ELECTROCATALYST THEORIES BASED ON LOCAL REACTION CENTER MODELS, LINEAR GIBBS ENERGY RELATIONSHIPS, AND NOW THE FULL GIBBS ENERGIES

Alfred B. Anderson

Chemistry Department, Case Western Reserve University
10900 Euclid Avenue, Cleveland OH 44106-7078

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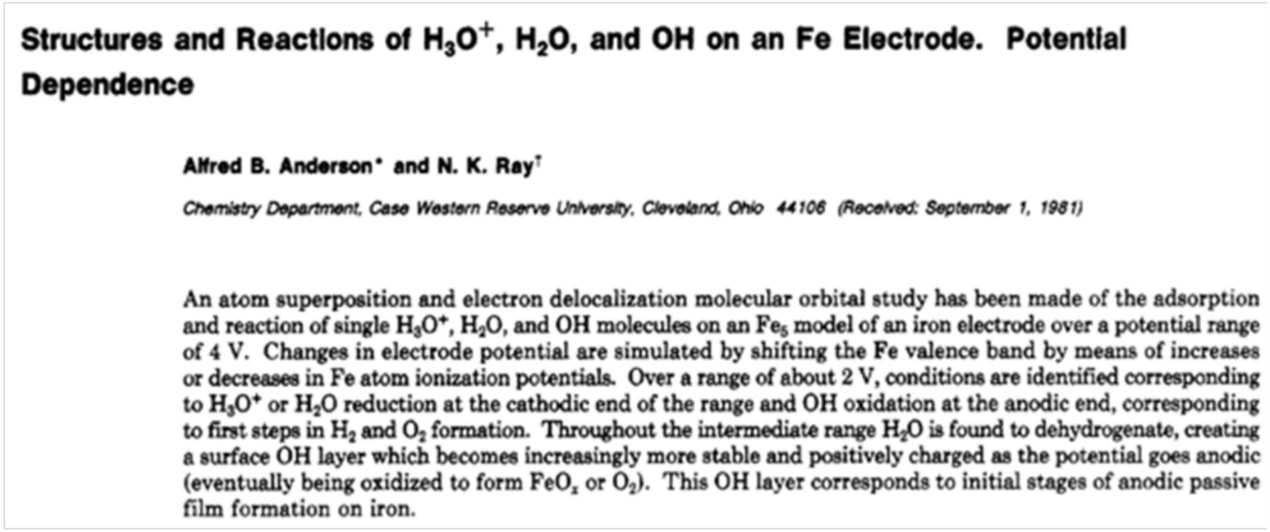
How simple can we get and still have something?

We have worked up from the phenomenological level of freshman chemistry texts to advanced *ab initio* modeling.

- *Fair.* Since the Fermi level shifts when the potential changes, calculate with the semiempirical ASED MO theory the dependence of properties of adsorbed molecules on pushing the Fermi level up and down.
- *Good.* Since bond strengths are the ingredient of many explanations in chemistry at the freshman level, lets see what we can say about the electrochemical interface using just internal energies for the reactions exactly as written in a text, without including the solvating molecules.
- *Better.* Include solvating molecules.
- *Best.* Add electrode surface charging, double layer, thermal and entropy contributions to achieve the Gibbs energies.

Getting started with semiempirical MO theory



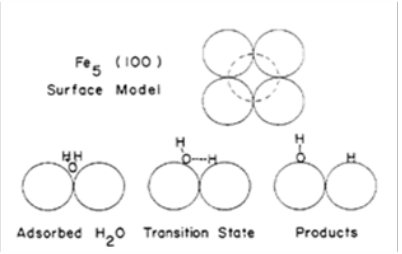
Structures and Reactions of H_3O^+, H_2O, and OH on an Fe Electrode. Potential Dependence

Alfred B. Anderson* and N. K. Ray†

Chemistry Department, Case Western Reserve University, Cleveland, Ohio 44106 (Received: September 1, 1981)

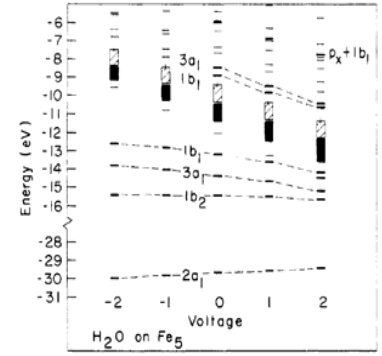
An atom superposition and electron delocalization molecular orbital study has been made of the adsorption and reaction of single H_3O^+, H_2O, and OH molecules on an Fe_5 model of an iron electrode over a potential range of 4 V. Changes in electrode potential are simulated by shifting the Fe valence band by means of increases or decreases in Fe atom ionization potentials. Over a range of about 2 V, conditions are identified corresponding to H_3O^+ or H_2O reduction at the cathodic end of the range and OH oxidation at the anodic end, corresponding to first steps in H_2 and O_2 formation. Throughout the intermediate range H_2O is found to dehydrogenate, creating a surface OH layer which becomes increasingly more stable and positively charged as the potential goes anodic (eventually being oxidized to form FeO_x or O_2). This OH layer corresponds to initial stages of anodic passive film formation on iron.

Make a model



Add potential by shifting the valence band

490 *The Journal of Physical Chemistry, Vol. 86, No. 4, 1982*



Calculate properties and explain with MO theory

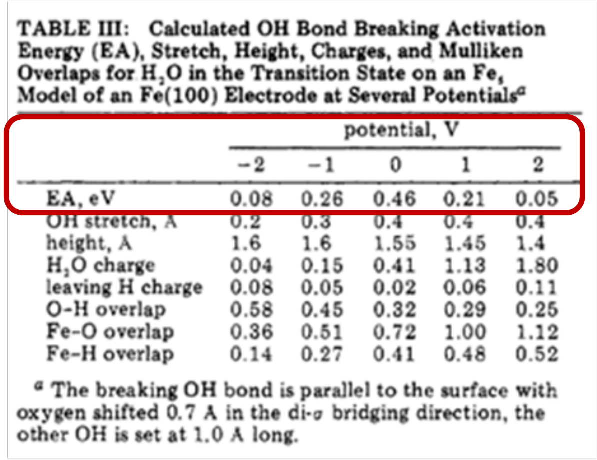


TABLE III: Calculated OH Bond Breaking Activation Energy (EA), Stretch, Height, Charges, and Mulliken Overlaps for H_2O in the Transition State on an Fe_5 Model of an Fe(100) Electrode at Several Potentials[a]

	potential, V				
	−2	−1	0	1	2
EA, eV	0.08	0.26	0.46	0.21	0.05
OH stretch, Å	0.2	0.3	0.4	0.4	0.4
height, Å	1.6	1.6	1.55	1.45	1.4
H_2O charge	0.04	0.15	0.41	1.13	1.80
leaving H charge	0.08	0.05	0.02	0.06	0.11
O-H overlap	0.58	0.45	0.32	0.29	0.25
Fe-O overlap	0.36	0.51	0.72	1.00	1.12
Fe-H overlap	0.14	0.27	0.41	0.48	0.52

[a] The breaking OH bond is parallel to the surface with oxygen shifted 0.7 Å in the di-σ bridging direction, the other OH is set at 1.0 Å long.

Qualitative at best

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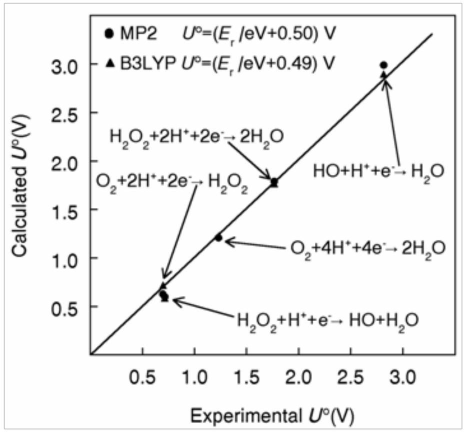
Linear Gibbs Energy Relationship

Bulk Solution

About 10 years ago we thought it worthwhile to develop simplified models for electrochemical reactions using internal energies rather than Gibbs energies.

We found the following linear relationship held for reducing O_nH_m molecules:

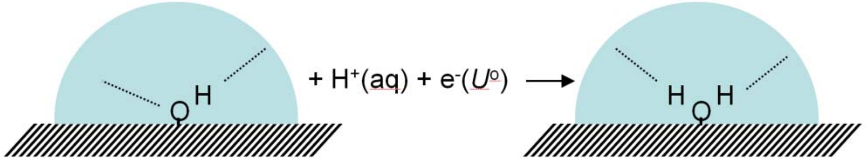
$U^o \approx -(\text{reaction internal energy})/nF + c$



Anderson, A. B.; Albu, T. V., *J. Am. Chem. Soc.*, **1999**, *121*, 11855-118863.

Surface

The reaction $OH + H^+ + e^- \rightarrow H_2O$ becomes, on the surface,



Part of the solvation shell replaced by bond to electrode:

$$Ox(aq) + H^+(aq) + e^- \rightleftharpoons Red(aq), \quad \Delta G^o, \quad U^o = -\frac{\Delta G^o}{nF}$$

Becomes, assuming c has the same value on the surface,

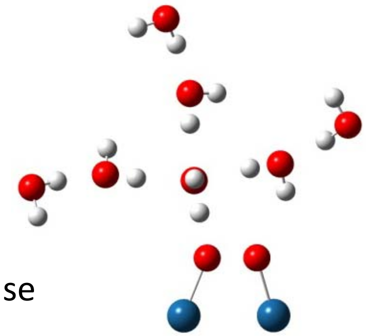
$$Ox(ads) + H^+(aq) + e^- \rightleftharpoons Red(ads), \quad U^{rev}_{surf} \approx U^o + \frac{\Delta E_{ads}}{nF}$$

ΔE_{ads} is the adsorption energy of the product minus that for the reactant and U^o is a known standard value .

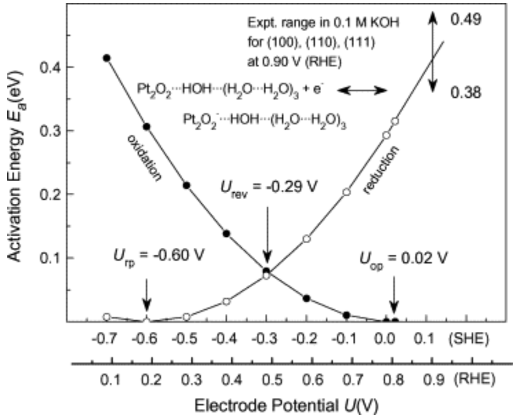
Many applications of the linear Gibbs energy relationship have been made to oxygen reduction reaction steps over a variety of electrocatalysts including Pt, Pt alloys, graphite, Cu^{I} clusters, and Co chalcogenides. Errors in reversible potential predictions are typically limited to 0.2 V, making it possible to characterize differences in electrocatalysts.

Local Reaction Center Model for Electron Transfer Reactions

Reactant and product with limited solvation
Bond strengths and ionization properties
Constrained variation theory

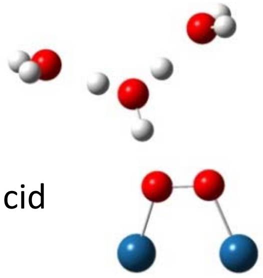


O_2^- formation in base

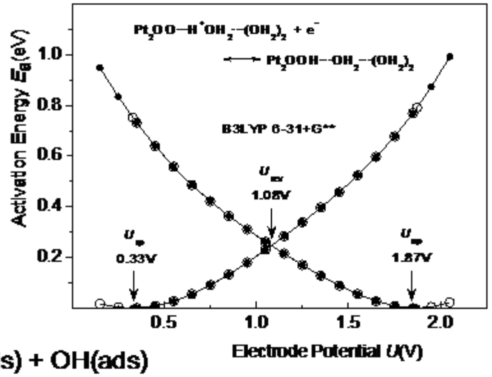


T. Zhang and A. B. Anderson, Electrochim. Acta 52, 982-989 (2007).

$Pt_2O_2\text{--}H_2O\text{--}(H_2O\text{--}H_2O)_3 + e^- \rightleftharpoons Pt_2O_2^-\text{--}H_2O\text{--}(H_2O\text{--}H_2O)_3$



OOH formation in acid



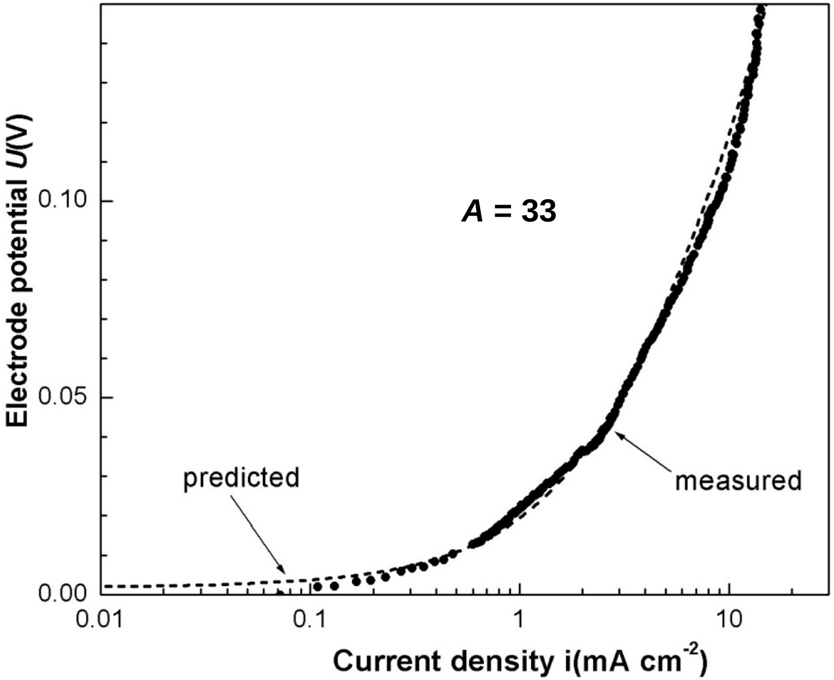
$Pt_2O_2\text{--}H_3O^+\text{--}(H_2O)_2 + e^- \rightleftharpoons Pt_2OOH\text{--}H_2O\text{--}(H_2O)_2 \longrightarrow O(ads) + OH(ads)$

Calculating Tafel Plots from Activation Energies

Hydrogen oxidation on platinum

$\text{Pt-H}\cdots\text{H}^+\text{-OH}_2(\text{H}_2\text{O})_2 + e^- \rightleftharpoons \text{Pt}\cdots\text{H-H}\cdots\text{OH}_2(\text{H}_2\text{O})_2$

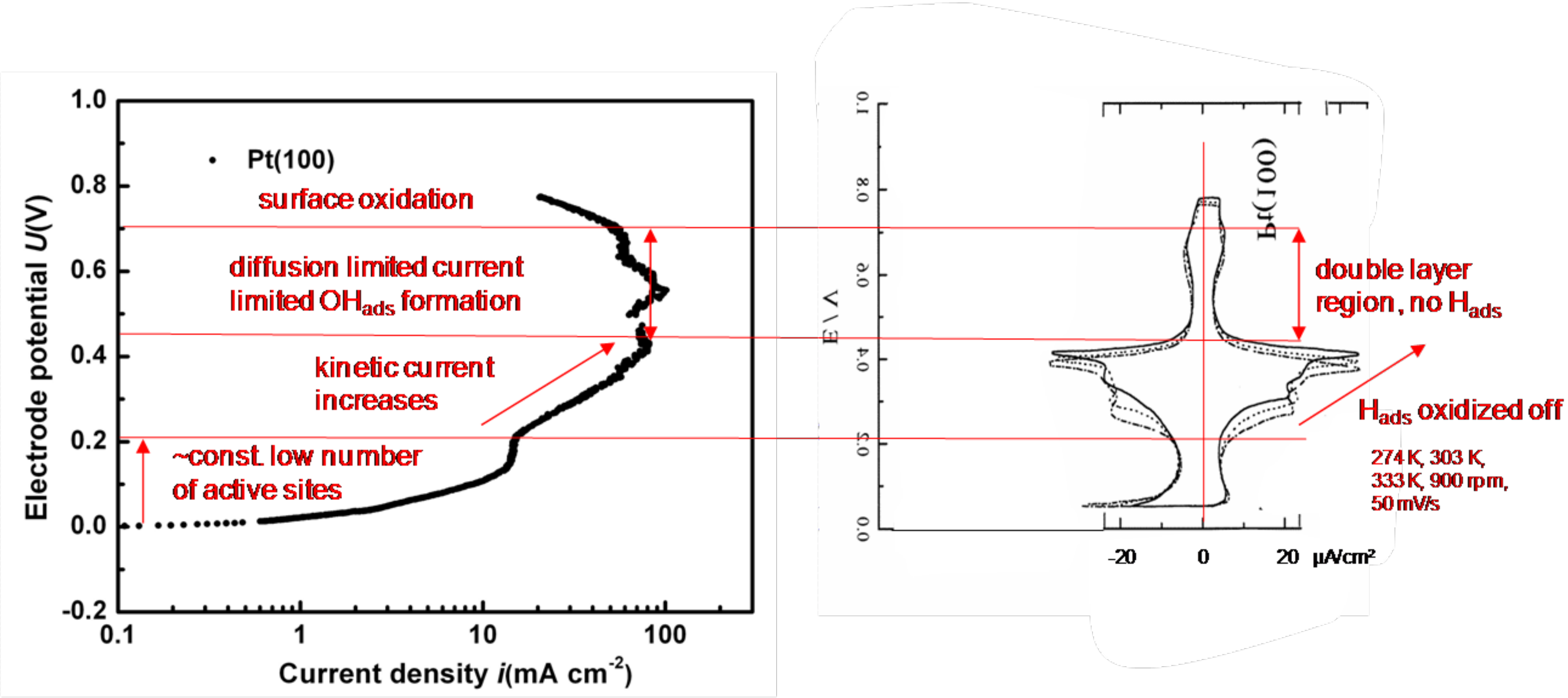
$$i = \left| i_{ox} - i_{red} \right| = A \cdot \left| \exp(-E_a^{ox}(U)/RT) - \exp(-E_a^{red}(U)/RT) \right|$$



A. B. Anderson and Y. Cai, *J. Phys. Chem. B* **108**, 19917 (2004).

Measured points for Pt(100) from Markovic et al., *J. Phys. Chem. B* **101**, 5405 (1997) and a private communication.

Overall Picture for Hydrogen Oxidation



The local reaction center model yields approximate results with higher uncertainties in reversible potential predictions compared to the linear Gibbs energy relationship. Accuracy of activation energies is generally uncertain, in part due to the lack of needed temperature-dependence studies by electrochemists. Developing a self-consistent treatment of the whole electrochemical interface is the next step for theory.

Aqueous and Surface Redox Potentials from Fully Modeled Self-Consistently-Determined Gibbs Energies

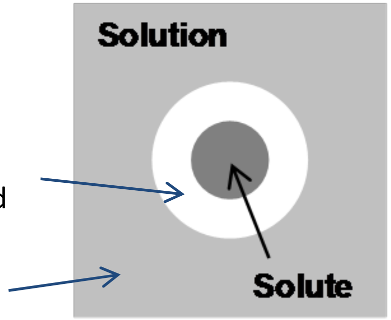
The full Gibbs energy change for a reduction reaction, including potential dependence, is given by

$$\Delta G(U) = \{G_{\mathrm{Red}}(U) - G_{\mathrm{Ox}}(U)\} + n(\varphi + FU)$$

where $-(\varphi + FU)$ is the energy of an electron on the vacuum scale, φ being the thermodynamic workfunction of the standard hydrogen electrode.

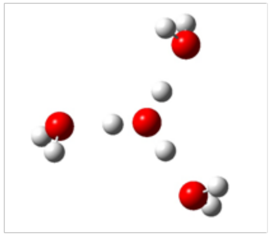
A new program, Interface 1.0, calculates $\Delta G(U)$ by this equation. The surface potential is adjusted by adding surface charge and a counter charge distribution in the double layer is determined self-consistently using a modified Poisson-Boltzmann theory within a dielectric continuum model.

Bulk Solution and Surface Models



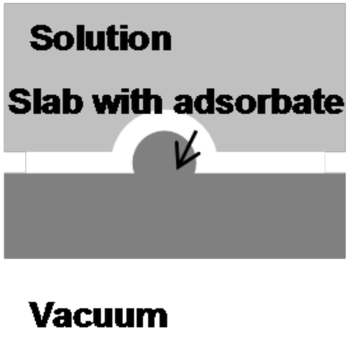
Smooth dielectric model function used

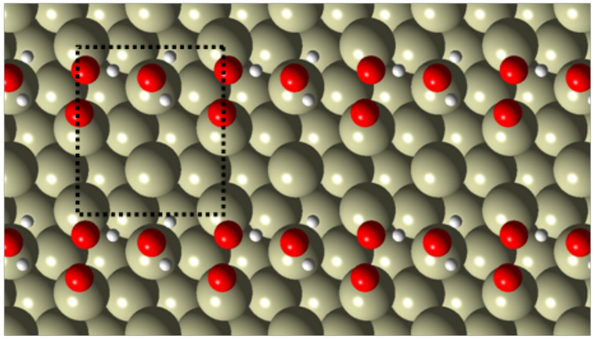
Dielectric continuum



Hydronium ion

Two-dimensional density functional band theory used

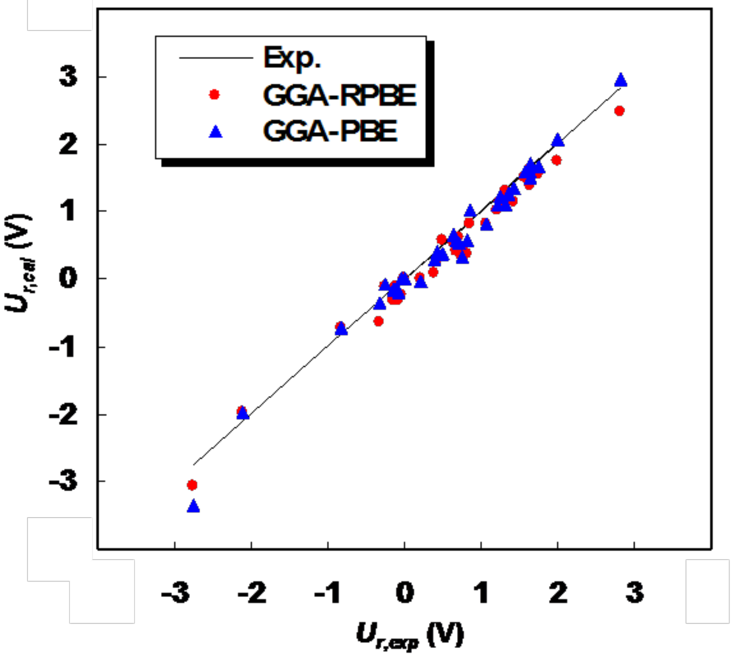




OOH(ads) with H_2O(ads)

Predictions for Bulk Solution

Reactions	PBE	RPBE	Exp.[a]
$O_2(g)+H^+(aq)+e^- \leftrightarrow O(g)+OH(g)$	-3.35	-3.08	-2.76
$H^+(aq)+e^- \leftrightarrow H(g)$	-1.98	-2.00	-2.11
$H_2O(aq)+e^- \leftrightarrow 1/2H_2(g)+OH^-(aq)$	-0.71	-0.73	-0.83
$O_2(g)+e^- \leftrightarrow O_2^-(aq)$	-0.37	-0.65	-0.33
$HO_2^-(aq)+H_2O(aq)+e^- \leftrightarrow OH(g)+2OH^-(aq)$	-0.09	-0.13	-0.25
$1/2O_2(g)+H_2O(aq)+e^- \leftrightarrow 1/2H_2O_2(aq)+OH^-(aq)$	-0.16	-0.33	-0.13
$H_2O_2(aq)+e^- \leftrightarrow OH(g)+OH^-(aq)$	-0.17	-0.11	-0.11
$1/2O_2(g)+1/2H_2O(aq)+e^- \leftrightarrow 1/2OH^-(aq)+1/2HO_2^-(aq)$	-0.20	-0.32	-0.06
$O_2(aq)+H^+(aq)+e^- \leftrightarrow HO_2(aq)$	0.00	-0.25	-0.05
$H^+(aq)+e^- \leftrightarrow 1/2H_2(g)$	0.00	0.00	0.00
$O_2^-(aq)+H_2O(aq)+e^- \leftrightarrow HO_2^-(aq)+OH^-(aq)$	-0.03	0.00	0.20
$O_2(g)+H^+(aq)+e^- \leftrightarrow 1/2O_3(g)+1/2H_2O(aq)$	0.28	0.06	0.38
$1/4O_2(g)+1/2H_2O(aq)+e^- \leftrightarrow OH^-(aq)$	0.40	0.24	0.42
$O_3(g)+H_2O(aq)+e^- \leftrightarrow O_2(g)+OH(g)+OH^-(aq)$	0.37	0.55	0.51
$1/3O_2^-(aq)+2/3H_2O(aq)+e^- \leftrightarrow 4/3OH^-(aq)$	0.65	0.53	0.64
$1/2O_2(g)+H^+(aq)+e^- \leftrightarrow 1/2H_2O_2(aq)$	0.55	0.39	0.70
$H_2O_2(aq)+H^+(aq)+e^- \leftrightarrow OH(g)+H_2O(aq)$	0.54	0.62	0.71
$HO_2(aq)+e^- \leftrightarrow HO_2^-(aq)$	0.31	0.33	0.74
$HO_2(aq)+O_2(g)+H^+(aq)+e^- \leftrightarrow O_3(g)+H_2O(aq)$	0.56	0.38	0.81
$1/2HO_2(aq)+1/2H_2O(aq)+e^- \leftrightarrow 3/2OH^-(aq)$	0.99	0.80	0.87
$1/2H_2O_2(aq)+e^- \leftrightarrow OH^-(g)$	0.95	0.81	0.93
$1/2HO_2(aq)+H^+(aq)+e^- \leftrightarrow 1/2OH(g)+1/2H_2O(aq)$	0.82	0.83	1.07
$1/4O_2(g)+H^+(aq)+e^- \leftrightarrow 1/2H_2O(g)$	1.08	1.01	1.23
$1/2O_3(g)+1/2H_2O(aq)+e^- \leftrightarrow 1/2O_2(g)+OH^-(aq)$	1.22	1.14	1.24
$O_3(g)+H^+(aq)+e^- \leftrightarrow O_2(g)+OH(g)$	1.08	1.28	1.34
$1/2Cl_2(g)+e^- \leftrightarrow Cl^-(aq)$	1.26	1.21	1.36
$HO_2(aq)+H^+(aq)+e^- \leftrightarrow H_2O_2(aq)$	1.34	1.14	1.44
$1/4HClO_2(aq)+3/4H^+(aq)+e^- \leftrightarrow 1/4Cl^-(aq)+1/2H_2O(aq)$	1.58	1.51	1.58
$HClO(aq)+H^+(aq)+e^- \leftrightarrow 1/2Cl_2(g)+H_2O(aq)$	1.58	1.50	1.63
$1/3HO_2(aq)+H^+(aq)+e^- \leftrightarrow 2/3H_2O(aq)$	1.48	1.37	1.65
$1/2H_2O_2(aq)+H^+(aq)+e^- \leftrightarrow H_2O(aq)$	1.66	1.54	1.76
$1/3HClO_2(aq)+H^+(aq)+e^- \leftrightarrow 1/6Cl_2(g)+2/3H_2O(aq)$	1.68	1.61	1.66
$OH(g)+e^- \leftrightarrow (aq)$	2.08	1.72	1.98
$OH(g)+H^+(aq)+e^- \leftrightarrow H_2O(aq)$	2.96	2.45	2.81
Mean absolute error	0.13	0.19	-



PBE functional slightly better for bulk and RPBE slightly better for surface

R. Jinnouchi and A. B. Anderson, J. Phys Chem. C, 112, 8487-8750 (2008).
R. Jinnouchi and A. B. Anderson, Phys. Rev. B77, 2454170-24541718 (2008).

Predictions for Pt(111) Electrode Surface

No coadsorbed H_2O

	RPBE				Exp.
	(i)	(ii)	(iii)	(iv)	
$H^+(aq) + e^- \rightleftharpoons H(ads)$	0.35	0.20	0.19	0.19	0.32
$H^+(aq) + O_2(g) + e^- \rightleftharpoons HO_2(ads)$	0.84	-0.01	0.09	0.12	-
$H^+(aq) + OH(ads) + e^- \rightleftharpoons H_2O(aq)$	0.92	1.08	0.88	0.84	0.68
$H^+(aq) + O\ (ads) + e^- \rightleftharpoons OH(ads)$	0.74	0.50	0.61	0.61	~1.0
Mean absolute error	0.18	0.34	0.24	0.23	-

(i) Δ*E* of adsorbates on neutral surface

(ii) Δ*G* of adsorbates on neutral surface

(iii) Δ*G* of adsorbates on neutral surface + MPB solvation free energies

(iv) Δ*G* of adsorbates on charged surface + MPB solvation free energies

Predictions for Pt(111) Electrode Surface

With coadsorbed H_2O

	RPBE				Exp.
	(i)	(ii)	(iii)	(iv)	
$H^+(aq) + e^- \rightleftharpoons H(ads)$	0.50	0.21	0.15	0.27	0.32
$H^+(aq) + O_2(g) + e^- \rightleftharpoons HO_2(ads)$	1.09	0.24	0.19	0.34	-
$H^+(aq) + OH(ads) + e^- \rightleftharpoons H_2O(aq)$	0.31	0.47	0.47	0.47	0.68
$H^+(aq) + O\ (ads) + e^- \rightleftharpoons OH(ads)$	1.48	1.24	1.11	1.12	~1.0
Mean absolute error	0.34	0.19	0.16	0.13	-

Δ*E* of adsorbates on neutral surface

Δ*G* of adsorbates on neutral surface

Δ*G* of adsorbates on neutral surface + MPB solvation free energies

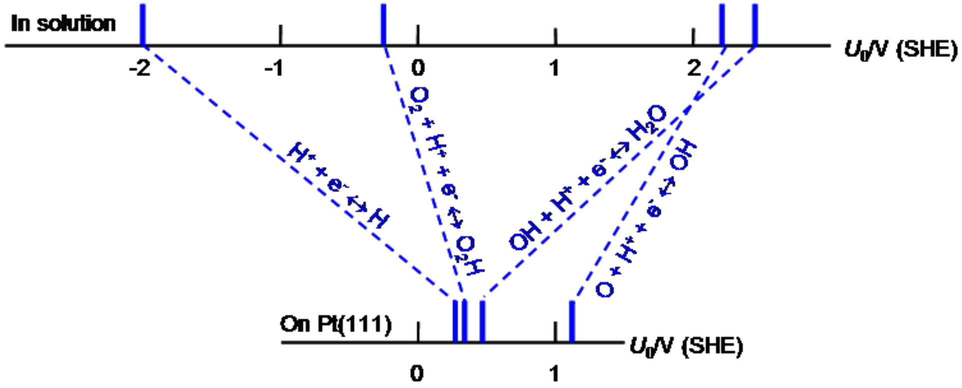
Δ*G* of adsorbates on charged surface + MPB solvation free energies

Conclusions

Contributions from thermal corrections and entropies, solvation free energies, and surface charging to redox potentials.

Type of E_{xc}	PBE			RPBE		
Type of contributions	$-(\Delta H_{corr}-T\Delta S)/nF$	$-\Delta G_{solv}/nF$	$-\Delta G_{sc}/nF$	$-(\Delta H_{corr}-T\Delta S)/nF$	$-\Delta G_{solv}/nF$	$-\Delta G_{sc}/nF$
Mean absolute contributions	0.33	0.45	0.05	0.35	0.37	0.07

Relationship between reversible potentials for reactions in solution and on a Pt surface.



Summary

- The corrections to the linear Gibbs energy approach largely cancel one another, which justifies focusing on bond energies and ionization energies of the chemical constituents as a starting point for thinking about electrocatalysis.
- A full self-consistent treatment of the electrochemical interface has been achieved and is accurate for predicting potentials within about 0.2 V.
- Extension of the self-consistent theory to calculate transition states and activation energies for electron transfer reactions will be useful.

Acknowledgments: There were many contributors to the research, some of them named in references above. Special thanks go to Dr. Ryosuke Jinnouchi for creating the Interface 1.0 computer program and to Yu Morimoto of Toyota Central R&D, Inc. for giving leave to Dr. Jinnouchi to come to Case to do the work. There have been many sources of support over the years for electrochemical theory in my lab, including NSF, ARO, DOE, and ONR. Recent development and applications have been supported by an ARO MURI grant to Case.