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ELECTROCATALYST POTENTIAL DEPENDENT ACTIVATION BARRIERS
APPROXIMATED WITH DENSITY FUNCTIONAL THEORY

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ABSTRACT

Density functional theory (DFT) studies of electrocatalytic systems are widespread, but the calculation of activation barriers for elementary steps involving electron and ion transfer remains challenging. A simple and transferable DFT approach to estimate these barriers for inner sphere electrochemical reactions, focusing on approximating the electron transfer coefficient, was studied. The challenge of finding a transition state for an electrochemical reaction step ($A^*+H^++e^- \rightarrow AH^*$) is met by breaking the electrochemical step down into one electrochemical step ($A^*+H^++e^- \rightarrow A^*+H^*$) and one non-electrochemical step ($A^*+H^* \rightarrow AH^*$). The transition state of the non-electrochemical step can be found relatively easily. It is assumed that the transition states for these two reactions are identical at the specific electrode potential (U^0) where the true reactant state ($A^*+H^++e^-$) and the intermediate state (A^*+H^*) have the same free energy. Once the transition state is located, the activation barrier, E_{act}^0 , can be calculated at that potential, U^0 . The activation barrier can be extrapolated as a function of electrode potential using Butler-Volmer theory, with the symmetry factor estimated by examination of the transition state and reaction coordinate. The methods used to calculate the symmetry coefficient, β , yield values that make sense and fit well with the other data. The first elementary step of CO_2 reduction, the hydrogenation of CO_2^* to $COOH^*$, will be used as a detailed example case for the development of the β calculation methods.

TABLE OF CONTENTS

List of Figures	iii
List of Tables	iv
Acknowledgements.....	v
Chapter 1 Introduction	1
Chapter 2 Methods.....	6
Chapter 3 Results and Discussion.....	11
3.1 CO ₂ * → COOH*	11
3.2 Symmetry Coefficient.....	13
Chapter 4 Conclusions and Further Work	21
Appendix A Derivation of Equation 5	23
BIBLIOGRAPHY	25

LIST OF FIGURES

Figure 1. An example of a plot illustrating the Marcus theory representation an electron transfer reaction.

Figure 2. Reaction energy diagram for an electroreduction reaction of an adsorbate.

Figure 3. Materials Studio Images of (a) the initial state with H^* , (b) the found transition state, and (c) the final state of the first electrochemical reaction step in the electroreduction of carbon dioxide over a copper catalyst, with a single water molecule.

Figure 4. Materials Studio Images of (a) the initial state with H^* , (b) the found transition state, and (c) the final state of the first electrochemical reaction step in the electroreduction of carbon dioxide over a copper catalyst, where the hydrogen starts on the surface and shuttles through two water molecules.

Figure 5. Materials Studio Images of (a) the initial state with H^* , (b) the found transition state, and (c) the final state of the first electrochemical reaction step in the electroreduction of carbon dioxide over a copper catalyst, where the hydrogen starts as part of a $H_5O_2^+$ in solution and shuttles through two water molecules.

Figure 6. A plot of the activation barrier of a system against the potential of the system.

Figure 7. The parabolas fit to the values given in Table 2.

Figure 8. The activation barrier of the reaction plotted against electrode potential.

Figure 9. A plot of the symmetry coefficient against the electrode potential.

Figure 10. A plot of activation barrier against electrode potential, calculated via three different methods.

LIST OF TABLES

Table 1. Calculated values^[1] for the system with both one and two water molecules, with and without a water bilayer.

Table 2. Values relevant to the fitting of the parabolas for the calculation of β .

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Chapter 1

Introduction

Arguably the greatest challenge of the 21st century is meeting the world's increasing energy demands. The limits of fossil fuels require that new technologies be developed in order to meet this challenge, and electrochemical devices could play a major role. Electrochemical devices involve reactions that are distinguished from general chemical reaction steps because they involve the transfer of an electron, rather than just the breaking and forming of bonds. The study of electrocatalysis and the kinetics of electrochemical reactions is important for these applications, particularly for fuel cells.

One particularly interesting electrochemical system involves the electroreduction of carbon dioxide to methane/methanol. The reaction is not energy efficient, but the ability to convert carbon dioxide into a fuel would be a significant contribution to resolving the energy crisis. Much research is being done to better understand the mechanism and kinetics of this reaction, in the hopes that an improved catalyst or certain reaction conditions can improve the energy efficiency of the reaction. In this study the first step of this reaction, the hydrogenation of CO_2^* to COOH^* was evaluated over a copper [1 1 1] surface in order to analyze and improve the methods used to calculate the potential dependence of activation barriers of electrochemical reaction steps.

Electrocatalysis is a key component of fuel cell and electrolysis devices. Improved catalysts directly lead to better, more efficient electrochemical devices. Catalysts lower the activation barrier of reaction steps, so improving the catalysis improves the kinetics of the overall reaction. This effectively makes the entire cell more efficient. Understanding the mechanisms and

principles of catalysis allows for the improvement of catalysts, both in terms of activity and selectivity. More active catalysts will motivate the reaction more easily, making them more effective in lowering the activation barrier of a reaction. Some materials will catalyze multiple reactions, but if only one reaction is desired then it is important for the catalyst to be selective toward that reaction.

A critical component in the study of electrocatalysis is the calculation of the activation barrier of overall reactions and of individual reaction steps, since catalysts work by lowering this energy barrier. Lowering activation barriers is the main target in improving catalyst design, specifically improving the rate of the rate limiting step. The thermodynamics of a reaction are also very important to understand how it will behave in a physical system, but catalysts have no effect on the overall thermodynamics of a reaction, so the focus in this study was placed on the reaction kinetics.

Potential for improvement exists in the approximation, calculation, and prediction of activation barriers. If this can be understood well, the kinetics of the reaction can truly be understood and better catalysts can be developed. The distinguishing characteristic of an electrochemical step is that it involves the transfer of an electron, which has an energy that will vary with the potential of the electrode involved in the reaction. In the case of hydrogenating CO_2^* , the electron is considered a reactant of this step. Therefore, the energy of the initial state will vary with potential, and it is this variation that causes the activation barrier to vary with potential, since the barrier is ultimately equal to the energy difference between the transition state and the initial state.

Marcus theory provides a framework that allows for the consideration of the rate of an electron transfer reaction^[1]. In Marcus theory, the initial and final states of a reaction are represented by parabolas on a plot of free energy against charge, as shown in Figure 1. Density functional theory (DFT) provides the ability to calculate electronic structure, and therefore system

energy, as a system moves along a reaction path. A number of people, including the Anderson^[2], Goddard^[3], Rossmeisl^[4], and Norskov^[5] groups, have used DFT to approximate electrocatalytic barriers. Each of these methods is complex and suffers from a lack of general applicability.

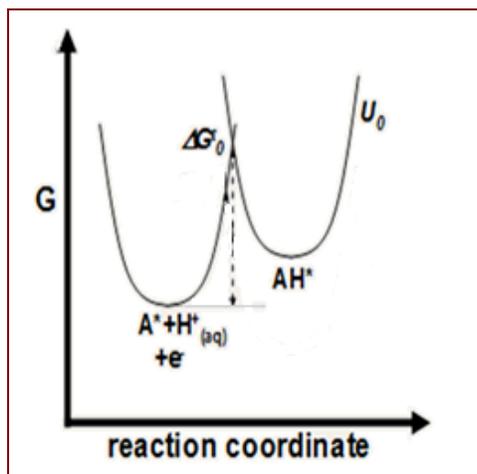


Figure 1. An example of a plot illustrating the Marcus theory representation of an electron transfer reaction.

The intersection of these parabolas represents the activation energy of the reaction. It is challenging to calculate the transition state of an electrochemical step, but relatively straightforward to find the transition state of the analogous non-electrochemical step. Therefore, it is useful to break the reaction modeled in Figure 1 down into two reaction steps, one electrochemical and one non-electrochemical, as shown in Figure 2.

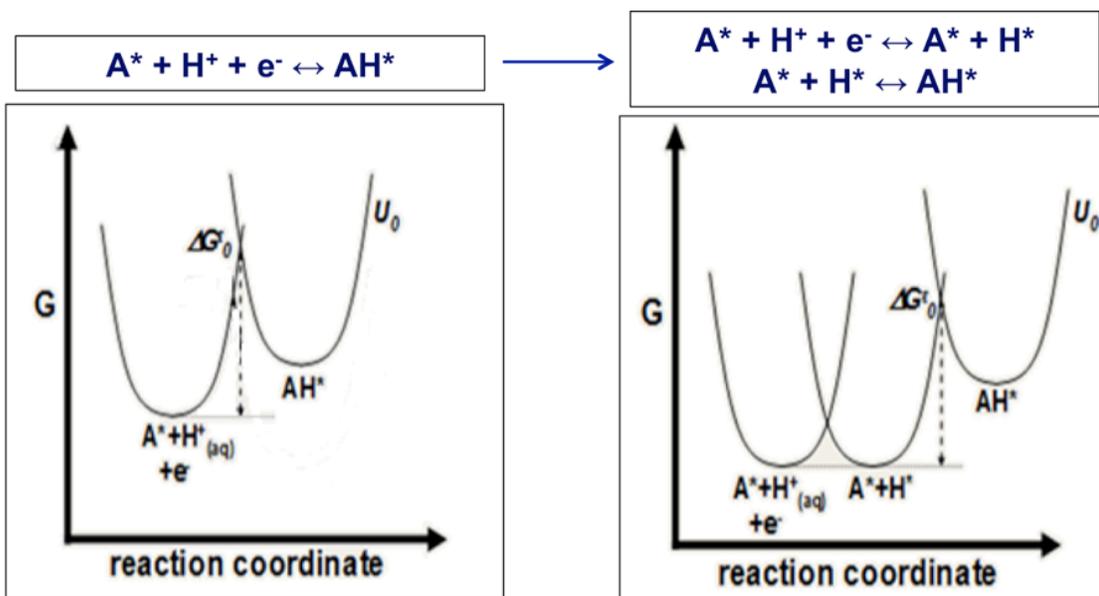


Figure 2. Reaction energy diagram for an electroreduction reaction of an adsorbate. In this case A represents CO_2 . The right hand diagram illustrates the concept of an equilibrium potential at which the $(A^*+H^++e^-)$ and (A^*+H^*) states are equivalent.

At a specific equilibrium potential (U^0), the initial state ($A^*+H^++e^-$) and the intermediate state A^*+H^* have the same free energy. The true initial state includes an electron, and its energy varies with electrode potential. At U^0 , the energy change of the non-electrochemical step ($A^*+H^* \rightarrow AH^*$) is equivalent to the energy change of the electrochemical step ($A^*+H^++e^- \rightarrow AH^*$). Therefore an activation barrier can be calculated at the equilibrium potential (E_{act}^0) that is equal to difference between the energy of the transition state and the energy of the initial state. Because the energy of the reactant varies with potential, the activation barrier does as well. Once U^0 and E_{act}^0 are calculated, an expression can be developed to determine the activation barrier at any potential.

This potential dependence can be clearly observed graphically in Figure 2. Free energy is plotted on the y-axis, and as mentioned the energy of the reactant state depends on the potential of the system. Therefore if the potential is changed, the reactant parabola will experience a vertical shift. Geometrically, this means that the intersection of the two parabolas will experience a shift

as well. In order to account for this shift, a symmetry coefficient is included in the expression for activation energy as a function of potential.

In Figure 2, all the parabolas are shown to have the same curvature. Because of this, if the reactant parabola experienced a vertical shift due to a change in potential, the intersection will experience a vertical shift with a magnitude that is exactly half of the shift that the parabola experienced. In this case, the symmetry coefficient β is equal to exactly 0.5. If one parabola were wider or narrower than the other, this would not be true, as the intersection would shift by some calculable fraction of the parabola's shift. Generally, the parabolas have a similar enough shape that it is reasonable to assume a value of 0.5 for β and use this in calculations. However if a more accurate value can be approximated for β , it results in more accurate calculations of the activation barriers of electrochemical reaction steps. Ultimately, this leads to a better understanding of electrocatalysis, and therefore better and more efficient electrochemical cells.

Chapter 2

Methods

The Vienna ab initio simulation program (VASP) was used to perform all calculations, evaluating the electronic structure by expansion on a plane wave basis. The results obtained included the energy and charge distribution of the system, which were used in subsequent calculations. The VASP was used to optimize structures and to find the transition state between two optimized states. These VASP files were converted to obtain images of the states, and all structural figures were made with Materials Studio.

A plane wave basis set was used, with an energy cutoff of 400 eV, and with the projected augmented wave (PAW) pseudopotentials supplied by VASP. A Monkhorst-pack grid was utilized, with a 3x3x1 k-point setting. All calculations were performed on a Cu(1 1 1) surface. There were four layers of copper atoms in each 3x3 surface cell.

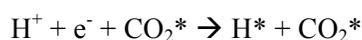
The limitations of the model lie in its inability to accurately represent the length and time scales of real systems. In a real physical system, the molecules are constantly moving, but the model used does not account for these dynamics. In order for the model to be effective, ions in solution must be concentrated enough so that there is an ion in every cell, but this represents an unrealistically high concentration.

The electrochemical reaction step that these calculations focus on is the first step in the electroreduction of carbon dioxide (CO_2^*) to methane/methanol over a copper catalyst. The first step in this reaction is the hydrogenation of the carbon dioxide to an intermediate species, COOH^* . This reaction step was modeled with a varying amount and orientation of surrounding water molecules, and the activation barrier was calculated at each.

Our method^[6,7,8] for calculating the activation barrier of an electrochemical reaction step begins with the optimization of both the initial and final states of the reaction step. The initial state modeled was a CO₂* molecule above the copper surface, and the final state was the COOH* molecule bonded to the surface. At least one water molecule was present in the model throughout the reaction, so it was included in the optimization. The initial state was optimized both with and without the proton present in the cell. These two versions of the initial state represent the two parabolas in Figure 2.

Once these three states (initial without H*, initial with H*, and final) were optimized, a CI-NEB (climbing image – nudged elastic band)^[9,10] transition state search was performed. The state found was considered to be a true transition state only if it met certain criteria. Logical predictions for the transition state could generally be made, so if the transition state was drastically different from this prediction, it was investigated further. The transition state is defined as a maximum in the energy curve of the reaction, so the tangent forces on all of the atoms had to be very close to zero for the transition state found to be considered accurate. Additionally, frequency calculations were performed, and the presence of one imaginary frequency confirmed that a true transition state had been found. Frequency calculations were performed on all states (initial with H*, initial without H*, transition, and final) so that the Gibb's free energy of the state could be obtained. An example transition state is shown below, with one water molecule enabling the proton transfer.

Once the vibrational corrected energies were obtained and the Gibb's energy of a hydrogen (H₂) molecule was calculated, a value for U⁰ could be calculated. For the following electrochemical step:



U⁰ can be calculated by the following equation:

$$U^0 = G_{\text{H}^*+\text{CO}_2^*} - G_{\text{CO}_2^*} - \frac{1}{2}G_{\text{H}_2} \quad (1)$$

Again, this is the potential where the true initial state and the intermediate (A^*+H^*) state had the same energy. E_{act}^0 can also be calculated. Using the ZPVE corrected energies, it can be calculated by the following equation:

$$E_{act}^0 = G_{TS} - G_{IS} \quad (2)$$

where G_{TS} is the energy of the transition state, and G_{IS} is the energy of the initial state. Because the calculation is performed at U^0 , the energies of the initial states with and without H^* should be equivalent, so either value can be used in this calculation.

The following expression, derived from Butler-Volmer theory, then gives the activation energy at any potential:

$$E_{act}(U) = E_{act}^0(U^0) + \beta e(U - U^0) \quad (3)$$

β here represents a symmetry coefficient. It takes on values between 0 and 1, and loosely represents where the transition state falls between the initial and final states. It is often assumed to have a value of 0.5, but can be estimated by a number of different methods.

One of the methods that has been used for approximating β is to calculate the activation barrier for the same system at different potentials; that is finding different values for E_{act}^0 at different values of U^0 . This leads to multiple data points, which can be plotted. A linear relationship emerges, as shown in Figure 6 in the results section, and β emerges as the slope of the line by equation 4:

$$E_{act}^0_1 = E_{act}^0_2 + \beta(U^0_1 - U^0_2) \quad (4)$$

This method works for some systems, but is not easily generalizable. In this case, it was used for the hydrogenation of CO_2 over a copper surface with two water molecules involved in shuttling the hydrogen. Two cases were available, one with the hydrogen initially as a proton on the copper surface, and one with the hydrogen floating in the solution as part of a $H_5O_2^+$ molecule. This allowed for two different activation barriers to be calculated at two different U^0 's, but this kind of analysis will not be possible for reactions if multiple cases cannot be found.

Another method for the approximation of the symmetry coefficient relates back to Figure 2, shown again here for reference.

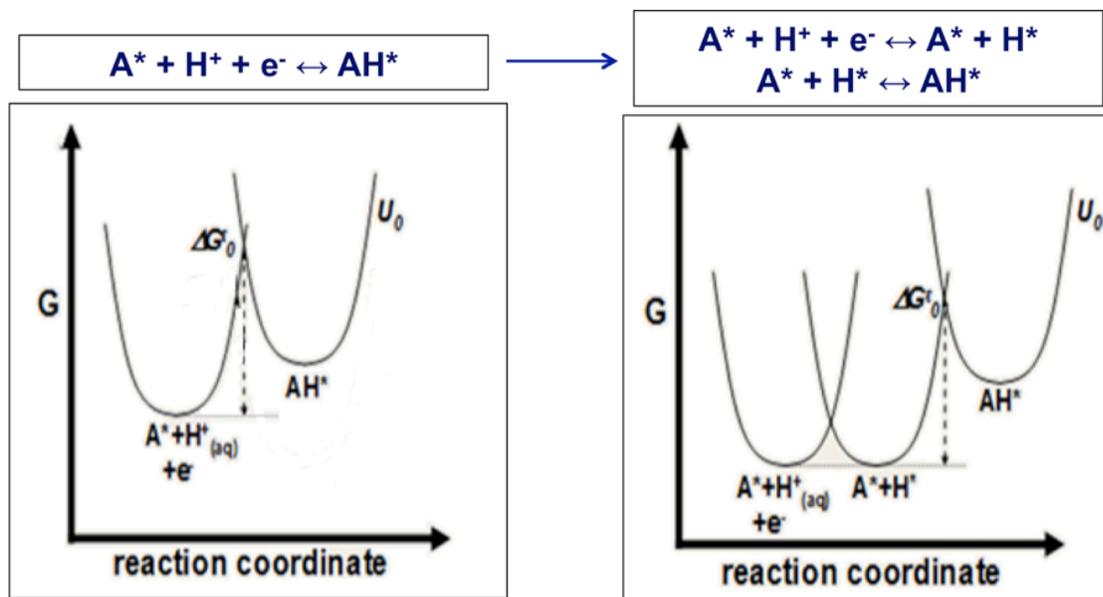


Figure 2. Reaction energy diagram for an electroreduction reaction of an adsorbate. In this case A represents CO_2 .

An available reaction coordinate must be chosen. In this case charge, approximated by the Bader method, was used. These numbers can be easily found in VASP, and the sum of the charge over the atoms involved in the reaction (all but the copper surface) was used as the charge of the state in all calculations. These values correspond to the points along the x-axis in Figure 2 where the minima of the parabolas occur. Therefore, if both the charges and the energies of the initial and final states are known, as well as the charge of the transition state (the intersection of the two parabolas), the parabolas can be fit. Their intersection represents the transition state of the reaction step, and therefore allows for the calculation of the activation barrier. A value for β can be approximated by comparing the intersection to the initial state, represented by the minimum in the first parabola in Figure 2.

The next step is to incorporate potential dependence. It is assumed that the final state is independent of potential, so a change in potential will only affect the energy of the initial state,

because the electron involved in the reaction is considered a reactant. Graphically, this means that only the parabola representing the initial state will experience a vertical shift when the potential is changed, as will the intersection of the two parabolas. The comparison between the shifting of the intersection and the parabola itself is truly where the value of β is derived from. Then, the potential dependence of β and can be mathematically incorporated into the expression, so that β can be known as a function of potential. A derivation can be found in Appendix A.

Chapter 3

Results and Discussion

The methods in this project were developed using the electroreduction of carbon dioxide to methane/methanol over a copper catalyst surface. Specifically the first step in the reaction was studied, the hydrogenation of CO_2^* to COOH^* . Values for the activation energy were initially calculated with a symmetry coefficient of 0.5 and are discussed below. The symmetry coefficient was then further evaluated by two different methods so that more realistic numbers could be attained, as discussed in this chapter.

3.1 $\text{CO}_2^* \rightarrow \text{COOH}^*$

Initially, activation barriers were calculated using equations (1-3) with an assumed value of 0.5 for β . This calculation was performed on the three systems shown below, in Figures 3-5, where each has a different configuration of water molecules. The path shown in Figure 5 shows the hydrogen as part of a H_3O_2^+ molecule in solution, rather than starting on the surface, and Figures 4 and 5 both show the hydrogen atom shuttling through two water molecules. This was found to be a favorable path for the reaction to follow^[6], as opposed to shuttling through one water molecule while the other solvated the reaction. This difference is illustrated in the table below, which shows calculated values for the system with varying water configurations, shown in Figures 3-5.

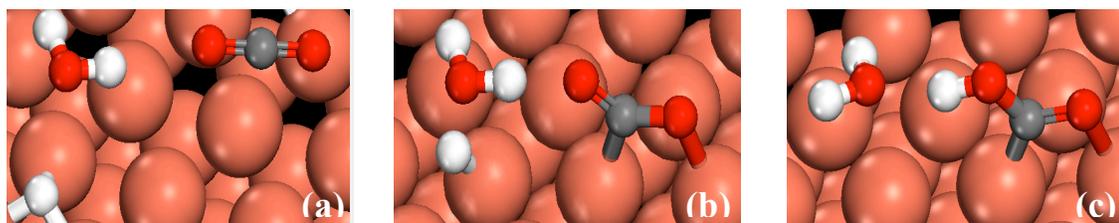


Figure 3. Materials Studio Images of (a) the initial state with H^* , (b) the found transition state, and (c) the final state of the first electrochemical reaction step in the electroreduction of carbon dioxide over a copper catalyst, with a single water molecule. This orientation is referred to as Model A in Table 1.

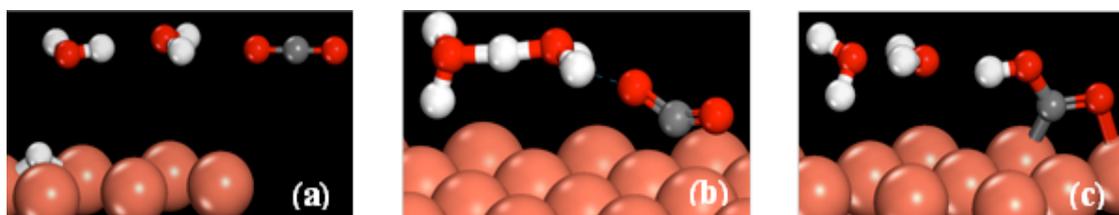


Figure 4. Materials Studio Images of (a) the initial state with H^* , (b) the found transition state, and (c) the final state of the first electrochemical reaction step in the electroreduction of carbon dioxide over a copper catalyst, where the hydrogen starts on the surface and shuttles through two water molecules. This orientation is referred to as Model C in Table 1.

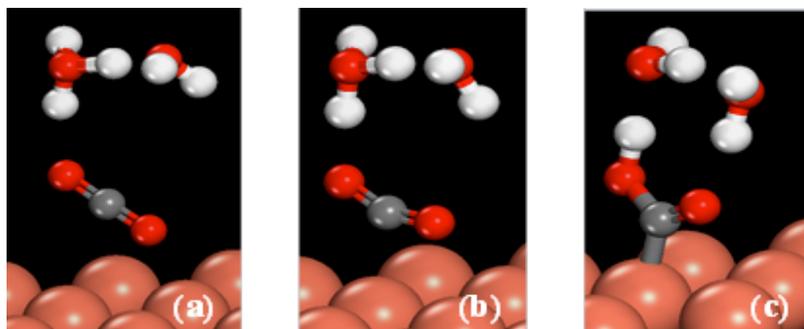


Figure 5. Materials Studio Images of (a) the initial state with H^* , (b) the found transition state, and (c) the final state of the first electrochemical reaction step in the electroreduction of carbon dioxide over a copper catalyst, where the hydrogen starts as part of a $H_5O_2^+$ in solution and shuttles through two water molecules. This orientation is referred to as Model E in Table 1.

Table 1. Calculated values for the system with both one and two water molecules, with and without a water bilayer. The two-water scenario listed involves one water solvating the system while the other shuttles the hydrogen to the CO₂ molecule. The second two-water scenario has the hydrogen starting in solution, and then shuttling through both water molecules to the CO₂ molecule.

<i>Model</i>	<i># and orientation H₂O</i>	U^0 (<i>V-RHE</i>)	E_{act}^0 (<i>eV</i>)	$E_{act}^0 - 0.65$ <i>V-RHE</i>	ΔG_{rxn} (U^0)	$\Delta Charge$ (<i>IS-TS</i>)
A	1	-0.11	1.10	0.83	--	--
B	1 with 6 H ₂ O bilayer ^a	-0.01	0.96	0.64	--	--
C	2 with H ⁺ on surface	-0.11	0.90	0.63	>0	0.83
D	2 with 6 H ₂ O bilayer ^a	-0.02	0.74	0.43	--	--
E	2 with H ⁺ in solution	-2.19	0.0075	0.78	<0	0.39

(a) These data were calculated by our collaborators at Ohio State University, in the Asthagiri group.

An interesting result lies in the relationship between the ΔG_{rxn} and the $\Delta Charge$ (IS to TS). This $\Delta Charge$ value is simply the difference in the Bader charge on the transition state and on the initial state (without H^{*}). For Model C, the ΔG_{rxn} is greater than zero, indicating that the reaction is not favorable. The change in charge from the initial state to the transition state is 0.83, which is relatively close to one. One total electron is transferred in this reaction, so this indicates that the transition state is more similar to the final state than it is to the initial state. For Model E, the opposite is true. The ΔG_{rxn} is less than zero, and the change in charge is only 0.39, indicating that the transition state is closer to the initial state than the final state. Both of these facts indicate a favorable reaction.

3.2 Symmetry Coefficient

The symmetry coefficient for electrochemical reaction activation barriers can be approximated in several different ways. The first that is evaluated here involves comparing the activation barrier for different equilibrium potentials. If one system can be set up in multiple ways such that different U^0 values can be found, then this method is applicable. The activation barrier,

E_{act}^0 , can be calculated at each U^0 . In this case, the system with two water molecules involved in the reaction step was studied. There were two distinct cases for this system (Model C and Model E). In the first case, the proton began on the copper surface and shuttled through two water molecules to the CO_2 molecule. In the second case, the proton began in solution, as part of a H_5O_2^+ molecule floating above the CO_2 molecule, and shuttled through both water molecules before moving to the carbon dioxide.

The equilibrium potential, U^0 , was calculated for each case, as was the activation barrier at the equilibrium potential, E_{act}^0 . These values were shown in Table 1, and are plotted in Figure 6 below.

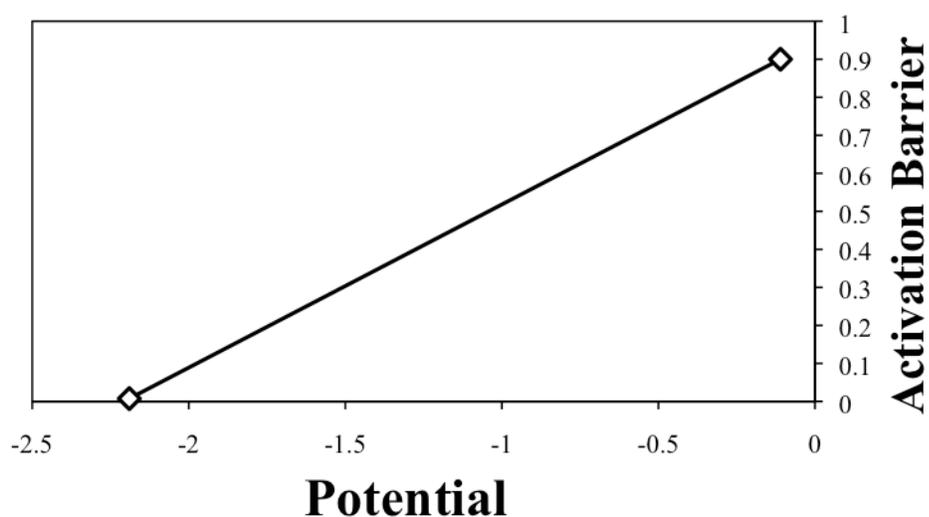


Figure 6. A plot of the activation barrier of a system against the potential of the system. The slope of this line gives the symmetry coefficient, β .

The values of the equilibrium potential and activation barrier at these points were plugged into equation 4, with the following result:

$$\text{Equation 4: } 0.9 = 0.0075 + \beta(-2.19 + 0.11)$$

$$\beta = 0.43$$

This value of 0.43 for the symmetry coefficient is fairly close to the previously assumed value of 0.5. This is reassuring for the method, in that it yielded a reasonable value for β , and it also confirms that previous calculations using a β value of 0.5 were realistic.

Because any two points create a linear plot, an attempt was made to determine an intermediate case, to make the plot more robust. This could be done by creating an initial state in which the hydrogen began in solution again as part of an H_5O_2^+ molecule, but with the molecule next to the carbon dioxide, rather than floating above it. This would put the proton closer to the copper surface, and result in an intermediate value for U^0 . However, any attempt to optimize this intermediate reactant case fell back to one of the previously studied cases, so it was not possible to add another point to the plot in Figure 6. This situation illustrates the lack in generalizability that is the major obstacle for this method. It can only be applied to systems where multiple cases can be optimized and studied, and this is not always possible.

The symmetry coefficient β can also be determined by fitting the parabolas representing the initial and final states of the reaction, as in Figure 2. Charge was assigned to each species using the Bader method, and this was used as the reaction coordinate for the system. As an example, the system with a proton starting on the copper surface and shuttling through two water molecules was studied (Model C, shown in Figure 4 above). The relevant values are shown in Table 2.

Table 2. Values relevant to the fitting of the parabolas for the calculation of β . The charge is the sum of the Bader charges on all atoms involved in the reaction, which includes every atom in the cell except for the copper surface.

<i>State</i>	<i>Energy</i> (<i>eV</i>)	<i>Charge</i> (# <i>electrons</i>)
Initial (with H*)	-179.904	33.2909
Initial (without H*)	-176.523	32.0183
Transition	-179.128	32.8394
Final	-179.513	33.4388

These values were used in order to specify the general parabolas shown in Figure #. The actual parabolas for this system were fit in Mathematica, and are pictured below. Using the analysis shown in Appendix A, the initial and final state parabola energies are given by

$$G_{IS}(q) = A(q - q_{IS})^2 \quad (5)$$

$$G_{FS}(q) = \Delta G_{rxn}^0 + C(q - q_{FS})^2 + e(U_{RHE} - U^0) \quad (6)$$

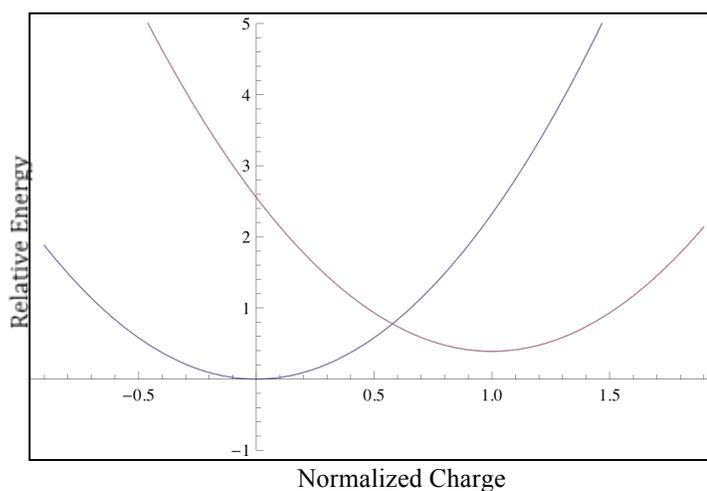


Figure 7. The parabolas fit to the values given in Table 2. The values were normalized so that the minimum of the reactant parabola was the origin of the coordinate system. Therefore the energies shown are relative to the energy of the optimized initial state.

This provides a relationship between the activation barrier and potential, as in Figure 8, because the intersection of the two parabolas represents the transition state of the reaction. The activation barrier is just equal to the energy difference between the transition state and the initial state.

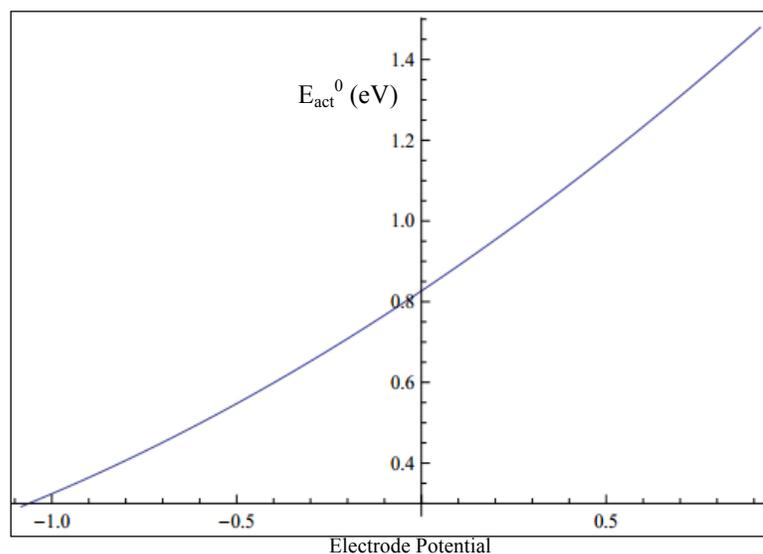


Figure 8. A plot of the symmetry coefficient against the electrode potential. The parabolas fit in Figure 7 were analyzed so that β could be obtained as a function of potential. The full derivation is given in Appendix B.

The intersection of these two parabolas is representative of the transition state, and comparing it to the initial state yields a value for β at U^0 . The result for β here is 0.58, which again is reasonably close to the previously assumed value of 0.5. This means that the previous assumption was reasonable, and the method was successful in predicting a reasonable value for β .

The potential dependence must be taken into account, so that β can be calculated at any potential. The dependence of this intersection on potential is based on the shape of the parabolas and the initial state's dependence on the potential of the system. This potential dependence can be incorporated into the parabolic equations, and the following plot can be obtained as well as an expression for β as a function of potential. A complete derivation can be found in the Appendix A.

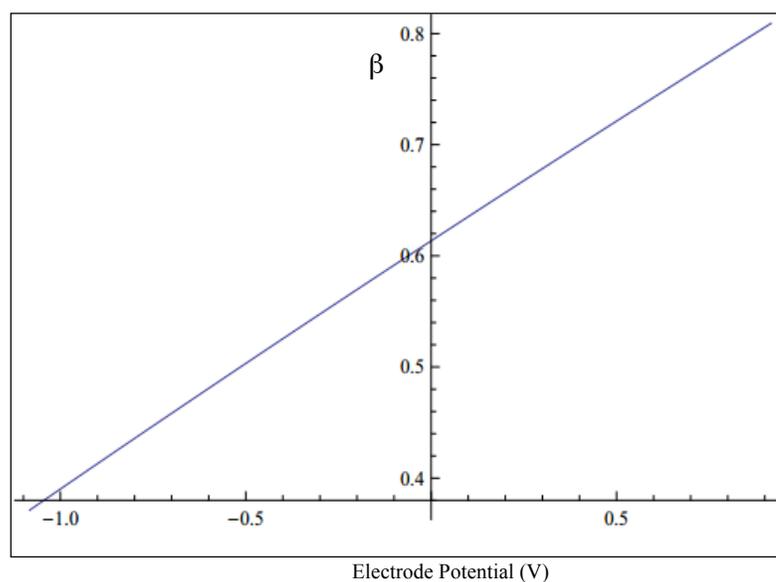


Figure 9. A plot of the symmetry coefficient against the electrode potential. The parabolas fit in Figure 7 were analyzed so that β could be obtained as a function of potential. The full derivation is given in Appendix B.

This relationship is the ultimate result of the study. It allows for the calculation of the symmetry coefficient for a reaction at any potential, but it also has limitations. When an inverse region exists, or the barrier is non-existent, the method breaks down. There are other potential scenarios when the method might fail, but more testing must be done to determine the true abilities and limitations of this method.

A plot of E_{act} against electrode potential can be created for each method, and provides a convenient comparison. Two lines were added to the plot in Figure 7 in Figure 10. The dotted line in Figure 10 represents the data obtained when a value of 0.5 is assumed for the symmetry coefficient β . The solid line is produced by the method which simultaneously analyzes two distinct cases of a system (in this case Model C and Model E above) to determine a value for β . Finally, the curve represents an activation barrier calculated by fitting the parabolas for the initial and final states of the reaction and analyzing their intersection to find E_{act} and β as functions of

electrode potential.

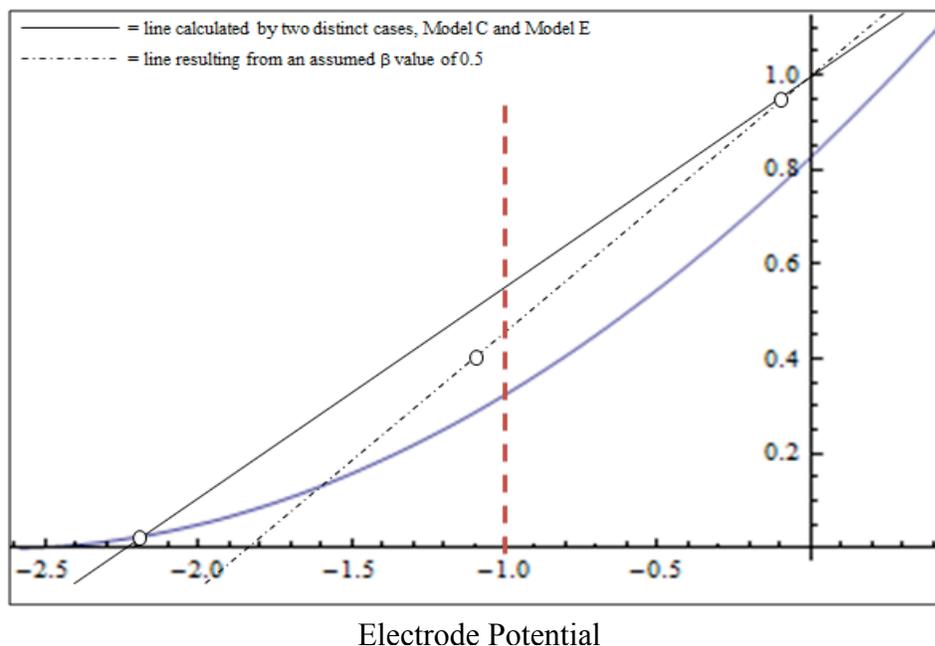


Figure 10. A plot of activation barrier against electrode potential, calculated via three different methods. The dotted line is produced assuming a value of 0.5 for b , while the solid line is determined by studying two distinct cases of a system. The blue curve is the relationship between E_{act} and potential that emerges from fitting the initial state and final state parabolas.

The image above shows the relationships between activation barrier and electrode potential that emerge as the result of three separate methods. They are reasonably close, as illustrated by the vertical dashed line placed on the plot. The points at which the three curves intersect this dotted line represent the activation barrier at an electrode potential of -1.0 V-RHE. Using one calculated point and extrapolating with an assumed value of 0.5 for β gives the dotted line, and an activation barrier of approximately 0.45 eV. The same graphical analysis of the solid line, produced by calculating the activation barriers and equilibrium potentials for two cases of the same system, yields an E_{act} of 0.55 eV. The third curve on the graph, produced through the fitting of the initial and final state parabolas, gives an activation barrier of approximately 0.33 eV.

These numbers are in reasonable agreement with each other, so it can be concluded that each of the methods is successful in approximating a value for the activation barrier as a function of electrode potential.

Chapter 4

Conclusions and Further Work

These methods can be used to capture the potential dependence of the symmetry factor and to calculate a value for β at varying potentials. Both methods used for approximating β result in reasonable values, relatively close to the previously assumed value of 0.5. This is encouraging, but both methods need to be tested further. The method utilizing the ability to plot different activation barriers at different potentials requires that multiple cases with different U^0 values exist for the given systems. This is not very generalizable. The second method discussed, which requires the fitting of parabolas representing the initial and final states, may be generalizable, but it must be evaluated further.

This method should be applied to various systems and reaction steps in order to test it. There are scenarios where the method will break down, and these must be found and understood so that we can fully understand where the method can successfully be applied. It appears to work well for the system evaluated in Chapter 3, but it is too soon to determine whether it is widely applicable.

The values of β calculated from these different methods should also be compared with each other and with the value of 0.5 in the subsequent calculations of the activation barriers. The activation barriers calculated at various potentials can then be compared to each other and to values determined from other methods, so that the numbers, and the method used to obtain them, can truly be tested.

These results are very important, because they describe the dependence of activation barriers on potential and provide an opportunity to study and understand this dependence. These

systems would ultimately be applied in a fuel cell, where the electrode potential would play an important role. The strong dependence of the activation barrier on the potential is a factor in electrocatalysis because the electrochemical reaction step involves the transfer of an electron. Electrons' energies depend on the potential of the system, so the energy of the state including the electron (the reactants in this case) varies with potential. This dependence is an important factor in electrocatalysis, and if it can be modeled with higher accuracy it could improve the understanding of electrocatalysis. This increased understanding could lead to the development of more active and selective catalysts for electrochemical reactions, ultimately leading to increased efficiencies in fuel cells.

Appendix A

Derivation of Equation 5

Parabolas for the reactant and product states could be fitted by writing parabolic expressions for the free energy of the initial and final states as a function of the charge of the system, where the charge is determined by the Bader method.

$$G_{IS}(q) = A(q - q_{IS})^2$$

$$G_{FS}(q) = \Delta G_{rxn}^0 + C(q - q_{FS})^2 + e(U_{RHE} - U^0)$$

Where G_{rxn}^0 indicates the reaction free energy calculated at the equilibrium potential U^0 . The free energy of the initial state is set to a reference value of 0. The fit constant A is defined by setting the initial state parabola to intersect the transition state, and the constant C was determined by a similar approach for the final state parabola.

$$A = \frac{E_{act}^0}{(q_{TS} - q_{IS})^2}$$

$$C = \frac{E_{act}^0 - \Delta G_{rxn}^0}{(q_{TS} - q_{FS})^2}$$

Substituting these values into the parabolic expressions above gives the following equations

$$G_{IS}(q) = E_{act}^0 \frac{(q - q_{IS})^2}{(q_{TS} - q_{IS})^2}$$

$$G_{FS}(q) = \Delta G_{rxn}^0 + (E_{act}^0 - \Delta G_{rxn}^0) \frac{(q - q_{FS})^2}{(q_{TS} - q_{FS})^2} + e(U_{RHE} - U^0)$$

The transition state of the reaction is represented graphically as the intersection of the two parabolas given in Figure 7. The x-coordinate (charge) of this intersection will change with a vertical shift caused by a change in potential, unlike the x-coordinate of either the reactant or product parabolas. The

value q_{TS} represents the charge on the transition state at the equilibrium potential, but q^* will be used to indicate the charge of the transition at any potential. A and C were substituted back into the expression for simplicity. The equation for the intersect of the two parabolas at q^* for any potential U is

$$q^{*2} (A - C) + 2q^* (Cq_{FS} - Aq_{IS}) + Aq_{IS}^2 - Cq_{FS}^2 - \Delta G_{rxn}^0 - e(U_{RHE} - U^0) = 0$$

The quadratic equation was used to solve the above expression for q^* . This was then used to determine the activation energy (E_{act}^0) as a function of potential. This is given by plugging q^* into the equation for the initial state parabola, where q^* is a function of potential U.

$$E_{act}(U) = E_{act}^0 \frac{(q^* - q_{IS})^2}{(q_{TS} - q_{IS})^2}$$

This equation is plotted in Figure 8, for the system analyzed above (Model C). The symmetry factor β can be calculated as the derivative of $E_{act}(U)$ with respect to U, as is clear mathematically from equation 3. β is plotted as a function of potential in Figure 9.

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