

Compensation Effect in the Hydrogenation/Dehydrogenation Kinetics of Metal Hydrides

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Received: September 13, 2004; In Final Form: December 9, 2004

The possible existence of a compensation effect, i.e. concurrent changes in activation energy and prefactor, is investigated for the hydrogenation and dehydrogenation kinetics of metal hydrides, by analyzing a series of reported kinetic studies on Mg and LaNi₅ based hydrides. For these systems, we find a clear linear relation between apparent prefactors and apparent activation energies, as obtained from an Arrhenius analysis, indicating the existence of a compensation effect. Large changes in apparent activation energies in the case of Mg based hydrides are rationalized in terms of a dependency of observed apparent activation energy on the degree of surface oxidation, i.e., a physical effect. On the other hand, we find the large concurrent changes in apparent prefactors to be a direct result of the Arrhenius analysis. Thus, we find the observed compensation effect to be an artifact of the data analysis rather than a physical phenomenon. In the case of LaNi₅ based hydrides, observed scatter in reported apparent activation energies is less pronounced supporting the general experience that LaNi₅ is less sensitive toward surface contamination.

1. Introduction

Soaring oil-prices—driven by limited supply, terrorist threats, and growing energy demands in Asia—has sparked intense research efforts in alternative energy carriers for the future. In particular, hydrogen stored in complex or metal hydrides has been the subject of multiple research projects. To be of practical interest for storage purposes these materials must willingly take up hydrogen and subsequently release it again at a sufficiently high rate. Thus, the kinetics of metal hydrides have been investigated extensively in order to map the reaction mechanisms of hydrogen absorption and desorption, respectively, and to identify possible rate limiting steps to ultimately take steps toward improving the kinetics. Interestingly, obtained kinetic data are scattered extensively, even for similar systems. Thus, reported apparent activation energies are often scattered, and discrepancies among which steps are suggested as controlling the overall rate are often encountered.^{1–3}

In this paper we investigate the possible existence of a compensation effect in the kinetics of the metal–hydrogen reaction viz. hydrogenation of metals and dehydrogenation of metal hydrides (see for instance refs 1 and 4–9 for detailed information).

In a simplified manner, the reaction rate, r , is usually expressed as the product of a rate constant, k , some functional, f , dependent on temperature, T , and concentration, θ , and an approach to equilibrium, β :

$$r = kf(\theta, T)\beta \quad (1)$$

Depending on the nature of the reaction, f can be a functional of gas-phase pressures of the reactants and products, and surface

coverages of reaction intermediates (heterogeneous catalysis) or the bulk concentration of adsorbed atoms (gas–solid reactions). The approach to equilibrium accounts for the rate decrease near equilibrium and secures that the equilibrium limit is not crossed.

The rate constant of most thermally activated processes is usually described well by an Arrhenius relationship

$$k = A \exp\left(\frac{-E_A}{RT}\right) \quad (2)$$

where A is denoted the prefactor and E_A is the activation energy. The prefactor may be interpreted as the potential reaction rate if the temperature is significantly higher than E_A . By taking the natural logarithm of eq 2:

$$\ln(k) = \ln(A) - \frac{E_A}{RT} \quad (3)$$

the Arrhenius relationship implies that a plot of the measured rate constants as a function of the reciprocal temperature will result in a straight line with slope E_A/R and intercept $\ln(A)$. Henceforth we will use the terms “apparent activation energy”, E_A^{app} , and “apparent prefactor”, A_{app} , since k values obtained from kinetic studies can potentially be a sum of several reaction steps.

In some reaction systems, it has been observed that the apparent activation energy varies under different measuring conditions. It is also found that the variation in apparent activation energy is accompanied by a change in A_{app} , i.e., a large apparent activation energy is accompanied by a large prefactor and vice versa;^{10,11} a phenomenon often referred to as the compensation effect (CE).

In some cases, the changes in prefactor and apparent activation enthalpy display a linear dependency according to the Cremer–Constable relation.¹¹

$$\ln A_{app} = aE_A^{app} + b \quad (4)$$

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TABLE 1: Corresponding Values of Apparent Prefactors and Apparent Activation Energies for Hydrogenation (h)/Dehydrogenation (d) of Magnesium Based Hydrides^a

host	method	$\ln(A_{app})$	E_A^{app} [kJ/mol]	comment	temp [K]	P [bar]	sample	ref
Mg–Al	XRPD	20.65	160	d	643–673	0 ^b	A	28
Mg/MgCu ₂	XRPD	21.11	160	d	633–663	0 ^b	B	29
Mg/Mg ₂ Cu	XRPD	12.20	108	d	643–673	0 ^b	C	29
Mg	XRPD	46.04	296	d	633–673	0 ^b	D	30
Mg(Ni)	XRPD	37.45	249	d	623–663	0 ^b	E	30
Mg	TG	19.22	119	d	608–641	3.84	F	32
Mg	Sievert	23.67	167	d	613–643	0.25–6	G	33
Mg	TG	36.44	230	d	635–663	1.5	H	34
Mg(foil)	TG	49.23	284	h	650–700	10–30	I	35
Mg(foil)	TG	53.37	308	h	650–700	10–30	J	35
Mg(Ni)	PCI	9.53	66	h	543–616	1–13	K	36
Mg	Sievert	10.40	91	h	614–648	5–21	L	33

^aIf not otherwise stated, the samples are in powder form. Mg(Ni): Nickel doped magnesium. TG: Thermogravimetry. PCI: pressure–composition isotherm apparatus. XRPD: Parameters determined from quantitative analysis of in situ time resolved X-ray powder diffraction. ^bDehydrogenation in an argon flow 10 mL/min with a pressure of 1 bar. The background pressure of hydrogen was not measured.

The relation implies that values of the natural logarithm of the prefactor plotted against the apparent activation energy (denoted a Constable plot), as obtained from an Arrhenius plot, fall on a straight line with slope a and intercept b .

Although the compensation effect has been known and studied for almost 100 years and been observed in a variety of different fields of science, including electron emission,¹² heterogeneous catalysis,^{10,11,13–18} homogeneous catalysis,¹⁹ temperature-programmed desorption,^{20,21} and diffusion,^{22,23} no consensus on the nature of CE has been reached. However, a number of different explanations for observed compensation effects have been suggested (most of them applicable to heterogeneous catalysis): (i) oversimplified data analysis;^{24,25} (ii) heterogeneity in activity and distribution of active sites;¹⁸ (iii) a correlation between applied reactant pressures and measured apparent activation energy due to coverage dependent terms;^{11,14,15,17} (iv) a change in anharmonicity in the adsorbate–surface bond changes the activation enthalpy of dissociation;²⁶ (v) the enthalpy–entropy relationship;^{10,11} (vi) the heat bath concept;²⁷ (vii) the Brønsted–Evans–Polanyi relation.¹⁶

Our recent findings of large variations (approximately 200 kJ/mol) in the apparent activation energy for dehydrogenation of Mg-based hydrides,^{28–30} prompted us to investigate the possible existence of a compensation effect in metal hydride systems.

2. Results and Discussion

To investigate the potential existence of a CE in metal–hydrogen systems, we review the literature on kinetics studies for two of the most investigated systems, viz., Mg and LaNi₅ based hydrides; in particular the kinetics of the magnesium based hydrides has been investigated thoroughly in the past.³¹

2.1. Mg-Based Hydrides. Corresponding values of $\ln(A_{app})$ and E_A^{app} along with information about the experimental method and reaction conditions (T, P) are presented in Table 1. The values of A_{app} and E_A^{app} in Table 1 are obtained by fitting eq. 3 to reported Arrhenius plots viz. $\ln(k)$ vs $1/T$ data from the references also given in the table. In a single case,³⁴ no Arrhenius plot was reported, only raw kinetic data, i.e., reacted fraction vs time. To extract the desired data, a kinetic expression was fitted to the raw kinetic data. For this purpose we have chosen a conventional Johnson–Mehl–Avrami^{37–40} nucleation and

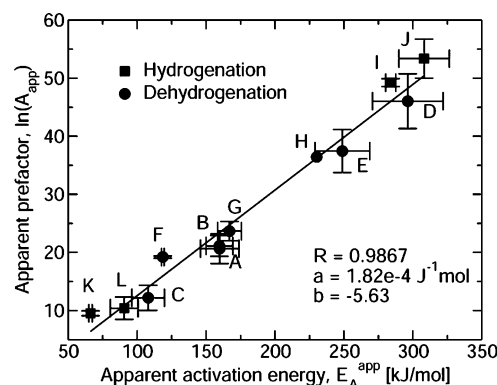


Figure 1. Constable plot of reported values of A_{app} vs E_A^{app} from Table 1 for magnesium based hydrides. Data points are assigned sample letters.

growth kinetic expression (also referred to as the Johnson–Mehl–Avrami–Kohlmogorov equation⁴¹) of the form

$$\alpha(t) = 1 - \exp(-(kt)^n) \quad (5)$$

where $\alpha(t)$ is the time-dependent phase fraction of magnesium hydride. The parameters describing nucleation and growth rates are contained within an effective kinetic parameter, k , and an exponent, n , often referred to as the Avrami exponent.⁴¹ Although the Avrami exponent is sometimes ascribed physical nature in terms of nucleation and growth,⁴² the derived k values are quite insensitive to the value of n , hence both k and n were fitted. A_{app} and E_A^{app} were determined by an Arrhenius analysis of fitted values of k vs $1/T$. This method of data analysis is analogous to the applied analysis in refs 28–30. Minor variations in the kinetic expressions used in the extraction of rate constants in the other references in Table 1 is possible. However, it is generally found that the temperature dependence of the extracted rate constants is rather insensitive to the choice of kinetic expressions.^{30,32,43} This allows for comparison of reported values of A_{app} and E_A^{app} between all the reported data, although the kinetic analysis may differ slightly.

A Constable plot of the values of A_{app} and E_A^{app} in Table 1 has been constructed in Figure 1. It is clearly observed from the figure that the apparent prefactor is linearly correlated with the apparent activation energy, having a correlation coefficient of $R \approx 0.99$.

Thus, in the case of hydrogenation/dehydrogenation of magnesium based hydrides a clear compensation effect according to the Cremer–Constable relation (eq. 4) is observed. From Figure 1 and Table 1 it also seen that the apparent activation energy covers a range of 66–308 kJ/mol for hydrogenation and 118–296 kJ/mol for dehydrogenation, respectively. The corresponding range in apparent prefactors is 19 orders of magnitude for hydrogenation and 12 orders of magnitude for dehydrogenation, respectively. Error bars for both apparent activation energies and apparent prefactors are based on standard deviations of fitted parameters from linear regression analysis. The error bars clearly indicate that observed scatter in apparent activation energies and apparent prefactors is *real* and not due to experimental uncertainties.

A physical explanation for the possible existence of two—or more—kinetic regimes is therefore warranted, at least in the case of apparent activation energies.

To explain the variation in apparent activation energies we will focus on the pretreatment of the samples also termed the *activation procedure*. The samples from Table 1 are ordered as *activated* and *nonactivated* samples in Figure 2. The term

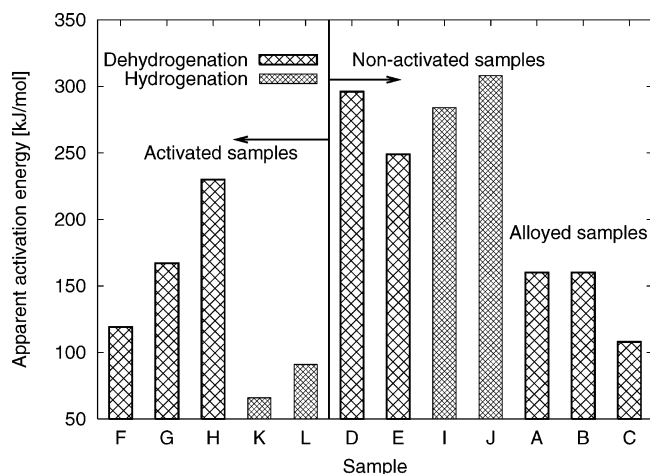


Figure 2. Apparent activation energy, E_A^{app} , from Table 1 for magnesium based hydrides. Data points are assigned sample letters and grouped after pretreatment procedure.

nonactivated implies that the kinetics are measured for the first hydrogenation or first dehydrogenation cycle. The term *activated* implies that the sample is hydrogenated/dehydrogenated for several cycles prior to kinetic measurements. The activation process covers different phenomena and includes penetration of the natural oxide layer on as-prepared samples (if previously exposed to air), followed by complete hydride formation, which leads to cracking of the particles, due to the expansion associated with the hydrogenation process combined with the brittle nature of most metal hydrides.^{1,6} During the first hydrogenation/dehydrogenation cycles, the reaction rate increases due to the creation of a fresh contamination-free surface and/or smaller particles (higher surface area and shorter diffusion paths) until a steady-state is reached. A potential physical explanation for the observed variations in $\ln(A_{\text{app}})$ and E_A^{app} , are therefore likely to depend on sample treatment and cleanliness.

For the nonalloyed Mg samples (D–L) in Figure 2, a trend of higher apparent activation energy for the *nonactivated* samples than the *activated* samples for both hydrogenation and dehydrogenation is observed. The high apparent activation energy of the nonactivated samples may be accounted for by the presence of an oxide shell/layer surrounding the bulk magnesium particles. For sample D and E the presence of MgO was confirmed by X-ray powder diffraction and energy dispersive X-ray spectroscopy (EDX).³⁰ Likewise, for samples I and J, the production method and sample handling makes formation of a surface oxide with low defect density highly probable.⁴⁴

It is known that hydrogen diffusion in the close packed MgO is extremely slow⁴⁵ and strongly thermally activated, when compared to diffusion of hydrogen in Mg⁴⁶ and MgH₂.⁴⁷ The formation of MgO at the surface is therefore expected to contribute to a higher apparent activation energy. The observed lower activation energies for the activated samples are thus probably due to the creation of a fresh, oxide free surface from cracked particles, and new hydrogen diffusion channels in the interface regions. Quantifying the effect of *activation* on the apparent activation energy is, however, difficult due to the various procedures used on the samples. Other effects may also be important, such as particle morphology, presence of other impurities both in bulk samples and in the surrounding gas phase of H₂/inert, etc.

The alloyed and nonactivated Mg samples (A–C), MgH₂/Al, MgH₂/MgCu₂, and MgH₂/Mg₂Cu, respectively, do not seem to fit the trend in applied activation procedure. The explanation probably relies on the fact that alloying with Cu and Al produces

TABLE 2: Corresponding Values of Apparent Prefactors and Apparent Activation Energies for Hydrogenation of LaNi₅ Based Hydrides^a

host	$\ln(A_{\text{app}})$		$E_A^{\text{app}}T$	sample	ref
LaNi ₅	11.87	32	271–360	M	49
LaNi ₅	9.35	33	289–352	N	50
LaNi ₅	3.79	19	294–333	O	3
LaNi ₅	17.37	53	267–333	P	51
LaNi ₄ Al _y	5.31	24	246–281	Q	52
LaNi ₅	10.79	37	245–293	R	53
LaNi ₅	11.26	38	245–293	S	54

^a For sample Q: $x = 4.75$ and $y = 0.25$. Sample P is for dehydrogenation. E_A^{app} is in kJ/mol and T is in Kelvin.

a compound less sensitive toward oxygen contamination; no crystalline MgO was found in the air-exposed samples by X-ray powder diffraction.^{28,29} Furthermore, it has also been suggested by Karty et al.⁴³ that the presence of Mg₂Cu provides an oxide free surface and favorable hydrogen diffusion paths. Effectively, the result of alloying with Al is the same as for Mg₂Cu/MgCu₂, although the physical explanation is likely different, since the marginal stability of the Mg–Al alloys does not block oxide formation.²⁸ With both Al and Mg present in the surface layers, the formation of amorphous or hydrogen porous alumina, Al₂O₃, and MgAl₂O₄ spinel is possible;^{48a} both structures and their interface regions with MgO have improved hydrogen diffusion channels.^{48b}

We therefore propose that the vast difference in apparent activation energies is a consequence of the level of MgO formation, which strongly inhibits hydrogen diffusion. For the activated or and alloyed samples, hydrogen dissociation is expected to be rate-limiting, whereas hydrogen diffusion through MgO-rich surfaces limits the kinetics for the nonactivated samples.

2.2. LaNi₅ Hydrides. To investigate the possible existence of a compensation effect in other metal hydride systems, we have reviewed a number of reported kinetic studies on LaNi₅ based hydrides from the literature. This particular hydride was chosen since it is not prone to oxide formation, and ample kinetic data are available.

Corresponding values of $\ln(A_{\text{app}})$ and E_A^{app} along with information about reaction temperature and the origin of the data are presented in Table 2. As for the Mg-based samples the values of $\ln(A_{\text{app}})$ and E_A^{app} are obtained by fitting eq 3 to reported values of $\ln(k)$ vs $1/T$. In a single case (sample S) the values have been obtained by first fitting eq 5 to raw kinetic data, extracting k at different temperatures, and thus finally performing an Arrhenius analysis.

The data of $\ln(A_{\text{app}})$ and E_A^{app} is used to construct a Constable plot as shown in Figure 3. Again, we observe a compensation effect in the reported data according to the Cremer–Constable relation. However, it is also noticed that the apparent activation energies for LaNi₅ span a much smaller interval (19–38 kJ/mol for hydrogenation) and cover only 4 orders of magnitude in apparent prefactor. Even with the uncertainty on the derived values of E_A^{app} , the compensation effect is found to be statistically significant. Thus, the smaller changes in apparent activation energy of the LaNi₅ compared to Mg could be an indicator of the fact that LaNi₅ is more easily activated and less sensitive toward oxidation and contamination.

2.3. Discussion. In the case of magnesium based hydrides, a probable physical explanation can be established for the large variation in apparent activation energy, whereas the pronounced changes in apparent prefactor seem unlikely to be explainable on the basis of, e.g., changes in vibrational frequencies.¹⁶

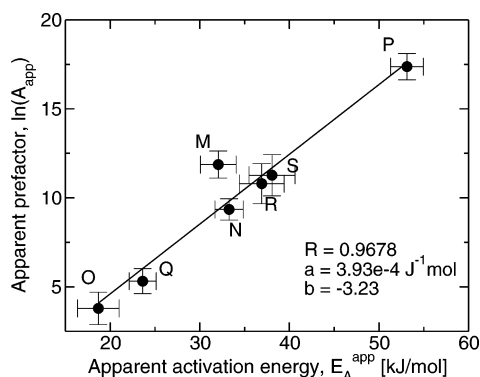


Figure 3. Constable plot of reported values of A_{app} vs E_A^{app} from Table 2 for LaNi₅ based hydrides. Data points are assigned sample letters.

TABLE 3: Constable Plot Slope a and Corresponding Values of T_m and $T_m(exp)$ for Mg and LaNi₅ Based Hydrides

metal hydride	a [J ⁻¹ mol]	T_m [K]	$T_m(exp)$ [K]
MgH ₂	1.82×10^{-4}	661	643
LaNi ₅	3.93×10^{-4}	306	293

Whether the observed compensation effect is an artifact of the derivation of $\ln(A_{app})$ from an Arrhenius plot, where $\ln(A_{app})$ is the intercept (the natural logarithm to the rate constant extrapolated to infinite temperature), is investigated in the following.

Recently, it have been shown⁵⁵ for heterogeneous catalytic reactions that changes in apparent activation energies due to variations in reaction conditions or changing the catalyst material always leads to a compensation effect when the corresponding apparent prefactors are determined from an Arrhenius analysis. Further, it was shown by algebraic derivation that the slope in such a Constable plot is $a = (RT_m)^{-1}$, where T_m may be interpreted in terms of a mean experimental temperature. Thus, it was concluded that the observed compensation effect could be explained by the method of data analysis rather than a physical effect.

The theoretical observation of $a = (RT_m)^{-1}$ prompted us to investigate whether the Constable plots presented in this paper displayed this correlation. The slope, a , in Figures 1 and 3 and the derived T_m for both Mg and LaNi₅ are shown in Table 3. Also shown is the true experimental mean temperature $T_m(exp)$ for Mg and LaNi₅. From Table 3 we notice that there is good agreement between the calculated and experimental value of T_m for both Mg and LaNi₅. The larger slope in the Constable plot of LaNi₅ compared to Mg is thus simply accounted for by the lower temperature applied during experiments; i.e., the slopes are equal to $(RT)^{-1}$.

Having shown that the slopes in the Constable plot are in fact equal to $(RT)^{-1}$ enables us to take the data analysis a step further. From eq 3, $\ln(A_{app})$ is given by

$$\ln(A_{app}) = \frac{E_A^{app}}{RT} + \ln(k) \quad (6)$$

To quantify the relative contributions to $\ln(A_{app})$, a modified Constable plot is constructed, where the data from Table 1 is compared to E_A^{app}/RT_m (Figure 4, upper).

From the figure we note that E_A^{app}/RT is by far the most important contribution to $\ln(A_{app})$. Even though the rate constant, k_m , calculated for the different samples at T_m using the derived values of apparent activation energy and apparent prefactors varies by 3 orders of magnitude (cf. Figure 4 lower) this is still only a minor contribution to $\ln(A_{app})$. This observation can

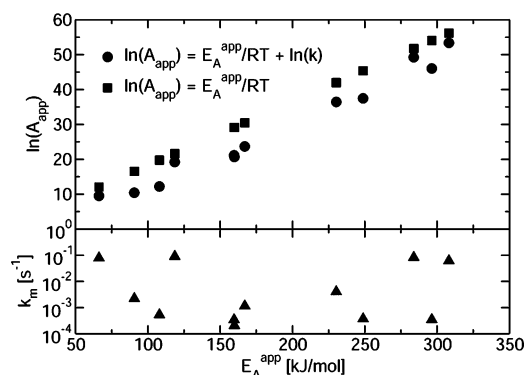


Figure 4. Constable plot of reported values of A_{app} vs E_A^{app} from Table 1 for Mg based hydrides compared with (E_A^{app}/RT_m) (upper).

explain why the slope in a Constable plot is simply $(RT)^{-1}$, since discarding $\ln(k)$ in eq. 6 introduces only minor errors in $\ln(A_{app})$.

The described decomposition of the apparent prefactor strongly indicates that the observed compensation effect, does not rely on a physical phenomenon, but is simply a consequence of the simultaneous determination of E_A^{app} and $\ln(A_{app})$ from an Arrhenius analysis. In this context it is important to note that an Arrhenius analysis is often the only method available to determine both the activation energy and the prefactor. Thus, caution should be exercised when drawing conclusions based on such an analysis. Taking into account that numerical values of reported rate constants often lay within a limited range (where the lower limit is determined by the instrumental time-resolution and the upper limit is determined by the patience of the experimentalist), the use of an Arrhenius analysis will often result in an apparent compensation effect.

3. Conclusion

In this paper, we have reviewed the kinetics in terms of apparent activation energies and apparent prefactors of two of the most investigated metal–hydrogen systems: magnesium and LaNi₅ based hydrides. For both systems we find that the values of the apparent activation energies are scattered. In the case of Mg we suggest that variations in reported apparent activation energies correlate with the presence of a MgO surface layer inhibiting diffusion of hydrogen. Thus, oxidized samples show large apparent activation energies and well activated samples show smaller activation energies. The observed scatter is most pronounced for the magnesium based hydrides. We take this as evidence for the fact that LaNi₅ is much more easily activated and less sensitive toward oxidation and contamination than Mg.

Further, we have investigated the existence of a compensation effect in the formation/decomposition of metal hydrides. We find a clear compensation effect in the case of both magnesium and LaNi₅ based hydrides. The origin of this compensation effect is the simultaneous determination of the apparent prefactor and apparent activation energy from an Arrhenius analysis. It is found that the slope in the Constable plots of both magnesium based hydrides and LaNi₅ based hydrides is equal to $(RT)^{-1}$. Whenever apparent activation energies and apparent prefactors are linked directly through an Arrhenius analysis, the observation of a potential compensation effect should be examined for a $(RT)^{-1}$ correlation.

Acknowledgment. This work has received financial support from the The Danish Technical Research Council, through the Center of Excellence *Toward a hydrogen based society*, and

the Danish Research Agency and Danfoss Corporate Ventures A/S through Grant No. 2013-01-0043.

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