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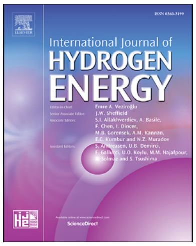

Analysis of hydrogen desorption from linear heating experiments: Accuracy of activation energy determinations

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ABSTRACT

Through performing hydrogen desorption experiments at different heating rates, β, the (effective) activation energy, E, of the desorption process can be determined from the shift of a characteristic temperature, T_f, of the hydrogen evolution effect with heating rate. In the literature various methods have been employed, and in the present work the accuracy of these methods is investigated. The Kissinger-Akahira-Sunose, Flynn-Wall-Ozawa, Starink, Kissinger and Choo-Lee methods all employ approximations which cause deviations in the activation energy determination, which increase drastically as E/RT (R is the gas constant) becomes smaller. It is shown that for various hydrogen desorption reactions reported in the literature, deviations in reported E between ~1 and ~20% can occur due to inappropriate use of methods. It is shown that the Ozawa and Flynn-Wall-Ozawa methods are highly inaccurate and particularly for hydrogen evolution, where E/RT is often smaller than 15, they are in most cases inappropriate. The Kissinger peak method is accurate for first order reactions, but as hydrogen evolution reactions generally are not first order reactions, application of this method will result in inaccuracies which increase for decreasing E/RT. In general the magnitude of the deviations of such a peak method are not predictable, as this depends on the reaction mechanism. In many cases the Kissinger peak method is inappropriate for high accuracy determination of activation energy for hydrogen evolution reactions. Amongst the methods that provide an activation energy directly from a slope (i.e. without iterative procedures) the Starink method provides the best accuracy of activation energy analysis methods studied in the literature. It provides an accuracy that is better than 2% for $E/RT > 6$, which covers all known hydrogen desorption reactions, whilst correction for residual errors are possible.

Introduction

Analysis of the mechanisms of absorption and desorption of hydrogen in materials is important as it improves our understanding of two key areas of technology: solid-state hydrogen storage for cleaner energy applications and hydrogen assisted embrittlement (HAE) in structural materials. In the energy application, hydrogen storage systems are a crucial part to allow a hydrogen economy to work, and

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material with a high storage capacity are required [1,2]. In structural materials, hydrogen absorption can lead to HAE and premature, unexpected failure of structural components. In both cases, the activation energies of absorption and desorption are particularly important parameters. For hydrogen storage materials a low activation energy is indicative of good applicability of the material for hydrogen storage systems [1]. In studies of hydrogen assisted embrittlement (HAE) in structural materials, determination of the activation energy, E, provides information on the trap states of the H atoms [3].

A regularly employed method for analyses of hydrogen desorption kinetics is linear heating hydrogen desorption measurements. Through performing experiments at several heating rates, β, the (effective) activation energy of the process can be determined from the shift of a characteristic temperature, T_f, of the hydrogen evolution effect with changing heating rate [4,5]. (Often T_f is taken as the temperature of a (local) maximum in H evolution rate, i.e. a peak temperature T_p.) In a range of works (e.g. Refs. [5–10]) such an activation energy determination has been performed with the aid of an analysis method that is generally known as the Kissinger method, i.e. plots of $\ln(T_p^2/\beta)$ versus $1/T_p$ are made, and the slope of the straight line is taken to equal E/R (R is the gas constant). Also the Ozawa method has been regularly employed, see e.g. Ref. [11], as well as the Starink method [12]. The thus obtained (apparent) activation energies have been discussed in terms of operating mechanisms and compared with theoretically derived trap energies and chemical bonding states [13]. Materials for hydrogen storage include materials based on chemical storage processes (e.g. in metal hydrides) and by physisorption processes (e.g. in carbon materials: fullerenes, nanotubes, grapheme; zeolites) [2,14,15]. Promising new developments to improve hydrogen sorption include application of reactive hydride composites (RHC) [16,17] and the use of nanoconfinement in porous material, e.g. in a (meso)porous medium [18,19]. Published desorption data relevant for the present analysis of kinetics includes materials based on Mg–Li (e.g. $Mg(NH_2)_2/LiH$ [20,21]) and Mg–Ti ([22,23]) systems. For structural materials published data on H desorption includes work on Al alloys and steels [24–26].

Whilst this approach has often appeared to be fruitful, it appears to be generally ignored that all the above mentioned activation energy determination methods have a limited accuracy [27–30]. In this contribution, the accuracy of the activation energy analysis methods for linear heating experiments relevant for H desorption will be assessed. It will be shown that accuracy of reported activation energies varies, and in several cases reported measured apparent activation energies will be in error by 4–6%, and corrections for these deviations are presented. Also, improved methods with higher accuracy are identified.

In addition to the special importance of these activation energy determination methods in the analysis of H desorption, the methods have been widely applied to a wide range of other reactions. Just as for H desorption studies the methods are generally applied with little or no reference to their accuracies. In chemistry, the Ozawa (and related Flynn-Wall-Ozawa) method still finds substantial application, even though it has been shown the method is the most inaccurate of its group [27]. A further aim of the present work is thus to further clarify the accuracies of the activation energy determination methods.

Derivations of the methods

Model-free methods

In general it is beneficial to calculate the activation energy using a method that does not depend on the reaction model/mechanism, i.e. a model-free method. The general derivation of model-free activation energy analysis methods has been presented in detail elsewhere [27]. The main elements relevant for hydrogen absorption and desorption studies is summarised in this chapter.

In deriving model-free activation energy analysis methods the transformation rate (e.g. the rate of hydrogen desorption) is considered to be the product of two functions, one depending solely on the temperature, T, and the other depending solely on the fraction transformed, α [27,31]:

$$\frac{d\alpha}{dt} = f(\alpha)k(T) \tag{1}$$

where $f(\alpha)$ is the transformation function. The temperature dependent function is assumed to follow an Arrhenius type dependency:

$$k = k_o \exp\left(-\frac{E}{RT}\right) \tag{2}$$

Inserting Eq. (2) into Eq. (1) and taking the logarithm provides

$$\ln\frac{d\alpha}{dt} = -\frac{E}{RT_f} - \ln f(\alpha) \tag{3}$$

To address reactions occurring during heating at a constant heating rate, β, Eq. (2) is inserted in Eq. (1) and this is integrated by separation of variables:

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{k_o}{\beta}\int_0^{T_f}\exp\left(-\frac{E}{RT}\right)dT = \frac{Ek_o}{R\beta}\int_{y_f}^{\infty}\frac{\exp(-y)}{y^2}dy \tag{4}$$

where $y = E/RT$, $y_f = E/RT_f$, T_f is the temperature at an equivalent (fixed) state of transformation. The integral on the right hand side is generally termed the (Arrhenius) temperature integral, $p(y)$:

$$\int_{y_f}^{\infty}\frac{\exp(-y)}{y^2}dy = p\left(y_f\right) \tag{5}$$

A range of approximations of the temperature integral $p(y)$ have been suggested in the literature. The asymptotic expansion after a single integration in parts provides:

$$p(y) = \frac{\exp(-y)}{y^2}\left(1 + \frac{2!}{-y} + \frac{3!}{(-y)^2} + \frac{4!}{(-y)^3}\cdots\right) \tag{6}$$

The first term in the expansion in Eq. (6) is the approximation used by Murray and White [32]: