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**A Simple Rule of Thumb for Diffusion on Transition-Metal Surfaces\*\****Anand Udaykumar Nilekar, Jeff Greeley, and Manos Mavrikakis\**

Diffusion of adsorbed species on solid surfaces involves the thermally activated lateral motion of these species. Among others, diffusion on surfaces plays an important role in many industrial heterogeneously catalyzed reactions and in crystal growth and aggregation processes.<sup>[1]</sup> Furthermore, an improved understanding of surface diffusion phenomena is relevant for characterizing the local deformation of metal surfaces,<sup>[2]</sup> and for analyzing the dynamics of metal corrosion.<sup>[3]</sup> Similarly, surface diffusion plays a key role in the transport of species in catalytic reactions,<sup>[4,5]</sup> as well as in the growth of surface nanostructures and the accumulation of subsurface/bulk species below metal surfaces.<sup>[6–9]</sup> Because of its importance in several areas, surface diffusion has been the focus of many experimental and theoretical studies involving a variety of adsorbates and surfaces, and there are many comprehensive reviews of the subject.<sup>[10–17]</sup> In spite of this widespread interest, however, very few general principles for diffusion on surfaces have been identified. Herein, we propose and provide quantitative evidence for two important principles: 1) that there is a simple correlation between the diffusion barrier and the binding energy of various species on transition-metal surfaces, and 2) that there is practically no compensation effect between the preexponential factor and the activation energy barrier for diffusion of adsorbed species on transition-metal surfaces.

Recent theoretical studies of surface-catalyzed bond-breaking reactions of diatomic molecules have elucidated some simple linear correlations between the transition-state (TS) energy and the final-state (FS) energy of the respective elementary steps. These Brønsted–Evans–Polanyi-type correlations span a wide range of energies and include several metal and alloy surfaces, which suggests the existence of a universality class for these simple catalytic reactions.<sup>[18–20]</sup> This universality reflects an inherent similarity between the TS and the FS structures. Such correlations are of great practical relevance to experimentalists, as they provide convenient

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tools for predicting reaction activation energies on the basis of reaction thermochemistry, and therefore offer a useful platform for catalyst screening and design.<sup>[21]</sup>

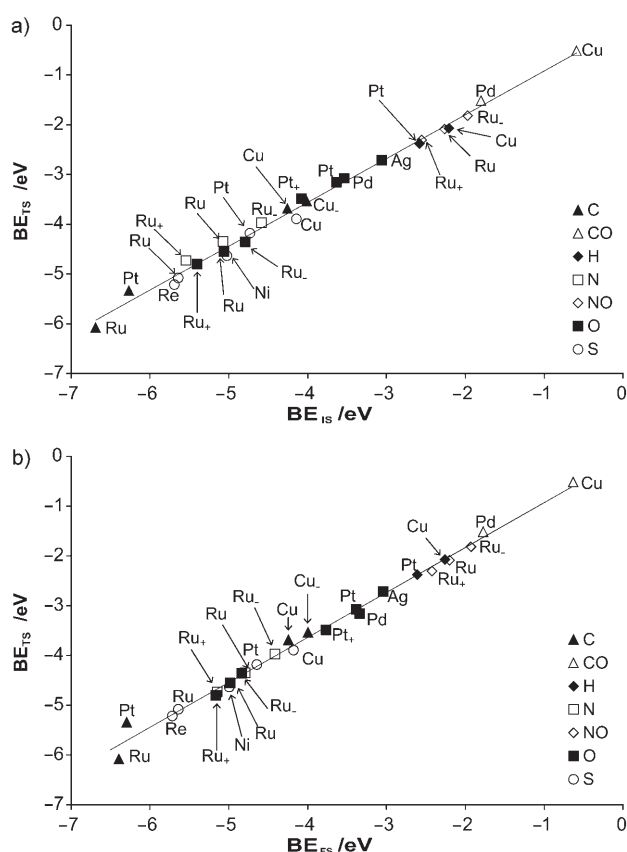
Herein, we systematically demonstrate using periodic, self-consistent density functional theory (DFT) calculations (see Methods section for details) that a similar, universal relationship exists between the surface diffusion TS energy and the adsorption energy of the diffusing species. This relationship is established by analyzing the minimum-energy diffusion path for a large number of adsorbates on a variety of close-packed metal surfaces, including those modified by strain. More specifically, our study included 26 different adsorbate/surface pairs on seven different transition metals (Ru(0001), Re(0001), Cu(111), Pt(111), Pd(111), Ni(111), Ag(111)) with varying levels of surface strain, and seven different diffusing species, both atomic (O, N, H, C, S) and molecular (NO, CO). We deliberately chose many of the adsorbate/metal pairs so that our data would cover a wide range of adsorbate binding energies (−7 to 0 eV), and accordingly, the range of applicability of the final correlation derived from our studies would be quite broad.

A summary of our DFT results obtained for the diffusion barrier of various adsorbate/surface pairs, all at the low-coverage limit ( $\theta=1/8$  ML), is given in Table 1. Figures 1a and 1b show the relation between the binding energy of the

**Table 1:** Experimentally estimated and calculated<sup>[a]</sup> diffusion barriers for adsorbate/metal pairs at various degrees of strain.<sup>[b]</sup>

Adsorbate/metal	% Strain	$\log_{10}(k)^{[c]}$	$E_{\text{DFT}}^*$	$E_{\text{exptl}}^*$
C/Cu	−5.00	12.70	0.46	
C/Cu	0.00	12.71	0.56	
C/Pt	0.00	12.74	0.91	1.3 <sup>[36]</sup>
C/Ru	0.00	12.72	0.60	
CO/Cu	0.00	13.09	0.06	0.10 <sup>[37]</sup>
CO/Pd	0.00	12.72	0.27	0.52 <sup>[38]</sup>
H/Cu	0.00	12.78	0.12	
H/Pt	0.00	12.72	0.18	0.30 <sup>[39]</sup>
N/Ru	−5.11	12.72	0.60	
N/Ru	0.00	12.73	0.71	0.94 <sup>[40]</sup>
N/Ru	5.11	12.73	0.79	
NO/Ru	−5.11	12.42	0.14	
NO/Ru	0.00	12.38	0.16	
NO/Ru	5.11	12.48	0.23	
O/Ag	0.00	12.61	0.33	
O/Pd	0.00	12.66	0.44	
O/Pt	0.00	12.67	0.46	
O/Pt	5.00	12.69	0.58	
O/Ru	−5.11	12.67	0.42	
O/Ru	0.00	12.69	0.49	0.70 <sup>[41]</sup>
O/Ru	5.11	12.67	0.59	
S/Cu	0.00	12.45	0.23	0.25 <sup>[41]</sup>
S/Ni	0.00	12.53	0.37	0.30 <sup>[42]</sup>
S/Pt	0.00	12.59	0.54	0.57 <sup>[43]</sup>
S/Re	0.00	12.56	0.46	0.80 <sup>[44]</sup>
S/Ru	0.00	12.54	0.55	

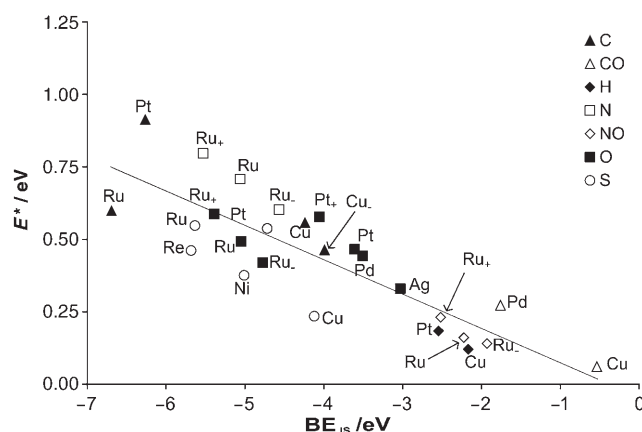
[a] With zero-point energy corrections. [b] At a coverage of  $\theta=1/8$  ML and on static slabs. The diffusion coordinate proceeds from the most-stable to the second-most-stable site for the adsorbate on the metal surface. Model slabs represent the closest-packed surfaces of the respective metals (fcc(111) and hcp(0001)). [c]  $k$  = preexponential factor for diffusion.



**Figure 1.** a) Binding energy of the transition state ( $BE_{\text{TS}}$ ) for diffusion of the adsorbate from the most-stable site to the next-most-stable site on the metal surface plotted against the binding energy of the adsorbate in its initial state, that is, most favorable site ( $BE_{\text{IS}}$ ). A + or − subscript on the metal label signifies expansive or compressive strain, respectively; the exact strain level is provided in Table 1. The absence of a + or − subscript indicates a surface with the equilibrium lattice constant. Linear regression gives the relation  $BE_{\text{TS}} = 0.91 BE_{\text{IS}} - 0.02$  with  $R^2 = 0.99$ . b) The binding energy of the transition state ( $BE_{\text{TS}}$ ) for diffusion of the adsorbate plotted against the binding energy of the diffusion final state ( $BE_{\text{FS}}$ ) on the metal surface. The derived linear-regression line is  $BE_{\text{TS}} = 0.91 BE_{\text{FS}} - 0.07$  with  $R^2 = 0.99$ .

adsorbate in the transition state ( $BE_{\text{TS}}$ ) and that in the initial ( $BE_{\text{IS}}$ ) and final states ( $BE_{\text{FS}}$ ) of the diffusion path, respectively. Despite the very broad range of energies covered, both graphs suggest that there is an excellent correlation ( $R^2 = 0.99$ ) between these values for atomic as well as molecular adsorbates on all the metal surfaces considered, including those surfaces with significant lateral strain (both compressive and expansive). The large variety of metal/adsorbate pairs, strain levels, and binding energies included in our study implies that a universal principle that governs the energetics of surface diffusion on metals may, in fact, exist.<sup>[22]</sup>

Having calculated the  $BE_{\text{TS}}$  and  $BE_{\text{IS}}$  values accurately, and by defining  $E^* = BE_{\text{TS}} - BE_{\text{IS}}$  as the diffusion activation energy barrier, we then attempted to correlate  $E^*$  with the  $BE_{\text{IS}}$  for all systems studied (Figure 2). In view of the broad range of adsorbate binding energies covered (ca. 7 eV), the scatter around the best fit line is only modest. For most



**Figure 2.** The diffusion barrier ( $E^*$ ) plotted as a function of the binding energy of the adsorbate in its most-stable site on the metal surface ( $BE_{IS}$ ). The linear-regression line obtained is  $E^* = -0.12 BE_{IS} - 0.02$  with  $R^2 = 0.72$ .

practical purposes, one can now correlate the diffusion activation energy barrier for common catalytic atoms and molecules with their binding energy on the respective surface. In particular, the line of best fit suggests that one can fairly accurately estimate the diffusion barrier of atomic and molecular species on transition-metal surfaces by simply taking 12 % of the binding energy of the respective species. A rule of thumb for diffusion on metal surfaces has been established from experimental studies,<sup>[17]</sup> whereby the diffusion barrier is between 0.1 and 0.2 times the adsorbate binding energy. However, to our knowledge, this is the first example of such a relationship from rigorous quantitative studies of a broad range of catalytically relevant systems. Nevertheless, the considerable scatter found for some systems shown in Figure 2 shows that this correlation is only a rule of thumb, rather than a fundamental physical principle.

Table 1 shows a comparison of our calculated results with available experimental data. Estimates from experimental data were taken from the literature and rely on a variety of experimental techniques. Accordingly, the accuracy of the experimental estimates for diffusion barriers can vary significantly. We found that, in most cases, the calculated diffusion barriers are lower than the corresponding estimates drawn from experiments. The differences between experimental and theoretical results can be attributed to a number of factors, such as the use of static metal slabs in the calculations and the nonuniform accuracy of the experimental methods used.<sup>[23]</sup>

We now turn our attention to whether mutually compensatory changes exist for the activation energy barrier ( $E^*$ ) and the preexponential factor for diffusion on metal surfaces, in general, and as a function of strain, in particular. The latter effect was studied for N, NO, and O on Ru(0001) ( $\pm 5.11$  % strain), O on Pt(111) (5 % strain), and C on Cu(111) ( $-5$  % strain). In general, and in good agreement with experimental results,<sup>[24]</sup> we found that compressive strain on the surface reduces the diffusion barrier, whereas expansive strain increases that barrier. The calculated preexponential factors,

however, remain practically invariant with surface strain (Table 1). Furthermore, despite the fact that our studies were designed to cover a wide range of adsorbate binding energies, and in contrast to experimentally determined values, which often show large variation in estimates of the preexponential factor, the calculated preexponential factors for diffusion remain very close to  $10^{13} \text{ s}^{-1}$ . As a result, the activation energy barrier alone should determine trends in diffusion on metal surfaces.

In summary, the following conclusions may be drawn: 1) that there is an excellent correlation between the binding energy of the adsorbed state and the binding energy of the respective transition state for diffusion; and 2) that the diffusion activation energy barrier can be estimated fairly accurately as approximately 12 % of the binding energy of the adsorbed state. This rule-of-thumb estimate for the diffusion barrier could be of fundamental importance for metal-catalyzed surface reactions. Finally, through the detailed calculation of preexponential factors and activation energy barriers, we showed that there is no compensation effect for diffusion on close-packed transition-metal surfaces. To our knowledge, this is the first systematic first-principles study to elucidate these general principles of diffusion on transition-metal surfaces.

## Methods Section

All calculations were performed by using DACAPO, a periodic, self-consistent, DFT-based total-energy code.<sup>[25,26]</sup> A static, three-layer ( $4 \times 2$ ) surface unit cell was used to model the adsorbate-metal systems. The effect of strain was simulated by implementing the specific lateral strain while keeping the metal interlayer distance fixed at the equilibrium value.<sup>[9,27]</sup> Adsorption was allowed on only one of the two metal surfaces exposed per slab, and the electrostatic potential was adjusted accordingly.<sup>[28]</sup> Ionic cores were described by ultrasoft pseudopotentials,<sup>[29]</sup> and the Kohn–Sham one-electron valence states were expanded in a basis of plane wave functions with kinetic energy below 25 Ry. The surface Brillouin zone was sampled by using a Monkhorst–Pack<sup>[30]</sup> grid of size  $2 \times 4 \times 1$ . The exchange correlation was described by the generalized gradient approximation (GGA-PW91).<sup>[31,32]</sup> The self-consistent PW91 density function was determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ( $k_B T = 0.1 \text{ eV}$ ), and Pulay mixing of the resulting electronic density.<sup>[33]</sup> All total energies were extrapolated to  $k_B T = 0 \text{ eV}$ . Binding energies (BEs) were calculated by Equation (1), in which  $E_{\text{ads}}$ ,  $E_{\text{clean}}$ , and  $E_{\text{gas}}$  are the total energies of the slab with adsorbate, the slab without adsorbed species, and the adsorbate species in the gas phase, respectively.

$$BE = E_{\text{ads}} - E_{\text{clean}} - E_{\text{gas}} \quad (1)$$

BEs were found to be well-converged with respect to the calculation parameters. All binding-energy values were adjusted to reflect harmonic zero-point-energy corrections, but the slab chemical potentials were not corrected for finite temperature and pressure effects. Bollinger et al. estimated that such effects are much less significant than the corresponding gas-phase effects.<sup>[34]</sup> We used the climbing-image nudged elastic band (CI-NEB) method to estimate the diffusion barrier.<sup>[35]</sup> In all cases, the diffusion of the adsorbate from the most-stable site to the second-most-stable site on the metal surface was studied. The diffusion preexponential factor ( $A$ ) was calculated by using Equation (2), in which  $S_{\text{vib}}^{\ddagger}$  and  $S_{\text{vib}}$  represent the

vibrational entropy of the transition state and the initial state for the diffusive jump, respectively.

$$A = \frac{k_B T}{h} \exp\left(\frac{S_{\text{vib}}^{\ddagger} - S_{\text{vib}}}{R}\right) \quad (2)$$

Both  $S_{\text{vib}}$  and  $S_{\text{vib}}^{\ddagger}$  were calculated using Equation (3), in which  $x_i$  is defined as  $\frac{h\nu_i}{k_B T}$  for each vibrational frequency  $\nu_i$ .

$$R \sum_i^{\text{\# of modes}} \left( \frac{x_i}{\exp(x_i) - 1} - \ln(1 - \exp(-x_i)) \right) \quad (3)$$

Vibrational frequencies were calculated by numerical differentiation of the forces by using a second-order finite-difference approach with a step size of 0.015 Å. The Hessian matrix was mass-weighted and diagonalized to yield the frequencies and normal modes for each system.

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