

## Supplementary material to

### Analysis of thermal desorption of hydrogen in metallic alloys

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#### Appendix A: Kinetics of trapping and detrapping

The rate at which hydrogen atoms are trapped per unit volume is defined as

$$\dot{n}_t = \underbrace{(\theta_L \beta N_L)}_{(1)} \cdot \underbrace{\nu \exp\left\{\frac{-E_t}{RT}\right\}}_{(2)} \cdot \underbrace{\left[\frac{(1-\theta_T)\alpha N_T}{\beta N_L + \alpha N_T}\right]}_{(3)} \quad (\text{A.1})$$

where the part labelled (1) on the right-hand side of this equation represents the number of hydrogen atoms in lattice sites per unit volume, (2) is the probability of capturing an atom per second, and (3) gives the probability that the atom can jump into a neighbouring empty trap site. The rate at which hydrogen atoms are detrapped per unit volume is likewise defined as

$$\dot{n}_d = \underbrace{(\theta_T \alpha N_T)}_{(4)} \cdot \underbrace{\nu \exp\left\{\frac{-E_d}{RT}\right\}}_{(5)} \cdot \underbrace{\left[\frac{(1-\theta_L)\beta N_L}{\beta N_L + \alpha N_T}\right]}_{(6)} \quad (\text{A.2})$$

where (4) is the number of hydrogen atoms in trap sites per unit volume, (5) is the probability of releasing an atom per second, (6) gives the probability of a neighbouring empty lattice site.

The net rate of change of trapped population can be written as

$$\alpha N_T \dot{\theta}_T = \dot{n}_t - \dot{n}_d = -\beta N_L \dot{\theta}_L \quad (\text{A.3})$$

Substitution of (A.1) and (A.2) into (A.3) gives

$$\dot{\theta}_T = \nu \left[ \exp\left\{\frac{-E_t}{RT}\right\} \theta_L (1-\theta_T) - \exp\left\{\frac{-E_d}{RT}\right\} \theta_T (1-\theta_L) \right] \left( \frac{\beta N_L}{\beta N_L + \alpha N_T} \right) \quad (\text{A.4})$$

and this can be re-written in the concise McNabb & Foster form

$$\dot{\theta}_T = [A\theta_L(1-\theta_T) - B\theta_T(1-\theta_L)]\nu \quad (\text{A.5})$$

where the constants  $A$  and  $B$  read

$$A = \left( \frac{\beta N_L}{\beta N_L + \alpha N_T} \right) \exp\left\{ \frac{-E_t}{RT} \right\} \quad \text{and} \quad B = \left( \frac{\beta N_L}{\beta N_L + \alpha N_T} \right) \exp\left\{ \frac{-E_d}{RT} \right\}. \quad (\text{A.6})$$

Equation (A.5) states that the net rate is  $\dot{\theta}_T = g\nu$  where  $g$  denotes the term in square brackets.

It is shown here that the local equilibrium equation (3) is the limit of equation (A.5) when the vibration frequency  $\nu \rightarrow \infty$  at finite  $\dot{\theta}_T$ . Consequently,  $g \rightarrow 0$  and local equilibrium implies that

$$\frac{\theta_T}{1-\theta_T} = \frac{\theta_L}{1-\theta_L} \cdot \exp\left\{ \frac{-\Delta H}{RT} \right\}, \quad (\text{A.7})$$

where the trap binding energy is  $\Delta H = E_t - E_d$ . Now introduce the non-dimensional groups, as identified in Section 2.3, such that (A.3) can be re-written as

$$\frac{\partial \theta_T}{\partial \bar{t}} = \frac{\bar{\nu}}{1+\bar{N}} \left[ \exp\left\{ \frac{-\bar{E}_t}{\bar{T}} \right\} \theta_L(1-\theta_T) - \exp\left\{ \frac{\bar{\Delta H} - \bar{E}_t}{\bar{T}} \right\} \theta_T(1-\theta_L) \right], \quad (\text{A.8})$$

where the non-dimensional frequency is  $\bar{\nu} \equiv \nu L^2 / D_0$  and the trapping activation energy is  $\bar{E}_t \equiv E_t / RT_0$ .

Additional TDS full numerical simulations have been performed using (A.8) and (8), with the choice of parameters:  $\bar{N} = 10^{-4}$ ,  $\bar{\Delta H} = -15$ ,  $\bar{E}_t = 0$ ,  $\bar{Q} = 2.75$ ,  $\theta_L^0 = 10^{-6}$ ,  $\bar{\phi} = 0.1$  and selected values of  $\bar{\nu}$ . The predictions are given in [Figure S1](#) along with the numerical solution to the diffusion equation (9) assuming local equilibrium. It is concluded that, for  $\bar{\nu}$  over a very wide range of  $10^9$ - $10^{15}$  (i.e.  $\nu = 10^8 \text{ s}^{-1}$  to  $\nu = 10^{14} \text{ s}^{-1}$  for  $D_0 = 10^{-7} \text{ m}^2 \text{ s}^{-1}$  and  $L = 1 \text{ mm}$ ), the finite trap kinetics play a negligible role: local equilibrium is satisfied provided

$\bar{\nu}$  exceeds  $10^6$ .

## B: Analytical solution to reduced ODE in regime I

Recall that, in Regime I, the traps are shallow and  $K\theta_L^0 \ll 1$ . Additionally, if the trap density is sufficiently high that  $K\bar{N} \gg 1$ , then the ODE (16) reduces to

$$\frac{df}{d\bar{t}} + \left( \frac{\overline{\Delta H \bar{\phi}}}{\bar{T}^2} \right) f = - \left( \frac{\pi^2 \bar{D}_L}{K\bar{N}} \right) f, \quad (\text{B.1})$$

where  $\bar{D}_L$ ,  $K$  and  $\bar{T}$  evolve with time  $\bar{t}$ . The ODE (B.1) can be integrated explicitly from time 0 to  $\bar{t}$  by making the substitution

$$y \equiv \frac{1}{\bar{T}} = (1 + \bar{\phi}\bar{t})^{-1} \quad (\text{B.2})$$

Introduce the notation  $\bar{D}_L / K = e^{\psi y}$ , where  $\psi = \overline{\Delta H} - \bar{Q}$ . Then, integration of (B.1) gives

$$\ln(f) = \overline{\Delta H}(y-1) + \frac{\pi^2}{\bar{\phi}\bar{N}} \left[ -\frac{e^{\psi y'}}{y'} + \psi \text{Ei}(\psi y') \right]_{y'=1}^{y'=y}, \quad (\text{B.3})$$

where  $f(\bar{t}=0) = 1$ ,  $y(\bar{t}=0) = 1$  and the exponential integral  $\text{Ei}(\psi y')$  is defined in the usual way by

$$\text{Ei}(x) = - \int_{-x}^{\infty} \frac{e^{-\zeta}}{\zeta} d\zeta. \quad (\text{B.4})$$

Note that the non-dimensional flux  $\bar{J}$  is related directly to  $f$  by  $\bar{J} = \pi \bar{D}_L \theta_L^0 f$  upon making use of (14) and (15). Consequently, the maximum flux can be written as  $\bar{J}_{\max} = \pi \bar{D}_L \theta_L^0 f_{\max}$ , and, upon writing  $y = 1/\bar{T}_{\max}$  as the upper limit in (B.3), we obtain

$$\ln(f_{\max}) = \overline{\Delta H} \left( \frac{1}{\bar{T}_{\max}} - 1 \right) + \frac{\pi^2}{\bar{\phi}\bar{N}} \left[ -\frac{e^{\psi y'}}{y'} + \psi \text{Ei}(\psi y') \right]_{y'=1}^{y'=\frac{1}{\bar{T}_{\max}}}. \quad (\text{B.5})$$

A comparison of the numerical solution of the PDE (9) with the analytical solution (B.3) in

regime I is given in **Figure S2**, assuming  $\theta_L^0 = 10^{-6}$ ,  $\bar{Q} = 2.75$ ,  $\bar{\phi} = 0.1$  and  $\bar{N} = 10^{-3}$ . The agreement is adequate.

## Figures

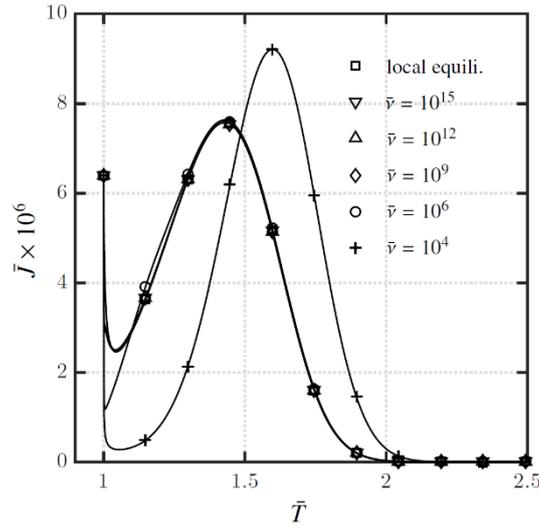


Figure S1: Comparison of solutions of coupled diffusion equations with trap kinetics (8) and (A.8) for different values of normalised jump frequency  $\bar{\nu}$  with the diffusion equation considering local equilibrium (9) for  $\bar{Q} = 2.75$  kJ/mol. Trap kinetics solution is identical to local equilibrium solution except for very low (unphysical) jump frequency.

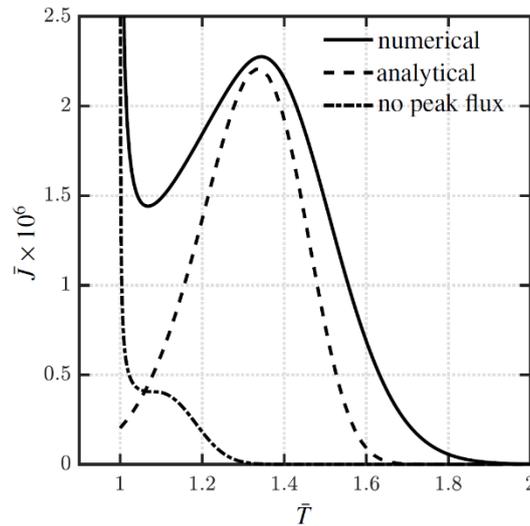


Figure S2: Comparison of analytical (B.5) and numerical (9) solutions of TDS flux versus temperature in regime I ( $\Delta H = -10$ ). The parameters used are  $\theta_L^0 = 10^{-6}$ ,  $\bar{Q} = 2.75$ ,  $\bar{\phi} = 0.1$  and  $\bar{N} = 10^{-3}$ . A numerical solution for the TDS flux, with no maximum, is included for comparison: it is obtained at  $\bar{N} = 8 \times 10^{-4}$ .