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Mixed mechanisms controlling hydrogen–metal reactions under steady state conditions: the diffusion–interface mechanism

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Abstract

Hydrogen–metal reactions (forming metal hydrides) which progress by a "contracting-envelope" morphology under steady state conditions (*i.e.* at a constant velocity of the reaction front) may be controlled by different rate-limiting steps. Usually, a single-step mechanism (*e.g.* diffusion, interface processes, etc.) is considered for the interpretation of experimental kinetic data. In the present work a more generalized mixed mechanism which involves simultaneous contributions of two microscopic processes (*i.e.* diffusion and interface emission) is treated. The single-step mechanisms are derived as particular extreme cases of the generalized formalism. The requirements which establish the existence of either a single or a mixed mechanism are evaluated and the experimental kinetic behaviour is discussed.

1. Introduction

Heterogeneous reactions between a certain gas and a metal proceed by a complex process consisting of a sequence of microscopic steps (*e.g.* chemisorption, transport, phase transformations, etc.) leading to precipitation of the product in the reacting metal matrix. Many gas–solid reactions (especially reactions of bulk samples with well-defined geometrical shapes) progress by the so-called "contracting-envelope" morphology (see *e.g.* ref. 1). In these cases a continuous product layer is formed on the surface, with the product–reactant interface moving into the bulk of the reacting sample. The sequence of main steps involved in the kinetic process are then:

(1) Chemisorption of the gas phase on the product layer surface (usually dissociative chemisorption);

(2) Penetration into the subsurface region;

(3) Diffusion across the product layer (*i.e.* towards the product–reactant interface);

(4) Transfer across the product–reactant interface;

(5) Dissolution of the gas phase atoms in the reacting matrix and a phase transition leading to precipitation of the product (at the interface).

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The velocity U of the interface may be either time dependent, *i.e.* $U(t)$, or constant. When a constant velocity is maintained, the reaction proceeds under steady state conditions.

The conventional approach of different kinetic models is based on the assumption that one of the microscopic steps involved in the reaction is much slower than all the other steps, being the rate-determining step of the overall process. Formulations based on a single-step controlling mechanism can then be derived [2] relating the measured kinetic parameters (*e.g.* U) to the applied experimental conditions (*i.e.* temperature and pressure). In certain systems such single-mechanism models fit well the kinetic behaviour of the system over a wide range of temperatures and pressures.

As pointed out previously [3], under steady state conditions all the atom fluxes involved in the different microscopic steps are actually equal. Thus the term a rate-determining step does not mean that the particular flux is lower but that the corresponding rate constant associated with that step is much smaller than the other rate constants associated with all other steps.

Generally, a situation may arise where the relative magnitudes of the different rate constants (associated with the different microscopic steps) are comparable. Moreover, since the relative magnitudes of the different rate constants may change with a variation of the experimental conditions, a corresponding change of the controlling mechanism may occur. Such a change from one single-step controlling mechanism to another single-step mechanism also involves an intermediate region where both steps dominate. Thus possible cases of mixed controlling mechanisms should be treated as a more generalized formalism of the single-step mechanisms.

In the present work such a mixed controlling mechanism is demonstrated for a system reacting under a "contracting-envelope" morphology with a constant (steady state) interface velocity. Mixed diffusion–interface-controlling steps are simultaneously treated. The requirements which establish either a single-step or a mixed mechanism are evaluated and the experimental kinetic behaviour which may be anticipated is discussed. The model presented is most appropriate to hydrogen–metal reactions, where simplified diffusion equations may be applied [2]. However, its qualitative trends may also be adapted to other types of gas–solid reactions.

2. The model

Assume a planar metal sample reacting with hydrogen gas at a pressure P and temperature T. A continuous hydride layer is formed on the sample, progressing inwards into the bulk.

Under steady state conditions the hydride layer attains an apparently constant thickness l_h owing to the simultaneous compensating effects of hydride progression (at the hydride–metal interface) and hydride cracking (at the outer side of the layer). The thickness of this steady state layer may either be temperature dependent, *i.e.* $l_h(T)$, or temperature invariable. We shall further assume that only a single hydride phase is thermodynamically stable, with a homogeneity range extending from H:M $=Y(T)$ (*i.e.* the lower composition limit at temperature T) up to H:M $=S$ (*i.e.* the upper composition limit attained at infinite pressure). Thus under a given set of experimental conditions (P, T) a concentration gradient of hydrogen (dissolved in the hydride beyond the lower composition limit) is maintained across the hydride layer. Denoting the excessive hydrogen concentration in the hydride by $Z(P,T)$, *i.e.* under the given experimental conditions the equilibrium stoichiometry of the hydride is $MH_{Y(T)+Z(P,T)}$, we shall label the excessive concentrations at the gas–hydride surface and hydride–metal interface by $Z_0(P,T)$ and $Z_i(P,T)$ respectively. Assuming a linear concentration gradient across the layer, the hydrogen diffusion flux is given by

$$J_d = \frac{d_h}{M_h} \frac{D(T)\Delta Z(P,T)}{l_h} \tag{1}$$

where J_d ((g atom H) cm^{-2} s^{-1}) is the diffusion flux, d_h (g cm^{-3}) is the weight density of the hydride, M_h is the molecular weight of the hydride, $D(T)$ (cm^2 s^{-1}) is the diffusion constant of hydrogen in the hydride and $\Delta Z(P,T)$ (H:M, dimensionless) is given by

$$\Delta Z(P,T) = Z_0(P,T) - Z_i(P,T) \tag{2}$$

At the hydride–metal interface the flux J_i ((g atom H) cm^{-2} s^{-1}) of hydrogen surmounting the boundary may be approximated by [2]

$$J_i = \frac{d_h}{M_h} bk_i(T)Z_i(P,T) \tag{3}$$

where b (cm) is the distance between two adjacent layers of diffusing hydrogen atoms (in the hydride) and $k_i(T)$ (s^{-1}) is the boundary transfer rate constant.

Under steady state conditions the fluxes given by eqns. (1) and (3) are equal, yielding the following relation [2] between Z_i and Z_0:

$$\frac{Z_i}{Z_0} = (1+\xi)^{-1} \tag{4}$$

where ξ is a dimensionless quantity given by

$$\xi(T) = bl_h \frac{k_i(T)}{D(T)} \tag{5}$$

This quantity can also be expressed as

$$\xi(T) = n \frac{k_i(T)}{D(T)/b^2} = n \frac{k_i(T)}{k_d(T)} \tag{6}$$

where n is the number of mobile hydrogen layers composing the total hydride thickness (*i.e.* $l_h = nb$) and $k_d(T)$ (s^{-1}) is the diffusion rate constant.

The value of the parameter ξ determines which controlling mechanism dominates. For $\xi \ll 1$, from eqn. (4) we derive $Z_i \approx Z_0$, which means that an almost even distribution of hydrogen is maintained across the hydride layer as a result of fast diffusion; hence a pure interface-controlled mechanism takes place. On the other hand, for $\xi \gg 1$, eqn. (4) yields $Z_i/Z_0 \ll 1 \approx 0$; thus a pure diffusion-controlled mechanism dominates. For ξ values around unity a mixed diffusion–interface-controlled mechanism should be considered.

In order to calculate the hydride–metal interface velocity U (cm s^{-1}), we shall use the relation [2]

$$U(P,T) = AJ \tag{7}$$

Where J is the steady state hydrogen flux (given by either eqn. (1) or eqn. (3)) and A (cm^3(g atom H)$^{-1}$) is a proportionality constant given by

$$A = \frac{M_m}{d_m} \frac{1}{Y(T) + Z_i(P,T)} \tag{8}$$

Substituting eqn. (4) into eqn. (1), the expression for the steady state flux J takes the form

$$J = \frac{d_h}{M_h} \frac{D(T)Z_0(P,T)}{l_h} \frac{\xi(T)}{1 + \xi(T)} \tag{9}$$

Which by substituting into eqn. (7) and utilizing relation (8) yields

$$U(P,T) = \frac{M_m}{d_m} \frac{d_h}{M_h} \frac{D(T)Z_0(P,T)}{l_h[Y(T) + Z_i(P,T)]} \frac{\xi(T)}{1 + \xi(T)} \tag{10}$$

Equation (10) is a generalized form from which the extreme cases for $\xi \gg 1$ (diffusion-controlled mechanism) and $\xi \ll 1$ (interface-controlled mechanism) can be easily derived.

Thus for $\xi \gg 1$ eqn. (10) reduces to

$$U(P,T) \approx \frac{M_m}{d_m} \frac{d_h}{M_h} \frac{D(T)Z_0(P,T)}{l_h Y(T)} \tag{11}$$

Which is the result obtained for a pure diffusion-controlled mechanism [2]. For $\xi \ll 1$ eqn. (10) takes the form

$$U(P,T) \approx \frac{M_m}{d_m} \frac{d_h}{M_h} b \frac{Z_0(P,T)k_i(T)}{Y(T) + Z_0(P,T)} \tag{12}$$

which represents an interface-controlled process.

3. Generalized temperature dependence

The interpretation of the experimental kinetic data (*i.e.* the measured U values) usually involves Arrhenius-type plots of ln U *vs.* $1/T$. The slopes of these plots are regarded as representing some apparent "activation barriers" for the reaction, from which the controlling mechanisms may be postulated.

It is evident from eqn. (10) that even if each of the rate constants appearing in that expression obeys an Arrhenius-type relation, for the mixed mechanism deviations from a linear Arrhenius dependence are still anticipated.

Let us analyse first the temperature dependence in the two extreme cases of the single-step controlling mechanisms, *i.e.* eqns. (11) and (12) respectively.

In the following discussion the hydride layer steady state thickness l_h is assumed to be temperature independent. This assumption is not always valid, as demonstrated recently for the titanium–hydrogen reaction [4], where a significant $l_h(T)$ temperature dependence modified the ln U *vs.* $1/T$ plots.

Assuming that the kinetic rate constants $k_d(T)$ (or $D(T)$) and $k_i(T)$ obey an Arrhenius-type relation, the question of whether eqns. (11) and (12) also follow an Arrhenius-type behaviour depends on the temperature behaviour of the composition ratio terms in these equations (*i.e.* Z_0/Y in eqn. (11) and $Z_0/(Y+Z_0)$ in eqn. (12)). In many hydrogen–metal systems the homogeneity range of the hydride is much smaller than the lower composition limit of that phase (*i.e.* $Z_0 \ll Y$). Hence for simplicity we shall approximate the term $Z_0/(Y+Z_0)$ in eqn. (12) by Z_0/Y and treat the temperature behaviour of that term (common to both eqns. (11) and (12)).

We shall further assume that the outer surface of the hydride is under equilibrium conditions with the gas phase, *i.e.* that $Z_0(P,T)$ is close to its equilibrium value. A crude and simplified relation linking the equilibrium hydride composition with P and T may be applied [5]:

$$\ln P^{1/2} = -\frac{\Delta H_H}{RT} + \frac{\Delta S_H}{R} + \ln\left(\frac{\rho_h}{1-\rho_h}\right) \tag{13}$$

Where R is the gas constant, ΔH_H is the relative partial molar enthalpy of the excess hydrogen dissolved in the hydride phase, ΔS_H is the corresponding excess entropy and ρ_h is the normalized composition of the hydride, defined as

$$\rho_h(P,T) = \frac{Y(T)+Z_0(P,T)}{S} \tag{14}$$

With S the saturation H:M value (at infinite pressure).

Using eqn. (13) and substituting $P_d(T)$, the dissociation equilibrium pressure conditions become

$$P = P_d(T)$$

$$Z_0(P,T) = 0 \tag{15}$$

$$\rho_h = \frac{Y(T)}{S}$$

The following relation is obtained:

$$\ln P_d^{1/2} = -\frac{\Delta H_H}{RT} + \frac{\Delta S_H}{R} + \ln\left(\frac{Y/S}{1-Y/S}\right) \tag{16}$$

On the other hand, the temperature dependence of the hydride dissociation pressure is also given by

$$\ln P_d = -\frac{\Delta H_f}{RT} + \frac{\Delta S_f}{R} \tag{17}$$

where ΔH_f is the enthalpy of formation of the hydride and ΔS_f is the corresponding entropy of formation. Using eqns. (16) and (17), we derive

$$\frac{Y(T)}{S} = \frac{K(T)}{1+K(T)} \tag{18}$$

with

$$K(T) = \exp\left(-\frac{\delta(\Delta S)}{R}\right)\exp\left(\frac{\delta(\Delta H)}{RT}\right) \tag{19}$$

$$\delta(\Delta H) = \Delta H_H - \frac{\Delta H_f}{2}$$

$$\delta(\Delta S) = \Delta S_H - \frac{\Delta S_f}{2} \tag{20}$$

Subtracting eqn. (13) from eqn. (16), rearranging the different terms and using eqn. (18) yields

$$\rho_h = \left[\frac{1}{K(T)}\left(\frac{P_d}{P}\right)^{1/2} + 1\right]^{-1} \tag{21}$$

From eqn. (14)

$$\frac{Z_0}{Y} = \frac{\rho_h}{Y/S} - 1 \tag{22}$$

Which by substituting eqns. (21) and (18) leads to

$$\frac{Z_0}{Y} = \frac{1-(P_d/P)^{1/2}}{K(T)+(P_d/P)^{1/2}} \tag{23}$$

In the temperature range where $(P_d/P)^{1/2} \ll 1$, *i.e.* when the applied hydriding pressure is much higher than the decomposition pressure of the hydride,

$$\frac{Z_0}{Y} \approx \frac{1}{K(T)} \tag{24}$$

Which by substituting into eqn. (11) or (12) indicates that for these single-step controlled mechanisms the ln U *vs.* $1/T$ curves do obey an Arrhenius-type dependence with slopes E_{ap}/R, where E_{ap} are apparent "activation barriers" given by

$$E_{ap(d)} = \delta(\Delta H) + E_d \tag{25}$$

for the diffusion-controlled case and

$$E_{ap(i)} = \delta(\Delta H) + E_i \tag{26}$$

for the interface-controlled case.

The terms E_d and E_i in eqns.(25) and (26) are the true activation barriers for diffusion and the hydrogen interface traverse respectively. As pointed out previously [6], the apparent activation barriers evaluated from the ln U *vs.* $1/T$ plots do not coincide with the true barriers of the rate-determining processes. Only when the additional enthalpy-related parameter $\delta(\Delta H)$ is small (which should be reflected by a very weak temperature dependence of the hydride composition limit Y) does the apparent activation energy correspond closely to the true activation barrier. An example where $\delta(\Delta H)$ contributes significantly to E_{ap} has been demonstrated for the uranium–hydrogen reaction [6], while examples for a small $\delta(\Delta H)$ contribution are given by the titanium–hydrogen [4] and hafnium–hydrogen [7] reactions.

It should be realized that as the reaction temperature is increased (and assuming that the controlling mechanism is not altered over the whole temperature range), the decomposition term $(P_d/P)^{1/2}$ in eqn. (23) starts to contribute and deviations from the Arrhenius relation are displayed. Actually, at a certain temperature U starts to decrease with increasing temperature, approaching zero as P approaches P_d. Nevertheless, as long as the hydride thickness l_h is not too dependent on temperature and the same single-step mechanism is involved, these deviations due to the $(P_d/P)^{1/2}$ term start to contribute only at temperatures where P_d is at least a few per cent of P (see *e.g.* Fig. 1, where the maxima in the curves occur at about 1050–1100 K where $P_d/P \approx 0.02$–0.03).

So far, the conventional single-step controlling mechanisms have been discussed. Let us now consider the possibility that changing the reaction temperature induces a change in the controlling mechanism. According to eqn. (5) (or eqn. (6)), the parameter $\xi(T)$ obeys an Arrhenius-type relation (again, as long as l_h does not vary much with temperature). Thus we can write

$$\xi(T) = \xi_0 \exp\left(\frac{\Delta E_{id}}{RT}\right) \tag{27}$$

where ξ_0 is a temperature-independent dimensionless constant and ΔE_{id} is the activation energy difference

$$\Delta E_{id} = E_d - E_i \tag{28}$$

When $E_d > E_i$ (*i.e.* $\Delta E_{id} > 0$), $\xi(T)$ decreases with increasing temperature. Keeping in mind that for $\xi \gg 1$ the diffusion-controlled mechanism dominates whereas for $\xi \ll 1$ the interface-controlled mechanism takes place, the trend that $\xi(T)$ decreases with increasing temperature enables the possible conversion of a diffusion-controlled mechanism prevailing in the lower temperature regime into interface-controlled mechanism operating in the higher temperature regime (with a lower activation barrier). It should be emphasized that such a conversion will not necessarily occur even for $E_d > E_i$ and it occurrence depends also on the value of the pre-exponential factor ξ_0 in eqn. (27). Only for $\xi_0 \ll 1$ can such a conversion take place. Thus $E_d > E_i$ is a necessary but insufficient condition for conversion of the low temperature diffusion mechanism into the high temperature interface mechanism.

Figure 1 demonstrates the ln U *vs.* $1/T$ behaviour anticipated according to the generalized eqn. (10) for some given sets of parameters summarized in Table 1. The P–T dependence of the different composition terms was calculated by eqns. (4), (18) and (23). Figures 1(A) and 1(B) illustrate the case when $\xi_0 \gg 1$, *i.e.* when the pure diffusion-controlled mechanism dominates throughout the relevant temperature range. Conventional Arrhenius-type curves are then displayed with slopes $E_{ap(d)}/R$, where $E_{ap(d)}$ is given by eqn. (25). On the other hand, Figs. 1(C) and 1(D) illustrate the case when $\xi_0 \ll 1$. Deviations from a linear Arrhenius dependence are now displayed, starting at about 430 K. Below that temperature $\xi(T < 430\ \mathrm{K}) > 3.5$, thus the pure diffusion-controlled mechanism dominates, whereas above about 590 K $\xi(T > 590\ K) < 0.2$, hence a pure interface-controlled mechanism (with an apparent slope corresponding to eqn. (26)) takes place. In the temperature range 430–590 K an intermediate mixed mechanism operates, leading to a non-linear behaviour in the ln U *vs.* $1/T$ curves. It is further evident that the larger $\delta(\Delta H)$ is (as compared to E_d or E_i), the less pronounced is the change of apparent slope displayed upon the transfer of controlling mechanism (compare Figs. 1(C) and 1(D)).

It is note worthy to point to the different approximations applied in the calculations of the curves shown in Fig. 1. These approximations can be divided into two groups, one group leading to the derivation of the generalized equation of U (eqn. (10)) and the other group, the approximation in the analytical pressure–temperature–composition relations (*i.e.* eqn. (13)), leading to the expressions substituted for Z_0, Z_i and Y in eqn. (10). Among the former set of approximations one can point to:

(1) The assumption of a composition-independent diffusion constant, which for various hydride systems [7, 8] has been found to be a reasonable approximation*;

(2) The assumption of a linear concentration gradient across the hydride layer (eqn. (1)), which is justified under the considered steady state conditions;

(3) The assumption of an interface flux (eqn. (13)) proportional to the local concentration of hydrogen atoms at the hydride–metal boundary (*i.e.* Z_i), which for a single-atom "jump" mechanism seems to be quite a good approximation.

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*Even when a certain composition dependence was evaluated for D_0, it has been suggested [8] to be proportional to a term $1-\rho$. According to eqn. (14), since in most systems $Z_0 < Y$, such a dependence is not significant and cannot alter much the P–T dependence of U.

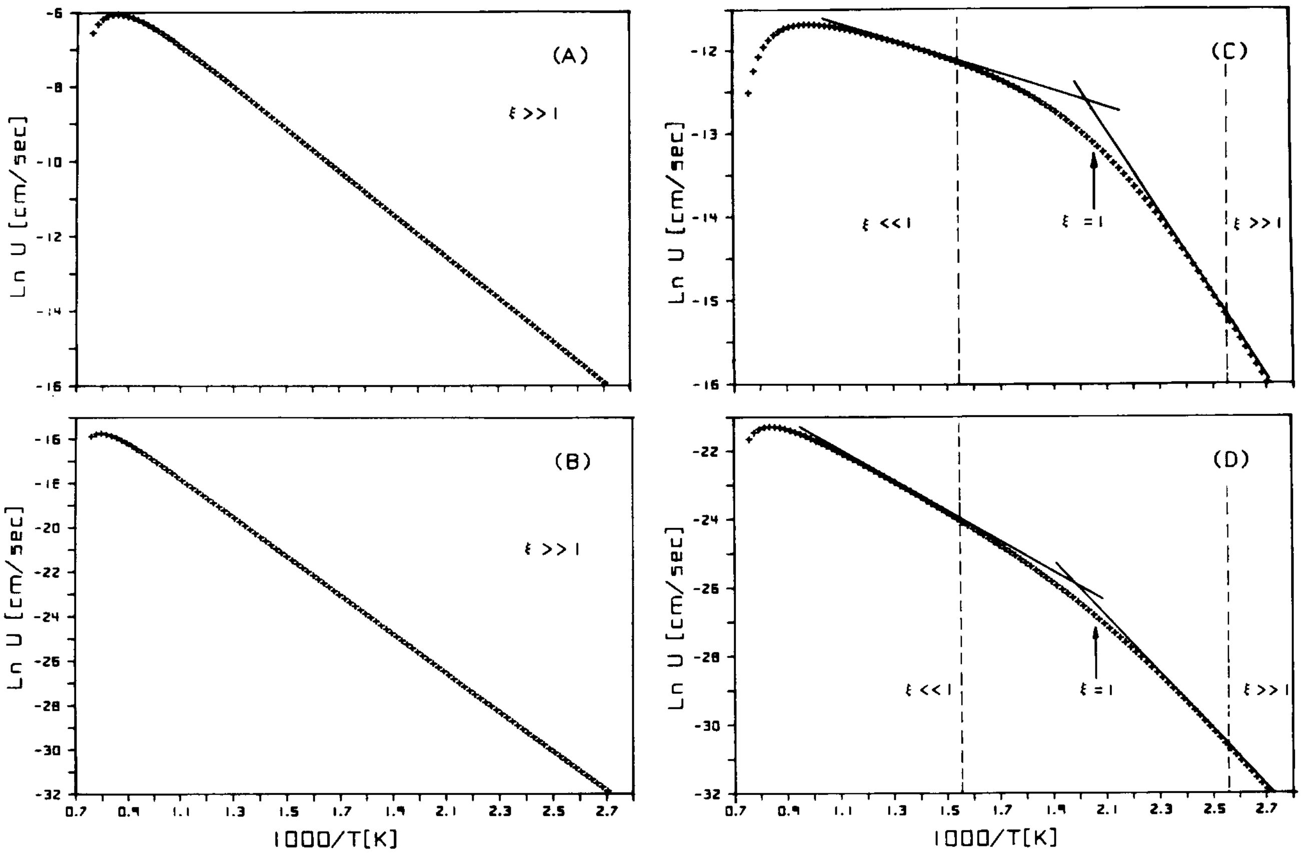

Fig. 1. Arrhenius plots of ln U *vs.* $1/T$ according to eqn. (10). The different composition terms in that equation were approximated by analytical expressions derived from eqn. (13). Numerical values of the different parameters are summarized in Table 1. (A) $\xi_0 = 10$, $\delta(\Delta H) = 1300$ kcal mole^{-1}. (B) $\xi_0 = 10$, $\delta(\Delta H) = 7600$ kcal mole^{-1}. (C) $\xi_0 = 10^{-4}$, $\delta(\Delta H) = 1300$ kcal mole^{-1}. (D) $\xi_0 = 10^{-4}$, $\delta(\Delta H) = 7600$ kcal mole^{-1}.

TABLE 1

Parameters utilized for calculations of ln *U* *vs.* 1/*T* curves (eqn. (10)) in Fig. 1

Parameters which are common to all curves in Fig. 1

Parameter	Units	Value
S	dimensionless (H:M)	2
$\delta(\Delta S)$	cal deg^{-1} mole^{-1}	0.8
ΔH_f	cal mole^{-1}	35000
ΔS_f	cal deg^{-1} mole^{-1}	25
P	atm	1
D_0	cm^2 s^{-1}	10^{-3}
E_d	cal (g atom)$^{-1}$	10000
E_i	cal (g atom)$^{-1}$	1000
l_h	cm	2×10^{-3}
$\frac{M_m}{d_m}\frac{d_h}{M_h}$	dimensionless	0.7

Parameters which are changed for each curve

ξ_0	dimensionless	10	10	10^{-4}	10^{-4}
$\delta(\Delta H)$	cal mole^{-1}	1300	7600	1300	7600

Equation (1) then is based on a reasonable set of approximations and can describe quite accurately the pressure–temperature behaviour of U (under the given model). On the other hand, in order to express analytically the P–T dependence of the different composition terms appearing in eqn. (1), a very crude approximation (eqn. (13)) has been applied. Actually, that approximation is valid only for an ideal solid solution without interactions between the dissolved hydrogen atoms and the metal sublattice or between H–H neighbours. Higher order approximations such as the Bragg–Williams [9] or Quasi-Chemical [10] approximations can be utilized. Alternatively, polynomial fits to the experimental $Y(T)$ and $Z_0(P,T)$ values can be substituted into eqn. (10). The curves illustrated in Fig. 1 thus demonstrate only a qualitative trend anticipated by the present model (*i.e.* the change of slope and the intermediate mixed mechanism region in the Arrhenius plots), whereas for a more quantitative analysis of some given experimental systems a more accurate substitution of these composition terms is required.

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