_{0,\ell}(t) - k^+(T)\left[1 - q_{0,\ell}(t)q_{\text{max}}^{-1}\right]c_{0,\ell}(t) = \mp D(T)c_x|_{0,\ell}.
\]

The value \( \theta(t) = q(t)/q_{\text{max}} \) means the degree of the surface covering. Flux density of atom \( H \) adsorption (dissociative hydrogen chemisorption on the surface) can be simulated by formula \( \mu s(T)p(t) [1 - \theta(t)]^2 \) in the balance equations (4), (5). But we have \( \theta \ll 1 \) for low level of hydrogen. It’s in good agreement with quadratic desorption, linear diffusion equation, \( D \neq D(c) \). In the context of current TDS-experiment it is convenient to take \( [p] = \text{Torr} \) and
Let us change variables so that boundary conditions in (6) become homogeneous:

\[ \mu(T) = (2\pi mkT)^{-1/2} \approx 2.484 \cdot 10^{22}/\sqrt{T}. \]

Here we have \( [\mu] = 1 \text{H}_2/(\text{Tor} \text{cm}^2 \text{s}), \) \( [T] = \text{K}, \)

\( k \) is the Boltzmann constant, \( m \) is mass of a hydrogen molecule. Variation of the kinetic constant with temperature \( (\mu \propto 1/\sqrt{T}) \) is usually neglected against exponential relation for \( s(T) \).

Saturation means that pressure \( \bar{p} \) of \( \text{H}_2 \) on both sides of the plate is constant at \( T = \text{const.} \)

Then (after a time) saturation concentration \( (\bar{c}) \) of dissolved atomic diffusivity hydrogen is established. Assuming zero derivatives in (3)–(5), we obtain \( \bar{c} = \Gamma\sqrt{\bar{p}}, \Gamma \equiv g/\mu s/b \quad (\bar{c} = gq). \)

Consequently the model is according to the Sieverts law adequacy range \( (\bar{c} \propto \sqrt{\bar{p}}) \).

Let us clarify the TDS-experiment. Plate of the material is placed into a chamber. Hydrogen gas is pumped into the chamber under relatively high pressure. The sample is heated to hasten sorption until the sample absorbs enough hydrogen (equilibrium gas saturation). Then heating current is shut off and the material is cooled. In such a case, the physico-chemical processes slow down sharply and significant amount of hydrogen remains inside the sample. The heating rate is low and constant. Molecular hydrogen pressure in the chamber is measured by a mass-spectrometer. The desorption flux from the surface is defined by pressure. The desorption flux density is denoted by \( J(t) = b(t)q^2(t) \) (usually \( J(t) \propto p(t) \)). From now on the contracted notation will be used for simplification: \( b(t) \equiv b(T(t)), D(t) \equiv D(T(t)), s(t) \equiv s(T(t)) \).

Parameter \( g \) of rapid dissolution (local surface-bulk equilibrium) is taken to be constant \( (E_{k-} = E_{k+}) \) near the TDS-peak. Symmetry conditions are fulfilled for the TDS method:

\[ p(t) = p_{0,x}(t), \quad q(t) = q_{0,x}(t), \quad c_0(t) = c_{0,\ell}(t), \quad D(t)c_x(t, 0) = -D(t)c_x(t, \ell), \quad \bar{c}(x) = \bar{c} = \text{const.} \]

The experiment end time \( t_\ast \) is defined by the degassing condition: \( p \approx 0, \quad c(t_\ast, x) \approx 0. \)

### 3. Integrodifferential equation

Suppose the TDS-degassing model:

\[ r(t) = \mu s(t)p(t), \quad J(t) = b(t)q^2(t), \]

\[ c_t = D(t)c_{xx}, \quad c(0, x) = \bar{c}, \quad c_{0,\ell}(t) = gq(t), \quad \dot{q}(t) = r(t) - b(t)q^2(t) + D(t)c_x(t, 0). \]

Vacuum system is assumed to be powerful enough. Hence resorption is neglected \( (r(t) = 0) \) for degassing. Values of \( J(t) \) are input data for the inverse problem of parametric identification.

In the paper we only present numerical simulation of TDS-spectrum \( J = J(T) \). It is needed as the iterative component of the identification algorithm. Heating is usually linear \( (T(t) = T_0 + vt). \)

Heating rate \( v \) is less than 1 K/s. Heating is stopped (although degassing is continued) if upper temperature limit \( T(t) = T_{\text{max}} \) is reached.

Let us formulate the mathematical problem. Difference schemes for the boundary-value problem (with different types of defects) solution was presented in [10]. But a curve of TDS-spectrum is determined by surface concentration \( (J = bq^2). \) Hence, we try to avoid the iterative solution of the boundary-value problem for the current approximations of the model parameters \( D_0, \quad E_D, \quad b_0, \quad E_b, \quad s_0, \quad E_s, \quad g. \) For this aim we perform the problem transformation. Finally, the modelling requires only integration of a nonlinear system of low order ordinary differential equations (ODE).

We replace time by \( t' = \int_0^t D(s) \, ds \) (keep previous notation \( t)): \n
\[ c_t(t, x) = c_{xx}(t, x), \quad c(0, x) = \bar{c}, \quad c_{0,\ell} = gq(t), \]  \hspace{1cm} (6)

\[ c_x|_0 = -c_{xx} = \dot{q}(t) + [J(t) - r(t)]D^{-1}(t). \]  \hspace{1cm} (7)

Let \( q(t) \) be functional parameter, formula (7) is additional relation to the linear problem (6). Let us change variables so that boundary conditions in (6) become homogeneous:

\[ \bar{c} = c(t, x) - gq(t), \quad \bar{c}_t(t, x) = \bar{c}_{xx}(t, x) + f(t), \quad f(t) = -g\dot{q}(t), \quad \bar{c}(0, x) = \bar{\varphi}(x) = 0, \quad \bar{c}_{0,\ell} = 0. \]
Write the solution using function of instantaneous source (Green’s function):
\[
\hat{c}(t, x) = \int_{t_0}^{t} \int_{0}^{L} G_1(x \xi, t - \tau) f(\tau) d\xi d\tau, \quad G_1(x \xi, t) = 2 \sum_{n=1}^{\infty} \exp \left\{ - \frac{n^2 \pi^2}{L^2} t \right\} \frac{\sin \frac{n \pi x}{L}}{n \pi} \sin \frac{n \pi \xi}{L}.
\]

Dynamical boundary conditions contain \( \hat{c}_x(t, 0) \):
\[
\hat{c}_x(t, 0) = - \frac{4g}{\ell} \int_{t_0}^{t} \hat{q}(\tau) \sum_{n=1}^{\infty} \exp \left\{ - \frac{n^2 \pi^2}{L^2} (\tau - t) \right\} d\tau, \quad \sum_{n=1}^{\infty} = \sum_{n=1,3,5,...}
\]
The series is divergent for \( \tau = t \) so that term-by-term integration is meant. For original time \( t \) we obtain \( c_x(t, 0) = \hat{c}_x(t, 0) = c_x(t, \ell) = \hat{c}_x(t, \ell) \),
\[
\dot{q}(t) = r(t) - b(t) \hat{q}^2(t) - \frac{4gD}{\ell} \int_{t_0}^{t} \hat{q}(\tau) \exp \left\{ - \frac{n^2 \pi^2}{L^2} \int_{\tau}^{t} D(s) ds \right\} d\tau.
\]
The equation and the original boundary-value problem are equivalent. This means that the solution \( \hat{q}(t) \) uniquely determines the solution \( c(t, x) \). An analogy to functional-differential equations of neutral type is due to impossibility to eliminate derivative \( \hat{q} \) in the right side of the equation due to divergent series. We are interested in the time interval \([t_1, t_2] \subset (0, t_*)\) near activity peak of thermal desorption (measurements for \( t \) near to \( 0, t_* \) are uninformative). Resorption is neglected (\( r(t) = 0 \)) for powerful vacuum system, thus the equation is simplified.

Dimensionless parameters are more convenient for numerical modelling. We use replaces: \( t' = \int_{t_0}^{t} D(s) ds / \ell^2 \), \( x' = x/\ell \), \( v = \hat{q} / \bar{c} \) (\( \bar{c} = \hat{q} \)). But notation of \( t \) is not changed. We obtain:
\[
\dot{\bar{v}}(t) = -\bar{b}(t) \bar{v}^2(t) - 4g \ell \int_{t_0}^{t} \dot{\bar{v}}(\tau) \exp \left\{ - \frac{n^2 \pi^2}{L^2} [t - \tau] \right\} d\tau, \quad \dot{\bar{v}} \equiv \frac{dv}{dt}, \quad \bar{b}(t) = \frac{b(t) \ell^2 \hat{q}}{D(t)}.
\]
Here \( v(0) = 1 \) is the initial condition. We only use first \( k \) terms of the series. Denote
\[
\bar{z}_i(t) = \int_{t_0}^{t} \bar{v}(\tau) \exp \left\{ - (2i - 1)^2 \pi^2 [t - \tau] \right\} d\tau.
\]
Differentiate \( \bar{z}_i(t) \) with respect to \( t \) and use \( \dot{\bar{v}}(t) \) from formula (9) (\( \max n = 2k - 1 \)):
\[
\dot{\bar{z}}_i = -\bar{b}(t) \bar{v}^2(t) - (2i - 1)^2 \pi^2 + 4g \ell \bar{z}_i - 4g \ell \bar{z}_{i-1} + ... + \bar{z}_1 + \bar{z}_k.
\]
The result is the following system of ordinary differential equations:
\[
\frac{d}{dt} \begin{pmatrix} \bar{v} \\ \bar{z}_1 \\ \vdots \\ \bar{z}_k \end{pmatrix} = -\bar{b}(t) \bar{v}^2(t) \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{pmatrix} - 4g \ell \begin{pmatrix} 1 & 1 & ... & 1 \\ \alpha_1 & 1 & ... & 1 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & ... & \alpha_k \end{pmatrix} \begin{pmatrix} \bar{z}_1 \\ \bar{z}_2 \\ \vdots \\ \bar{z}_k \end{pmatrix},
\]
where \( \alpha_i = 1 + (2i - 1)^2 \pi^2 / (4g \ell), \bar{v}(0) = 1, \bar{z}_i(0) = 0 \) (matrix size is \( (k + 1) \times k \)). The system is rapidly integrated using classic Runge-Kutta fourth-order method. We make calculations using Scilab 5.5. The system order is not large (compared with, e.g., the method of lines) due to measurement error is usually not less than 10% and the exponent function contains \( n^2 \).

Initial saturation by hydrogen and coefficient \( \bar{b}(t) \) of quadratic nonlinearity are focused. Initial saturation is conducted at high temperature \( T = \bar{T} = \text{const} \) and pressure \( \bar{p} = \text{const} \) (to stimulate sorption). After establishing of equilibrium concentration we obtain
\[
\mu(\bar{T}) s(\bar{T}) \bar{p} = b(\bar{T}) \bar{q}, \quad \bar{c} = g \bar{q} \quad (g = \text{const}) \Rightarrow \bar{c} = g \hat{t}_0^{-1/2} \sqrt{\mu s \bar{p}} \bar{T} \exp \left\{ E_b [2R \bar{T}]^{-1} \right\},
\]
\[
\bar{b}(t) = \bar{q} \bar{b}(t) \ell^2 D^{-1} = \bar{c} b(t) \ell^2 [g D(t)]^{-1} = \bar{b}_0 \exp \left\{ - E_b [RT(t)]^{-1} \right\},
\]
\[
E_b = E_b - E_D, \quad \bar{b}_0 = \ell^2 D_0^{-1} \sqrt{b_0 \mu s \bar{p}} \bar{T} \exp \left\{ E_b [2R \bar{T}]^{-1} \right\}.
\]
Formally let \( \tilde{b}(t) \equiv \tilde{b}(T(t)) \) be Arrhenius parameter, here \( E_b - E_D \) is activation energy. Usually \( E_b > E_D \) and surface processes are faster speeded up on heating. \((\tilde{b} = \ldots E_b T, D = \ldots E_D T)\), thus, \( E_b > 0 \). The pre-exponential factor \( \tilde{b}_0 \) depends on all parameters \( D_0, b_0, E_b, s_0, E_s \) (except \( E_D \)). Hence the coefficient \( \tilde{b} \) changed monotonically and limited \( 0 < \tilde{b} < \tilde{b}(t) < \tilde{b}^+ \).

The first approximation represents qualitative situation (factor \( n^2 \) in exponent for the second term of the series is an order of magnitude greater the similar factor in the first term):

\[
\dot{v}(t) = -\tilde{b}(t)v^2(t) - \pi \int_0^t \dot{v}(\tau) \exp\left\{ -\pi^2[\tau - t]\right\} d\tau, \quad \pi \equiv 4g\ell, \\
\dot{z}(t) = -\tilde{b}(t)\dot{v}(t) - \pi z(t), \quad z \equiv z_1, \\
\ddot{z}(t) = -\tilde{b}(t)v^2(t) - (\pi^2 + \pi z(t)), \quad v(0) = 1, \quad z_1(0) = 0.
\] (10)

The qualitative behaviour of the motion on phase plane \((v, z)\) is presented in Fig. 1. Dash-and-dot lines show parabolas \( \dot{v}, \dot{z} = 0 \): \( z = -\tilde{b}(t)\pi^{-1}v^2, -\tilde{b}(t)[\pi + \pi^2]^{-1}v^2 \).

Field of phase rate of the system (10) is nonstationary. But its change is monotonous and limited due to \( \tilde{b}(t) \in [\tilde{b}^-, \tilde{b}^+] \). Parabolas are moved left (for \( E_b > E_D \)) or right (for \( E_b < E_D \)). The second approximation of equation (9) is considered in the same way:

\[
\begin{align*}
\dot{v}(t) &= -\tilde{b}(t)v^2 - \pi z(t), \\
\dot{z}_1(t) &= -\tilde{b}(t)v^2 - [\pi + \pi z]z_1 - \pi z_2, \\
\dot{z}_2(t) &= -\tilde{b}(t)v^2 - \pi z_1 - [\pi + \pi^2]z_2.
\end{align*}
\] (11)

![Figure 1. Motion on phase plane](image1)

![Figure 2. Decrease of \(|z_i(t)|\)](image2)

4. Computer simulation results

Data for nickel [4] are used: \( D = 7.5 \times 10^{-3} \exp\{-40000/RT\} \) [cm²/s]; \( g = 100 \) [1/s]; \( b = 1.53 \times 10^{-14} \exp\{-43200/RT\} \) [cm²/s]; \( s = 1.8 \times 10^{-2} \exp\{-61400/RT\} \) [cm²/s]; \( \tilde{p} = 37.4 \) [Torr]; \( \ell = 0.02 \) [cm]; \( T = 770 \) [K], \( T(0) = 295 \) [K]; \( \tilde{T} = 0.5 \) [K/s]. Variation of parameters provides an opportunity to estimate the degree of sensitiveness (‘derivatives’) of TDS-spectrum to a selected limiting factors (Fig. 3–Fig. 6). We solved the system of 10–15 equations. In Fig. 6 we notice rise of an extra peak structure due to interplay between diffusion and desorption activation energies. Warning, this effect is usually interpreted by traps with different binding energies.

Conclusion

The paper presents a distributed boundary-value problem of thermal desorption with nonlinear dynamical boundary conditions for modelling the degassing TDS-spectrum of a hydrogen-presaturated structural material. The variation of parameters allows estimating the TDS-spectrum’s sensitivity to changes in the material service conditions and its composition.
The algorithm only requires integration of a nonlinear system of low order ordinary differential equations (compared, e.g., with the method of lines). The results of computer simulations using experimental data for nickel are presented. Researchers and experts in hydrogen interaction with solids are thus enabled to directly estimate transfer parameters using current experimental data, and no special software development is required for solving of boundary-value problem.

The main physical sense of the presented results is the following. Unexpectedly at first sight, flux decreases as the desorption coefficient increases. Taking into account initial saturation we conclude that the increase of $b_0$ prevents saturation to a greater extent than it enhances degassing.

We notice rise of an extra peak structure due to interplay between diffusion and desorption activation energies (but this effect is usually interpreted by traps with different binding energies).

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