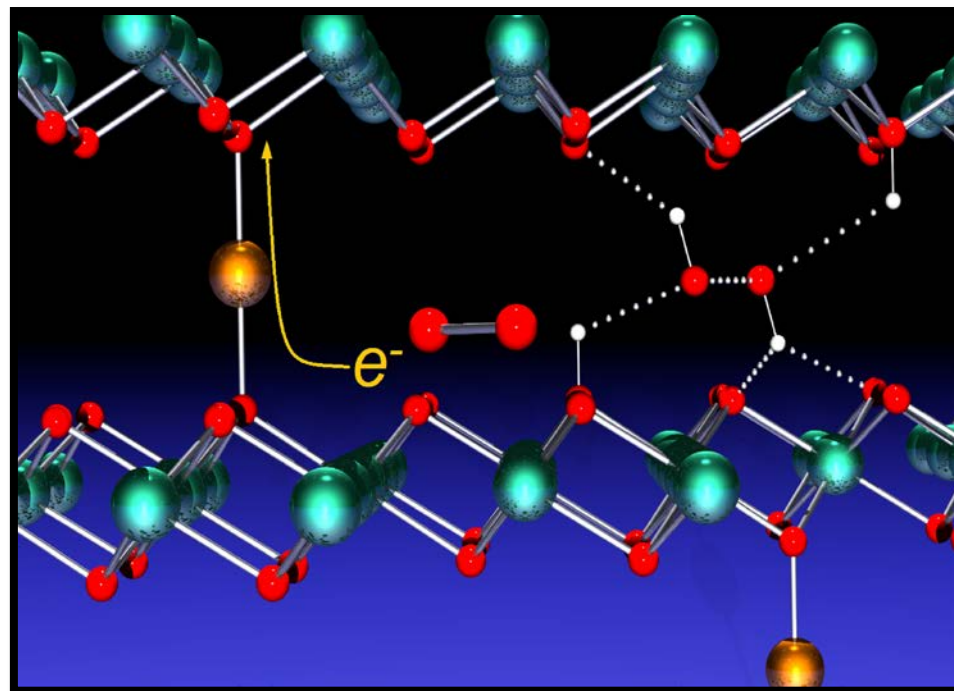
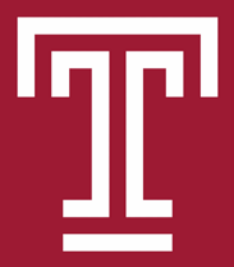


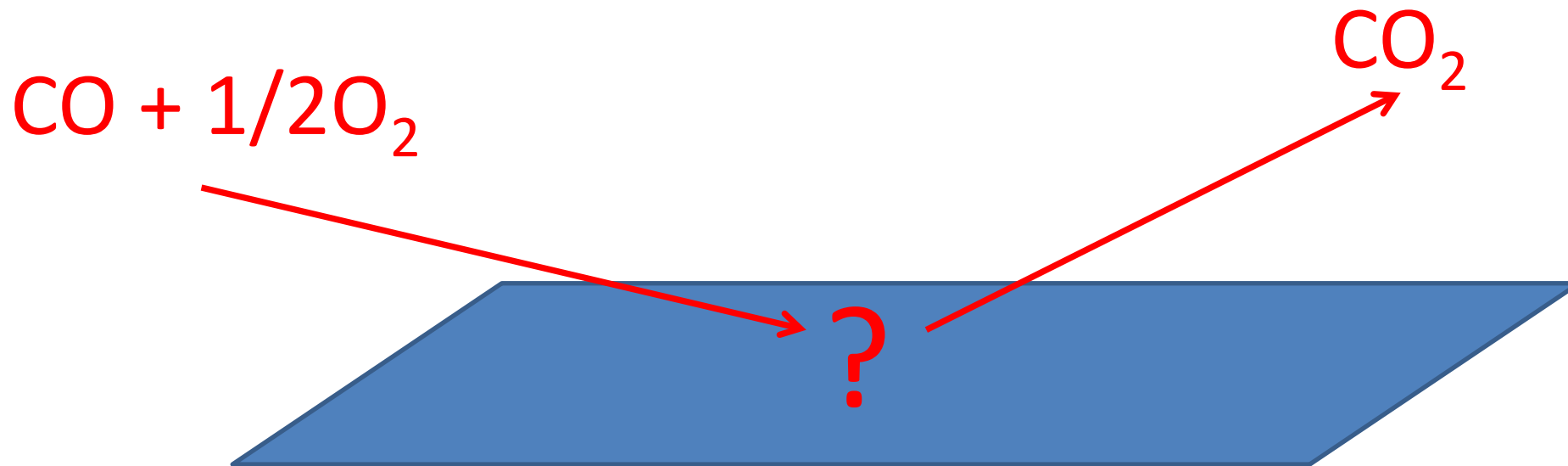
Kinetics and Catalysis with a nod toward water oxidation

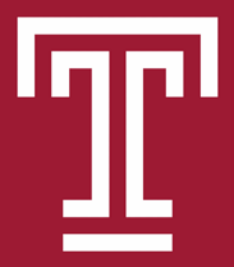


- Daniel Strongin
- 1/22/2016



Brief Introduction Surface Catalysis





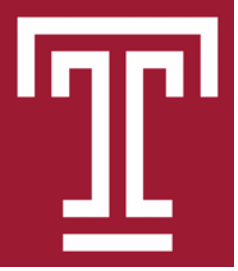
Terms

Adsorbed Phase - Atoms or molecules that are bound to a surface

Molecular Adsorption – Adsorbing molecule remains intact

Dissociative Adsorption – Bond breaks in adsorbed molecule

Surface Sites – Places on the surface where reactions occur



Types of Adsorption for Various Molecules

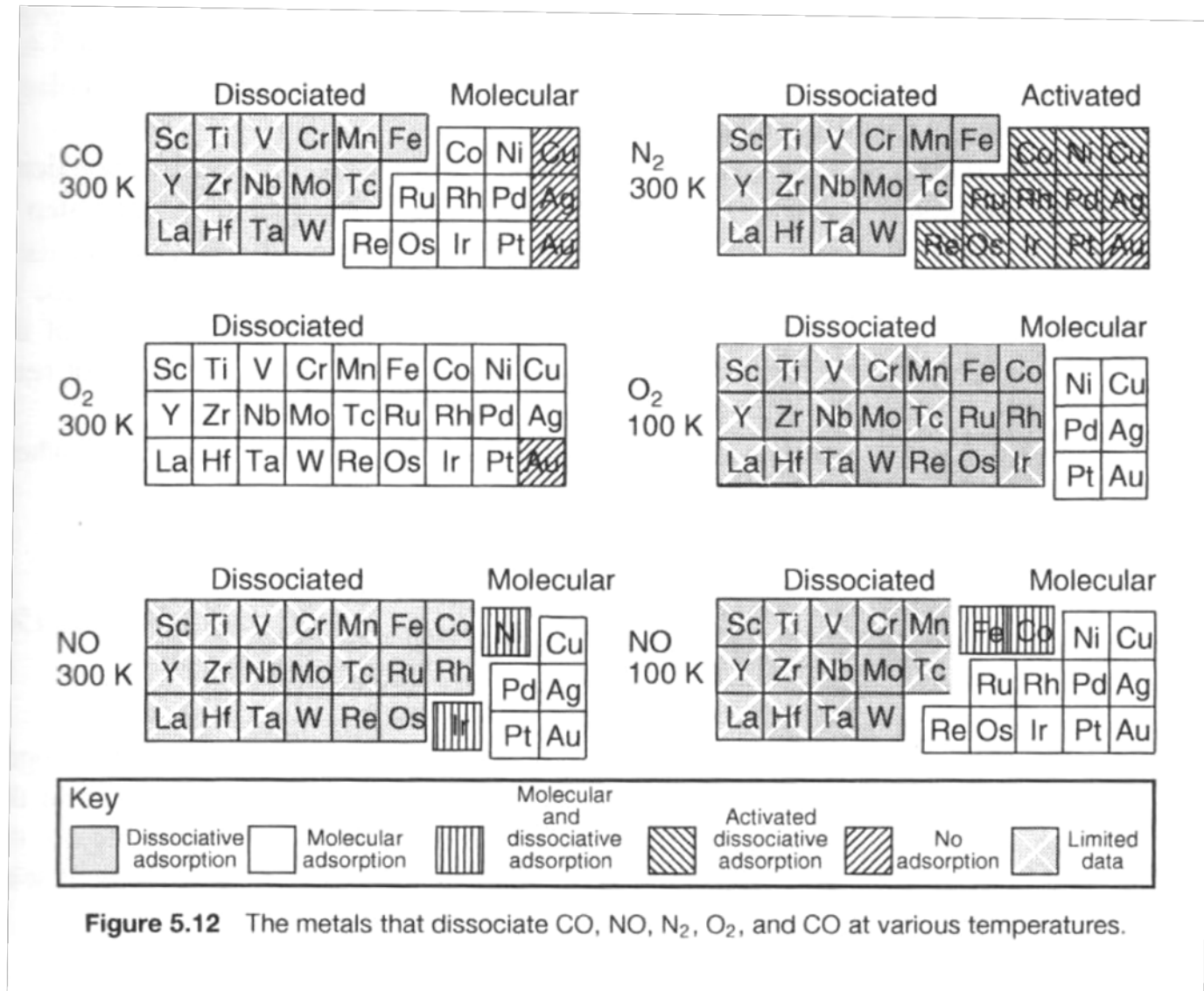
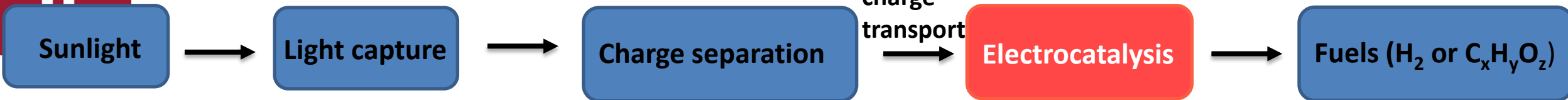


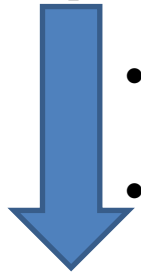
Figure 5.12 The metals that dissociate CO, NO, N₂, O₂, and CO at various temperatures.

Chemical Kinetics and Catalysis, Richard Masel, Wiley-Interscience, 2001

Solar to fuel conversion

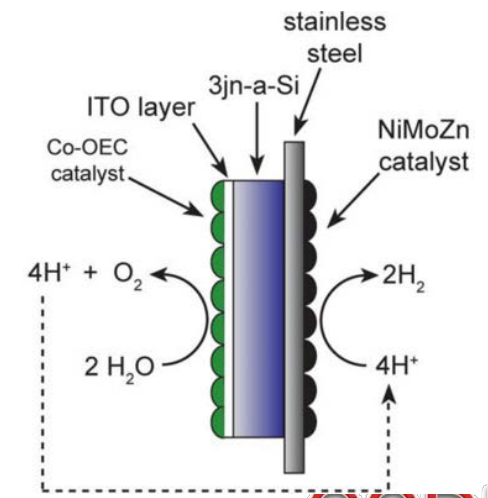
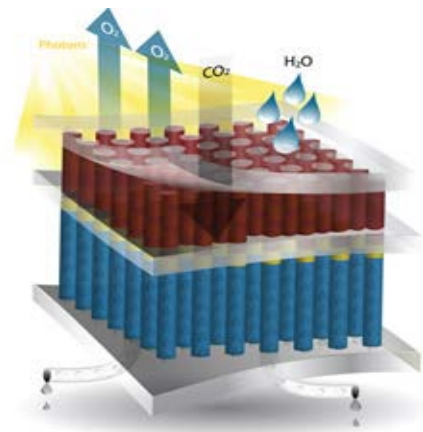
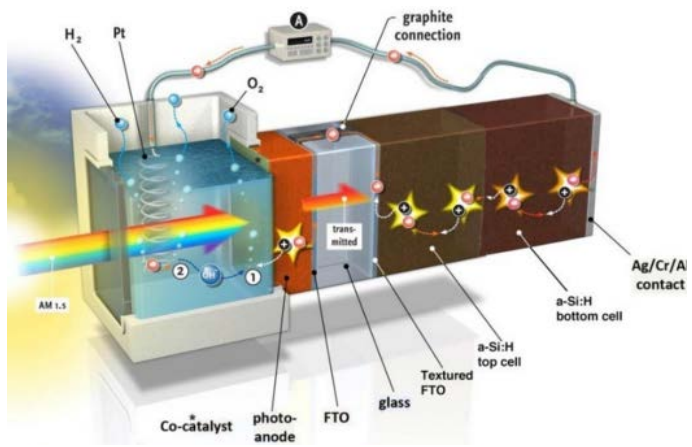


- ✓ High absorption
- ✓ Long diffusion lengths
- ✓ Minimal overpotential

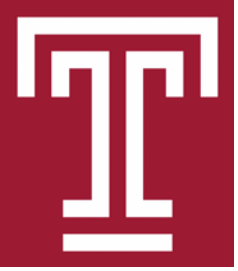


- Solar farms- tethering PV device with electrolyzes (inefficient) (solar energy → electricity → fuels)
- Advance technologies (with **single energy transformation**)

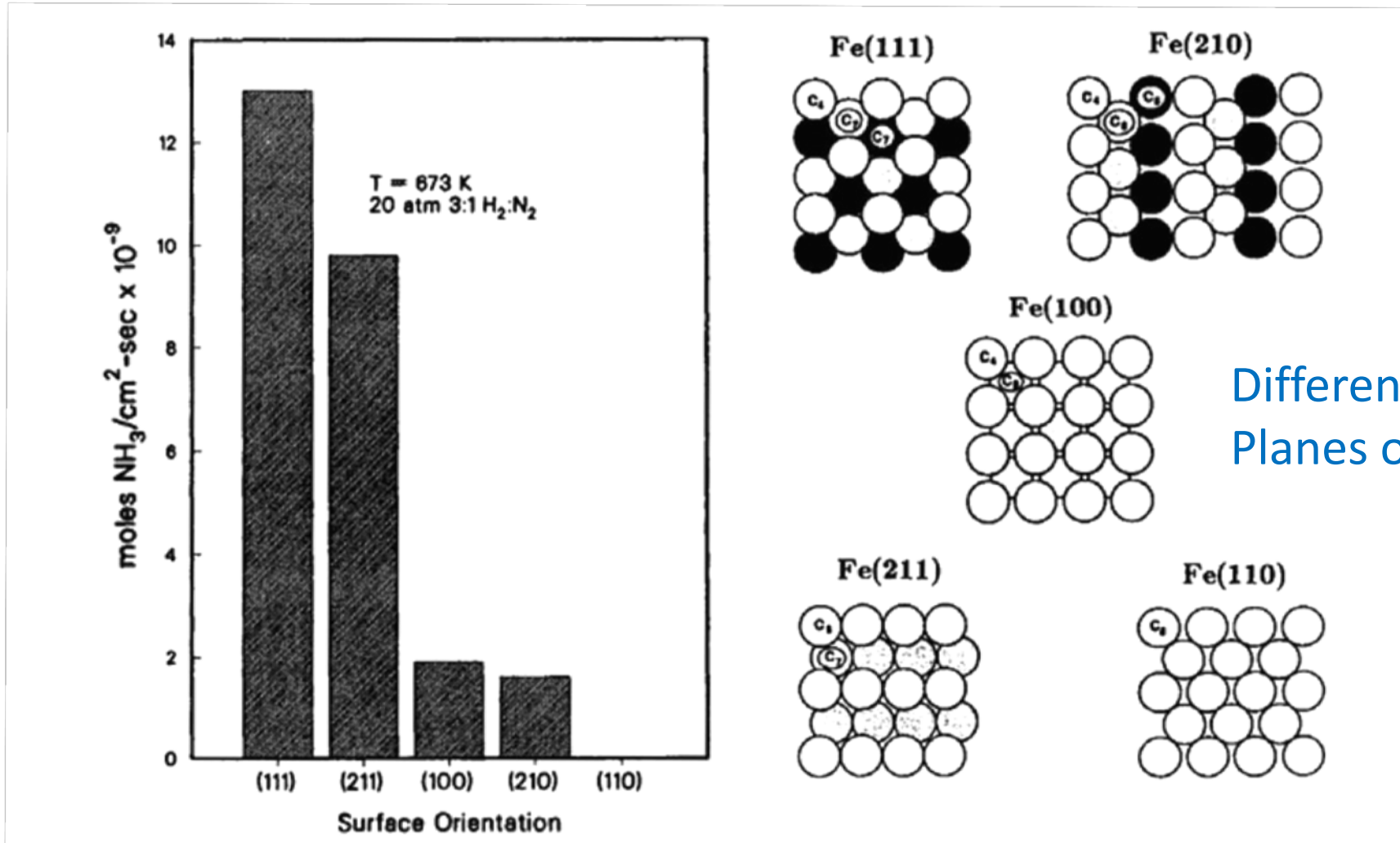
Photo-anodes with electrocatalysts



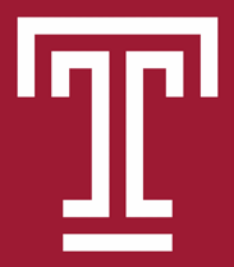
CCDM
(2011): 645



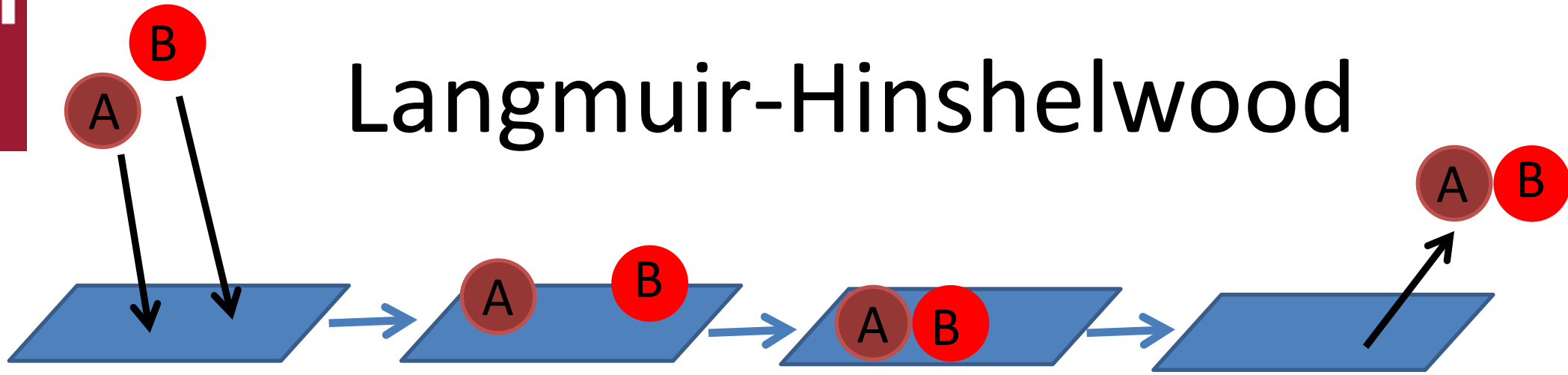
Catalysis may be very sensitive to surface structure



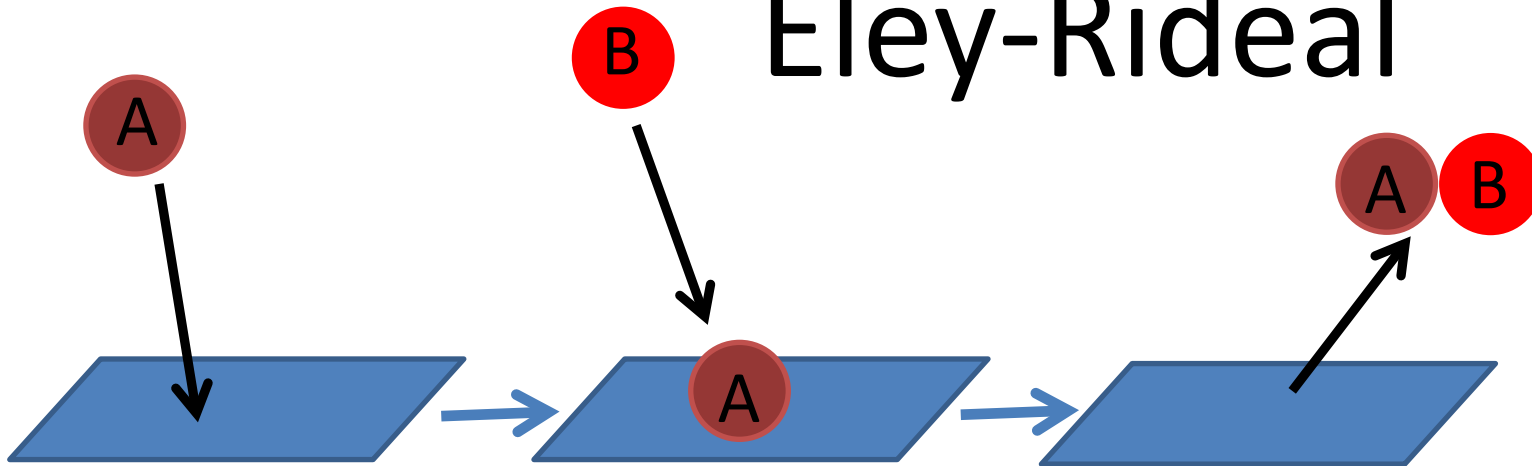
Strongin DR, Carrazza J, Bare SR, Somorjai GA (1987) J Catal 103:289

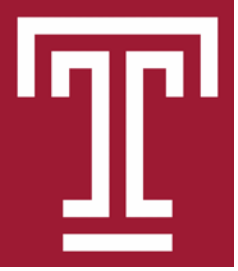


Langmuir-Hinshelwood



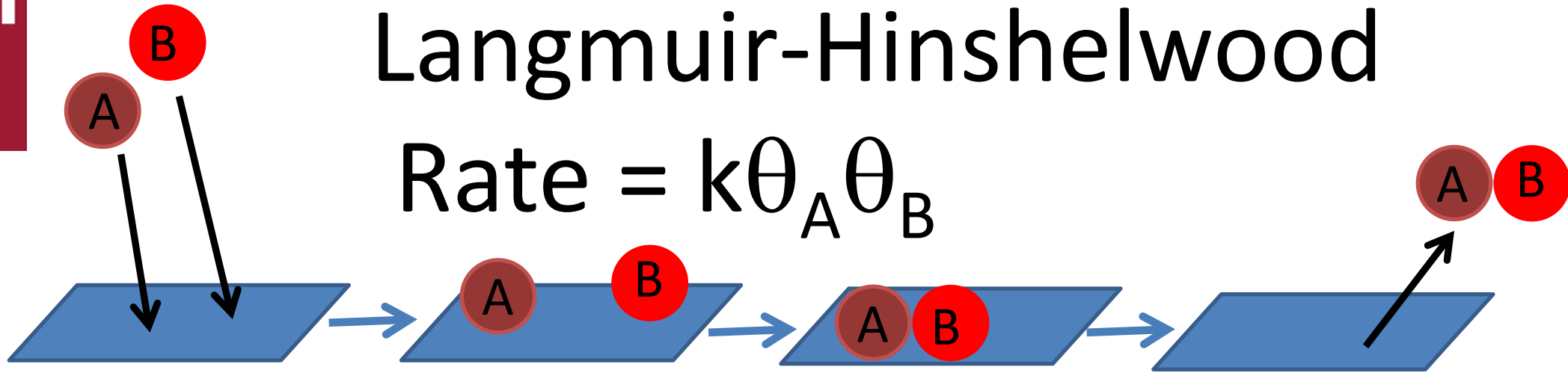
Eley-Rideal





Langmuir-Hinshelwood

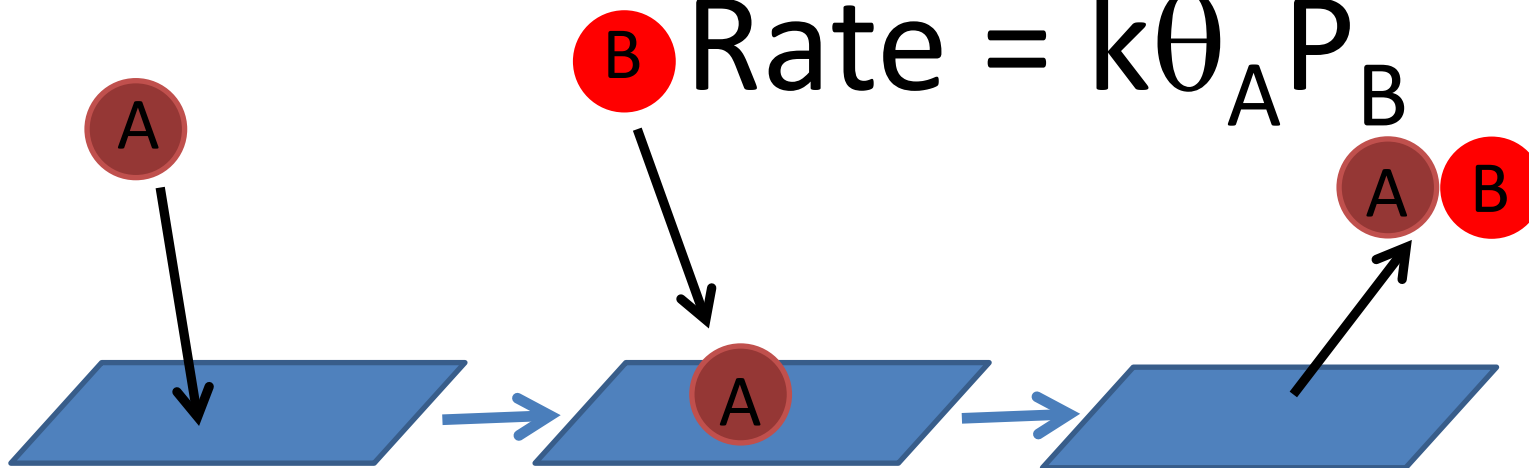
$$\text{Rate} = k\theta_A\theta_B$$

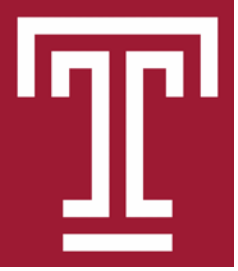


$$\theta = \frac{\# \text{ of sites occupied}}{\text{total \# surface sites}}$$

Eley-Rideal

$$\text{Rate} = k\theta_A P_B$$

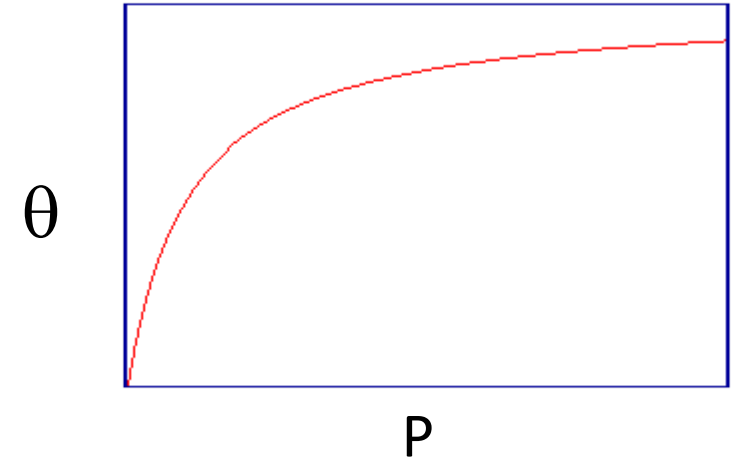




Langmuir Isotherm

At equilibrium: $r_{ad} = r_{des}$

$$\frac{P}{\sqrt{2\pi mkT}} \cdot S_0(1 - \theta) \cdot e^{-\Delta E_{ad} / kT} = v_{des} \cdot \theta \cdot e^{-\Delta E_{des} / kT}$$



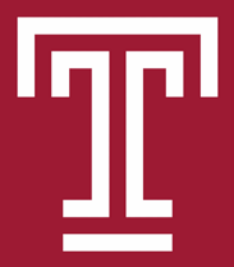
$$\theta = \frac{bP}{1 + bP} \quad ; \quad b = \frac{S_0 \exp(-\{\Delta E_{ad} - \Delta E_{des}\} / kT)}{v_{des} \sqrt{2\pi mkT}}$$

coverage

$$\theta = \frac{\sqrt{bP}}{1 + \sqrt{bP}}$$

Non dissociative adsorption

Dissociative adsorption



Catalysis on surfaces

Unimolecular decomposition



$$r_a = k_a P_a (1 - \theta)$$

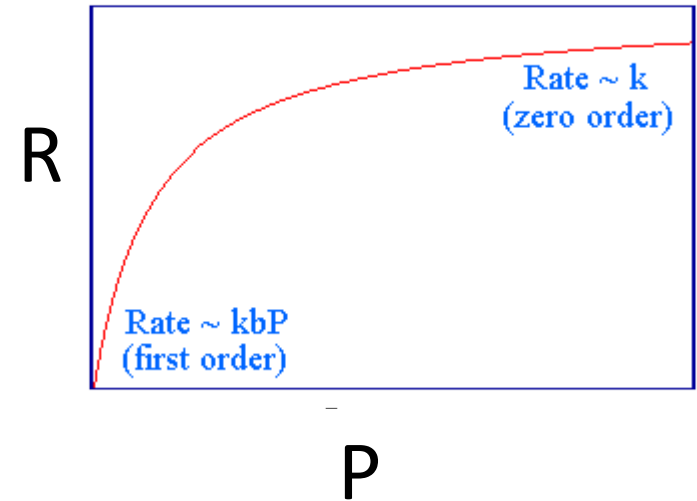
$$r_d = k_d \theta$$

$r_a = r_d$ at equilibrium

$$\theta = \frac{bP}{1 + bP}; b = \frac{k_a}{k_d}$$

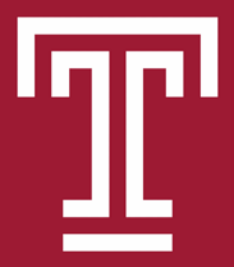
$$\text{Rate} = k\theta$$

$$\text{Rate} = k \frac{bP}{1 + bP}$$



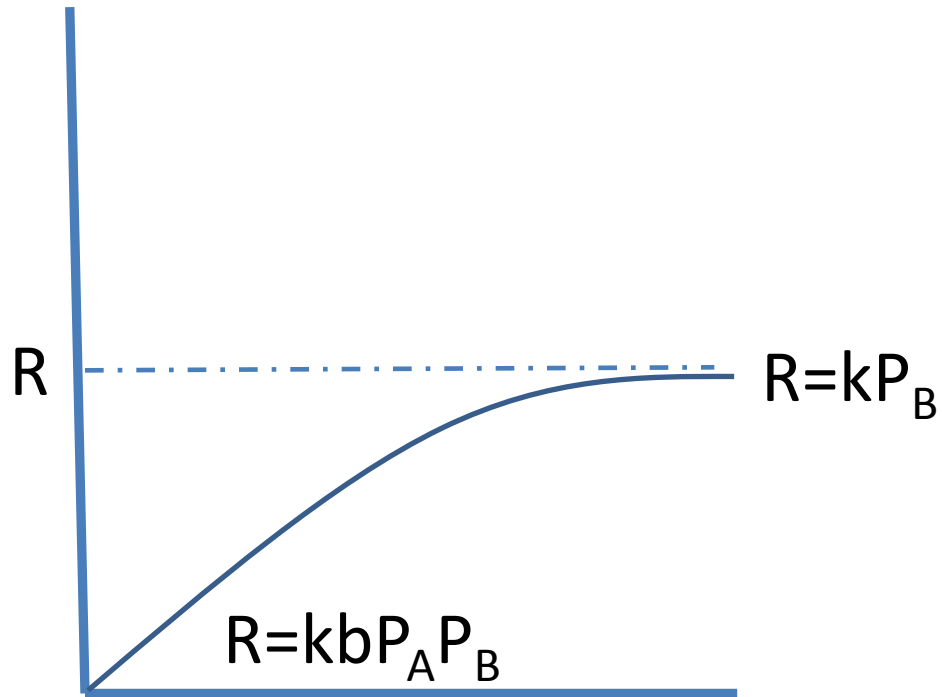
$$\theta = \frac{\# \text{ of sites occupied}}{\text{total } \# \text{ surface sites}}$$

<http://www.chem.qmul.ac.uk/surfaces/scc/>



Eley-Rideal

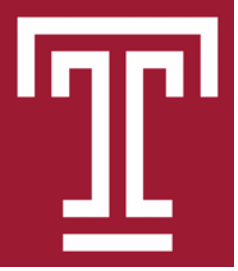
$$\text{Rate} = kP_B\theta_A$$



P_A \longrightarrow
 P_B is constant

$$\theta_A = \frac{bP_A}{1 + bP_A}$$

$$R = \frac{kbP_A P_B}{1 + bP_A}$$



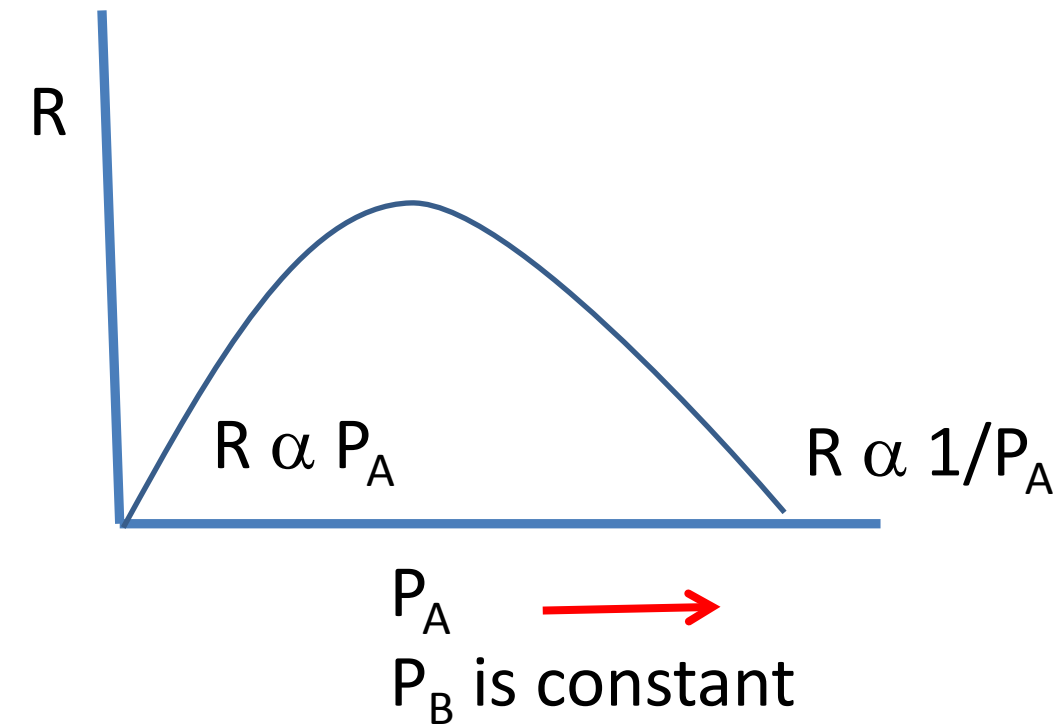
Langmuir-Hinshelwood

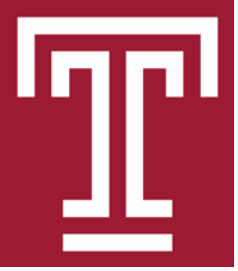
$$\text{Rate} = k\theta_A\theta_B$$

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B}; K_A = \frac{k_A}{k_{A,des}}$$

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B}; K_B = \frac{k_B}{k_{B,des}}$$

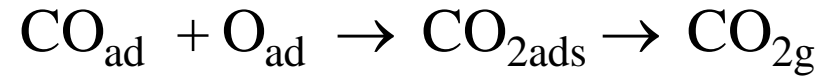
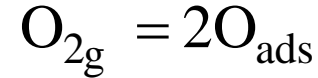
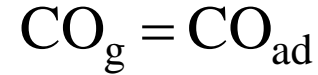
$$R = \frac{kK_A K_B P_A P_B}{(1 + K_A P_A + K_B P_B)^2}$$





Catalysis on surfaces

Bimolecular: Langmuir-Hinshelwood Reaction



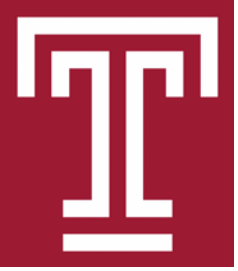
$$\theta_{\text{O}} = \frac{\sqrt{b_{\text{O}}P_{\text{O}_2}}}{1 + \sqrt{b_{\text{O}}P_{\text{O}_2} + b_{\text{CO}}P_{\text{CO}}}}; \theta_{\text{CO}} = \frac{b_{\text{CO}}P_{\text{CO}}}{1 + \sqrt{b_{\text{O}}P_{\text{O}_2} + b_{\text{CO}}P_{\text{CO}}}}$$

$$\text{Rate} = k\theta_{\text{CO}}\theta_{\text{O}} = \frac{kb_{\text{CO}}P_{\text{CO}}\sqrt{b_{\text{O}}P_{\text{O}_2}}}{(1 + \sqrt{b_{\text{O}}P_{\text{O}_2} + b_{\text{CO}}P_{\text{CO}}})^2}$$

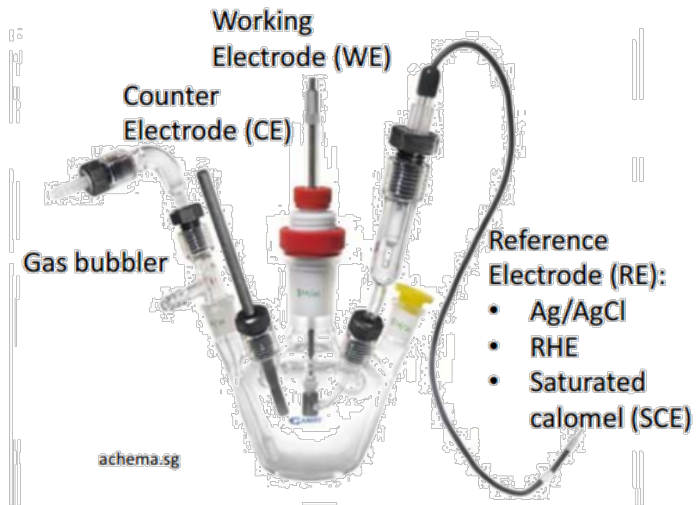
$$\text{Rate} = \frac{k\sqrt{b_{\text{O}}P_{\text{O}_2}}}{b_{\text{CO}}P_{\text{CO}}} = k' \frac{P_{\text{O}_2}^{5/2}}{P_{\text{CO}}}$$

CO strongly adsorbed

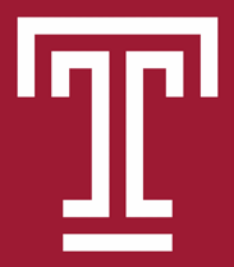
$$b_{\text{CO}}P_{\text{CO}} \gg (1 + \sqrt{b_{\text{O}}P_{\text{O}_2}})$$



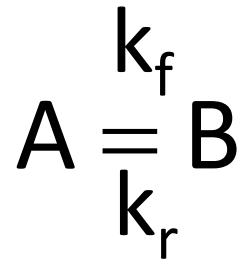
Brief Introduction to electrochemistry for electrocatalysts



Analysis adapted from
Bard and Faulkner, *Electrochemical Methods*, 2nd edition, 2001, John Wiley.



Consider the following reaction where A is in equilibrium with B



Where k_f and k_r are the forward and reverse rate constants.



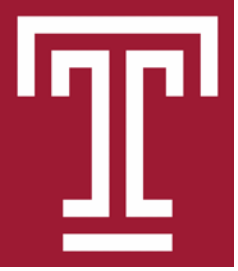
Reaction rate of forward and reverse reaction

- Rate of forward reaction is given by

$$R_f = k_f \cdot C_A$$

- Rate of reverse reaction is given by

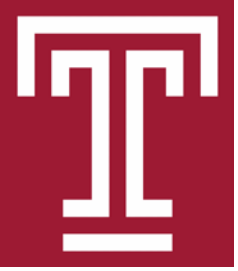
$$R_r = k_r \cdot C_B$$



What is the net reaction rate?

- $R_{\text{net}} = R_f - R_r$

- $R_{\text{net}} = k_f \cdot C_A - R_r = k_r \cdot C_B$



Equilibrium

Equilibrium is defined as the point at which the net reaction rate is zero

$$k_f / k_b = K = C_B / C_A$$

↑
Equilibrium constant

Rates of reactions



$$R_{for} = k_{for} [O] = \frac{i_c}{nF}$$

$$R_{rev} = k_{rev} [R] = \frac{i_a}{nF}$$

$$R_{net} = R_{for} - R_{rev} = (i_c - i_a) / nF$$

$$= (k_{for} [O] - k_{rev} [R])$$

Nernst Equation at Equilibrium

$$E_{eq} = E^0 - \frac{RT}{nF} \ln \frac{[R]}{[O]}$$

Where E^0 is standard potential, F is Faraday's constant, and n =#electrons transferred in equation

At Equilibrium

$$R_{for} = R_{rev} ; i_c = i_a$$

$$k_{for} [O] = k_{rev} [R]$$

$$\ln k_{rev} - \ln k_{for} = \ln \frac{[O]}{[R]} = \frac{F}{RT} (E - E^0)$$

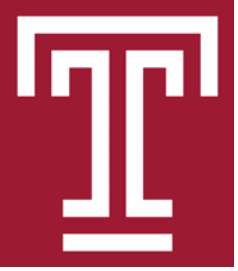
$$\frac{RT}{F} \left[\underbrace{\frac{d}{dE} \ln k_{rev}}_{1-\alpha} + \underbrace{\frac{d}{dE} \ln(1/k_{for})}_{\alpha} \right] = 1$$

Oxidative
Symmetry factor

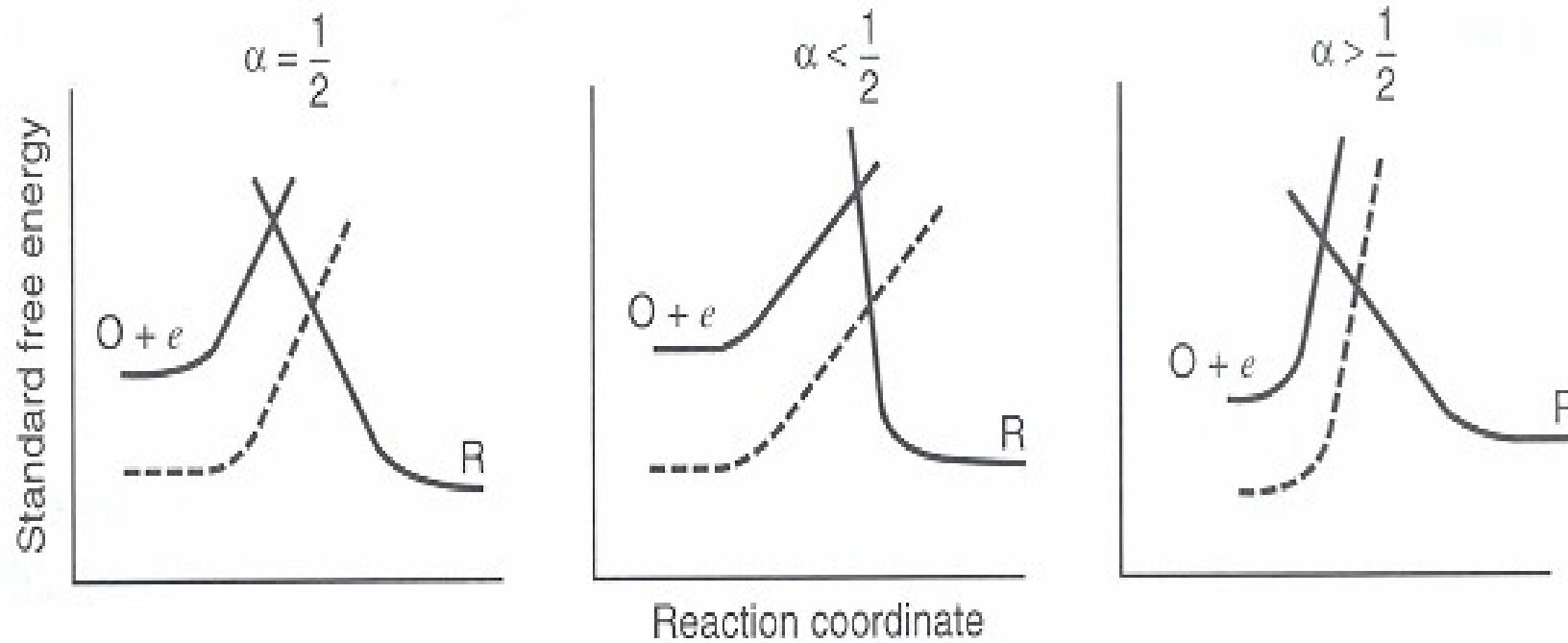
$1-\alpha$

Reductive
Symmetry factor

α



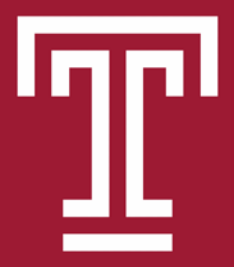
Symmetry Factor



O + e curve shifts as a potential becomes more positive

α Is the symmetry of the energy barrier for reaction. If both sides of barrier are same, $\alpha = .5$

Bard and Faulkner, Electrochemical Methods, 2nd edition, 2001, John Wiley.



Rate constants

$$\ln \frac{1}{k_{for}} = \frac{\alpha F E}{RT} + c$$

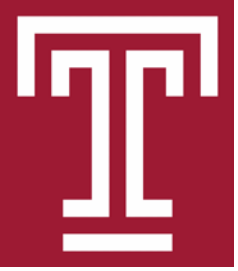
$$k_{for} = k_{for}^0 \exp\{-[\alpha F / RT](E - E^0)\}$$

$$k_{rev} = k_{rev}^0 \exp\{[(1 - \alpha)F / RT](E - E^0)\}$$

Where $k_f = k_f^0$ and $k_r = k_r^0$ when $E = E^0$

k_f^0 and k_r^0 are standard rate constants

When $[O] = [R]$ and $E = E^0$ then $k_f^0 = k_r^0$

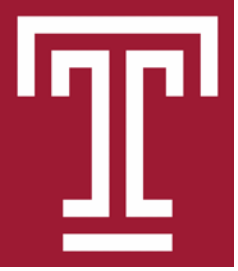


Rate constants

$$k_{for} = k^0 \exp\{-[\alpha F / RT](E - E^0)\}$$

$$k_{rev} = k^0 \exp\{-[(1 - \alpha)F / RT](E - E^0)\}$$

Small k^0 , large overpotential needed to get reaction
Going. Low efficiency



Tafel Equation

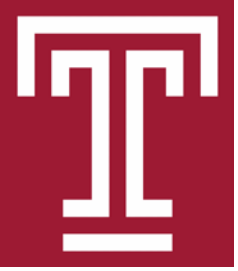
$$R_{net} = i / nF = [k_f[O] - k_r[R]]$$

$$i = nFk^0 \{ [O] \exp\{-[\alpha nF / RT](E - E^0)\} - [R] \exp\{[(1 - \alpha)nF / RT](E - E^0)\} \}$$

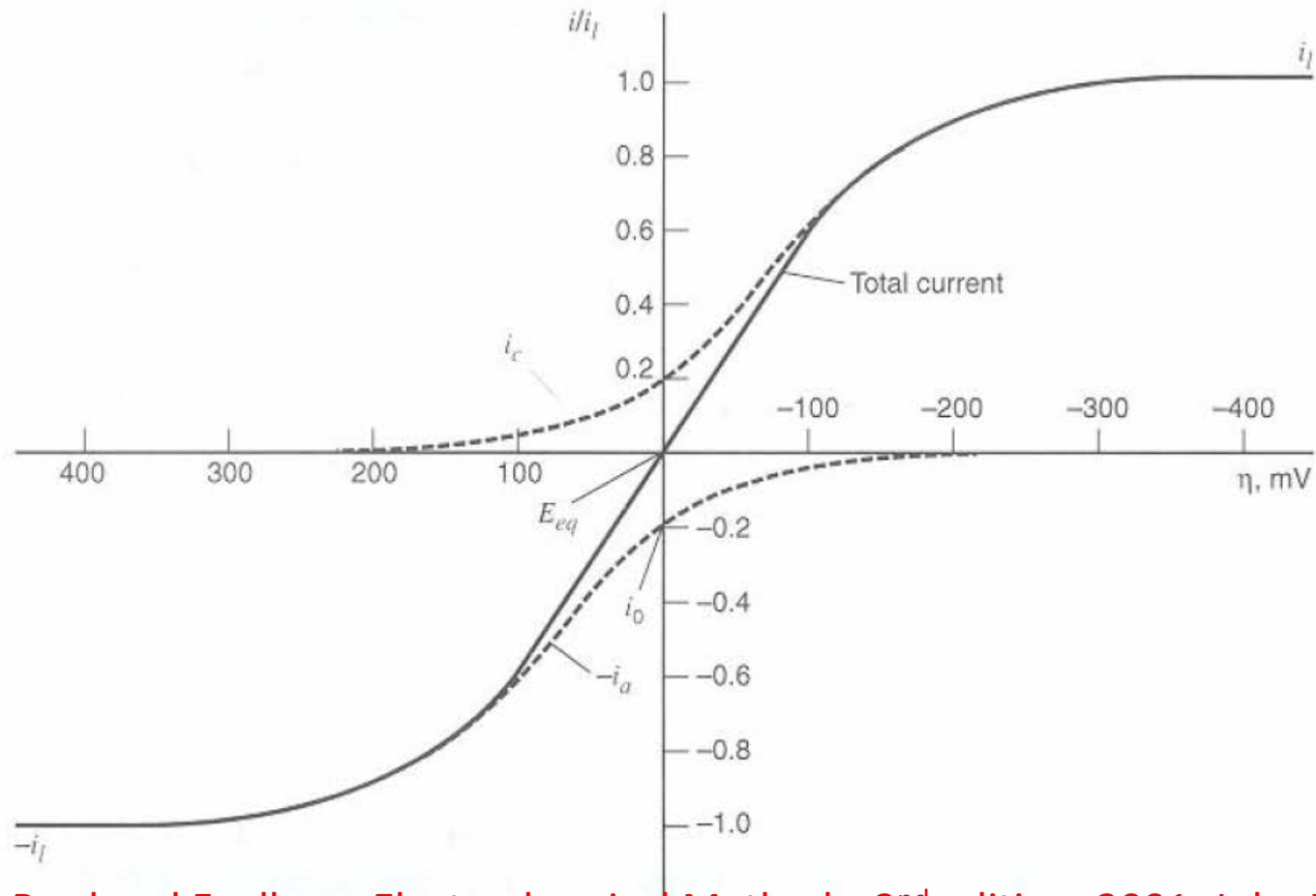
If we have a large overpotential, η , where $\eta = E - E^0$

Whether η is $<$ or $>$ 0

$\eta = a + b \log |i|$ (Tafel equation)



Current versus Overpotential

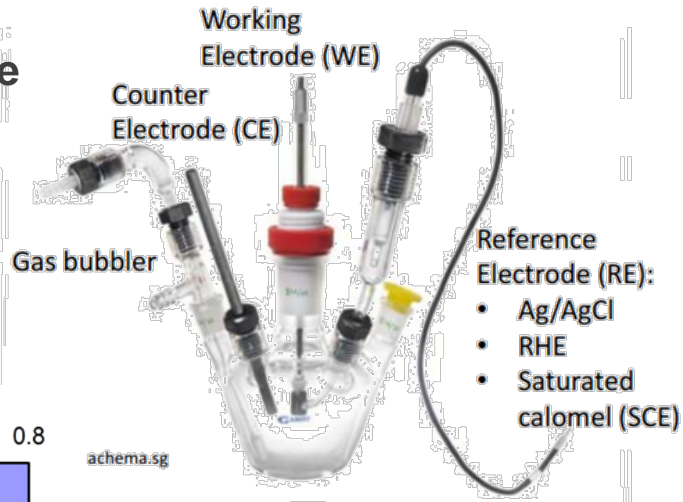


Bard and Faulkner, *Electrochemical Methods*, 2nd edition, 2001, John Wiley.



Testing catalyst

Glassy carbon working electrode

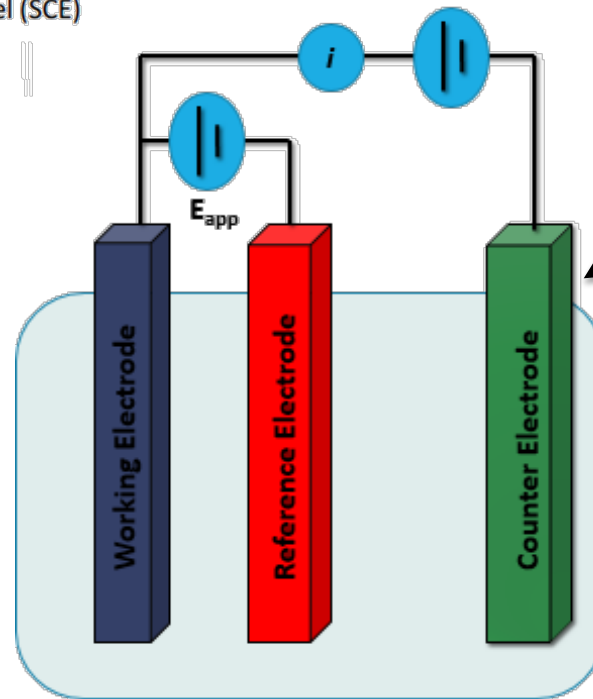


- Reference Electrode (RE):
- Ag/AgCl
 - RHE
 - Saturated calomel (SCE)

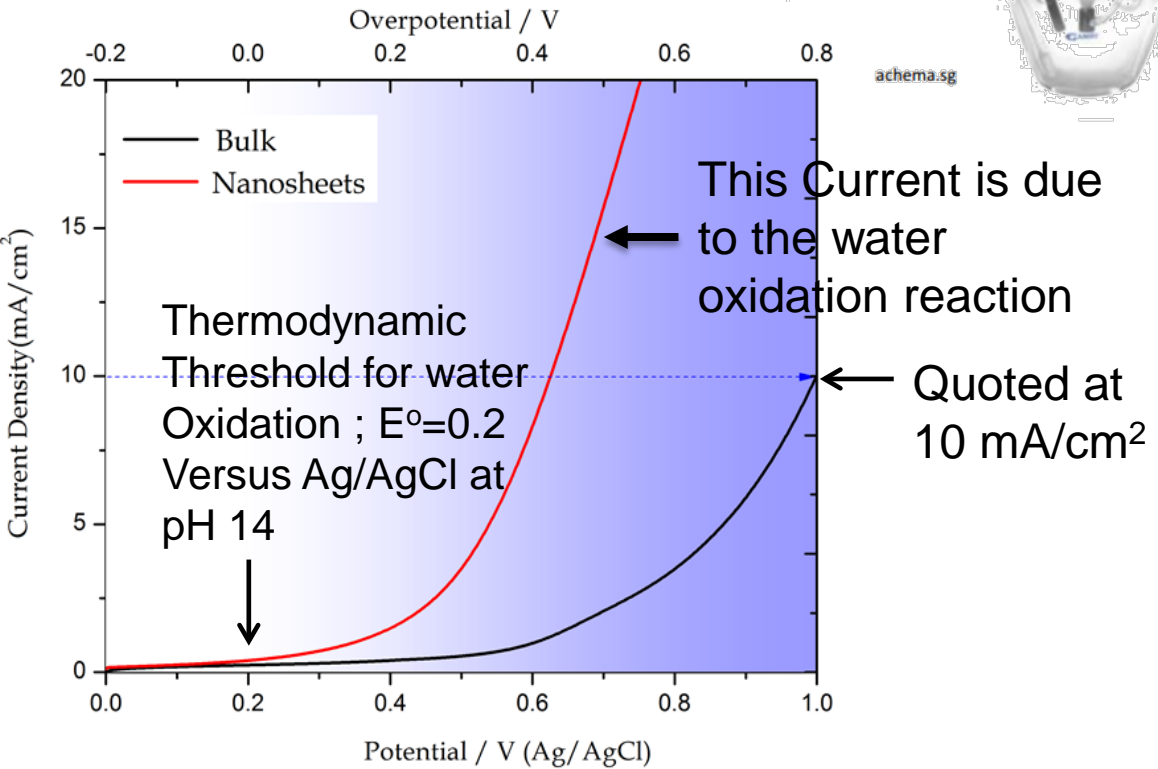
Potentiostat



Potentiostat is instrument that controls the voltage difference between a Working Electrode and a Reference Electrode.

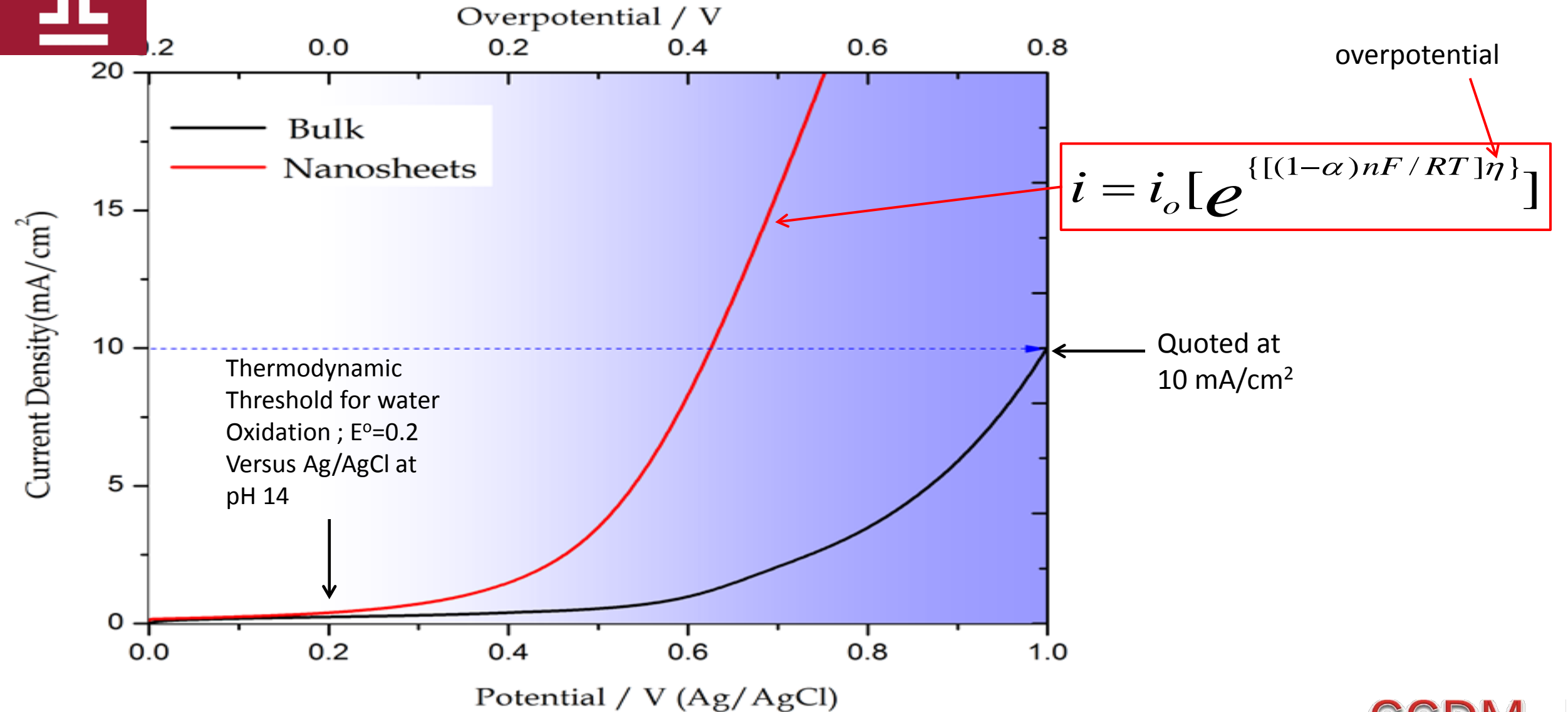


This voltage is set so the counter electrode can pass the same current as the working electrode.





Electrocatalysis Measurement

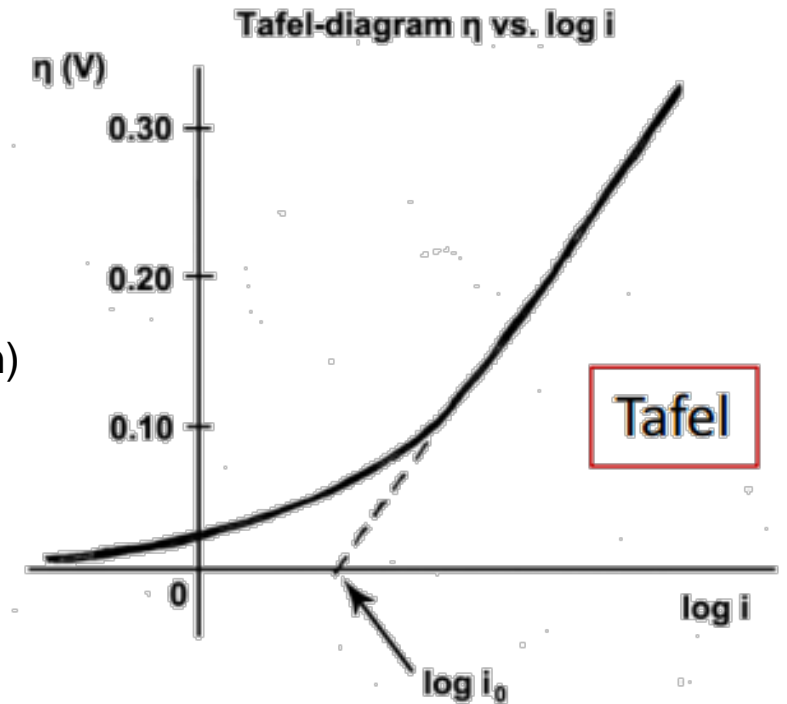




Electrocatalytic activity: Figures of merit

Primary figures of merit for electro-catalyst activity:

- Overpotential needed to reach a give current density
- Tafel slope, b (mV/dec) (relating the rate of an electrochemical reaction)
- Exchange current density i_0 (mA/cm²)

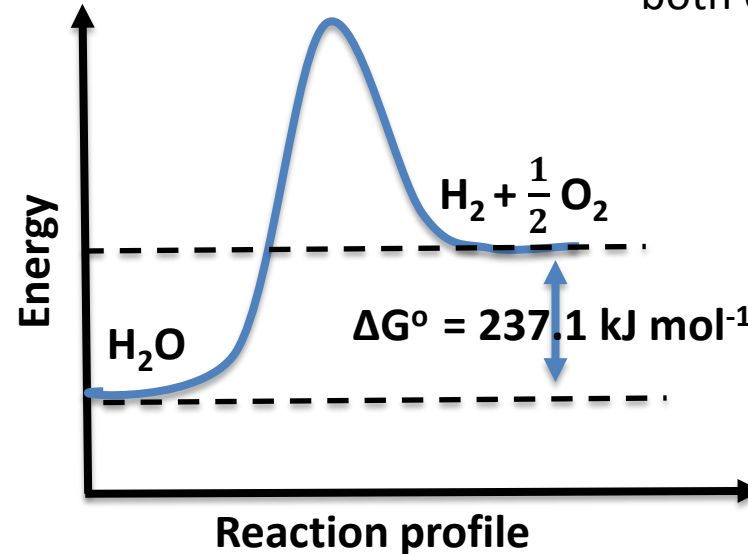
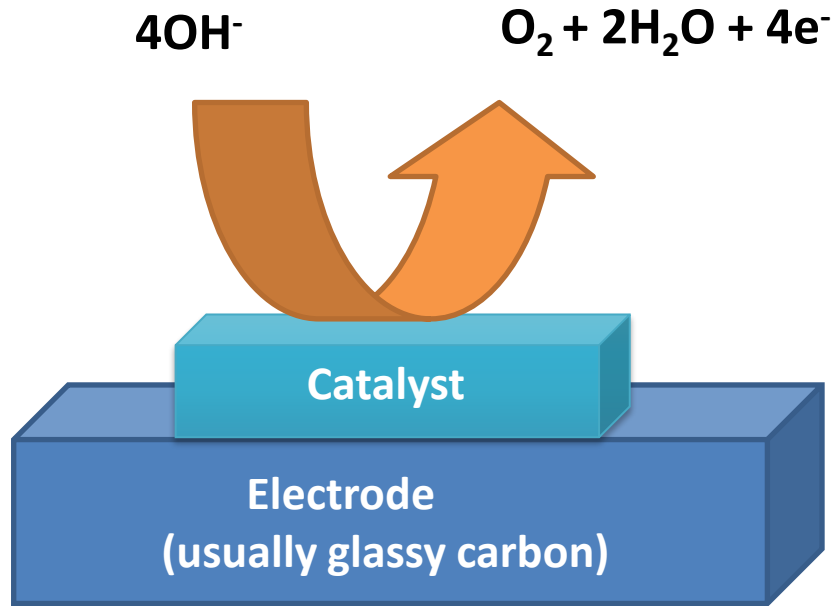




Thermodynamics of Water Oxidation Reaction



- A single catalyst cannot catalyze both oxidation and reduction reactions

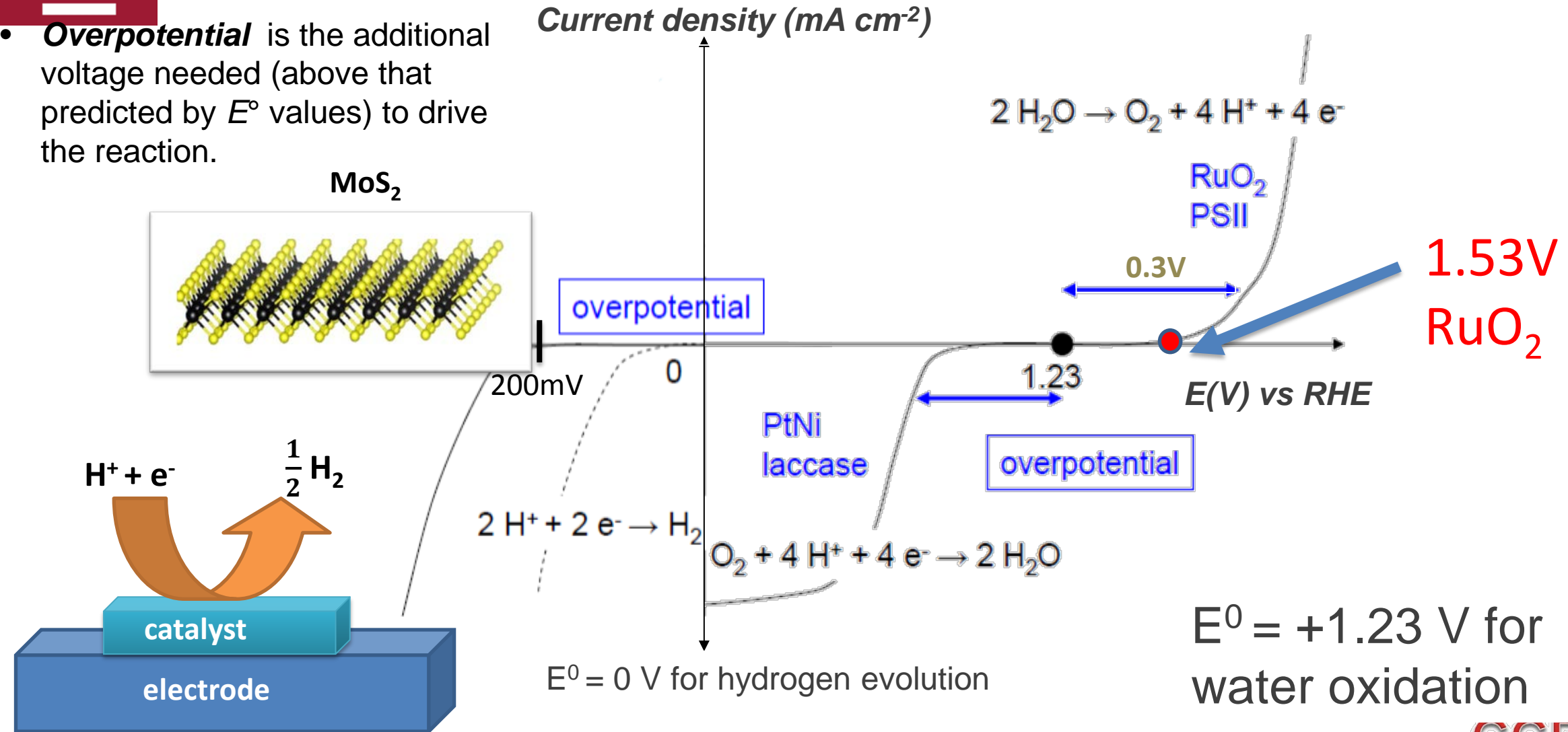


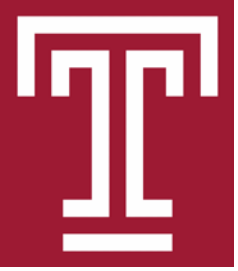
$$\Delta G > 0$$
$$E^0 = +1.23 \text{ V}$$



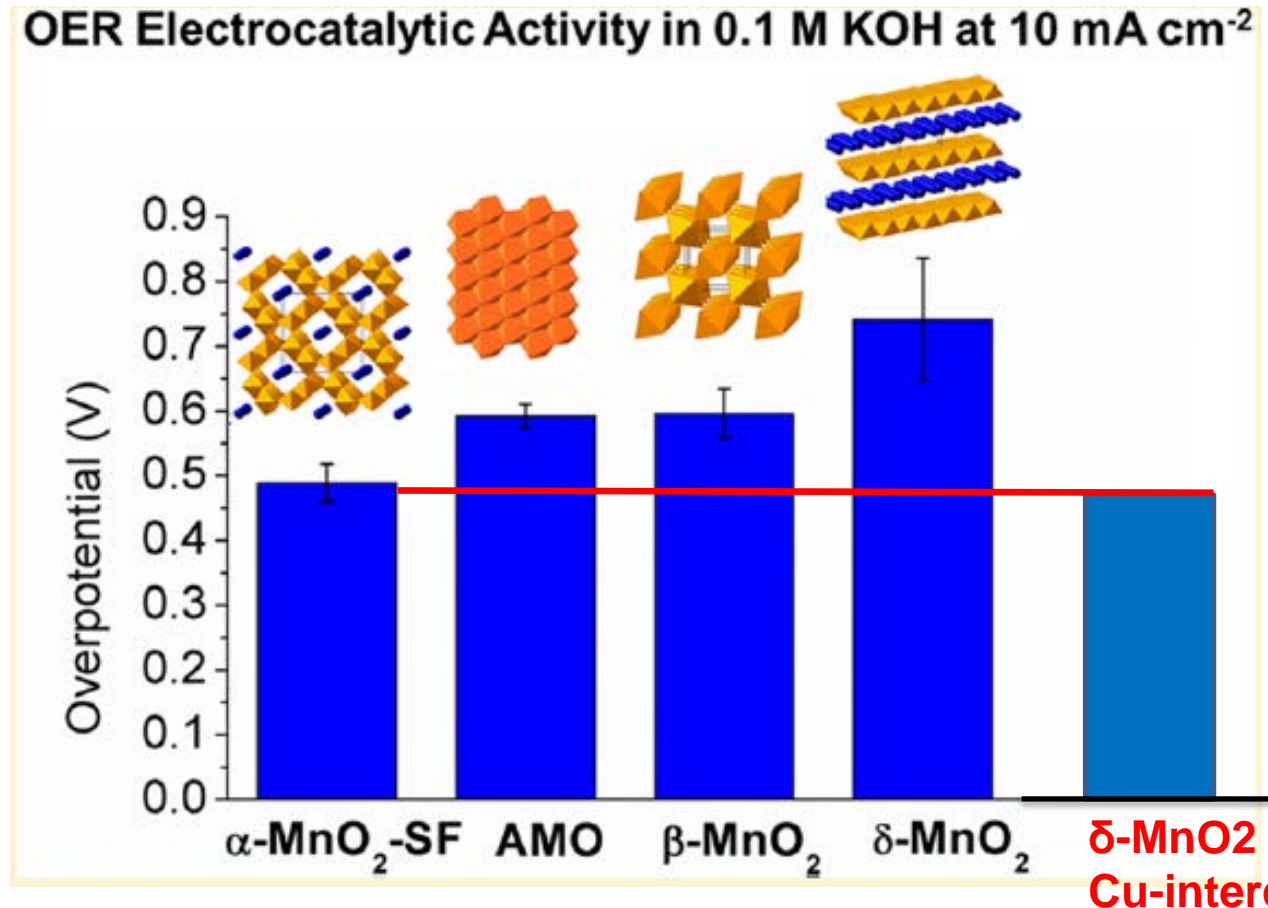
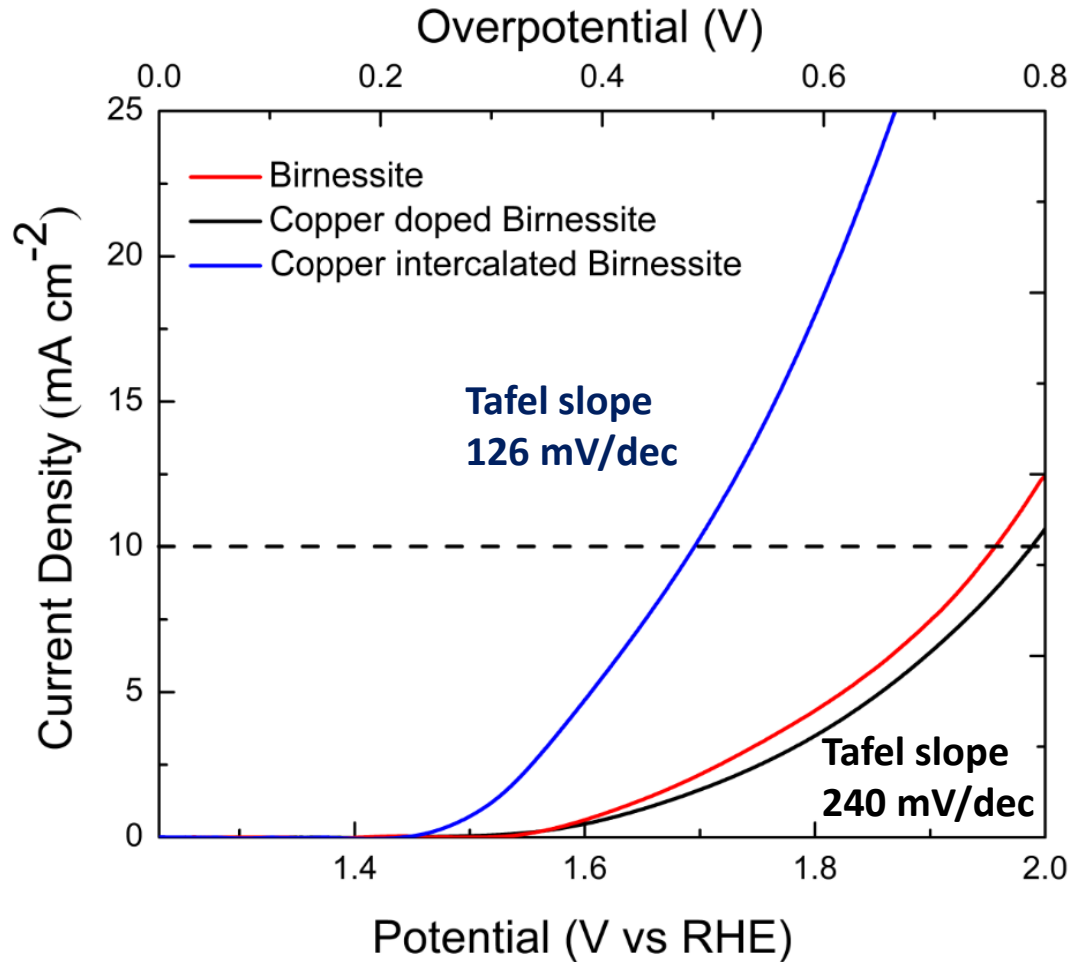
Concept of Overpotential

- Overpotential** is the additional voltage needed (above that predicted by E° values) to drive the reaction.





Zero valent copper intercalated Birnessite



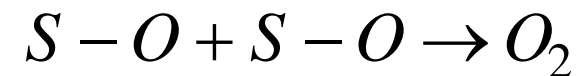
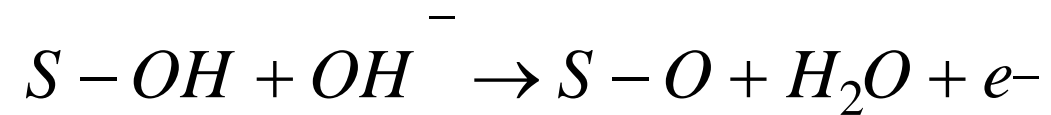
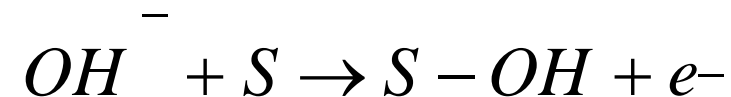
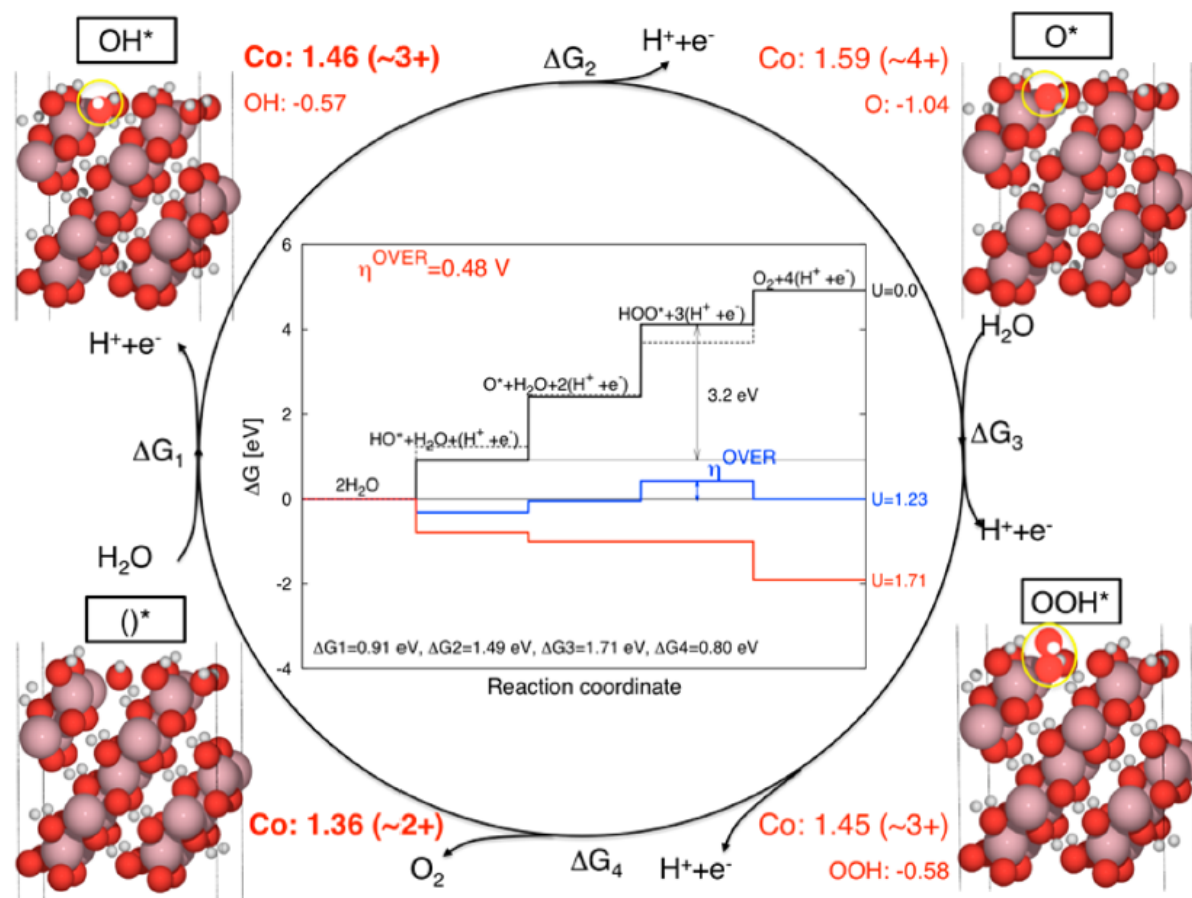
Theoretical Investigation of the Activity of Cobalt Oxides for the Electrochemical Oxidation of Water

Michal Bajdich,^{†,§} Mónica García-Mota,[‡] Aleksandra Vojvodic,[‡] Jens K. Nørskov,^{*,‡} and Alexis T. Bell^{*,†,§}

[†]The Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

[‡]SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States

[§]Department of Chemical and Biomolecular Engineering, University of California at Berkeley, Berkeley, California 94720, United States



And / Or

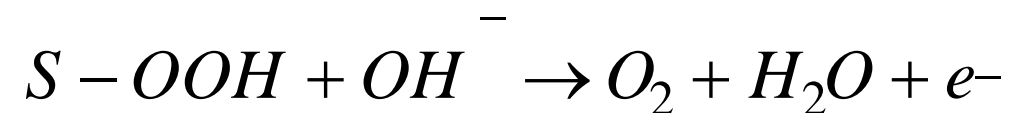
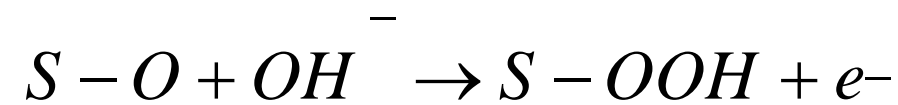
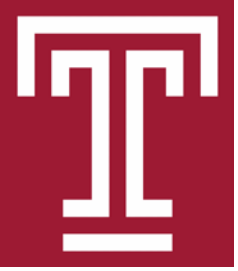
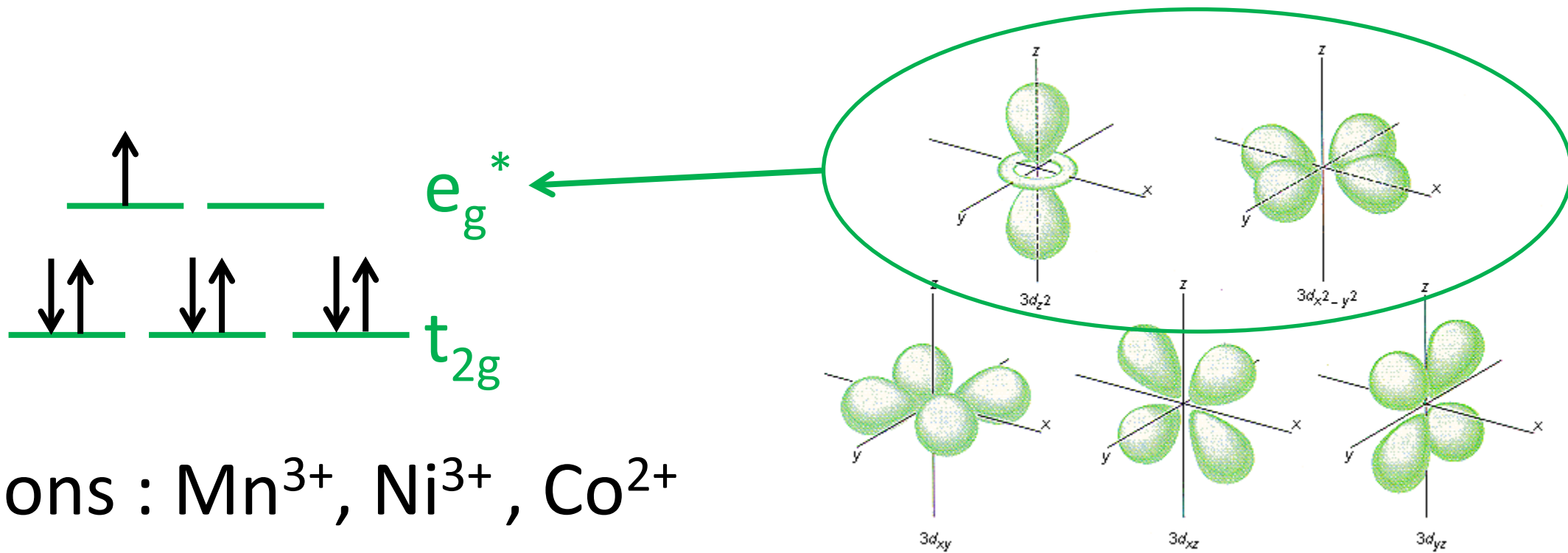


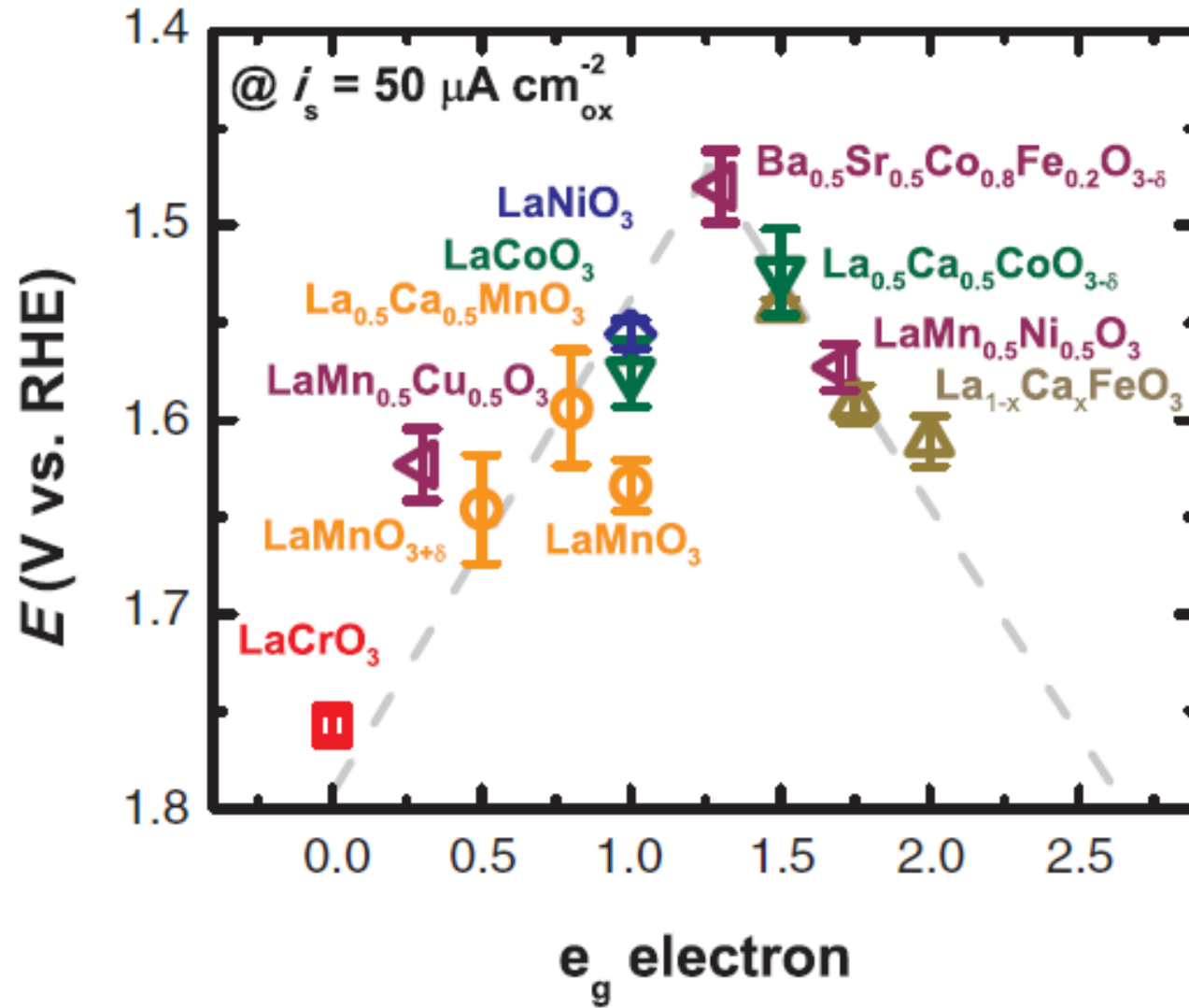
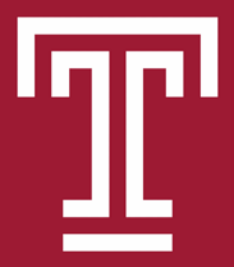
Figure 5. Schematic of the OER on the (10 $\bar{1}$ 4) surface. The inset shows the free-energy landscape compared to an ideal catalyst (dashed-line) for zero pH. Reaction 3 is the potential-limiting step. For $U > 1.71$ V, all steps are thermodynamically accessible. For each step, we list the measured Bader charge of the Co active site and of the adsorbed species (Table 3).

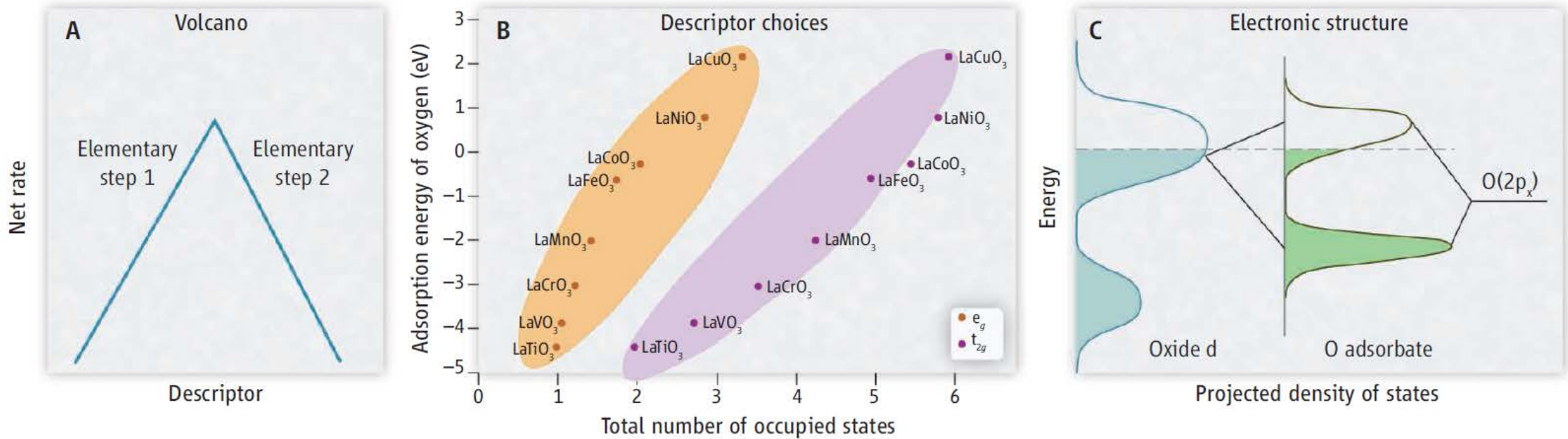


Descriptor for Catalysis Water Oxidation



<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/crystal.php>



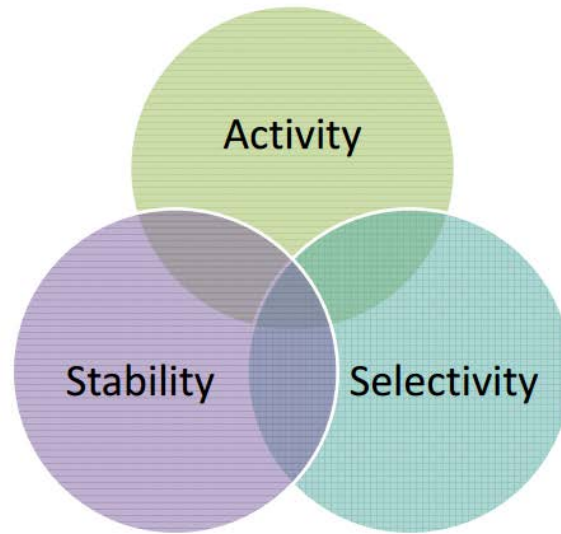


- 1) Intermediates *OH, *O, *OOH bond through O atom
*OH or *O from H₂O become easier due to the surface-O interaction
- 2) Steps like *O + H₂O → OOH⁻ + H⁺ + e⁻ is more difficult since surface-O bond is being broken.

Vojvodic and Norskov, Science (2011) vol. 334, p. 1355



Direction of Forum B



Criteria for the evaluation of layered Materials for OER.

- Lots of room for improvement, even for the best precious-metal based systems (eg: IrO_2 , RuO_2).
- Screening process using descriptors for water oxidation is needed to focus us on materials of interest
- New materials that can be synthesized that from computation have favorable properties