

Computational lab 3

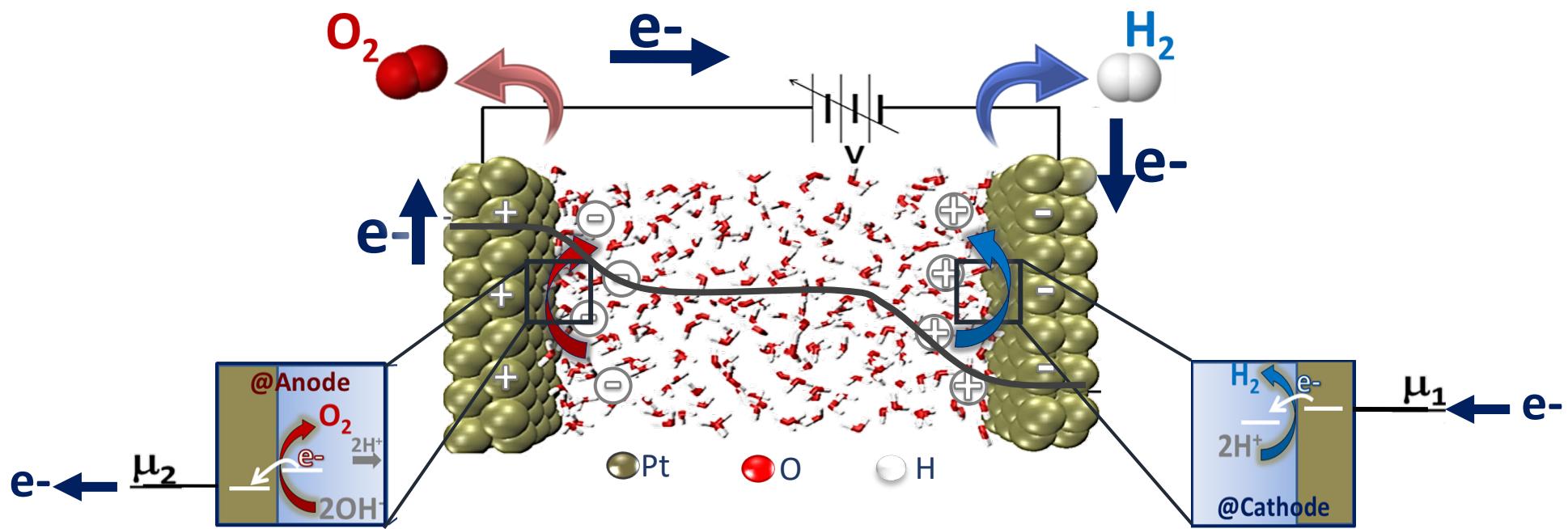
Understanding trends in catalytic activity for hydrogen evolution

Theoretical introduction

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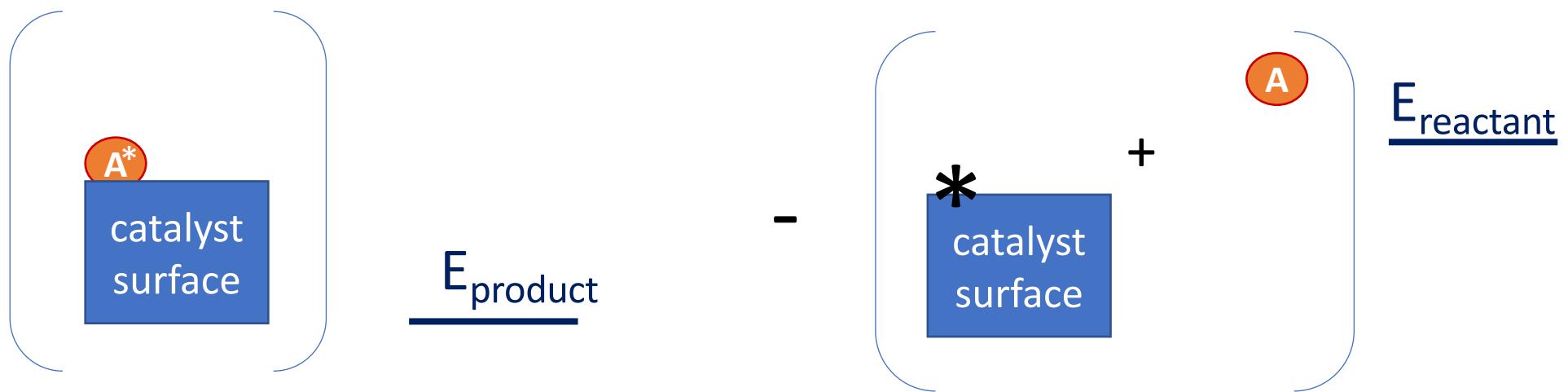
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Proton transfer reactions at metal water interfaces



Binding energies for adsorbates

Reference state: atom in gas phase

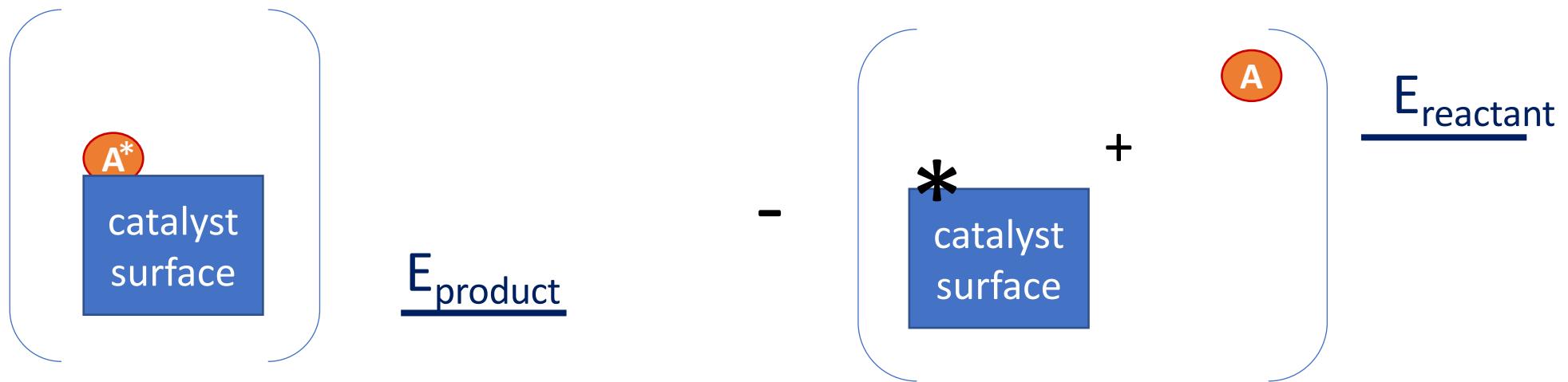


$$\Delta E = E_{final} - E_{initial} = E_{A^*} - (E_* + E_A)$$

$$\Delta E_{ads} = \frac{1}{n} \left(E_{surf+nH} - \left(E_{surf} + \frac{n}{2} E_{H_2} \right) \right)$$

Binding energies for adsorbates

Reference state: atom in gas phase



reaction energy

$$\Delta E = E_{product} - E_{reactant}$$

reaction free energy

$$\Delta G = G_{product} - G_{reactant}$$

$$\Delta G = 0$$

equilibrium

Thermodynamic quantities

Gibbs free energy $G = H - TS$

Enthalpy $H = U - pV$

Entropy $S = k_B \ln \Omega$

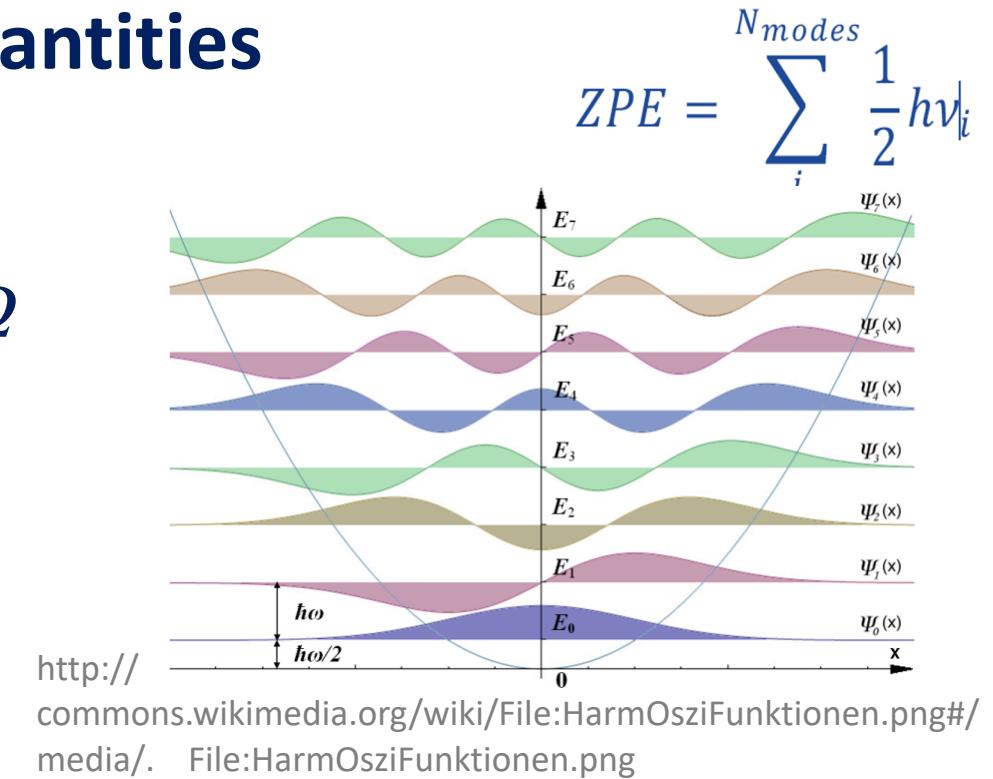
$U = E + ZPE + (\text{small thermal corrections})$

small
—

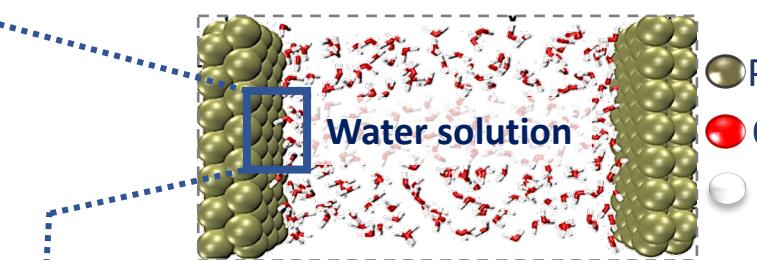
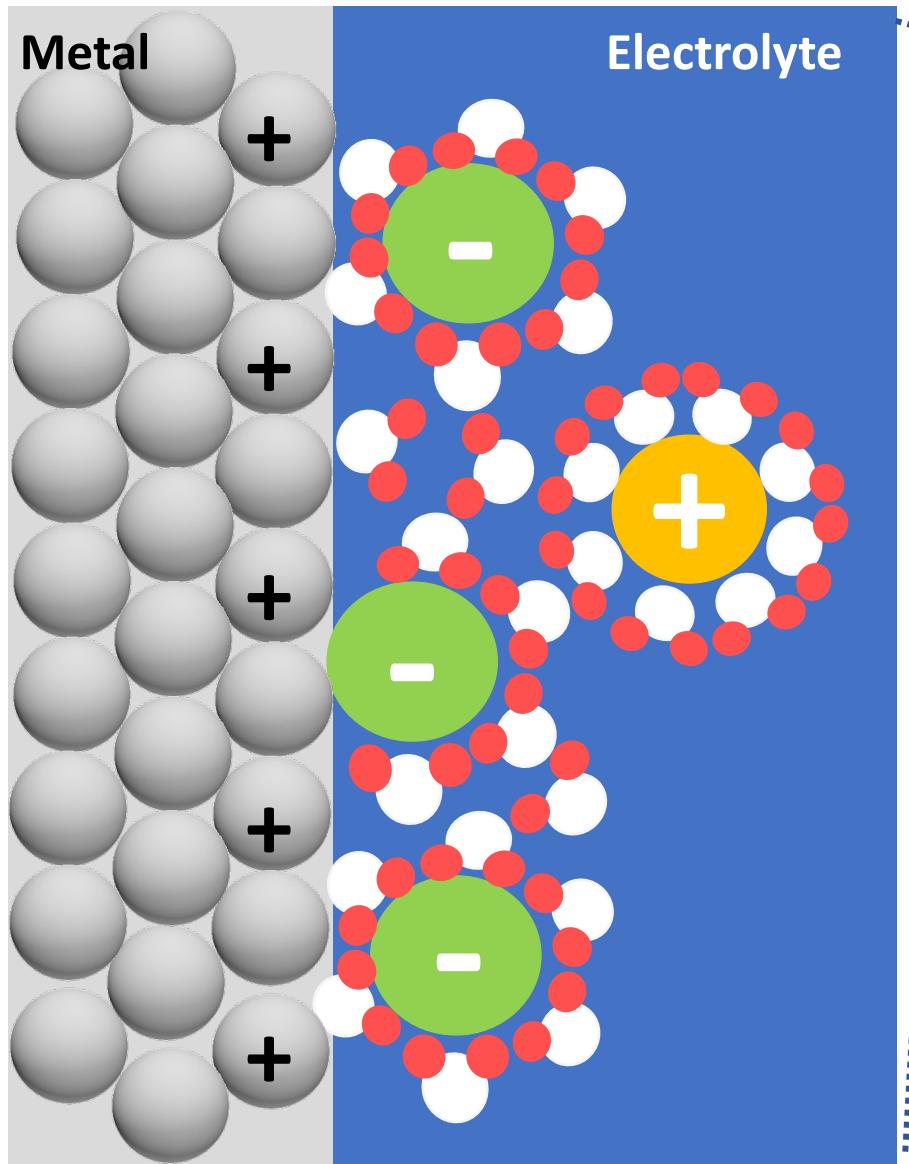
$$\Delta H = \Delta U + \Delta(pV) = \Delta E + ZPE$$

$$\Delta S = S_{\text{adsorbate}} - S_{\text{gas-phase}} \sim -S_{\text{gas-phase}}$$

$$\Delta G = G_{\text{product}} - G_{\text{reactant}} = \Delta E + ZPE + T\Delta S = \Delta E + \text{corrections}$$



Electrochemical and gas catalysis

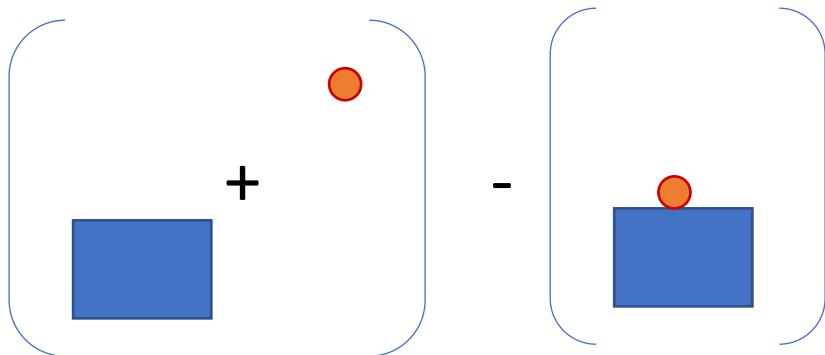


1. Electrode potential
2. Species solvated by the electrolyte
3. Solvation effects
4. Interfacial electric field
5. Electron transfer

Norskov, Fundamental Concepts in Heterogeneous Catalysis. Wiley

Computational hydrogen electrode

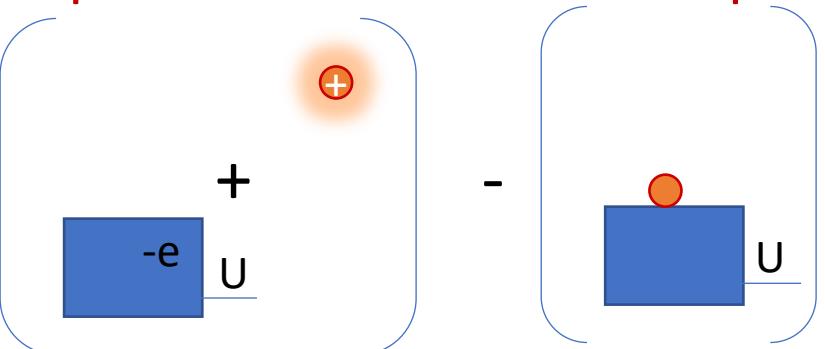
Reference state: atom in gas phase



$$\Delta G(\theta) = \Delta G_{gas}(\theta) = \Delta E_{ads}(\theta) + \Delta E_{ZPE} - T\Delta S_{ads}(\theta) + \varepsilon$$

Reference state in electrochemistry: atom in solution
in the presence of an electrode potential

$$\tilde{\mu} = \mu + neU$$



$$\Delta G(\theta, U, a_{H+}) = \Delta G_{gas}(\theta) \pm eU + k_B T \ln a_{H+} + \Delta E_{interface}$$

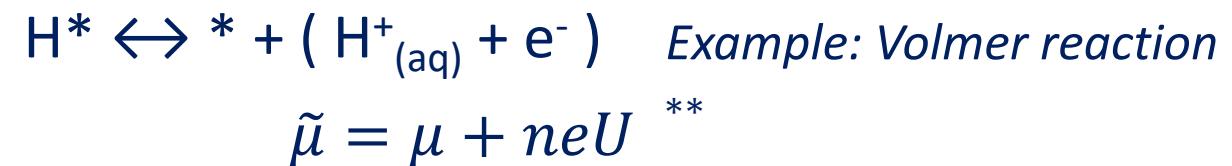
Free energy changes in electrochemistry

Computational hydrogen electrode

The hydrogen electrode provides a direct link between the free energies in gas-phase adsorption and those relevant in electrochemistry



Introduce CHE



$$\Delta G_g = \Delta E_{ads} + \Delta E_{ZPE} - T\Delta S_{ads} + \Delta E_{int}$$

$$\Delta G = k_B T \ln a_{H^+} - e n U_{SHE}$$

$$** \tilde{\mu}(H^+(\text{aq})) + \tilde{\mu}(e^-) = \frac{1}{2} \mu(H_2(\text{g})) - e n U_{SHE} + k_B T \ln a_{H^+}$$

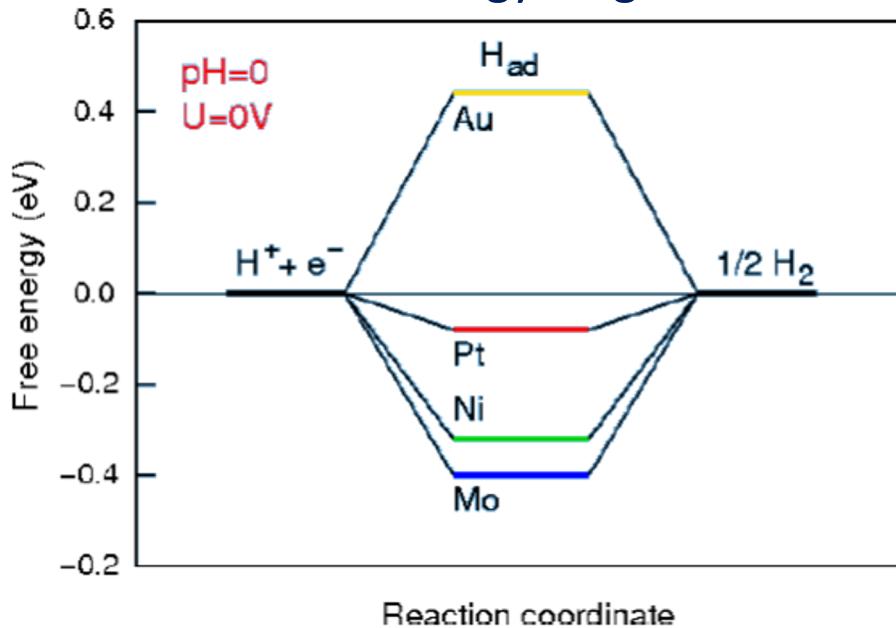
$$\Delta G = \Delta G_g(\theta) + n e (U_{RHE} - U^0) + \Delta G_{int}$$

Free energy changes in electrochemistry

Computational hydrogen electrode

$$\Delta E_{ads} = \frac{1}{n} \left(E_{surf+nH} - (E_{surf} + \frac{n}{2} E_{H_2}) \right)$$

Free energy diagram



Equilibrium at standard conditions



$$\tilde{\mu}(H^+(aq)) + \tilde{\mu}(e^-) = \frac{1}{2}\mu(H_2(g)) - eU_{SHE} - k_B T \ln a_{H^+}$$

Change in electron number n between reactants and product considered via

$$\begin{aligned} \Delta G(\theta, U, a_{H^+}) &= \Delta G_g(\theta) - eU + \Delta E_{int} = \Delta E_{ads}(\theta) + \Delta E_{ZPE} - T\Delta S_{ads}(\theta) + \Delta E_{int} - neU - k_B T \ln a_{H^+} = \\ &\quad \Delta G_g(\theta) + neU \end{aligned}$$

Norskov, Fundamental Concepts in Heterogeneous Catalysis. Wiley

A. Gross Theory of solid/electrolyte interfaces P-k highlight of the month 2015; J.K. Norskov et al., J. Phys. Chem. B 108, 17886 (2004)

Hydrogen reaction and electrocatalysis

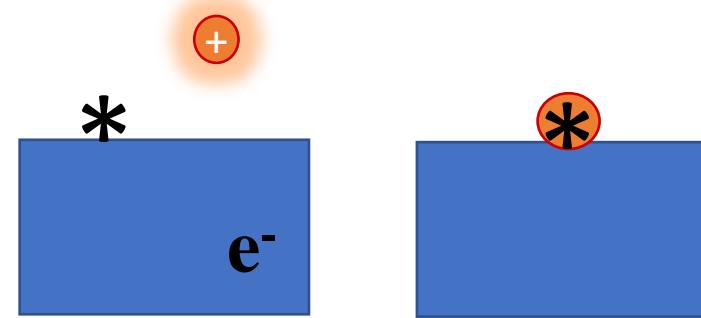
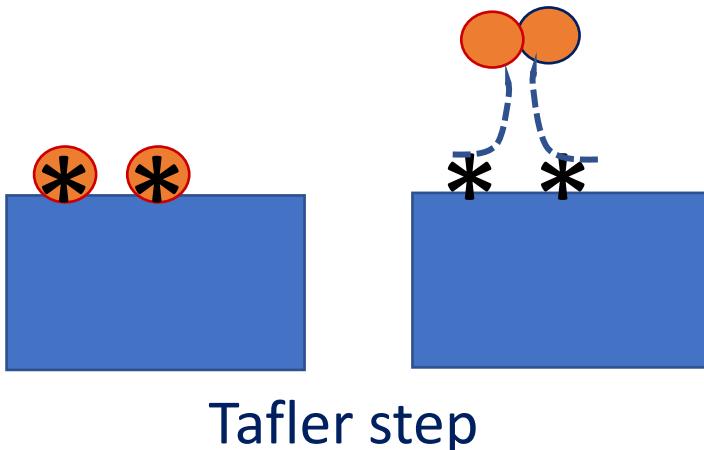
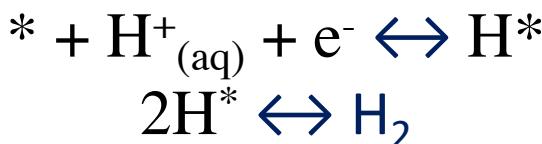
Reaction in acidic media



Reaction in alkaline media

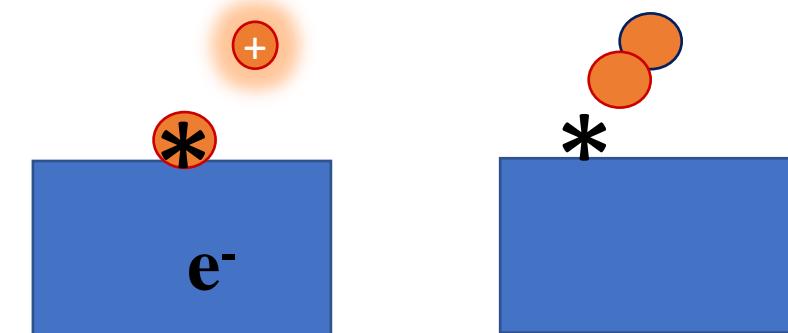
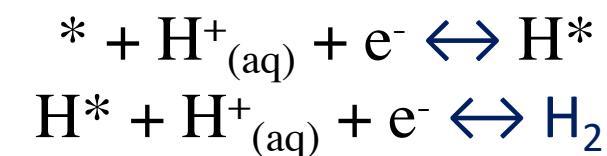


Volmer Tafler reaction



Volmer step

Volmer Heyrovsky reaction



Heyrovsky step

Volcano relation

- Experimental data differ
- qualitative understanding based on work function, presence of unfilled d orbitals, Volmer reaction is uphill
- High adsorption energy (high gain in energy)

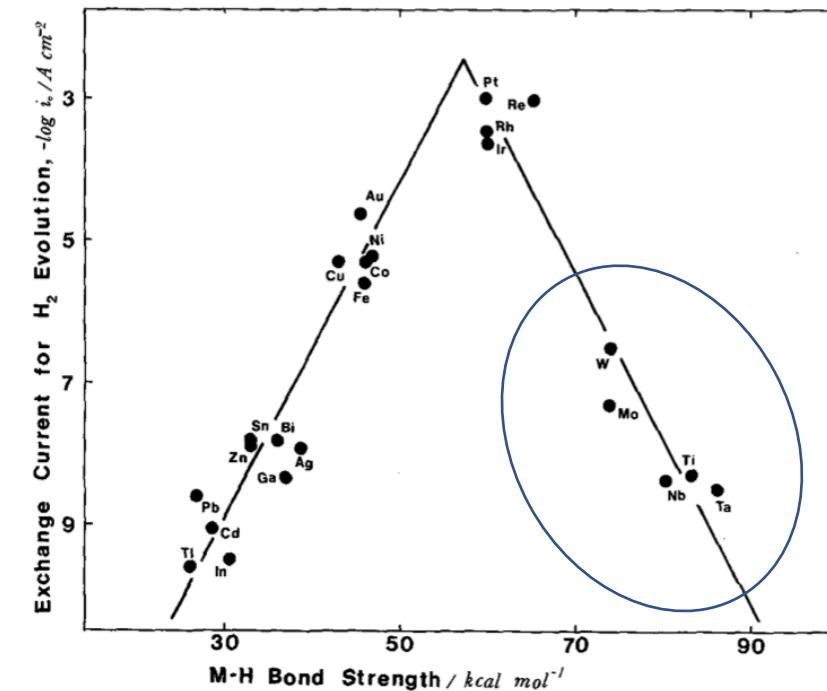


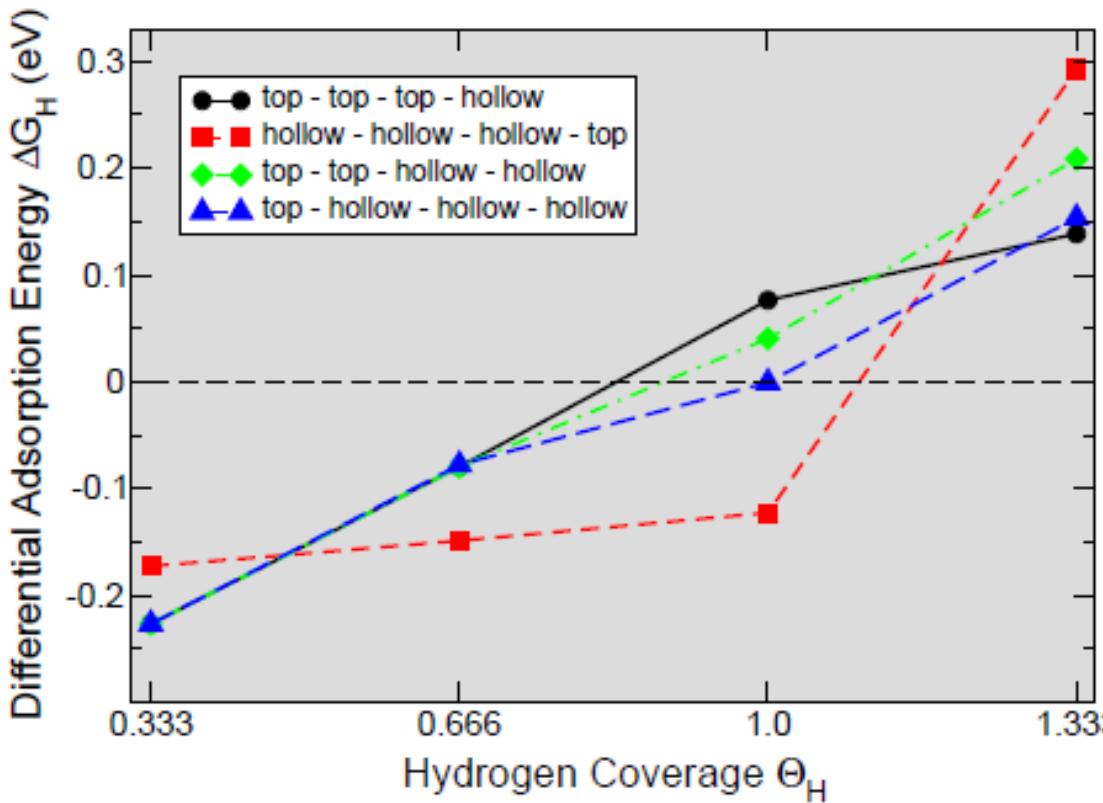
Fig. 3. Exchange currents for electrolytic hydrogen evolution vs. strength of intermediate metal-hydrogen bond formed during electrochemical reaction itself. $E(M-H)$ from Krishtalik²⁶.

Trasatti, J. Electroanal. Chem., 39 (1972)

Sabatier principle is valid: the interaction between the catalyst and the substrate should be neither too strong nor too weak

Coverage effects

Differential adsorption energies H/Pt(111)



Coverage of N adsorbates on N_0 sites:

$$\theta = N/N_0$$

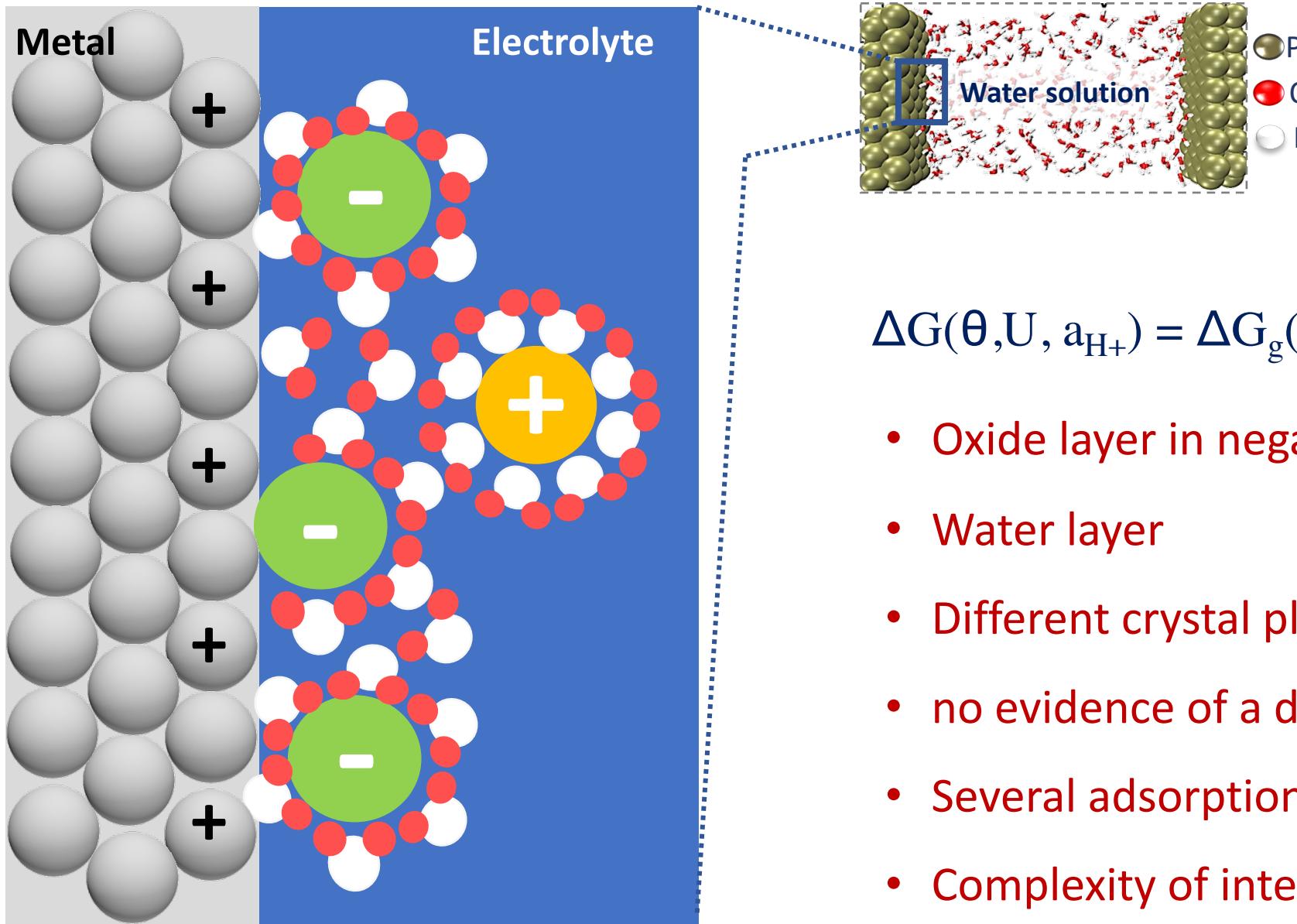
Average adsorption energy:

$$\Delta E_{av}(\theta) = \frac{E_{\text{surf.}+N*\text{ads.}} - E_{\text{surf.}} - N E_{\text{ads}}}{N}$$

Differential adsorption energy:

$$\Delta E_{diff}(\theta) = \frac{d(N \cdot \Delta E_{av})}{dN}$$

Possible issues with our model



$$\Delta G(\theta, U, a_{H+}) = \Delta G_g(\theta) - e(U=0) + \Delta E_{\text{interface}}$$

- Oxide layer in negative branch
- Water layer
- Different crystal planes
- no evidence of a decreasing branch
- Several adsorption states for H can compete
- Complexity of interactions at interfaces