On the Compensation Effect in Heterogeneous Catalysis

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For a class of heterogeneously catalyzed reactions, we explain the compensation effect in terms of a switching of kinetic regimes leading to a concomitant change in the apparent activation energy and in the prefactor for the overall rate of the reaction. We first use the ammonia synthesis to illustrate the effect. Both experiments and a detailed kinetic model show a compensation effect. Second, we use density functional theory calculations to show that the compensation effect is not only due to changes in the activation barrier and prefactor of the rate-determining step, N_2 dissociation. We compare N_2 dissociation on Ru and Pd. The barrier for dissociation differs by more than 2 eV (200 kJ/mol), but calculations of the prefactor based on harmonic transition-state theory shows a difference of less than 10%. To analyze the origin of the compensation effect, we construct a general kinetic model for a surface-catalyzed reaction and show that the effect can be related to a shift in kinetic regime, from one dominated by the rate of activation of the reactants to a regime where the stability of the reaction products on the surface becomes increasingly important. Finally, we present arguments why this should be a general effect for a broad class of reactions. We will show that the compensation effect in the rate is intimately linked to the underlying linear relationships between activation energy and stability of intermediates, which have been found to hold for a number of surface reactions.

Introduction

The rate of essentially all simple, thermally activated processes follows an Arrhenius law, which means that the rate, r, depends on temperature, T, as $r(T) = Ae^{-E_a^{app}/k_BT}$, where k_B is Boltzmann's constant. The apparent activation energy, E_a^{app}, determines the temperature dependence, and the prefactor, A, determines the overall rate. It is found empirically that, for some classes of systems with varying activation energies, there is a compensation effect, such that when the apparent activation energy changes, so does the prefactor. Moreover, the two parameters characterizing the system often depend linearly upon each other as

$$\ln A = aE_a^{app} + b \tag{1}$$

The compensation effect was first discovered in 1908 by Wilson[1] for the case of electron emission from a platinum surface heated in a hydrogen atmosphere. Later it was discovered in heterogeneous catalysis by Palmer and Constable[2,3] and has subsequently been found to hold for a large number of homogeneous as well as heterogeneous chemical reactions.[4−6] A compensation effect also exists for other thermally activated processes, such as bulk[7] and surface[8] diffusion, dielectric relaxation in polymers,[9] and electrical conduction in inorganic oxide semiconductors,[10] organic compounds,[11] and polymers.[9] Since the discovery of a compensation effect for the electrical conduction in TiO_2, Fe_2O_3, UO_2, and ZnO by Meyer and Neldel,[10] the linear compensation effect has often been referred to as the Meyer−Neldel rule, especially in relation to conduction and diffusion phenomena. In heterogeneous catalysis, the linear compensation

effect is often called the compensation law[12] or the isokinetic relationship.[4] The latter term is used because the linear compensation effect, eq 1, leads to the concept of a fictitious temperature, $T_{isokinetic}$, at which all the considered reactions would in principle have the same rate. The isokinetic temperature often lies outside the range of experimentally accessible reaction conditions. It was originally believed that for chemical processes the compensation effect would always lead to an actual compensation in the rate,[12] in the sense that the proportionality constant, a, in eq 1 would always be positive. Even if this is true in the large majority of cases, chemical reactions do exist for which a has a negative value.[13]

Many attempts have been made to explain the compensation effect for various processes. It has been argued that the nature of the Arrhenius law is such that the experimental determination of the activation energy and the prefactor are associated with large statistical uncertainties and that these by themselves give rise to a compensation effect.[13] It has also recently been discovered that the compensation effect observed for surface diffusion was based on prefactors that were wrong by several orders of magnitude due to limitations in the applicability of the standard nucleation-theory approach in analyzing experimental island-density data obtained from STM growth experiments.[14,15] The inherent uncertainties do, however, only explain few of the observations of the compensation effect and cannot in general explain why the proportionality factor, a, is predominantly positive. In heterogeneous catalysis, it has been suggested that a distribution of active sites with varying reactivity could explain the effect,[3] while others have suggested that the individual elementary processes could show a compensation effect related to the fact that for high-barrier processes there are more excitations in the catalyst that can feed energy into

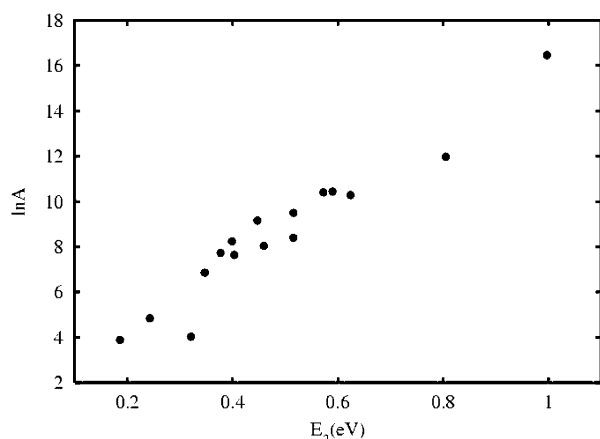* Corresponding author: e-mail norskov@fysik.dtu.dk.

Figure 1. Experimentally measured apparent activation energies E_a and prefactors A for ammonia synthesis over a number of bimetallic alloys (deduced from ref 22).

the reactions.[16,17] It must, however, be concluded that despite the intriguingly simple relationship and the generality of the effect, there is still no broadly accepted explanation.[17−19]

In the present paper we will show that for a broad class of catalytic reactions we can explain the compensation effect in terms of a switching of kinetic regimes. The reactions we consider are characterized by a monotonic relationship between the activation energy of the rate-limiting step and the stability of the reaction intermediates on the surface. Such a Brønsted−Evans−Polanyi relationship has been found recently to hold for a number of reactions[20,21] and expresses the fact that a decrease in the activation energy is accompanied by a similar increase in the stability of the reaction intermediates on the catalyst surface. We will show that the compensation effect in the rate is intimately linked to the underlying Brønsted−Evans−Polanyi relationship.

Our explanation goes in four steps. First, we use the ammonia synthesis reaction to illustrate the effect. Analysis of available experimental data[22] shows a clear compensation effect (see Figure 1), and we show that the kinetic model we have developed to describe trends in catalytic activity from one transition metal to the next on the basis of density functional theory calculations[23] also captures the effect. Second, we use detailed density functional theory calculations to show that the compensation effect is not likely to be due to a relationship between the activation energy and entropy for the rate-determining step, N_2 dissociation. We compare N_2 dissociation on Ru and Pd. The barrier for dissociation differs by more than 2 eV (200 kJ/mol), but calculations of the prefactor based on harmonic transition state theory shows a difference of less than 10%. To analyze the origin of the effect we construct a general kinetic model and invoke explicitly a Brønsted−Evans−Polanyi relationship. We show on this basis that the compensation effect can be related to a shift in kinetic regime, from a regime where the overall rate is dominated by the rate of activation of the reactants to a regime where the stability of the reaction products on the surface become increasingly important. Finally, we present arguments why this should be a general effect.

Compensation Effect for Ammonia Synthesis

Kinetic Model. We use the catalytic ammonia synthesis reaction to illustrate the compensation effect because we have an extremely detailed picture of this catalytic process.[18,23−26] In the present context the most important point is that we are able to describe the variation in the reactivity from one metal
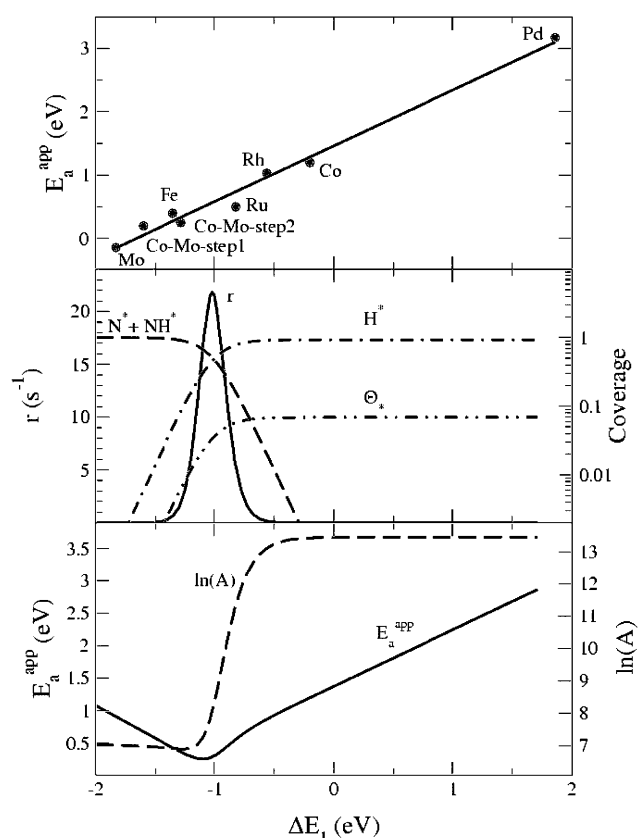

Figure 2. (a, top panel) Calculated activation energies for N_2 dissociation at steps on a number of different metal surfaces plotted as a function of the dissociative chemisorption energy of N_2 (in electron-volts per molecule). The convention is such that a negative value means that chemisorption is exothermic. (b, middle panel) Calculated turnover frequencies, r, from the kinetic model described in the text. Also shown are variations in the surface coverages. Reaction conditions are $T = 400$ °C, $H_2:N_2 = 3:1$, 1 bar, $\gamma = 0.2$. (c, bottom panel) Apparent activation energy for the overall reaction and the prefactor (eq 4).

to the next.[23] This is illustrated in Figure 2. The starting point is a set of density functional theory (DFT) calculations[23] showing that there is a linear (Brønsted−Evans−Polanyi) relationship between the activation energy for the rate-limiting step, which is N_2 dissociation,[27,28] and the stability of adsorbed N on the surface; see Figure 2a. The reason for this relationship is that the transition state for N_2 dissociation is very final-state-like. Therefore, the transition-state energy essentially follows the nitrogen adsorption energy from one metal to the next. The linear relationship means that one cannot find a catalyst with a lower barrier for N_2 dissociation, and thus a higher rate of the rate-limiting step, without having more stable nitrogen on the surface and thus a higher coverage and a lower concentration of free sites where the process can occur. This implies that the best catalyst is a compromise between having as low a barrier as possible and as low a stability of surface intermediates as possible. This results from combining the DFT calculations with microkinetic modeling show that there is a volcano-shaped relation between the ammonia synthesis activity of different catalysts and their nitrogen adsorption energy;[23] see Figure 2b. The model shows (in complete agreement with experimental evidence[29]) that Ru, Os, and Fe are the best catalysts among the pure metals.

The microkinetic model for ammonia synthesis assumes that the nitrogen dissociation step is rate-limiting for all metals of interest. This is a very well justified assumption around the top of the volcano and to the right of it.[24,30−32] All the other

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elementary reaction steps are considered to be in equilibrium and thus only important in the way that they are determining the number of free active sites available for nitrogen dissociation. In this model the turnover frequency is given by

$$r(T,\{P_x\}) = 2kP_{N_2}\theta_*^2\left(1 - \frac{P_{NH_3}^2}{K_{eq}P_{N_2}P_{H_2}^3}\right) = 2kP_{N_2}\theta_*^2(1-\gamma)$$

(2)

Here k is the N_2 dissociation rate constant, θ_* is the probability that an N-adsorption site is free (an active site consists of two N-adsorption sites), and K_{eq} is the equilibrium constant for the overall synthesis reaction $N_2 + 3H_2 \rightarrow 2NH_3$. P_x is the partial pressure of gas-phase species x.

To calculate the turnover frequency at a given set of conditions (temperature and partial pressures of N_2, H_2, and NH_3), expressions for the nitrogen dissociation rate at an active site and the equilibrium constants for the other elementary reaction steps are needed. In the microkinetic model the nitrogen dissociation rate is calculated from a preexponential factor and an activation energy, E_a. The equilibrium constants are calculated by statistical mechanics methods from the potential energies, rotational constants, and vibrational frequencies for all the reactants, intermediates, and products in the synthesis reaction. The combination of the microkinetic model with the Brønsted−Evans−Polanyi relation is realized by assuming that, on going from one metal to the next, all parameters are constant except for the activation energy and the potential energies of some of the adsorbed reaction intermediates.

The parameter values giving a good description of experimental data for ammonia synthesis over ruthenium[33] are used as a reference point. These values are all based on experimental observations. All parameters can be found in ref 33. The parameters are in good agreement with the DFT calculations for the active sites (which turn out to be the steps[25]) with respect to the values of both the activation energy and potential energies.

Apart from the activation energy of the rate-limiting step, E_a, and the dissociative chemisorption energy of N_2, E_{N*}, the energies most important for the turnover frequency are the potential energies of NH* and H*. We find that the adsorption energy of hydrogen does not vary much for the most relevant metal surfaces, and the potential energy of adsorbed hydrogen is therefore taken to be constant. NH, on the other hand, is very similar to N and it is assumed that the potential energy of adsorbed NH, E_{NH*}, follows E_{N*} (E_{NH*} = constant + E_{N*}). The potential energies of adsorbed NH_2 and NH_3 are assumed to be constant since they do not play any significant role for the turnover frequency.

With these assumptions it is possible to calculate the turnover frequency for ammonia synthesis under different synthesis conditions as a function of E_{N*}. The result is shown in Figure 2b for a typical set of conditions.

Compensation Effect. Since we have a model that describes the variations in catalytic activity from one system to the next, it is interesting to see whether it includes a compensation effect. Experimental data suggest that there should be one for ammonia synthesis; see Figure 1.

We define the apparent activation energy by

$$E_a^{app} = -\frac{\partial \ln(r)}{\partial(1/k_BT)}$$

(3)

This is the activation energy that would be measured experimentally as minus the slope in an Arrhenius plot of the logarithm
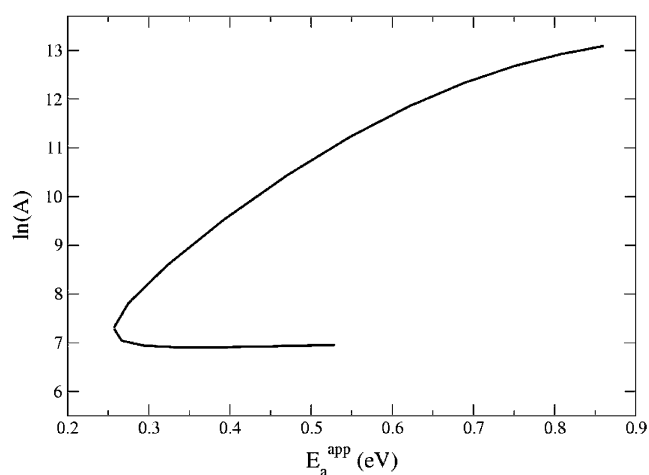

Figure 3. Logarithm of the apparent prefactor vs the apparent activation energy in the interval where the rate is greater than 1% of the maximum.

of the synthesis rate versus inverse temperature:

$$r(T) = Ae^{-E_a^{app}/k_BT}$$

(4)

A in eq 4 then defines the apparent prefactor for the overall reaction. A compensation effect would entail a monotonic correlation between E_a^{app} and $\ln A$.

Figure 2c shows the variation of E_a^{app} and $\ln A$ as a function of the nitrogen binding energy. Here and in the following we use the nitrogen binding energy to characterize the catalyst. The linear relationship between the binding energy and the other important parameter in the problem, the activation energy for nitrogen dissociation, ensures that specification of the nitrogen binding energy gives a unique characterization of the catalyst. Figure 2c shows that there are regions of binding energies where there is no correlation between E_a^{app} and $\ln A$ and others where there is such a correlation. It is clear, however, that around the maximum in the volcano curve and to the right of it, cf. Figure 2b, there is a compensation effect. This is illustrated in Figure 3, which shows a plot of $\ln A$ vs E_a^{app} for catalysts that have activities greater than 1% of the maximum. These are the most interesting catalysts and the ones for which measurements are most easily done. There is a clear linear region but also a flat part originating from the catalysts with the strongest bonding of nitrogen. This may be a sign that one cannot expect the compensation effect to hold for all catalysts, but it may also be that the catalysts that bind nitrogen most strongly are behaving differently. These catalysts tend to form nitrides under reaction conditions, and the catalysis takes place at nitrogen vacancies. Here interactions with the other nitrogen atoms will effectively shift the nitrogen binding energy and activation energy for dissociation up the linear Brønsted−Evans−Polanyi line as discussed in ref 20; that is, into a region where the compensation effect again becomes clear. The slope of the linear part of the $\ln A$ vs E_a^{app} in the model and the experimental data in Figure 1 are seen to be the same, which lends further credibility to the model.

We conclude that the model includes a compensation effect, and we can use the model to analyze the origin of the effect. It is worth pointing out that the compensation effect shown by the model is not part of the input. In fact we have assumed that the rate constant for the rate-limiting step

$$k = \nu e^{-E_a/k_BT}$$

(5)

has the same prefactor irrespective of the huge variations in
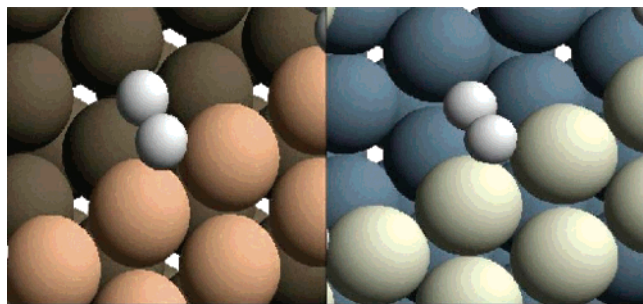
Figure 4. Transition states for N_2 dissociation at a Ru step (left) and at a Pd step (right).

the activation energy for dissociation; see Figure 2. In the following section we will show that this is a very good description.

Rate of Nitrogen Dissociation

One might think that the compensation effect is related to the properties of the transition state. In absolute rate theory, the prefactor for an elementary process is given by the difference in entropy from the initial state to the transition state. A high-energy transition state could be considered as a more loosely bound structure and therefore it might have higher entropy than the initial state. In the following we investigate this possibility in some more detail. We use absolute rate theory to get an estimate of the prefactor in the rate for N_2 dissociation on stepped Ru(0001) and Pd(111) surfaces, which have very different activation energies.

We have performed first-principles total energy calculations using density functional theory (DFT) to determine energies and N_2 vibrational frequencies in the transition state. These are the only properties that are needed in order to estimate prefactors and rate constants within transition-state theory. The DFT calculations were carried out with the dacapo code,[34] where the Kohn−Sham equations are solved in a plane wave basis restricted by the kinetic energy cutoff 25 Ry. We employed RPBE[35] generalized gradient correction self-consistently, and the core electrons of both the metal atoms and the N atoms were treated with Vanderbilt nonlocal ultrasoft pseudopotentials.[36] Sampling of 18 k-points was used together with a Fermi smearing of 0.1 eV. The stepped surface of fcc Pd(111) was modeled by a (2×1) unit cell of the Pd(211) surface, by use of a slab with three (111) atomic layers. The Ru steps were modeled by using Ru(0001) and a (4×2) surface cell where two close-packed rows were removed to give a step; see Figure 4. Again three layers were used. It has been shown that this gives a good description of N interaction with Ru(0001).[37]

The transition state was localized constraining the N−N distance and relaxing all other degrees of freedom, including the topmost two layers of the metal atoms. By varying the N−N distance, we localize the saddle point. In Figure 4 we give N_2 configurations for transition states on stepped Ru(0001) and Pd-(111) surfaces: the transition states are clearly seen to be similar on the two surfaces. The vibrational frequencies at the transition state were calculated by diagonalizing the Hessian matrix obtained by displacing one N atom at a time in the three different Cartesian directions around the saddle point. We find one imaginary frequency (the reaction coordinate) and five vibrational frequencies, shown in Table 1. The frequencies are almost identical for the two systems.

The activation barriers for N_2 dissociation on Ru and Pd surfaces, shown in Table 2, are calculated with respect to gas-phase N_2 and they differ from each other by about 2.1 eV (200 kJ/mol).

TABLE 1: Five Real Vibrational Frequencies of N_2 in the Transition State on Stepped Ru(0001) and Pd(111) Surfaces

N_2/Ru v (meV)	N_2/Pd v (meV)
53	45
55	59
58	62
65	65
73	67

TABLE 2: Activation Energies, Prefactors and Rate Constants for N_2/Ru and N_2/Pd Systems[a]

	N_2/Ru	N_2/Pd
E_a (eV)	0.4	2.5
A (1/s)	2.4×10^6	2.6×10^6
k (1/s)	3×10^3	1.3×10^{-12}

[a] Numbers for the N_2/Ru system are taken from ref 37.

According to transition-state theory,[38] the rate constant for dissociative chemisorption can be expressed as

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_{gas}} e^{-E_a/k_B T} \qquad (6)$$

where k_B is Boltzmann's constant, T is the temperature, and q_{TS} and q_{gas} are the partition functions for N_2 in transition state and gas phase, respectively. While we do not include the molecularly adsorbed state of N_2 in the description, eq 6 gives the rate of dissociative adsorption even if it is included, since N_2 is only weakly bound and in equilibrium with the gas phase.

Generally, the partition function is a product of translational, rotational, and vibrational partition functions. For N_2 in the gas phase, $q_v \approx 1$ (there is only one very high frequency mode, which cannot be excited thermally at the temperatures we consider) and q_{gas} can be written as

$$q_{gas} = \frac{k_B T}{2\epsilon_{rot}} \frac{k_B T}{P} \left(\frac{2\pi k_B T}{h^2} \right)^{3/2} \qquad (7)$$

where h is Planck's constant and P is the pressure. Here ϵ_{rot} is the rotational constant, which for gas-phase N_2 has the value 0.248 meV.[39] In our calculations we assume that the reaction takes place at $T = 700$ K and $P = 100$ bar, which correspond to industrial conditions during ammonia synthesis.

At the transition state both the translational and the rotational partition functions are close to unity, so q_{TS} features only the vibrational partition function and is given by

$$q_{TS} = \Pi_i \frac{1}{1 - e^{h\omega_i/2\pi k_B T}} \qquad (8)$$

where ω_i is a vibrational frequency.

A direct comparison between eq 6 and the Arrhenius law shows that the prefactor A has the following form:

$$A = \frac{k_B T}{h} \frac{q_{TS}}{q_{gas}} \qquad (9)$$

The calculated prefactors and rate constants are given in Table 2. Clearly, the data do not show any indication of a compensation effect: while the prefactors are almost identical, the rate constants differ by more than 15 orders of magnitude.

**Switching of Kinetic Regimes**

Having established that the compensation effect is included in our kinetic model for the ammonia synthesis, we can begin to analyze its origin. Since we have also shown—at least in the

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framework of harmonic absolute rate theory—that the prefactor in the expression for the rate of the rate-limiting step is independent of the activation energy, the compensation effect must lie in the fact that the actual kinetics (eq 2) is considerably more complex than the simple Arrhenius expression (eq 4), which is the basis for defining the apparent activation energy and prefactor.

An indication of the origin of the effect can be obtained by considering the variation in the coverages as the catalyst changes in Figure 2b. Clearly the coverages change dramatically in exactly the range where the apparent activation energy and prefactor change.

To bring out the origin of the compensation effect, we simplify the kinetic model even further. We do that in order to show that even the simplest possible, generic model of a surface-catalyzed reaction shows the effect.

Consider the following reaction sequence:

$$\text{reaction 1:} \quad A_2 + 2* \rightarrow 2A*$$

$$\text{reaction 2:} \quad A* + B \rightarrow AB + *$$
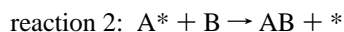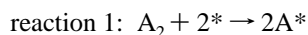
Here an asterisk represents a free active site on the surface. Let us assume in analogy with the ammonia synthesis reaction that the first step is rate-limiting. We will show later that this assumption is not important in the present context. In analogy with eq 2, the rate of the total reaction can then be written

$$r(T,P_x) = 2k_1 P_{A_2} \theta_*^2 \left(1 - \frac{P_{AB}^2}{K_{eq} P_{A_2} P_B^2}\right) = 2k_1 P_{A_2} \theta_*^2 (1 - \gamma) \tag{10}$$

Here

$$k_1 = \nu e^{-E_a/k_B T} \tag{11}$$

is the rate constant for reaction 1 in the forward direction, and γ measures the approach to equilibrium for the overall gas-phase reaction $A_2 + 2B \rightarrow 2AB$, K_{eq} being the corresponding equilibrium constant.

Since reaction 2 is at equilibrium, the coverage of free sites is given by

$$\theta_* = \frac{1}{1 + K_2(P_{AB}/P_B)} = \frac{1}{1 + \sqrt{K_1 P_{A_2} \gamma}} \tag{12}$$

where

$$K_1 = e^{\Delta S_1/k_B} e^{-\Delta E_1/k_B T} \tag{13}$$

is the equilibrium constant for reaction 1, with corresponding reaction entropies and energies ΔS_1 and ΔE_1, and similarly for reaction 2. As above, $\gamma = P_{AB}^2/(K_{eq} P_{A_2} P_B^2)$ is the approach to equilibrium for the gas-phase reaction. The last part of eq 12 separates the coverage dependence into two contributions, $P_{A_2}\gamma$ and K_1, where $P_{A_2}\gamma$ describes the reaction conditions while the variations between different catalysts are described by K_1. ΔS_1 will be essentially constant for different surfaces (see discussion above for the transition states), so the number of free sites primarily depends on the given surface through the dependence of K_1 on ΔE_1.

Equations 10−13 show that only two parameters involving the properties of the catalyst are needed, E_a and ΔE_1. We now invoke a linear relationship between the two, cf. Figure 2a:

$$E_a = \alpha \Delta E_1 + \beta \tag{14}$$
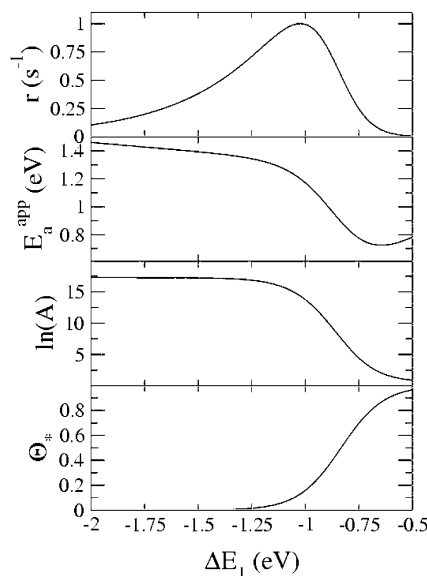

Weakly bound precursor

Figure 5. Plot of the rate r, the apparent activation energy, the prefactor, and the coverage of free sites for the simple model reactions 1 and 2. The parameters are specified by eq 14, with $\alpha = 0.87$ and $\beta = 1.3$ eV, and the reaction properties are $T = 300$ °C, $P_{A_2} = 0.01$ bar, $P_B = 0.01$ bar, and $\gamma = 0.01$.

Such a linear relationship has been found to hold for a number of different reactions,[20] with $\alpha = 0.87$ and $\beta = 1.3$ eV. The actual parameters of the line are not important in the present context. We note that the linear relationship allows us to use the binding energy ΔE_1 to characterize the system in question. Variation of ΔE_1 can now be used to investigate the effect of changing the catalyst for a given reaction, or to investigate changes in the reactants in a family of similar molecules (e.g., C−H or C−C bond splitting for hydrocarbons of varying composition).

In Figure 5 we show that the simple model also gives a volcano curve, just like the one found for ammonia synthesis (Figure 2b). It also shows a large variation in the activation energy and a concomitant variation in the prefactor. Despite its extreme simplicity, the model includes a clear compensation effect. Figure 6 shows that over a range of conditions it is of the type

$$\ln A = a E_a^{app} + b \tag{15}$$

A variation in the apparent activation energy of about 0.5 eV (50 kJ/mol) gives rise to a change in the apparent prefactor of more than 5 orders of magnitude ($\ln A$ varies by more than 10).

We note in Figure 5 that the switching in apparent activation energy and prefactor is associated with a change in the coverage in free sites, from no free sites for the most negative values of ΔE_1 to a coverage of free sites of one for the most positive ΔE_1. This switching also holds the key to understanding the changes in the apparent activation energy and prefactor. To see this, consider two limiting cases.

In the limit $\theta_* \rightarrow 1$ we have

$$r(T) \sim k_1 \sim \nu e^{-E_a/k_B T}$$

and the apparent activation energy is $E_a^{app} = E_a$, while $\ln A = \ln \nu$.
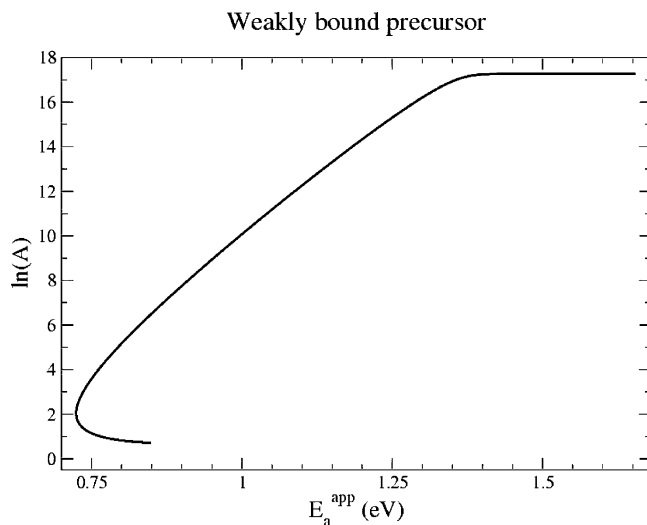
Weakly bound precursor

Figure 6. Compensation effect within the simple model based on reactions 1 and 2; see Figure 5. A clear linear relationship is observed between the logarithm of the apparent prefactor and the apparent activation energy.
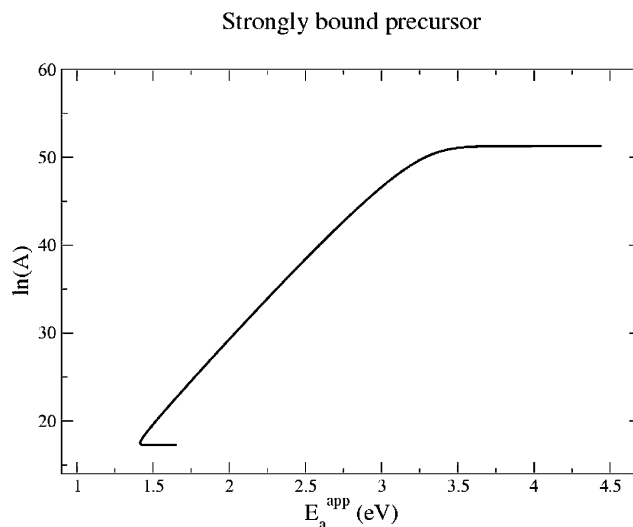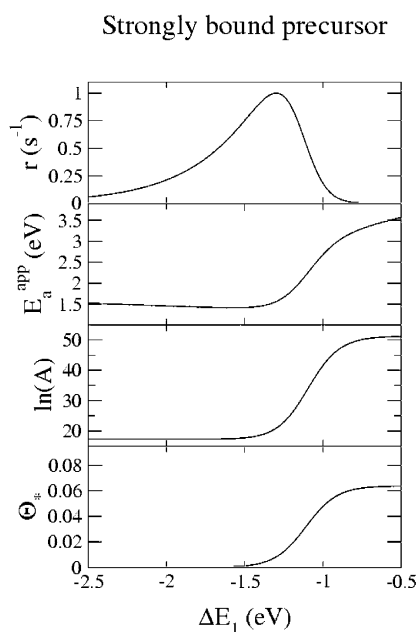
Strongly bound precursor

Figure 7. Plot of the rate r, the apparent activation energy, the prefactor, and the coverage of free sites for the simple model reactions 1a, 1b, and 2. The reaction parameters are the same as in Figure 5, and the stability of the molecular state is $\Delta E_{1a} = -1.5$ eV.

In the limit $\theta_* \to 0$ or $K_1 P_{A_2} \gg 1$, on the other hand, we have

$$ r(T) \sim k_1 \theta_*^2 \sim \nu e^{-E_a/k_B T} \left(\frac{1}{\sqrt{K_1}} \right)^2 \sim \nu e^{-\Delta S_1/k_B} e^{-(E_a - \Delta E_1)/k_B T} $$

and the apparent activation energy in this limit[27,29] becomes $E_a^{app} = E_a - \Delta E_1$. This value is larger than the value E_a found in the other limit, since the adsorption energy ΔE_1 must be negative in order to have adsorption at all. The apparent prefactor is also larger than in the other limit, $\ln A = \ln \nu - \Delta S_1 > \ln \nu$, since there is always a loss of entropy associated with adsorption from the gas phase, $\Delta S_1 < 0$. The change in apparent activation energy and prefactor is thus brought about by the same switching in kinetic regime and must therefore be correlated. The switching is given simply by the change in the coverage on the surface.

Strongly bound precursor

Figure 8. Compensation effect in the case of a strongly bound precursor; see Figure 7.

The effect is a real compensation effect where a change in activation energy is compensated for by a change in the activation entropy: the system switches from a low-coverage situation, where the activation energy and prefactor for the rate-limiting step determines everything, to a high-coverage situation, where the activation energy is the sum of the energy it requires to free a surface site by desorption and the activation barrier for the rate-limiting step. Since the heat of adsorption is negative in all cases of interest and adsorption is essentially always accompanied by a positive entropy change, the two effects compensate each other.

We note that the effect is not limited to the case where the first reaction is rate-limiting. If we complicate the reactions 1 and 2 slightly to include a strongly bound molecular precursor such that reaction 1 is split up into

$$ \text{reaction 1a: } A_2 + * \to A_2* $$

$$ \text{reaction 1b: } A_2* + * \to 2A* $$
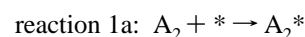
we get the results shown in Figure 7. The precursor hardly changes the volcano curve, but the variations in apparent activation energy and prefactor are completely different. In this case the apparent activation energy and prefactor decrease with increasing ΔE_1, for instance. Yet they again show a complete compensation effect; see Figure 8.

Discussion and Conclusions

We have shown that the simplest, generic surface-catalyzed chemical reaction, which involves an activated process coupled with competition for sites on the surface, can give rise to a compensation effect. We have also shown that the same holds true for a considerably more complex reaction scheme describing a real catalytic reaction in detail. The question now is whether this can be a general explanation for compensation effects in heterogeneous catalysis.

The key component in the effect described above is a switching in kinetic regime due to changes in surface coverage from one catalyst to the next or from one reactant to the next under a given set of conditions. The question is therefore whether such switching is found for many reactions and whether the interesting catalysts are always close to the switching regime. As can be seen from Figures 2, 5 and 7, there are also regimes far from the switching where there is no compensation effect.

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For the classes of reactions discussed above where there is a linear relationship between the important activation barrier(s) and adsorption energies, there will always be a switching and the most active catalysts will always be close to the switching regime. The reason is quite simple. A good catalyst must be as active as possible for the rate-limiting step, while not so chemically active that it binds reactants, intermediates or products so strongly to the surface that there are no free sites. The coupling between these two tendencies is what is expressed by the linear relationship between activation energies and chemisorption energies shown in Figure 2. For these classes of reactions there must always be a switching in kinetic regime when going from strong to weak bonding of the intermediates, and the best catalysts must be compromises (the Sabatier principle[40]) right in the range of switching from low to high coverage of the intermediates. This also means that the most interesting catalysts (perhaps the only ones where an activity can be measured) are close to the switching.

We would therefore expect that all processes where there is a linear relationship between the important activation barrier-(s) and adsorption energies should show a compensation effect. It has been found that a large number of reactions show such linear relationships, and undoubtedly more will be shown to have the same behavior. This alone suggests that a compensation effect due to kinetic switching for coupled surface reactions should be found quite generally. It does, however, not exclude that other factors could lead to additional compensation effects.

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(31) All the models discussed in the present paper assume that dissociation of a reactant molecule is rate-limiting. If we instead impose stationary coverages, the assumption of a rate-limiting step is no longer necessary. We have implemented the stationary coverage microkinetic model for reactions 1a, 1b, and 2. This model shows that under relevant reaction conditions the assumption of the rate-limiting step is well-justified and the qualitative behavior for the models discussed in the present paper stays unchanged in the relevant catalytic regime.

(32) Whereas the presented limit is correct for the model we discuss here, this limiting behavior is only correct when the dissociation of the reactant is the rate-limiting step. This is true close to the top of the volcano curve and to the right of it. A model that also takes the switching of the rate-limiting step into account[30] shows a different limiting behavior for very low coverages of free sites. This happens further to the left of the top of the volcano, but this regime is, hovever, probably not experimentally accessible, as the metal surfaces there will have a strong tendency to form nitrides, oxides, carbides, etc., depending on which reactants are used.

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