Functional differential equations of neutral type with integrable weak singularity: hydrogen thermal desorption model

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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 thermal desorption functional differential equations of neutral type with integrable weak singularity and a numerical method for TDS spectrum simulation, where only integration of a nonlinear system of low order ordinary differential equations (ODE) is required. This work is supported by the Russian Foundation for Basic Research (project 15-01-00744).

1. Introduction
Interaction of hydrogen and its isotopes with solids has many applications [1–5]. 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 [6,7]. Enthusiasts speak not only of hydrogen energy but also of hydrogen economy [4]. 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 or alloy sample (plate of thickness \( \ell \)). 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 (micro-defects). Let us assume a standard model for diffusion:

\[
c_t(t,x) = D(T)c_{xx}(t,x), \quad (t,x) \in Q_t, \tag{1}
\]
where $t$ is time, $Q_{\text{ads}} = (0, t_s) \times (0, \ell)$; $c(t, x)$ is concentration of dissolved atomic hydrogen. Diffusion coefficient $D$ is an Arrhenius function of temperature $T(t)$: $D = D_0 \exp \{-E_D/[RT(t)]\}$, $D_0$ and $E_D$ are the preexponential factor and activation energy.

Suppose the plate contacts with gas $H_2$ and surface is potential barrier (see [2, pp. 177–206]). Taking into account (de)absorption processes, we obtain the following boundary conditions:

\[ c(0, x) = \bar{c}(x), \ x \in [0, \ell], \ t \in [0, t_s], \]

\[ c_0(t) = g(T)q_0(t), \ c_\ell(t) = g(T)q_\ell(t), \]

\[ q_{0,\ell}(t) = \mu s(T)p_{0,\ell}(t) - b(T)q_{0,\ell}^2(t) \pm Dc_\ell \big|_{x=0, \ell}, \]

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3. Functional differential TDS-equation

Suppose the TDS-degassing model: \( r(t) \equiv \mu s(t)p(t) \), \( J(t) \equiv b(t)q^2(t) \),

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

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 \( J = J(T) \). 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 [8]. But a curve of TDS-spectrum is determined by surface concentration \((c)\). For this aim we perform the problem transformation. Finally, the modeling requires only integration of a system of low order ordinary differential equations (ODE).

We replace time by \( t' = \int_0^t D \, ds \) (keep previous notation \( t \)):

\[
c_t(t, x) = c_{xx}(t, x) \quad , \quad c(0, x) = \bar{c}, \quad c_{0, t} = gq(t), \quad c_x|_0 = -c_x|_\ell = \dot{q}(t) + [J(t) - r(t)]D^{-1}(t). \quad (5)
\]

Let \( q(t) \) be functional parameter, formula \((6)\) is additional relation to the linear problem \((5)\).

Let us change variables so that boundary conditions in \((5)\) become homogeneous:

\[
\hat{c} = c(t, x) - gq(t), \quad \hat{c}_t(t, x) = \hat{c}_{xx}(t, x) + f(t), \quad f(t) = -g\ddot{q}(t), \quad \hat{c}(0, x) = \hat{\varphi}(x) = 0, \quad \hat{c}_{0, \ell} = 0.
\]

Write the solution using function of instantaneous source (Green’s function):

\[
\hat{c}(t, x) = \int_0^t \int_0^\ell G_1(x, \xi, t - \tau)f(\tau)d\xi d\tau, \quad G_1(x, \xi, t) = \frac{2}{\ell} \sum_{n=1}^\infty \exp\left\{-\frac{n^2\pi^2}{\ell^2} t\right\} \sin \frac{n\pi x}{\ell} \sin \frac{n\pi \xi}{\ell}.
\]

Dynamical boundary conditions contain \( \hat{c}_x(t, 0) \):

\[
\hat{c}_x|_0 = -\frac{4g}{\ell} \int_0^t \hat{q}(\tau) \sum' \exp\left\{\frac{n^2\pi^2}{\ell^2} (\tau - t)\right\} d\tau, \quad \sum' = \sum_{n=1,3,5,\ldots}.
\]

The series is divergent for \( \tau = t \) so that term-by-term integration is meant. For original time \( t \) we obtain \( c_x(t, 0) = \hat{c}_x(t, 0) = c_x(t, \ell) = \hat{c}_x(t, \ell) \),

\[
\dot{q}(t) = r(t) - b(t)q^2(t) - \frac{4gD}{\ell} \sum' \int_0^t \hat{q}(\tau) \exp\left\{-\frac{n^2\pi^2}{\ell^2} \int_\tau^t D(s) \, ds\right\} d\tau. \quad (7)
\]

The equation and the original boundary-value problem are equivalent. This means that the solution \( q(t) \) uniquely determines the solution \( c(t, x) \). An analogy to functional-differential equations of neutral type is due to impossibility to eliminate derivative \( \dot{q} \) in the right side of the equation due to divergent series. We are interested in the time interval \([t_1, t_2] \subset (0, t_\ast)\) near activity peak of thermal desorption (measurements for \( t \) near to 0, \( t_\ast \) are uninformative). Resorption is neglected \((r(t) = 0)\) for powerful vacuum system, thus the equation is simplified.

Dimensionless parameters are more convenient for numerical modeling. We use replaces: \( t' = \int_0^t D(s) \, ds/\ell^2, \quad x' = x/\ell, \quad v = q/\bar{q} \quad (\bar{c} = g\bar{q}) \). But notation of \( t \) is not changed. We obtain:

\[
\dot{v}(t) = -\ddot{b}(t)v^2(t) - 4g\ell \sum' \int_0^t \dot{v}(\tau) \exp\left\{-n^2\pi^2[t - \tau]\right\} d\tau, \quad v(0) = 1, \quad \dot{v} \equiv \frac{dv}{dt}, \quad \ddot{b} = \frac{b(t)\ell^2\bar{q}}{D(t)}. \quad (8)
\]
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

\[
\mu(\bar{T})s(\bar{T})\bar{p} = b(\bar{T})q^2, \quad \bar{c} = g\bar{q} (g = \text{const}) \quad \Rightarrow \quad \bar{c} = g\bar{b}_0^{-1/2} \sqrt{\mu s \bar{p}} \exp \left\{ E_b[2\bar{R}\bar{T}]^{-1} \right\},
\]

\[
b(t) = q \bar{b}(t)\ell^2 D^{-1} = \bar{c} b(t)\ell^2[gD(t)]^{-1} = \bar{b}_0 \exp \left\{ -E_b[R\theta(t)]^{-1} \right\},
\]

\[
E_b \equiv E_b - E_D, \quad \bar{b}_0 \equiv \ell^2 D^{-1} \sqrt{\mu s \bar{p}} \exp \left\{ E_b[2\bar{R}\bar{T}]^{-1} \right\}.
\]

Formally let \( \bar{b}(t) \equiv \bar{b}(T(t)) \) 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. (\( \bar{b} = \ldots \bar{E}_b T, \: D = \ldots \bar{E}_D T \)), thus, \( E_b > 0 \). The pre-exponential factor \( \bar{b}_0 \) depends on all parameters \( D_0, \: b_0, \: E_b, \: s_0, \: E_s \) (except \( E_D \)). Hence the coefficient \( \bar{b} \) changed monotonically and limited \( 0 < \bar{b}^- \leq \bar{b}(t) \leq \bar{b}^+ \).

Hereinafter let us suggest that the limit of surface concentration is at \( q_{\text{max}} \sim 10^{15} - 10^{16} \) (monolayer in the context of geometrical statics). Where at the stage of initial saturation for selected model parameters we have \( q > 10^{14} \), for numerical simulations we must take into account the surface filling degree. In such a case, the formula \( \mu s \bar{p} = b q^2 \) is substituted with the ratio \( \mu s \bar{p}[1 - q q_{\text{max}}^{-1}]^2 = b \bar{q}^2 \) to estimate the initial value of \( \bar{q} \).

For extracting singularity let us clarify why the quite accurate approximation of the thermal desorption functional differential equation (8) still requires a large number of terms in \( \sum' \). The function

\[
\Theta(s) = 4 \sum' \exp \left\{ -n^2 \pi^2 s \right\}, \quad \sum' \equiv \sum_{n=1,3,5,..}
\]

has finite values for \( s > 0 \). The series is rapidly converging for large \( s \). Formally, substituting \( s = 0 \) (the integration variable reaches the upper limit of \( t \)) we obtain a divergent series. This can be fixed by term-by-term integration. We have \( \max |z_i(t)| = O(n^{-2}) \) \( (n = 2i - 1, \: i \geq 1) \), whereas convergence is slow. Let us run some transformations using the theory of Jacobi theta functions. More specifically, we will focus on

\[
\theta_3(t, x) = 1 + 2 \sum_{n=1}^{\infty} \exp \left\{ -n^2 \pi^2 t \cos(2n\pi x) \right\}, \: t > 0.
\]

We have an alternative presentation \( [10] \) for \( x = 0 \): \( \theta_3(t, 0) = \sum_{n=-\infty}^{+\infty} \exp \left\{ -n^2 / t \right\} / \sqrt{\pi t} \).

The series on the left is rapidly converging for large \( t \). But the series on the right is rapidly converging for small \( t \). Here we are only concerned with small \( t \). Defining \( \theta(t) = \sum \exp \left\{ -n^2 t \right\} \) \( (n \in \mathbb{Z}, \: t > 0) \) we obtain the formula \( \theta(1/t) = \sqrt{\pi} \theta(t) \) or \( \sqrt{\pi} \sum \exp \left\{ -n^2 t \right\} = \sum \exp \left\{ -n^2 / t \right\} \) \( (n \in \mathbb{Z}) \). This relation is known as functional equation for theta function \( [11] \).

Let us run auxiliary transformations. The series is split into odd and even terms:

\[
[\pi t]^{-1/2} \sum_{n=-\infty}^{+\infty} \exp \left\{ -n^2 / t \right\} = 1 + 2 \sum_{n=1}^{\infty} \exp \left\{ -n^2 \pi^2 t \right\}
\]

\[
= 1 + 2 \sum' + 2 \sum_{k=1}^{\infty} \exp \left\{ -k^2 \pi^2 4t \right\} = 2 \sum' + [4\pi t]^{-1/2} \sum_{n=-\infty}^{+\infty} \exp \left\{ -n^2 / 4t \right\}.
\]

With this in mind, the last series is subtracted from the first series and the result is doubled. The following expansion is obtained for \( s > 0 \):

\[
\Theta(s) \equiv 4 \sum' \exp \left\{ -n^2 \pi^2 s \right\} = \frac{1 - Q}{\sqrt{\pi s}}, \: Q(s) \equiv -2 \sum_{n=1}^{\infty} q^n, \: q \equiv - \exp \left\{ -(4s)^{-1} \right\}.
\]

The series \( Q \) is rapidly converging for small \( s \). As \( s \to +0 \) we have \( Q \to 0 \) and the integrable singularity \( \Theta \approx 1 / \sqrt{\pi s} \). Since the series is alternating, we have the inequalities \( Q > 0 \) (more exactly \( Q \in (0, 1) \)) and \( Q \leq 2|q| \). The graph for function \( Q(s) \) is an S-shaped saturation curve
and $Q(1) \approx 0.999$. Using the above-described presentation of $\Theta(s)$ we obtain the TDS functional differential equation of neutral type (terminology from \cite{9}):

$$\dot{v}(t) = -\ddot{b}(t) v^2(t) - \kappa \int_0^t \frac{1 - Q(t - \tau)}{\sqrt{\pi(t - \tau)}} \dot{v}(\tau) d\tau \quad (t \geq 0, \ v(0) = 1). \quad (9)$$

**Numerical method and computer simulation**

To be specific in the paper, we use experimental data for nickel and steel 12Cr18Ni10Ti \cite{3}. The assumed values of model parameters are the following: (steel) $\ell = 0.1$ cm, $T_0 = 300$ K, $b_0 = 1.28 \times 10^{-9}$ cm$^2$/s, $E_b = 90 \times 10^3$ J/mol, $D_0 = 3.09 \times 10^{-4}$ cm$^2$/s, $E_D = 31 \times 10^3$, $g = 50$ cm$^{-1}$, $s_0 = 0.6$, $E_s = 110 \times 10^3$, $\tilde{c} = 6 \times 10^{17}$ at.H/cm$^3$, $T = 170$ K, $\tilde{T} = 0.5$ K; (nickel) $\ell = 0.1$, $T_0 = 300$, $b_0 = 1.53 \times 10^{-14}$, $E_b = 43.2 \times 10^3$, $D_0 = 7.5 \times 10^{-3}$, $E_D = 40 \times 10^3$, $g = 100$, $s_0 = 1.8 \times 10^{-2}$, $E_s = 61.4 \times 10^3$, $\tilde{p} = 37.4$ Torr, $\tilde{T} = 770$, $\tilde{T} = 0.5$.

The main role in degassing dynamics belongs to quadratic desorption. So let us approximate the integral term in equation (9). The aftereffect horizon here is $h < 1 \ (\tau \in [t, t - h])$ for dimensionless $Q(1) \approx 0.999$. Let us fix $h \sim 0.3 - 0.4$ due to continuously differentiable function $Q(s)/\sqrt{s}$ graph and trapezoid rule for numerical integration. Then, TDS-equation (9) can be approximated by ODE system of low order one-by-one on time segments of length $h$.

The greatest contribution to the integral is made by the value $\dot{v}(\tau) (\tau \approx t)$ due to non-limited (but integrable) singularity. Thus, the quadratic approximation \vdot{}$\dot{v}(\tau) \approx \dot{v}(t) + A[t - \tau] + B[t - \tau]^2$ is used due to function $\dot{v}$ concavity. Let us consider the current period of time $t \in [kh, (k + 1)h]$, $k \geq 0$. The conditions $\dot{v}(\tau)_{kh} = \dot{v}(kh)$ and $\int_{kh}^t \dot{v}(\tau) d\tau = \dot{v}(t) - \dot{v}(kh)$ (here suppose $\dot{v}(t) \approx \dot{v}(kh) + \dot{v}(t)[t - kh]$) determine the sought values of $A(t), B(t) \ (\text{constant on } \tau)$:

$$\dot{v}(\tau) \approx \dot{v}(t) + 2 \frac{\dot{v}(t) - \dot{v}(kh)}{t - kh} [t - \tau] - 3 \frac{\dot{v}(t) - \dot{v}(kh)}{[t - kh]^2} [t - \tau]^2, \quad \tau \in [kh, t]. \quad (10)$$

Represent the integral as a sum $\tau \in [0, kh], \tau \in [kh, t]$. For the second additive, the singularity $\dot{v}(\tau)/\sqrt{t - \tau}$ is explicitly integrated by substituting (10). The trapezoid rule is used for the integral without singularity ($Q(+0)/\sqrt{0} = 0$). For approximation of the first integral

$$\int_0^{kh} \frac{1 - Q(t - \tau)}{\sqrt{\pi(t - \tau)}} \dot{v}(\tau) d\tau = 4 \sum_{2}^{kh} \int_0^{kh} \dot{v}(\tau) \exp \{-n^2 \pi^2 [t - \tau]\} d\tau$$

we use only several series terms (for definiteness $n = 1, 3$) on the right-hand side due to the exponent $n^2$. Thereby, the negative additives ($\dot{v} < 0$) are dropped. Let us compensate for that by replacing $kh$ with $t$, and introduce in addition variables $w_{1,2}$ (see below). As the result we obtain the ODE system:

$$\dot{v}(t) = -\ddot{b}(t) v^2(t) + \frac{\kappa}{\sqrt{\pi}} \left[ \frac{2}{15} + \frac{Q(0)}{2} \right] \sqrt{t - kh} \dot{v}(kh)$$

$$-4\dot{\kappa} \sum_{n=1,3} \int_0^t \exp\{-n^2 \pi^2 [t - \tau]\} \dot{v}(\tau) d\tau, \quad \dot{b} \equiv \frac{b}{1 + \frac{32\sqrt{2}T - kh}{19\sqrt{\pi}}}, \quad \dot{\kappa} \equiv \frac{\kappa}{1 + \frac{32\sqrt{2}T - kh}{19\sqrt{\pi}}}.$$

$$\dot{w}_1(t) = \ldots - 4\dot{\kappa} w_1(t), \quad \dot{w}_2(t) = \ldots - 4\dot{\kappa} w_1(t) - 4\dot{\kappa} w_2(t).$$

The ellipsis stands for the right-hand side of formula (11). The sought function $v(t) = q(t)/\bar{q}$ ($t = t', \ t' \in [kh, (k + 1)h], k \geq 0$) is computed by the standard Runge-Kutta 4th order method for integration of the ODE system (the authors used Scilab software). The numerically obtained
TDS-spectra nearly agree with experimental curves. If a TDS-spectrum has two peaks, then \( w_{3,4} \) should be additionally used to improve modeling accuracy. For a comparison, lines with marks in Fig. 1, 2 illustrate TDS-spectra simulated by numerical solution (based on difference scheme) of the original distributed boundary-value problem with dynamical boundary conditions (the algorithm, including the model with reversible trapping in the bulk, was presented in Ref. [8]).

**Figure 1.** Phase trajectories

**Figure 2.** TDS-spectrum, numerical simulation

### Conclusions

The paper presents a thermal desorption functional differential equation of neutral type with integrable weak singularity for modeling the degassing TDS-spectrum of hydrogen-presaturated structural materials. The proposed numerical method allows using a standard procedure for low order ODE system solving as an alternative to solving the original non-linear boundary-value problem with dynamical boundary conditions. One can thus quickly model TDS-spectra for a wide range of parameters, reveal the limiting factors and explore the material also under extreme conditions (where a natural experiment would be problematic).

The main physical sense of the results is the following. One cannot a priori rule out fluctuating thermal desorption, not even for defect-free materials with minor trapping of the diffusing hydrogen (the diffusion model in this paper is free of additives associated with traps). The problem for future research is to differentiate the peaks arising from “surface-volume” interaction dynamics from those induced by hydrogen release from traps with different binding energies.

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