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Metal Dissolution from First Principles: Potential-dependent Kinetics and Charge Transfer

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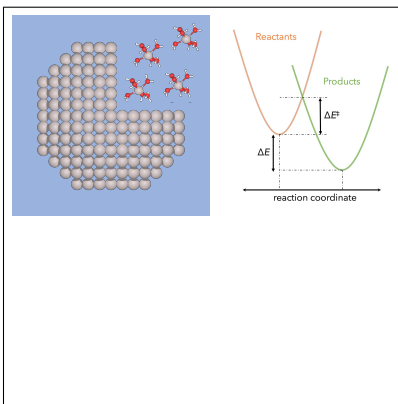
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Abstract

Metal dissolution and its inverse process are integral to both corrosion and electrodeposition; however, many mechanistic details regarding the dissolution process are challenging to decipher. These include how ion dissolution kinetics and charge transfer are influenced by the competition between metal and solvent interactions under an electrode potential. In this work, we introduce a computational framework based on density functional theory with grand-canonical treatment of electrons to directly predict the potential energy landscape for metal dissolution at a constant potential. Using aluminum as an example, we demonstrate that dissolution kinetics is governed by competing kinetics between two physical processes associated with metal-metal bond breaking and ion-migration within the electrical double layer, respectively. We identify a kinetic transition between regimes dominated by each of these processes and show that this transition depends on the operating electrode potential, among other key factors. It is further found that kinetics and thermodynamics of these processes can be described with a simple, one-parameter Marcus-theory-type model. Beyond offering new understanding of charge transfer during dissolution, our simulation protocol provides a recipe for directly predicting other important quantities in electrochemical reactions from first principles that are difficult to measure, such as the symmetry factor.

TOC Graphic



Introduction

Predicting and controlling metal dissolution is critical for a broad array of applications, from corrosion and electrodeposition to development of electrochemical energy systems. In these applications, dissolution kinetics is often an important parameter that determine key performance metrics, such as the corrosion rate of alloys in aqueous environments,¹ and stability of electrode materials in ion batteries^{2,3} and fuel cells.⁴ From an activity point of view, it has also been demonstrated that dissolution of surface atoms in electrocatalysts may lower the overpotential for hydrogen production, pointing to the infamous trade-off between stability and activity in these materials.^{5,6}

Experimentally, the thermodynamics of metal dissolution are well documented in terms of redox potentials;⁷ however, the kinetics of these processes are far more challenging to measure and unravel.^{8,9} Metal dissolution is notoriously complex, involving processes that are often competing and multiscale in nature. These include metal-metal bond breaking, formation of an ion solvation shell, and migration of the dissolved ion across the electrical double layer (EDL). This is further complicated by the fact that charge transfer accompanies dissolution, meaning both electronic and ionic contributions synergistically determine the dissolution energetics and the associated mechanism. For electrochemical systems relevant for energy storage and conversion, electrode materials are also subjected to an external voltage, which can magnify the driving force for dissolution.¹⁰⁻¹² Under open-circuit conditions, such as those that commonly accompany corrosion, intrinsic potential gradients can play an analogous role.¹³ As a result, dissolution kinetics depend both on the bias potential and the intrinsic reduction potential. Additional factors, such as surface orientation and defects, as well as solvent composition, further influence dissolution kinetics.

Some critical issues in understanding metal dissolution kinetics have been discussed by Gignea.¹⁴ One of the central questions regards the evolution of the metal charge state and hydration shell as the metal atom migrates from the substrate to the bulk solution during dissolution. A related question is how activation barriers are dictated by the competition

between metal-metal and metal-solvent interactions. In addition, a detailed mechanistic understanding of the kinetically limiting step that governs the overall dissolution process is largely lacking, particularly under an applied potential. This can be distributed to the lack of experimental probes with sufficient resolution and sensitivity to isolate the highly complex dissolution process.

Atomistic simulations can aid with detailed understanding of dissolution; however, several technical challenges remain. Most atomistic studies have focused on reproducing the thermodynamics of dissolution. Early theoretical investigations combined empirical embedded atom (EAM) potentials and stochastic dynamics to simulate deposition of silver and platinum on a gold surface at specific electrode potentials.¹⁵ Along similar lines, EAM variable charge-potentials were developed to provide a more realistic description of metal oxidation charge states during dissolution.¹⁶ While providing important insights, these studies did not explicitly account for the metal-metal bond breaking and ion hydration formation.¹⁷ With recent advancements in electronic structure methods, several attempts have been made to model metal dissolution or electrodeposition using first-principles approaches. For example, density functional theory (DFT) calculations were employed to predict trends in the thermodynamics of surface alloy dissolution in acidic media.¹⁸ Another study combined DFT with the Effective Screening Medium (ESM) approach to compute free corrosion potentials, although assumptions were introduced to account for the kinetic terms.¹⁹ By contrast, few attempts have been made to directly compute kinetics. Most notably, Taylor *et al.* used DFT to study dissolution kinetics of Cu and Ni—Cr alloy surfaces in liquid water.^{20,21} Although these studies directly accounted for the metal-metal bond breaking and ion hydration formation, the effects of constant electrode potential—a critical control knob in experimental setups—were not explicitly included. In another direction, Pinto and co-workers proposed a method that combines a model Hamiltonian, DFT and classical molecular dynamics (MD) simulations to predict dissolution kinetics for a series of monovalent and divalent metal ions.^{22,23} Within this approach, the electronic and solvent contributions to the model Hamiltonian are de-

rived separately using input parameters computed from DFT and force field simulations, respectively. More recently, Ma *et al.* developed an approach to predict the anisotropic anodic dissolution for metals, where the activation energy for dissolution is approximated through properties that are more straightforward to compute from first principles, including the surface energy density and work function.²⁴

Built on these studies, we present an alternative framework for directly evaluating the kinetics of metal dissolution from first principles under potentiostatic conditions that mimic realistic experimental setups. The approach is applied to elucidate previously unreported aspects of dissolution of an aluminum surface. We choose to study aluminum due to its importance in a wide range of technology and we expect that our study would present a baseline for understanding more realistic aluminum alloys. We show that aluminum dissolution is a double-barrier process, with the rate-limiting step switching between metal-metal bond breaking and ion migration across the EDL depending on the potential. Moreover, we discover that activation barriers associated with dissolution at a constant potential follow a quadratic and linear relationships with intermediate and large driving forces, respectively, and these relationships can be expressed with a single parameter that is functionally similar to a Marcus-theory type model. The computational framework also enables prediction of the symmetry factor governing macroscale reaction kinetics, which is found to be dependent on the potential energy difference between intermediate reaction steps as well as the bias.

Computational Methods

Throughout this work, we consider an oxide-free aluminum (Al) surface, which is particularly relevant for understanding corrosion under low pH conditions or in crevices where solution mass transport is inhibited.^{25–27} All calculations were carried out using DFT implemented in the Grid-Based Projector Augmented Wave (GPAW) code with a real-space grid basis set.^{28,29} The Perdew–Burke–Ernzerhof (PBE)³⁰ exchange–correlation functional was

employed with a real grid spacing of 0.18 Å, and an optimized lattice constant of $a = 4.03$ Å was used. The lattice constant optimization was performed with a $21 \times 21 \times 21$ k-point mesh while a $4 \times 4 \times 1$ mesh was used for the surface calculations. In addition, we chose to study the common Al(111) surface, which was modeled with a $3 \times 3 \times 3$ slab where the bottom-most layer of the slab was constrained in the bulk position. A distance of at least 50 Å was used between the periodic images of the slab in the direction normal to the surface. Atomic manipulations and visualizations were handled using the Atomic Simulation Environment (ASE).³¹

Constant potential (*i.e.*, grand-canonical) surface calculations were performed using the Solvated Jellium Method (SJM), which allows selective charging of the unit cell while maintaining charge neutrality by adding a localized jellium counter charge in the implicit solvent region of the cell.³² This method naturally localizes the excess charge only on the reactive side of the electrode, avoids spurious solvation effects, and solves the generalized Poisson equation to deduce the electrostatics. A dipole correction³³ is located between the jellium counter charge and the reverse of the periodic slab to isolate this counter charge and eliminate field effects on the reactive side. Energies for isolated systems, such as water molecules and $[\text{Al}(\text{H}_2\text{O})_n]^{3+}$ clusters that represent the solvation shell of the Al^{+3} ion, were performed using conventional canonical DFT with a constant charge of 0 and +3, respectively. For consistency, an implicit solvent scheme developed by Walter and Held was applied in all calculations except for in the case of bulk Al.³⁴ A dielectric constant, $\epsilon = 78.36$ and cavity shape parameter, $u_0 = 0.18$ eV was employed for describing the implicit water as provided in Ref. 34. In all calculations, thermal (vibrational) contributions to the free energy were omitted. However, since the potential dependence of G (*i.e.*, Gibbs free energy) is reflected in the potential energy, we do not expect a significant change in the observed trends.

It is necessary to emphasize that there are several approaches besides SJM that have been developed over the years which treat charged electrochemical interfaces under constant potential conditions.³⁵ These can be broadly divided into two categories *i.e.*, canonical and

grand-canonical methods. With canonical approaches, the reaction energetics are performed using conventional DFT using finite size unit cells that are extrapolated to the constant-potential limit through a cell-extrapolation^{36,37} scheme or using charge-extrapolation using interfacial capacitor models.^{38,39} Although relatively simple, these extrapolation schemes are limited by the high computational cost associated with increasing cell size or the accuracy of charge partitioning methodologies. Relatively more sophisticated, grand-canonical^{32,40–44} schemes, on the other hand, allow for explicit control of the electrode potential by allowing direct *charging* of the electrode interface while still maintaining charge neutrality to circumvent divergence issues for periodically repeated unit cells. Besides, explicit charging, most of the grand-canonical methods employ hybrid or continuum-solvation schemes that provide for adequate solvation as well as electrostatic *screening* effects resulting in a realistic representation of the EDL. The *charging* and *screening* schemes differ between implementations, but the unifying feature is to create a charge-compensating electrolyte which results in a charge neutral unit cell with a realistic electrostatic profile that mimics the EDL. Such charge-compensating electrolytes can be broadly classified into two categories: (i) localized *i.e.*, Gaussian-shaped^{45,46} or spatially constrained, solvent-immersed counter charges (as implemented in SJM), and (ii) Boltzmann-weighted counter-ion distributions based on Poisson-Boltzmann (PB) equation.^{42,47} Although less realistic than the PB approach, the appeal of SJM lies in its efficiency and stability for treating the electrostatic problem; for example, the generalized Poisson equation only needs to be solved once per self-consistent field step in SJM. By construct, the primary purpose of the implicit solvent in SJM is to provide a medium to generate a reasonable electrostatic profile rather than providing solvation effects to the system for which more sophisticated implicit/hybrid solvation models should be considered.³² In its current form, the implicit solvent scheme by Walter and Held³⁴ have a solvation Gibbs energy accuracy of approx. 5 and 13 kJ/mol for neutral molecules and cations, respectively, which is comparable to some of the other continuum solvation models.^{48,49} However, it is not recommended to apply the model to anions in water with-

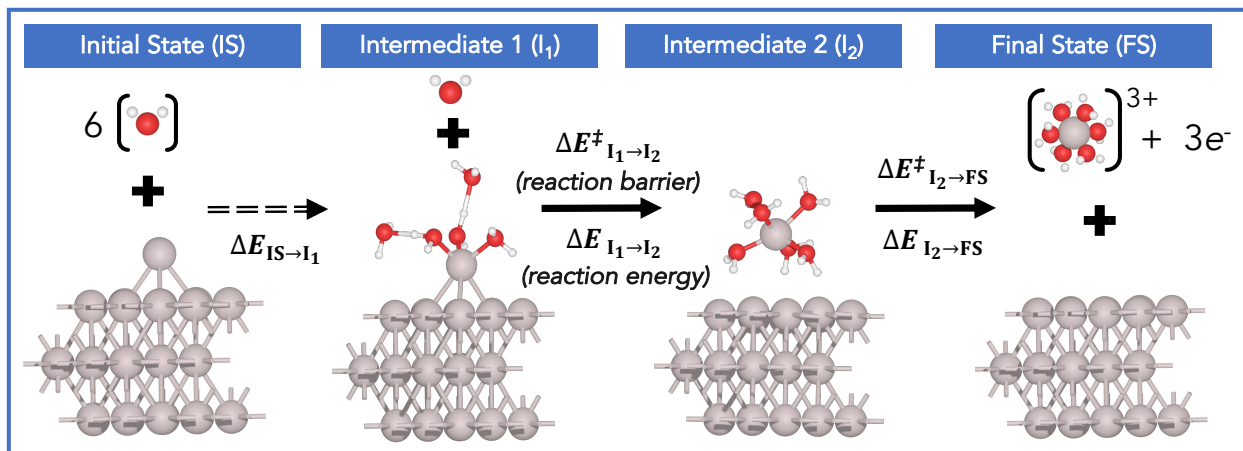


Figure 1: Schematic of atom-by-atom dissolution from the Al(111) surface, with the example shown for an initial adatom. The dissolution reaction can be divided into two steps: (i) breaking metal-metal bonds and forming a full ion solvation ($I_1 \rightarrow I_2$); and (ii) ion migration into the bulk solution ($I_2 \rightarrow \text{FS}$). Thermodynamic driving force for dissolution is defined as the reaction energy associated with the transition of an Al atom initially in the solid phase (IS) to an Al^{3+} ion immersed in the solvent (FS). For completeness, thermodynamic difference between IS and I_1 states is also included.

out further modification as short-range interactions between anions and water are not well represented. As we describe below, the inclusion of explicit water molecules in the first ion solvation shell is critical to achieve a good accuracy of dissolution energetics.

Results and Discussions

Figure 1 shows schematically how the atom-by-atom dissolution process proceeds from an intact Al(111) surface to a solvated Al^{3+} aqua complex. Using an adatom as an example, the dissolution process can be divided into two steps: (i) breaking of metal-metal bonds and formation of a full ion solvation, denoted by the reaction $I_1 \rightarrow I_2$; and (ii) ion migration into the bulk solution through the EDL, denoted by $I_2 \rightarrow \text{FS}$. The dissolution kinetics are determined by the evolution of this process, whereas the thermodynamic driving force for dissolution can be defined as the total reaction energy associated with the transition of an Al atom in the solid phase (IS) to an Al^{3+} ion immersed in the solvent (FS).

Before proceeding to study the surface and its associated kinetics, we first calculate the

Al/Al³⁺ redox potential, which provides a convenient reference to validate our simulated results. The potential was computed by evaluating the reaction energy associated with the transition of an atom in the interior of bulk metal to an Al³⁺ aqua ion complex immersed in the solvent, accompanied by three electrons transferred to the metal (see Supporting Information). We obtain a value of $-1.48 V_{\text{SHE}}$ for the redox potential, in reasonable agreement with the experimental value of $-1.68 V_{\text{SHE}}$.⁷ We point out that a purely implicit solvation model is not sufficient to accurately describe the solvated ion.⁵⁰ For example, as illustrated in Figure 2A and Figure S1, employing just a single explicit water molecule along with an implicit solvent model leads to a redox potential of $+2.09 V_{\text{SHE}}$, which is drastically higher than the experimental number. The discrepancy is largely corrected when the solvated ion is instead described using the [Al(H₂O)_{*n*}]³⁺ cluster with six explicit water molecules that form a complete solvation shell.⁵¹ This confirms that our approach that combines six explicit water molecules forming the first hydration shell along with implicit solvation can be reasonably used for assessing dissolution energetics of the metal. We note that agreement with experiment would likely be further improved by including explicit water molecules in the second ion hydration shell, and by accounting for entropic and/or thermal effects in the simulation model.

The results in Fig. 2A focus on the Al/Al³⁺ redox potential as a bulk property. In practice, dissolution is a surface phenomenon that is locally determined by the chemical bonding of the dissolving atoms (Figure 1). This in turn depends on multiple factors, such as surface orientation, the presence of grain boundaries and defects, and the specific solution environment. For example, it has been demonstrated that dissolution rates of Alloy 22 (nickel-chromium-molybdenum-tungsten-iron) scale inversely with the coordination number of surface atoms for a given grain orientation in aggressive acidic environments.⁵² Motivated by this study, we further investigate redox potentials of Al atoms with different coordination numbers. We focus on the defect free single-crystalline Al(111) surface for simplicity, and consider dissolution of an adatom and a surface atom that yield the lowest and highest pos-

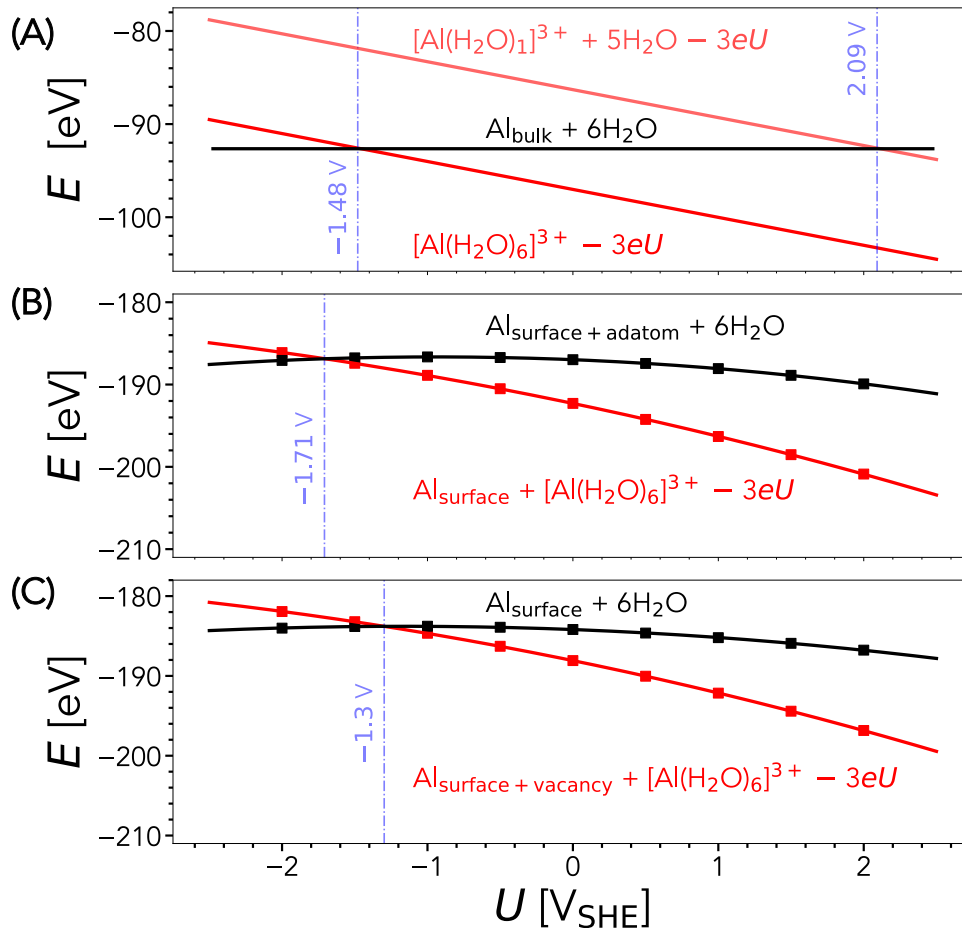


Figure 2: Dissolution reaction energies for (A) an atom in bulk Al, (B) an adatom on the Al(111) surface, and (C) an atom on the pristine Al(111) surface. The point of intersection between the black (initial state) and red lines (final state) represents the Al/Al³⁺ redox potential. For (A), the initial state is a bulk-phase atom, whereas the final state is a solvated ion in the implicit solvent with a specific number of explicit water molecules. For (B) and (C), the solvated ion is described by a complex with six explicit water molecules.

sible coordination numbers, respectively (see Figure S2). Calculation of the redox potential of these species is shown in Figure 2B & C. The potential was obtained by evaluating the difference in the energy between the initial state (IS) and the final state (FS) in Figure 1. As expected, dissolving a surface adatom requires much less energy (by 0.41 V) than for the surface atom. The dissolution potentials of these two limiting cases—the adatom and surface atom—bound the value obtained for the bulk.

Beyond the Al/Al³⁺ redox potential, our simulation protocol can be extended to access

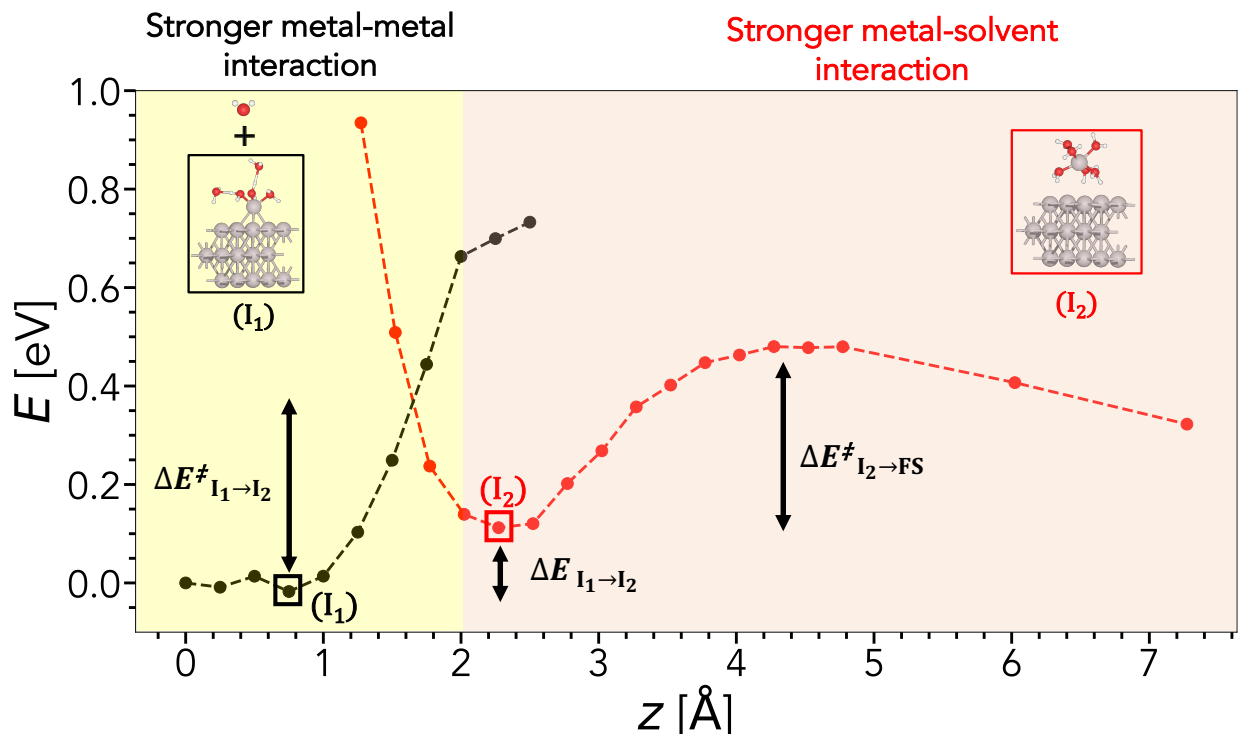


Figure 3: Dissolution kinetics at $-1 V_{\text{SHE}}$ as function of the distance (z) between the adatom and the Al(111) surface. The black and red lines represent energies of the $I_1|_z$ and $I_2|_z$ configurations with varying positions of the $[\text{Al}(\text{H}_2\text{O})_5]^{3+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complexes, respectively. Definitions of the intermediate-stage barriers $\Delta E_{\text{diss}}^\ddagger$ and $\Delta E_{\text{ion}}^\ddagger$ are shown, along with the potential difference ΔE_{diss} . For $\Delta E_{\text{diss}}^\ddagger$, the barrier and transition state are determined by the intersection between the $I_1|_z$ and $I_2|_z$ potential energy profiles. The representative models of I_1 and I_2 show the local minimum energy structures along the $I_1|_z$ and $I_1|_z$ pathways, respectively. Shaded regions delineate qualitative dominance of metal-metal (yellow) versus metal-solvent (pink) interactions.

kinetics of dissolution at a constant given potential. Here we focus on the adatom, shown in Figure 1, as our limiting case of interest. The dissolution process can be intuitively separated into two reaction stages: breaking of metal-metal bonds and formation of a complete ion solvation ($I_1 \rightarrow I_2$); and migration of the ion–water complex to bulk solution through the EDL ($I_2 \rightarrow \text{FS}$). Here, the I_1 state is modeled using five explicit water molecules that represent a partial solvation shell with an additional water molecule deep in the implicit solvent, whereas ion solvation of the I_2 state is modeled using six explicit water molecules. The I_1 and I_2

geometries represent the minimum energy structures on the potential energy wells obtained through incremental movement of $[\text{Al}(\text{H}_2\text{O})_5]^{3+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complexes represented by $\text{I}_1|_Z$ and $\text{I}_2|_Z$, respectively as shown in Figure 3. The potential energy profiles of $\text{I}_1|_Z$ and $\text{I}_2|_Z$ along the surface normal were then obtained by varying the position of the $[\text{Al}(\text{H}_2\text{O})_5]^{3+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complexes in the presence of an applied potential. At each step, configurations of these complexes were optimized with the adatom fixed in the z -direction. The $\text{I}_1|_{Z=0}$ structure was obtained by optimizing the structure shown in Figure S3, where the adatom was not allowed to relax in the direction normal to the surface. The transition state and the corresponding reaction barrier ($\Delta E_{\text{diss}}^\ddagger$) associated with the $\text{I}_1 \rightarrow \text{I}_2$ step was approximated as the intersection between the potential energy profiles of $\text{I}_1|_Z$ and $\text{I}_2|_Z$ configurations. In this way, kinetics associated with temporary reconfiguration of the ion solvation due to the presence of the sixth water molecule is not included in our simulations. Finally, the transition state associated with $\text{I}_2 \rightarrow \text{FS}$ and the associated reaction barrier ($\Delta E_{\text{ion}}^\ddagger$) was obtained from the potential energy profile of $\text{I}_2|_Z$ as a function of distance from the surface. The grand-canonical potential energy landscape as a function of the distance of the metal adatom from the surface is shown in Figure 3 for a representative applied potential of $-1 \text{ V}_{\text{SHE}}$. We note that a slow convergence of the energy of $\text{I}_2|_Z$ at a long distance is due to the electrostatic interaction between the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complex and a charged electrode (see Figure S4) *i.e.*, it is dependent on the electrostatic potential. To mitigate this slow convergence and be thermodynamically consistent, the Final State (FS) of $\text{I}_2|_Z$ was obtained by treating the electrode and aqua-ion complex separately at constant potentials and constant charge of +3, respectively.

Following this simulation protocol, we carried out Bader charge analysis to elucidate the spatial evolution of the charge state of the dissolved metal. The charge state associated with the $\text{I}_1|_Z$ and $\text{I}_2|_Z$ geometries as functions of distance from the surface are shown in Figure 4A & 4B, respectively. We find that the adatom (red lines) already exhibits cationic character with a charge state of around +1.1 in the $\text{I}_1|_{Z=0}$ configuration due to interactions

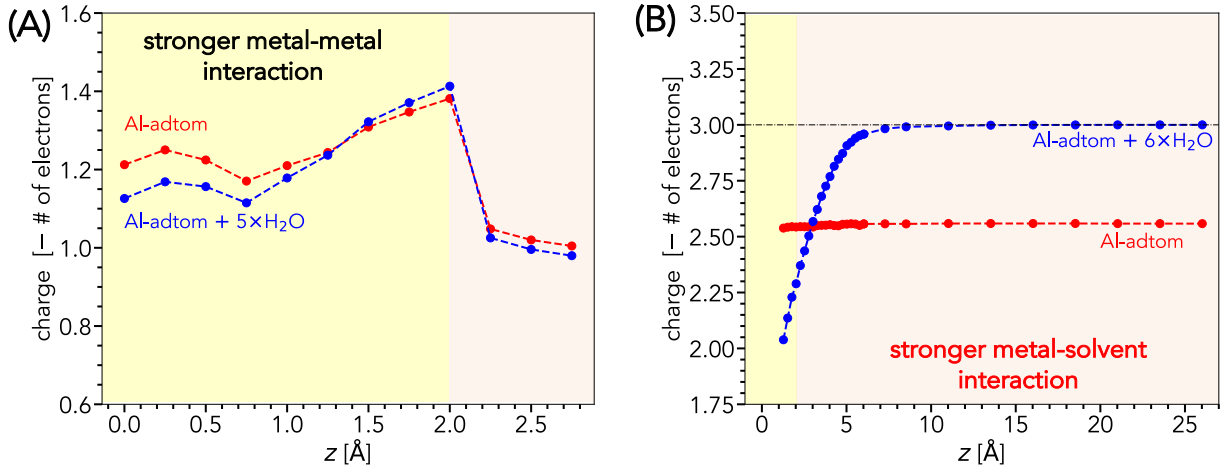


Figure 4: Bader charge analysis at $-1 \text{ V}_{\text{SHE}}$ for the (A) $I_1|_Z$ and (B) $I_1|_Z$ configurations as function of distance (Z) between the adatom and the Al(111) surface. The red and blue lines represent the charge of just the metal center and of the entire metal-water complex, respectively. Shaded regions delineate qualitative dominance of metal-metal (yellow) versus metal-solvent (pink) interactions.

with explicit waters and initial metal-metal bond stretching. As expected, the hydrated adatom becomes increasingly oxidized as the metal-metal bond continues to stretch until the bond is completely broken. The drop in the charge magnitude once the metal-metal bond breaks, shown in Figure 4A, is an artifact of not accounting for the full six-water solvation shell when $I_1|_Z$ enters the solution. On the other hand, the Al adatom with a full first hydration shell in $I_2|_Z$ (Figure 4B) yields a charge state of +2 when the ion complex transitions from the regime dominated by the metal-metal interaction to the one dominated by the metal-solvent interaction. This is an indication that as the metal dissolves, it evolves into the +2 state first before transitioning to the expected +3 state; the latter takes place as an outer-layer electron-transfer event as the metal ion migrates into the bulk solution. A lower charge state of the ion near the surface can be explained based on charge density analysis (Figure S5), which shows highly delocalized charge when the solvated ion is close to the metal surface, resulting in electron spilling from the surface to the metal ion. Our findings on the evolution of the charge state of the dissolved ion are consistent with Marcus theory, which suggests that dissolution of multivalent ions involves a series of one-electron

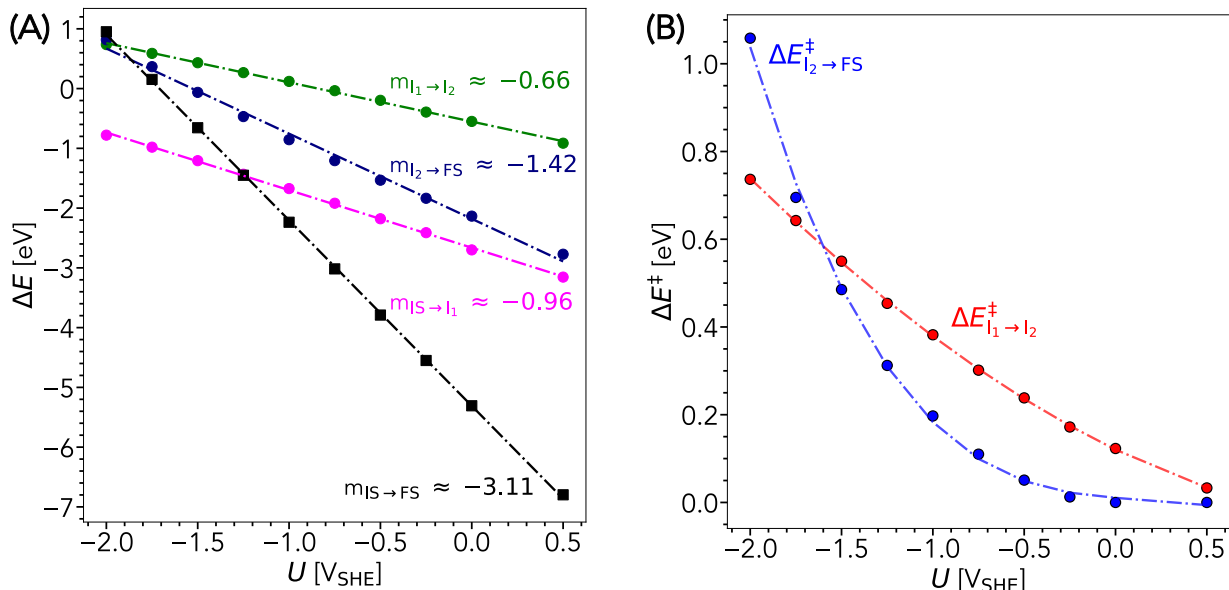


Figure 5: Potential (U) dependence of (A) reaction energies and (B) reaction barriers for the steps highlighted in Figure 1.

steps as the required reorganization energy would be much higher for a simultaneous transfer of multiple electrons. Our results are also in agreement with the make-before break concept proposed by Giladi,¹⁴ who likewise concluded that the formation of the hydration shell would start when the effective charge of the ion is slightly cationic.

Our analysis also points to fundamentally different natures of the charge transfer reaction between dissolution and ion migration regimes, represented respectively by the $I_1|_Z$ and $I_2|_Z$ configurations. For the former, metal-metal bonds dominate the charge transfer, resulting in similar charge states for the dissolving metal center and for the cumulative hydrated metal-ion complex, as represented by the red and blue lines in Figure 4A, respectively. On the other hand, because the ion is fully solvated in the I_2 configuration, the charge state of the metal-center remains stable at ≈ 2.6 , whereas the rest of the charge in the solvated complex is delocalized across the surrounding water molecules (Figure 4B). It is also found that it is the charge transfer between these water molecules and the metal surface that leads to the increase of the charge state of the entire ion complex to +3 as it migrates away from the surface.

The energetics of the entire dissolution process are summarized in Figure 5. It is found that the reaction energy differences associated each step shown in Figure 1 follow a simple linear relationship with respect to the applied potential (U). The slope of the each curve is the charge transfer associated with that step along the reaction coordinate, as obtained from SJM. For instance, the overall reaction from IS to FS yields a slope of ~ 3 (black line), consistent with a total of three electrons transferred during the entire Al dissolution process. Examination of the thermodynamic profiles reveals important additional findings. In particular, the transition from the Al adatom into a partially solvated ion ($\text{IS} \rightarrow \text{I}_1$, magenta line) is always energetically favorable. On the other hand, formation of a complete solvation shell by breaking the metal-metal bonds ($\text{I}_1 \rightarrow \text{I}_2$, green line) and migration of the solvated ion into the bulk solution through the EDL ($\text{I}_2 \rightarrow \text{FS}$, blue line) are thermodynamically unfavorable at very low potentials; they only become favorable around $-1.0 \text{ V}_{\text{SHE}}$ and $-1.5 \text{ V}_{\text{SHE}}$, respectively. Finally, it is shown that in the sampled potential range, the $\text{I}_1 \rightarrow \text{I}_2$ step is the most difficult during dissolution from a purely thermodynamic point of view.

The picture becomes more interesting when one also considers the impacts of kinetics. In particular, our simulations indicate that Al dissolution can be governed by either of two kinetically limiting processes, which are associated with metal-metal bond breaking and ion migration through the EDL (Figure 5B, red and blue lines, respectively). In contrast to thermodynamics, kinetic barriers exhibit a more nonlinear behavior with respect to the potential. Specifically, we find that ion migration is the rate-limiting process at potentials lower than $-1.7 \text{ V}_{\text{SHE}}$, whereas the process of forming a complete ion solvation shell by breaking the metal-metal bond dominates at more positive potentials. Collectively, these results indicate a complex dependence of dissolution kinetics on electrode potential, pointing to the importance of taking into account effects of potential bias in simulations involving electrochemical dissolution.

We further discuss the connection between results presented here and Marcus theory for predicting dissolution kinetics.^{53,54} For each transition step, we consider the initial and final

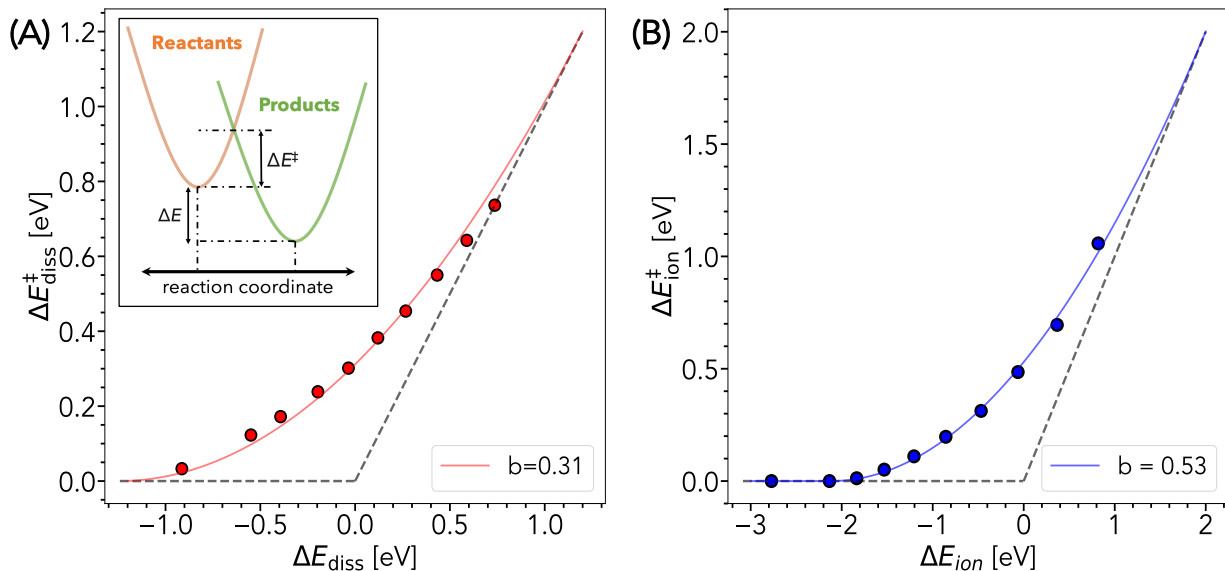


Figure 6: Reaction energies and barriers of the dissolution (A) and ion-migration (B) reactions in the functional form described in Eq 1. The relationship is quadratic for intermediate driving forces and linear for high magnitude driving forces. Inset of (A): Schematic showing reaction reactants and products to lie in the quadratic potential wells, and the reaction barrier is described by the point of intersection.

states to lie in a quadratic potential energy well (See Figure 6A, inset), with the reaction barrier described by the point of intersection. This simple analytical model captures the basics of the dissolution process in limiting cases: as the reaction energy becomes strongly exothermic ($\Delta E \ll 0$), the reaction smoothly approaches an activationless state ($\Delta E^\ddagger \rightarrow 0$). Similarly, when the reaction becomes highly endothermic ($\Delta E \gg 0$), the kinetics are dominated by the large energy change of the reaction ($\Delta E^\ddagger \rightarrow \Delta E$), again indicating a barrierless reaction in this limit.⁵⁵ Intermediate cases involve a competition between kinetic and thermodynamic factors for determining the overall energy landscape. This simple Marcus-theory-like relation can be described as:

$$\Delta E^\ddagger = \begin{cases} 0, & \Delta E < -4b \\ \frac{(\Delta E + 4b)^2}{16b}, & -4b \leq \Delta E \leq 4b \\ \Delta E, & \Delta E > 4b \end{cases} \quad (1)$$

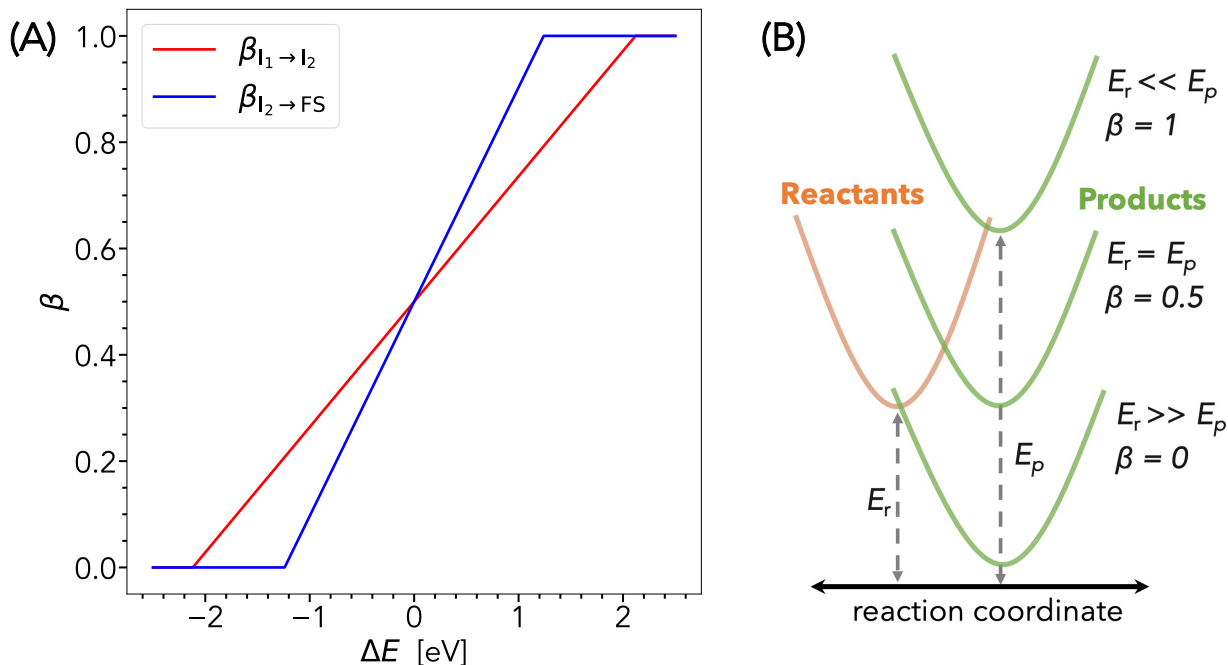


Figure 7: (A) Symmetry factors computed as a function of applied potentials for the dissolution (red) and ion-diffusion processes (blue), and (B) Schematic showing the influence on the symmetry factor with varying energetics of an elementary step.

where b can be interpreted as the intrinsic barrier, *i.e.*, the reaction barrier when the elementary step is thermoneutral ($\Delta E = 0$). As shown in Figure 6, we find that relation between reaction energies and barriers of the two kinetically limiting processes of Al dissolution can be well captured with this simple one-parameter model. The limiting behavior is evident from the dissolution and ion-migration reactions (See Figures 5B & 6); specifically, the reactions approach the barrierless and activationless regions for highly negative and positive potentials, respectively. Overall, our analysis indicates that Marcus theory can be used for a qualitative description of the kinetics-thermodynamics relationship and evolution of the ion charge state of Al dissolution.

Beyond providing a detailed understanding of energetics and charge transfer reaction during Al dissolution, our simulation protocol can also be used to compute quantities that are not easily accessed by experimental probes. These include the symmetry factor (β), which is a key factor in the Butler–Volmer (BV) equation that has been largely employed

for describing electrochemical reactions. The symmetry factor can be simply approximated as the rate of change of the activation energy with respect to the thermodynamic driving force for each of the electrochemical reactions:

$$\beta = \frac{d}{d\Delta E} (\Delta E^\ddagger) = \begin{cases} 0, & \Delta E < -4b \\ \frac{1}{2} + \frac{\Delta E}{8b}, & -4b \leq \Delta E \leq 4b \\ 1, & \Delta E > 4b \end{cases} \quad (2)$$

It can also be interpreted as the fractional charge transfer in the activation step of the electrochemical reactions. In practice, β is often assumed as 0.5 in the BV equation.⁵⁶ However, because our formalism gives a way of directly computing β for the two kinetically limiting processes of Al dissolution, we can assess and refine this approximation. Shown in Figure 7, our results confirm that $\beta = 0.5$ is indeed a good approximation for the thermoneutral reaction under no applied bias. However, β can significantly deviate from 0.5 for driven reactions, such as those under an applied potential that often occur under operation. Moreover, our simulations indicate that symmetry factor is generally not identical across different electrochemical reaction steps. This is indicated by the different slopes of β for the dissolution ($I_1 \rightarrow I_2$) and migration ($I_2 \rightarrow \text{FS}$) subprocesses discussed above. In particular, the migration step shows higher sensitivity of the symmetry factor to an applied bias, which reflects the particularly crucial role of the screened Coulomb interaction for determining the energy landscape for that process. Our analysis therefore indicates that the use of $\beta = 0.5$ for describing electrochemical processes must be practiced with care.

Conclusions

To conclude, we present a simple simulation protocol based on DFT with grand-canonical treatment of electrons to predict dissolution kinetics, charge transfer, and thermodynamics at constant bias potential. Applied to metallic Al as a demonstration case, our approach is used

to show that Al dissolution can be governed by either of two potentially kinetically limiting processes. These processes are associated with metal–metal bond breaking and ion migration through the electric double layer. Interestingly, the limiting step switches depending on the applied potential. Our findings are generally consistent with a simple Marcus-theory type interpretation, particularly regarding the kinetics-thermodynamics relationship and nature of the charge transfer process during dissolution. Nevertheless, the simulations point to key subtleties that arise from driving the reaction under an applied bias. One critical example is the effect on the symmetry factor, which cautions use of the commonly used approximation of 0.5.

In addition to the specific findings presented here, the generality and flexibility of our approach enables extraction of analytical relationships between kinetics and thermodynamics for electrochemical dissolution and charge-transfer reactions. Our approach also offers a promising avenue to compute other important parameters, including the symmetry factor, from first-principles. Such relationships can be used to bridge connections to higher-order theories, such as those proposed by Ref. 24, for a more holistic treatment of electrochemical kinetics under different driving forces. It is also important to note that although we have focused solely on the defect-free Al(111) surface here, our method can be straightforwardly applied to study dissolution as a function of more complex surface factors, including surface orientation, point defects, grain boundaries, and impurities. Surfaces with step/kink edges, or those with preformed oxide films, can likewise be studied. Along these lines, work is underway to simulate dissolution of metal with an oxide layer for different pH conditions and ion types. Looking forward, our simulation protocol can be used to elucidate the competition between oxide formation and metal dissolution, and to investigate how dissolution kinetics is governed by the interplay between interfacial chemistry, applied potentials, and solution chemistry. Finally, it is important to highlight some of the important factors that were beyond the scope of this study but could potentially influence dissolution kinetics. These include entropic effects, and kinetics associated with water transport and temporary recon-

figuration of the ion solvation, which could be highly relevant within the context of Marcus theory. Similarly, additional efforts are required to understand how dissolution kinetics can be influenced by the choice of implicit solvation model as well as the number of explicit water molecules used to represent the ion solvation. A better understanding of the possible impact on dissolution energetics due to charge delocalization error⁵⁷ — a well-known issue in DFT — is highly desirable as the use of semi-local (GGA) exchange-correlation functionals like PBE could lead to overly dispersed charge distribution or nonphysical charge transfer at the interface.

Acknowledgement

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Supporting Information Available

Information regarding calculating dissolution / redox potential, generating intermediate structures, convergence of energy profile, and, analysing charge density localization is provided in the Supporting Information.

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Supporting Information

Metal Dissolution from First Principles: Potential-dependent Kinetics and Charge Transfer

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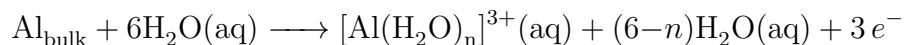
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Calculating Dissolution / Redox Potential for Al:

At any arbitrary potential U vs. standard hydrogen electrode (SHE), the dissolution of bulk aluminium was considered as



In terms of energies,

$$E_{\text{bulk}} + 6E_{\text{H}_2\text{O}} = E_{[\text{Al}(\text{H}_2\text{O})_n]^{3+}} + (6-n)E_{\text{H}_2\text{O}} - 3eU \quad (1)$$

The energetics associated with Al-bulk dissolution as a function of potential is in plotted

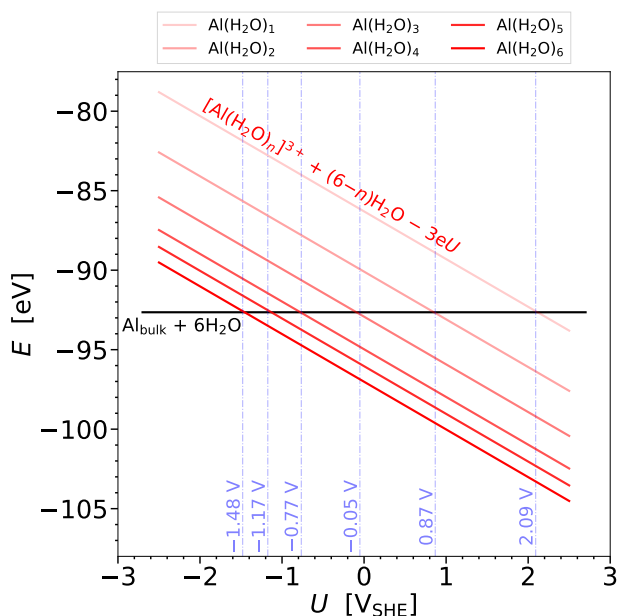


Figure S1: DFT calculated redox potential for bulk Al as a function of explicit water molecules used to describe the solvated metal-ion complex.

in Figure S1. The intersection of the two black (initial state) and red (final state) curves denote the theoretical redox potential at which the dissolution reaction is in thermodynamic equilibrium i.e.,

$$U_{\text{eq}} = (E_{[\text{Al}(\text{H}_2\text{O})_n]^{3+}} - nE_{\text{H}_2\text{O}} - E_{\text{bulk}}) / 3e \quad (2)$$

The experimentally known reduction potential for pure Al is known to be $-1.68 \text{ V}_{\text{SHE}}$. We observe that the theoretically obtained redox-potential approaches the experimental redox potential as we increase the number of explicit water molecules around the metal ion-center from one to a fully-hydrated solvation shell. We believe that the discrepancy between the experimentally reported and our calculated redox potentials could be further reduced by considering a second hydration shell. Moreover, our current calculations also neglect the energy corrections associated with thermalization and other degrees of movement which can further contribute towards bridging the gap between the theoretically computed and experimentally reported redox potential. Some of the other factors or parameters that can also influence the calculated redox potential is the exchange correlation functional and type of implicit solvation model employed. As for this work, we neglect the fine tuning of the redox potential and use the current methodology and parameters with reasonable accuracy to provide a general framework to approximate dissolution energetics.

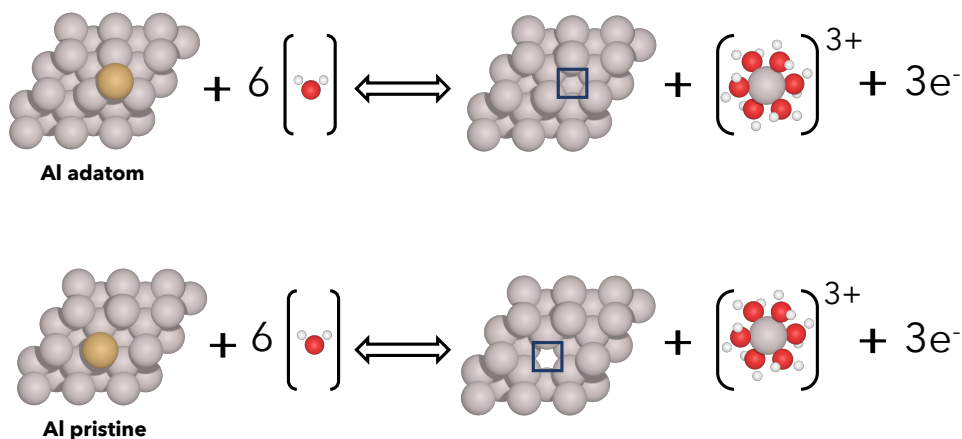


Figure S2: Schematic showing end states for the dissolution process of (A) an Al adatom, and, (B) an Al atom from a pristine Al(111) surface.

Similar to bulk Al, we compute the dissolution of a metal atom from Al surfaces for an adatom and pristine surface as shown in Figure S2. The dissolution potential was computed as:

$$U_{\text{eq}} = (\Delta E + E_{[\text{Al}(\text{H}_2\text{O})_n]^{3+}} - nE_{\text{H}_2\text{O}}) / 3e \quad (3)$$

Here, ΔE is the difference in potential energy between potential energy of surface post and pre-dissolution.

Generating structure $\text{I}_1^{Z=0}$

We generate the structure $\text{I}_1^{Z=0}$ described in the main text by performing a constrained relaxation on the geometry shown by Figure S3. A user intuition is used to enclose the adatom in contact with the surface with 5 water molecules. This geometry can be attributed as the replacing a water molecule from an isolated $\text{Al}[(\text{H}_2\text{O})_6]^{3+}$ ion with a surface-metal ion bond. Configuration $\text{I}_1^{Z=0}$ was obtained by relaxing the geometry shown in Figure S3 in all directions except the direction perpendicular to surface.

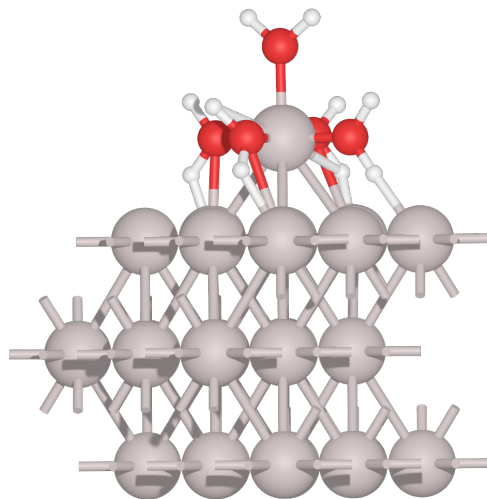


Figure S3: Starting geometry prior relaxation used to obtain the intermediate ($\text{I}_1^{Z=0}$) in the main text for the dissolution kinetics mechanism.

Convergence behavior of energy profile

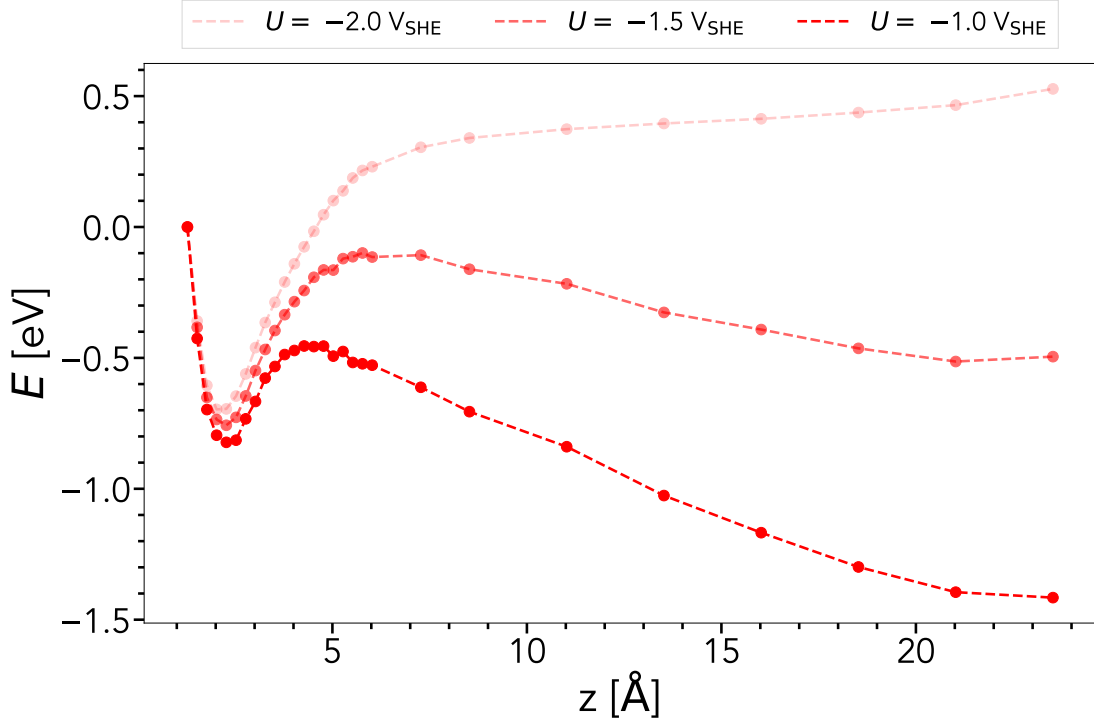


Figure S4: Energy profile for $I_2|_Z$ configuration at three arbitrary potentials as function of the distance (Z) between the adatom and the Al(111) surface.

Charge density localization/delocalization:

$$\Delta\rho^\phi(z) = \rho(z)\Big|_{\text{Al(111)} + [\text{Al}(\text{H}_2\text{O})_6]^{3+}}^\phi - \rho(z)\Big|_{\text{Al(111)}}^\phi - \rho(z)\Big|_{[\text{Al}(\text{H}_2\text{O})_6]^{3+}}^\phi \quad (4)$$

Here, $\rho(z)\Big|_{\text{Al(111)}}^\phi$ represent the x-y plane integrated electron-density as function of direction normal to the surface for the combined surface plus Al-water ion system. $\rho(z)\Big|_{\text{Al(111)}}^\phi$ represent the x-y plane integrated electron-density as function of direction normal to the surface for the Al. And, $\rho(z)\Big|_{[\text{Al}(\text{H}_2\text{O})_6]^{3+}}^\phi$ represent the x-y plane integrated electron-density as function of direction normal to the surface for the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ion. The simulation box and positions of atoms (*i.e.*, slab or hydrated metal ion-complex) are kept constant for all

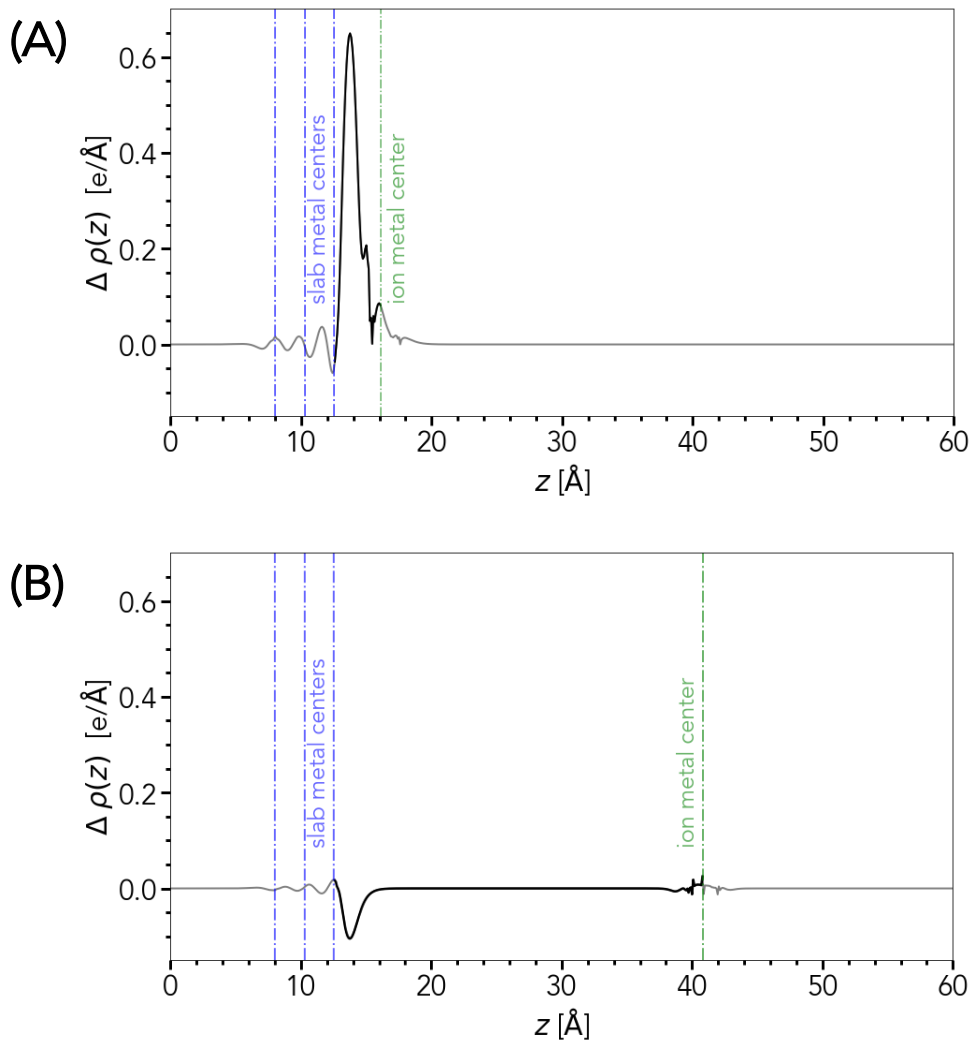


Figure S5: Difference in electron density at -1 V_{SHE} as described by Equation 4 for (A) when the metal-ion is close to the surface and, (B) when the metal ion is farther away from the surface.

the quantities in the right hand side of Equation 4. Our calculations show that there is high delocalization of electrons when the solvated ion is close to the metal surface resulting in electron spilling from the surface to the metal-ion. This can be attributed as a plausible explanation for the +2 (or fractional) charge of the solvated-ion when it is closer to the surface. On the other hand, metal ion is far away from the surface, we see that the +3 charge on the ion is localized within itself.