Simulations in computational electrochemistry

Katharina Doblhoff-Dier| Han-sur-Lesse winterschool 2025

Universiteit Leiden
The Netherlands

Computational electrochemistry

1. Electrochemistry: The basics
2. Computational catalysis and computational electrocatalysis
3. Beyond the computational hydrogen electrode method
4. Modeling the electrochemical double layer
5. Mass transport

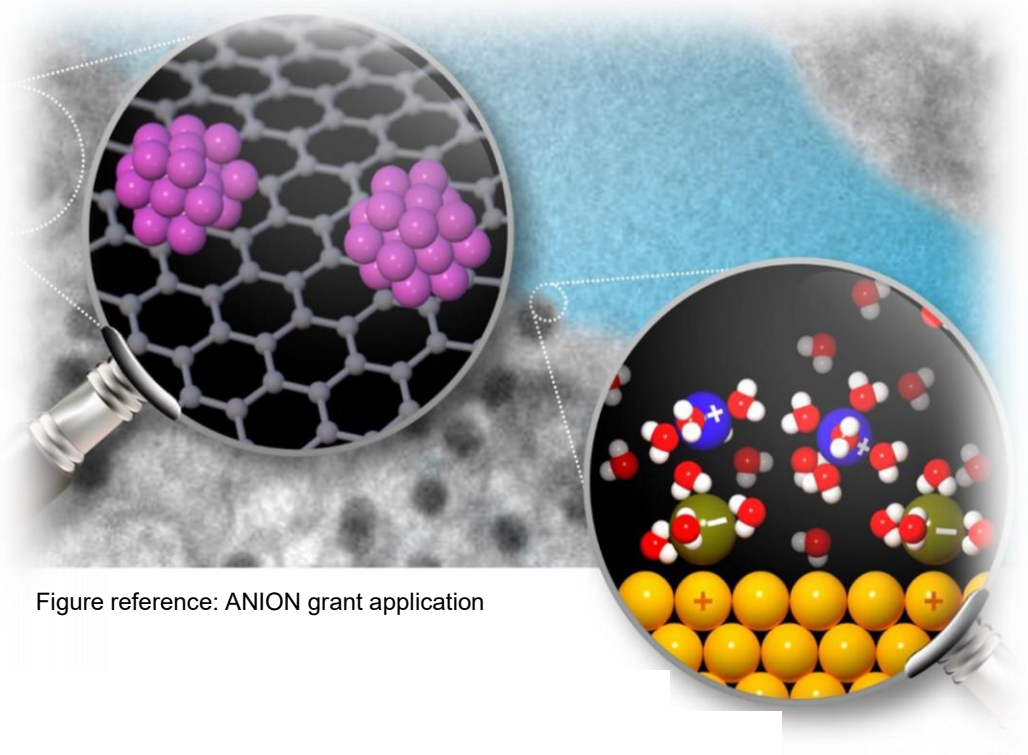

Figure reference: ANION grant application

Index

Part 1: The basics

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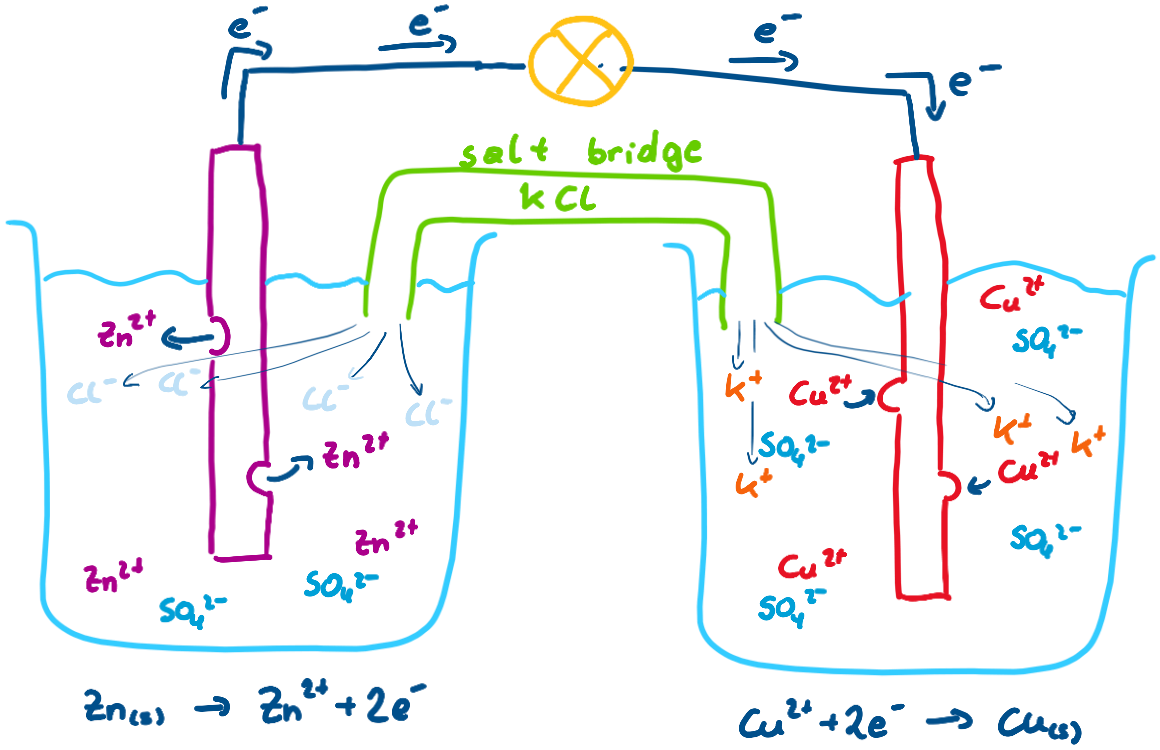
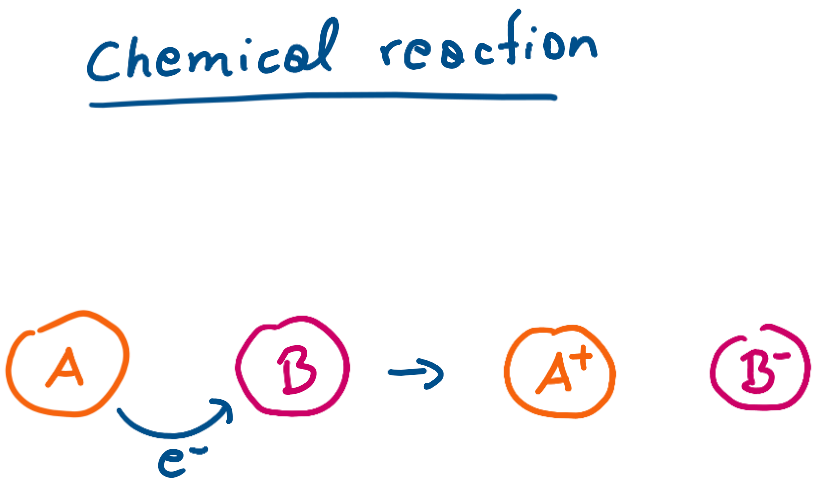
Computational electrochemistry

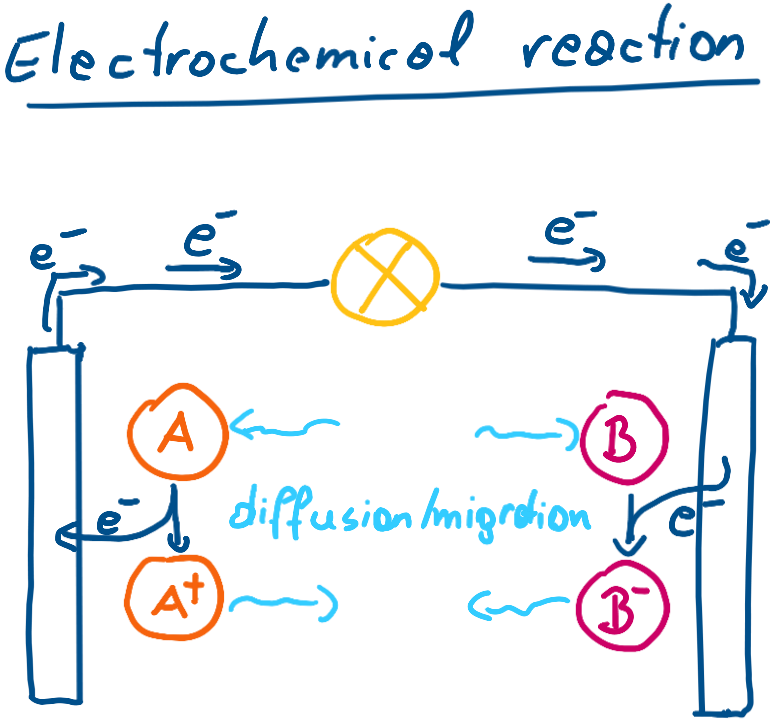
1. Electrochemistry: The basics
   - What is electrochemistry
   - (Half-)cell potentials
   - Reference potential
   - Computer exercise: Computing cell potentials/electrochemical stability windows
2. Computational catalysis and computational electrocatalysis
3. Beyond the computational hydrogen electrode method
4. When the electrolyte is key
5. Mass transport



Electrochemistry

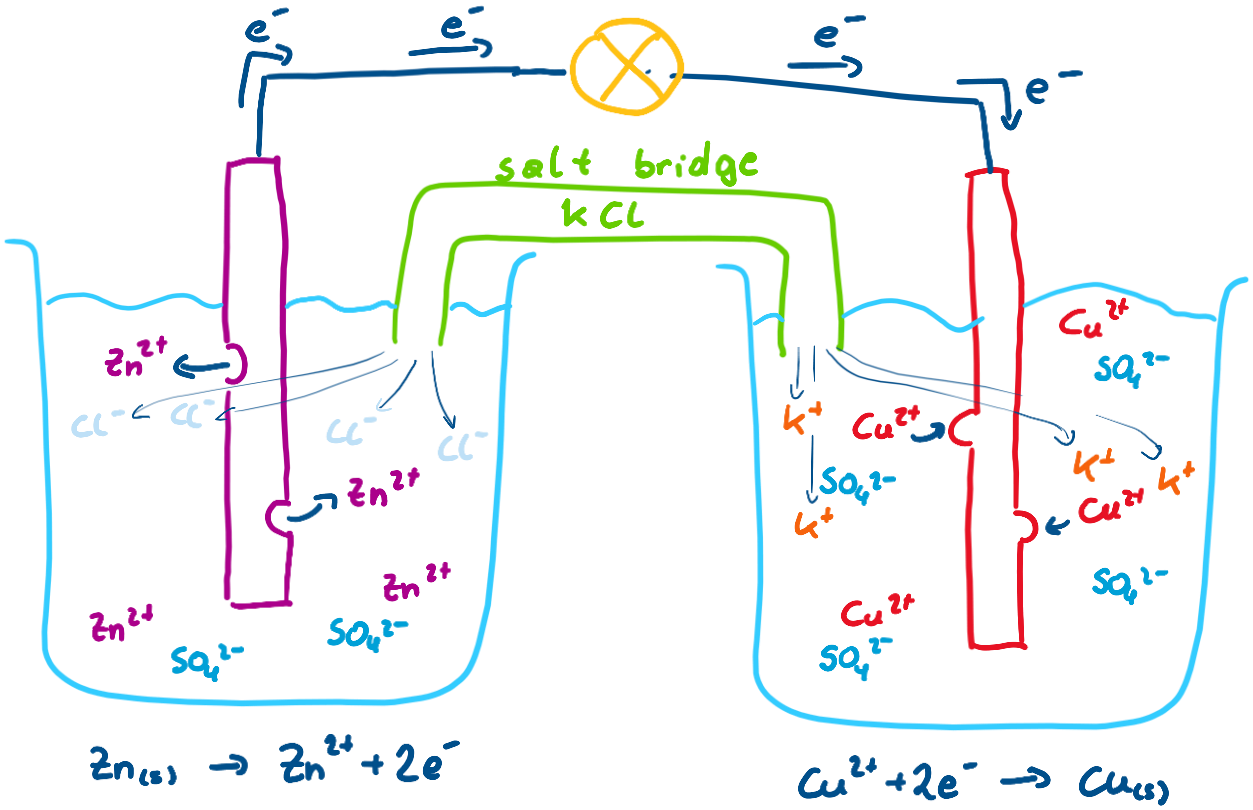
- Chemical reactions involving electrons that move via an electronically conducting phase between two electrodes that are separated by an electronically insulating (but ionically conducting) electrolyte.





Galvanic cell

Figure reference:CC-BY 3.0: Asim18;
https://commons.wikimedia.org/wiki/File:02_-_Single_Energizer_Battery.jpg

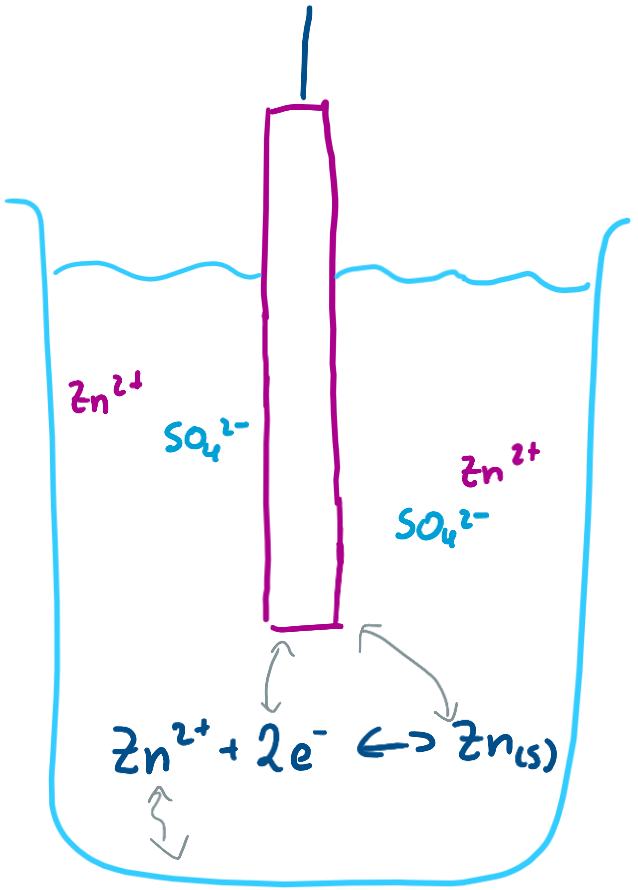


$Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$

$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

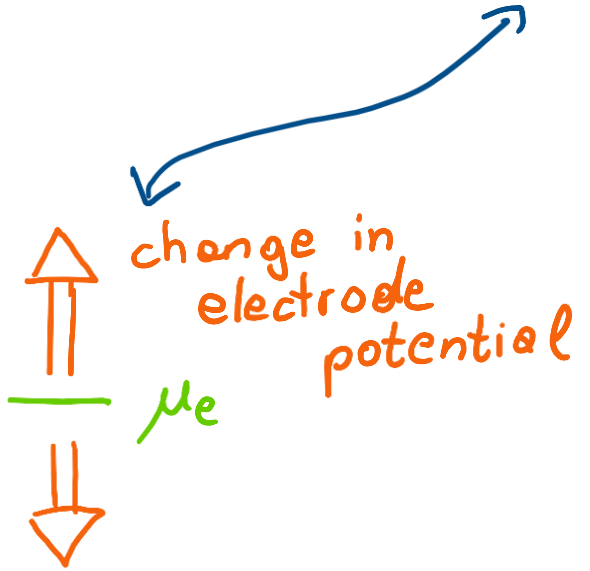
overall reaction: $Zn_{(s)} + Cu^{2+} \rightarrow Zn^{2+} + Cu_{(s)}$

Galvanic cell

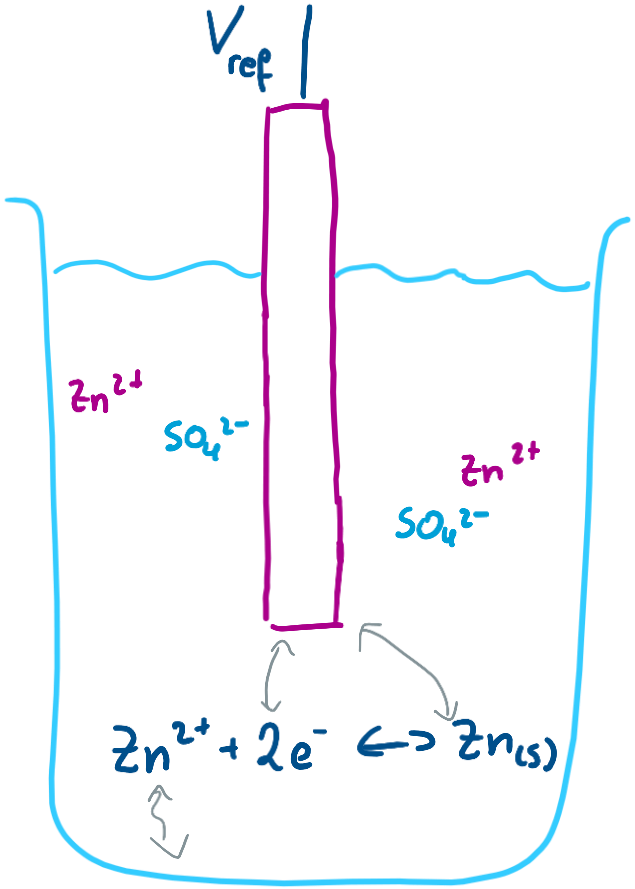


$$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$$

$$\Delta G_1 = G(Zn_{(s)}) - G(Zn^{2+}) - 2\mu_e$$



Galvanic cell



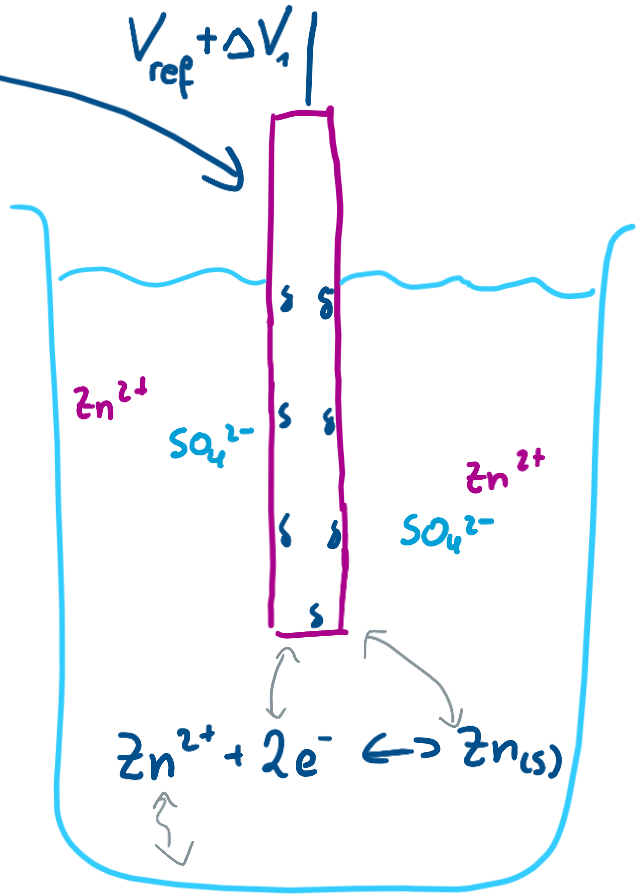
$@V^{ref}$:

$$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$$

$$\Delta G_1^{\mathrm{ref}} = G\left(Zn_{(s)}\right) - G(Zn^{2+}) - 2\mu_e^{ref}$$

Galvanic cell

Build-up of surface charge → potential change ΔV_1



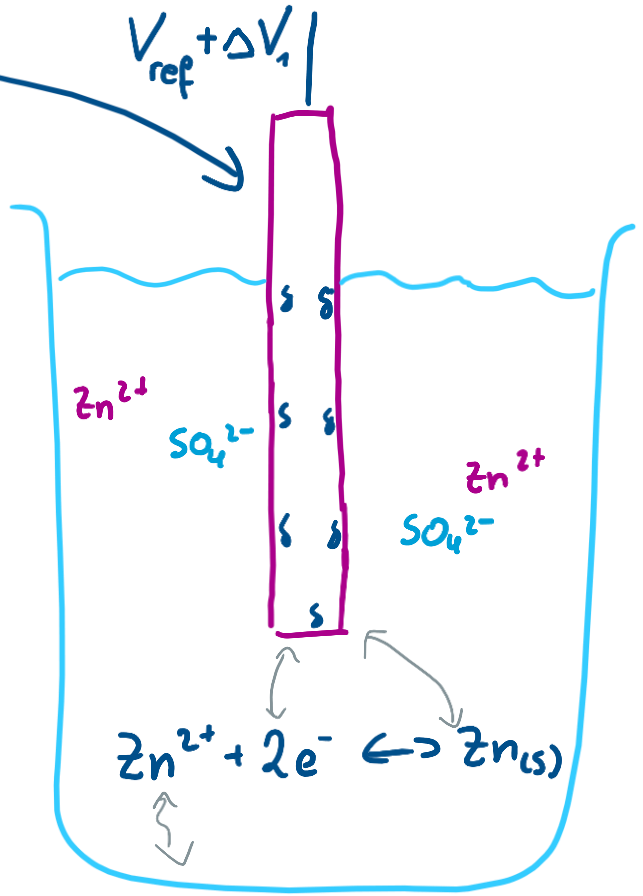
$$\mathrm{Zn}^{2+} + 2e^- \rightarrow \mathrm{Zn}_{(s)}$$

$@V^{ref}$: $\quad \Delta G_1^{\mathrm{ref}} = G(\mathrm{Zn}_{(s)}) - G(\mathrm{Zn}^{2+}) - 2\mu_e^{ref}$

$@V^{ref} + \Delta V_1$: $\quad \Delta G_1^{\mathrm{V_1}} = G(\mathrm{Zn}_{(s)}) - G(\mathrm{Zn}^{2+}) - 2\mu_e^{V_1}$

Galvanic cell

Build-up of surface charge → potential change ΔV_1



$$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$$

$@V^{ref}$: $\Delta G_1^{ref} = G(Zn_{(s)}) - G(Zn^{2+}) - 2\mu_e^{ref}$

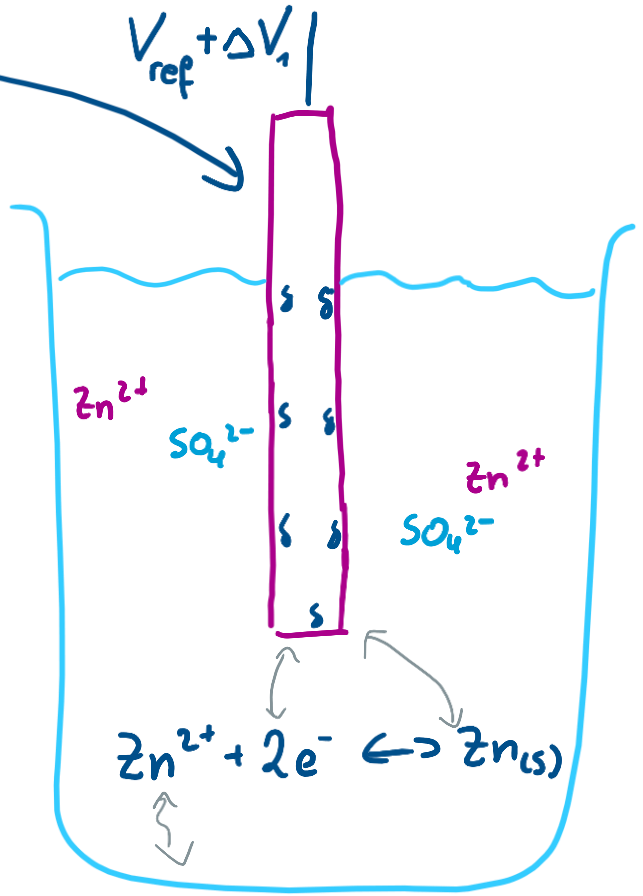
$@V^{ref} + \Delta V_1$: $\Delta G_1^{V_1} = G(Zn_{(s)}) - G(Zn^{2+}) - 2\mu_e^{V_1}$

$$\mu_e^{V_1} = \mu_e^{ref} - eN_A\Delta V_1$$

$$\Delta G_1^{V_1} = \Delta G_1^{ref} + 2eN_A\Delta V_1$$

Galvanic cell

Build-up of surface charge → potential change ΔV_1



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$@V^{ref}$: $\Delta G_1^{\mathrm{ref}} = G(Zn_{(s)}) - G(Zn^{2+}) - 2\mu_e^{ref}$

$@V^{ref} + \Delta V_1$: $\Delta G_1^{V_1} = G(Zn_{(s)}) - G(Zn^{2+}) - 2\mu_e^{V_1}$

$$\mu_e^{V_1} = \mu_e^{ref} - e N_A \Delta V_1$$

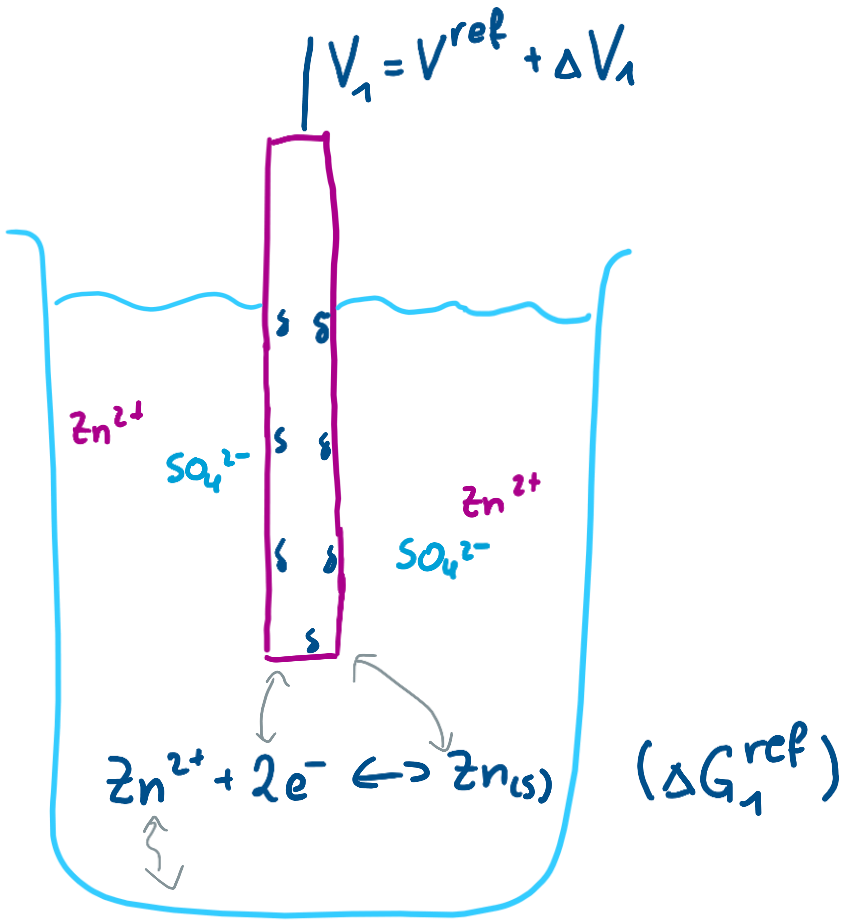
at equilibrium

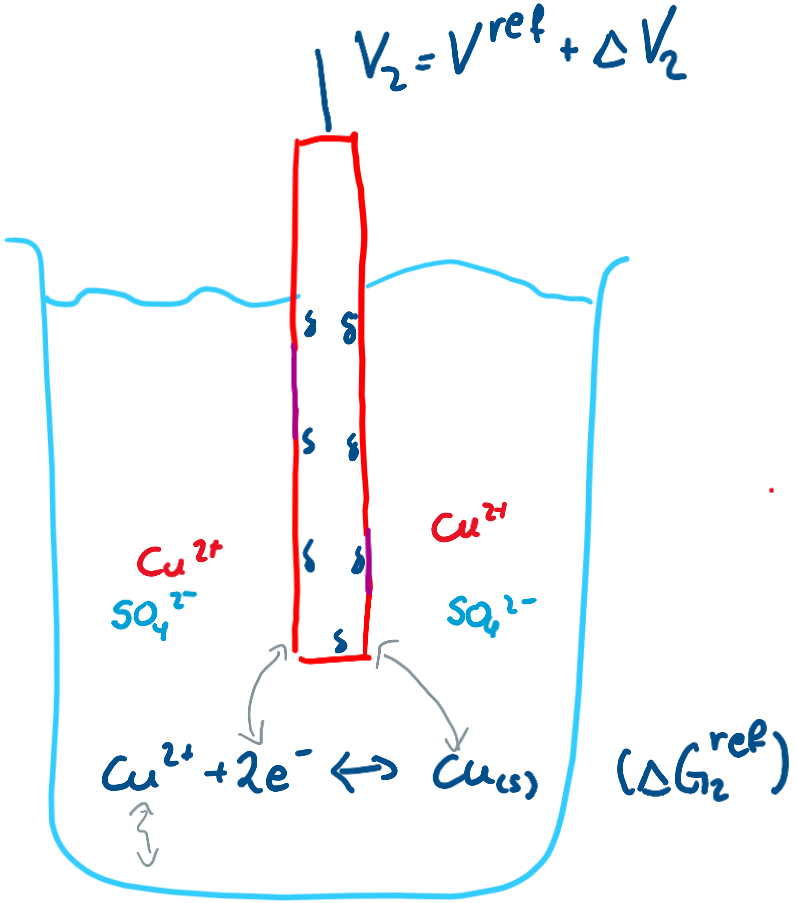
$$\Delta G_1^{V_1} = \Delta G_1^{ref} + 2 e N_A \Delta V_1 = 0$$

$$\Rightarrow \Delta G^{ref} = -2 e N_A (V - V_{ref})$$

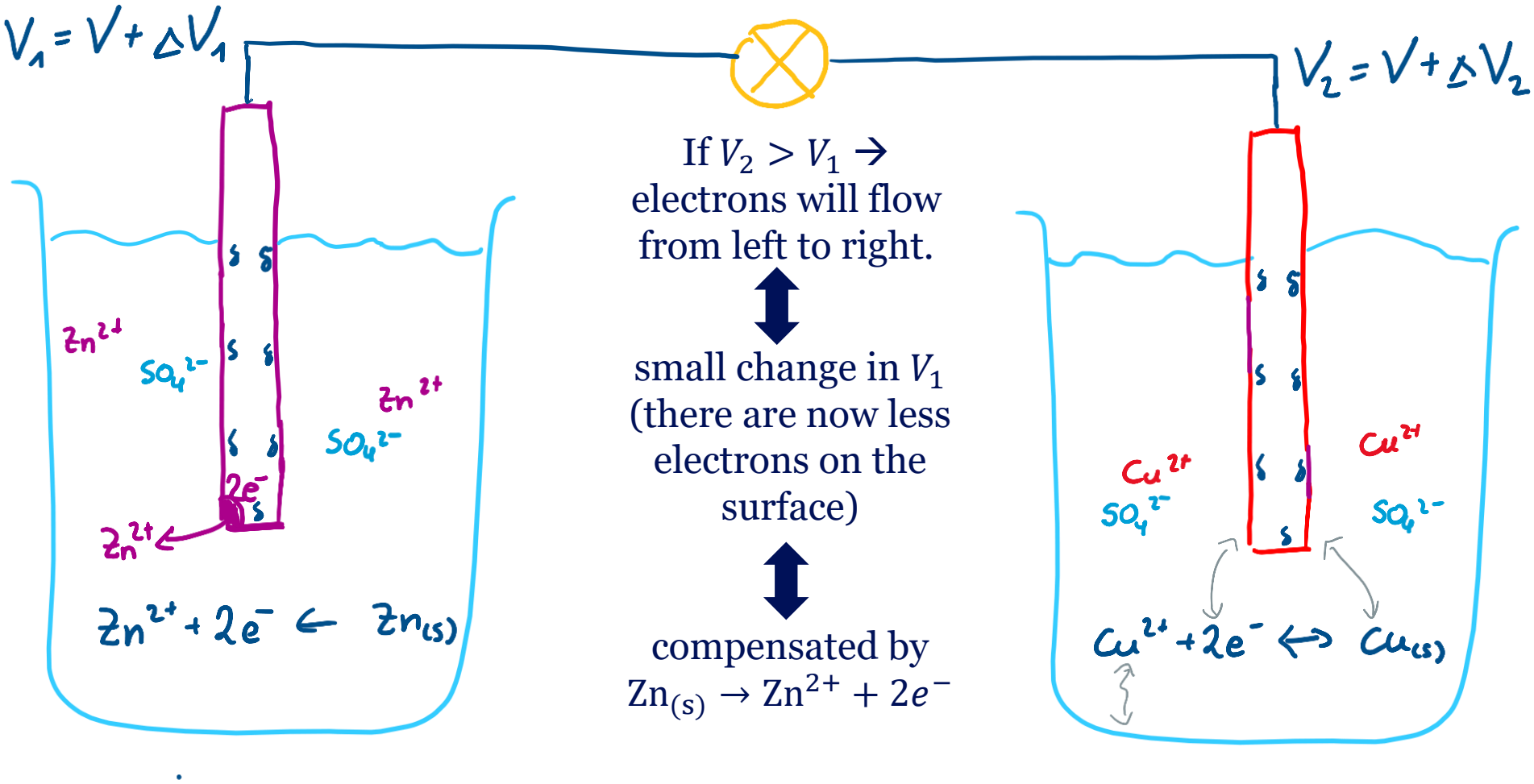
electrons

Galvanic cell





Galvanic cell



If $V_2 > V_1$ → electrons will flow from left to right.

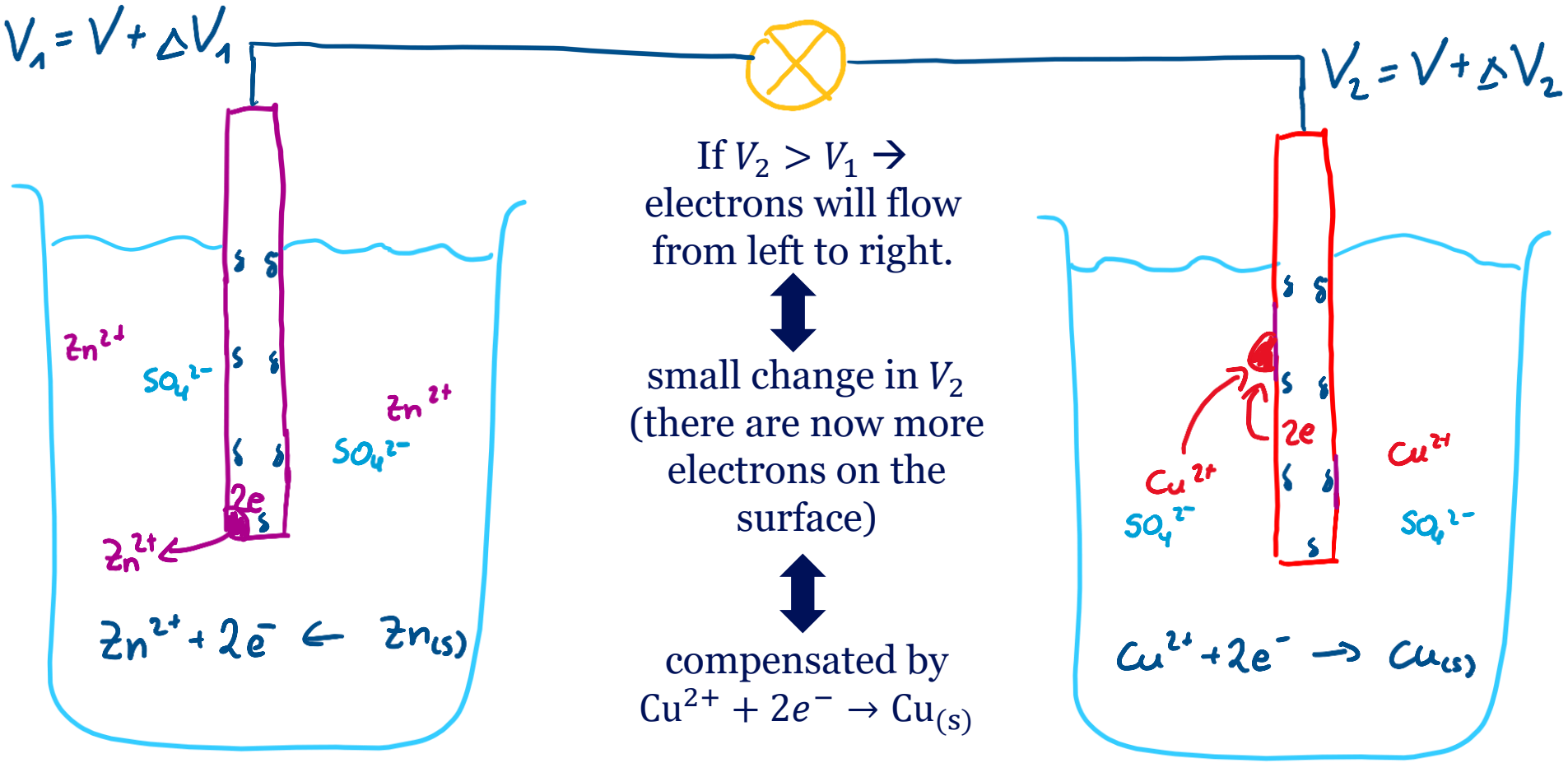
↕

small change in V_1 (there are now less electrons on the surface)

↕

compensated by $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$

Galvanic cell

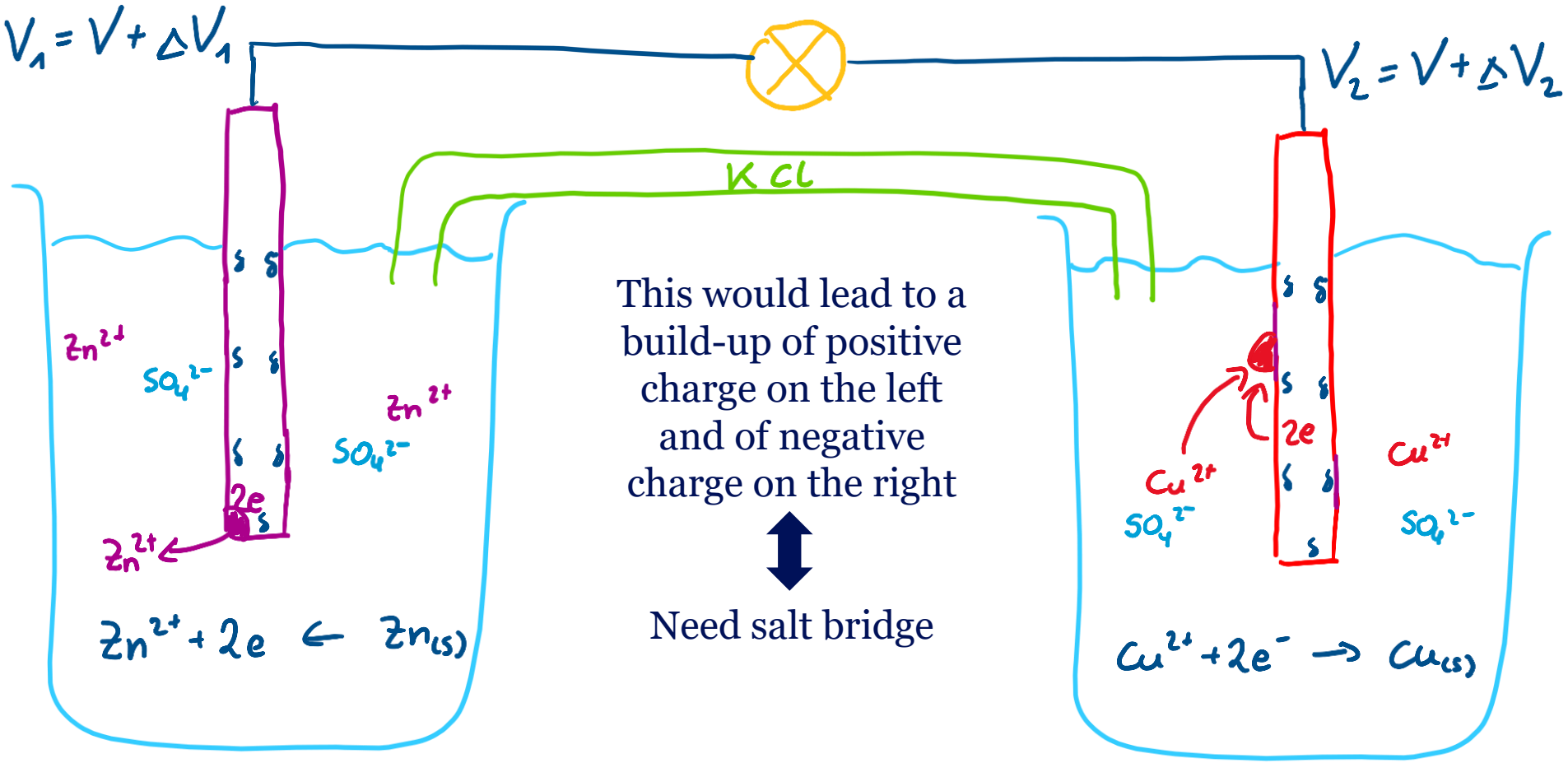


If $V_2 > V_1$ →
electrons will flow
from left to right.

small change in V_2
(there are now more
electrons on the
surface)

compensated by
$Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

Galvanic cell



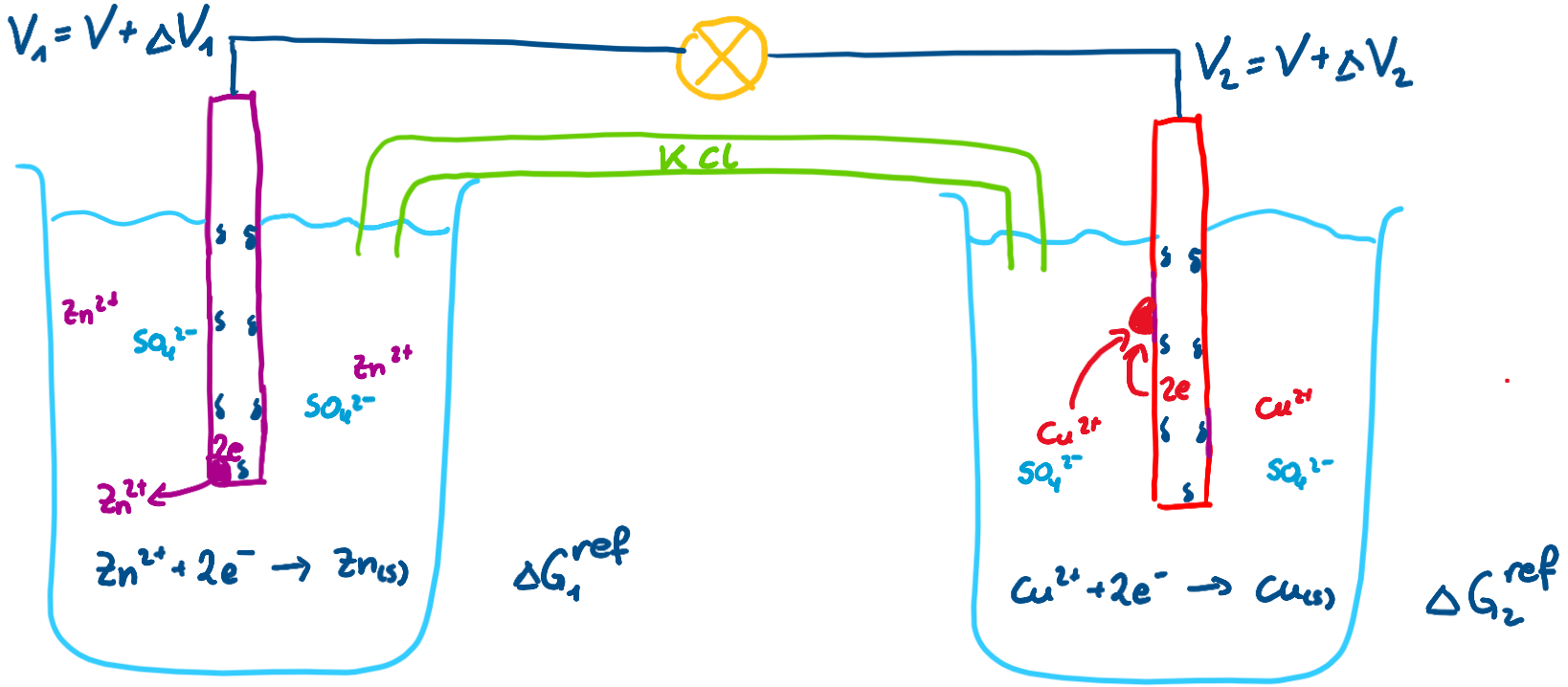
This would lead to a build-up of positive charge on the left and of negative charge on the right

↕

Need salt bridge

Galvanic cell

$$nN_A\underbrace{\Delta\mu_e}_{-e\Delta V_1} = \Delta G_1$$



Overall reaction:

$$R_2 - R_1 = \mathrm{Cu}^{2+} + \mathrm{Zn}_{(s)} \rightarrow \mathrm{Cu}_{(s)} + \mathrm{Zn}^{2+}$$

$$\Delta G = \Delta G_2 - \Delta G_1$$

$$E_0 = V_2 - V_1 = (V_2 - V^{ref}) - (V_1 - V^{ref}) = -\frac{1}{neN_A}\left(\Delta G_2^{ref} - \Delta G_1^{ref}\right) = -\frac{1}{neN_A}\Delta G$$

Galvanic cell

$$nF\Delta V = -\Delta G$$

- Standard reduction potentials $E°$:
  - Measured against the standard hydrogen electrode:

$$2H^+ + 2e \rightarrow H_2$$

$$\text{at } p(H_2) = 1 \text{ bar and } pH = 0$$

  - Tabulated:

$$Cu^{2+} + 2\,e^- \rightarrow Cu_{(s)} \qquad E° = \quad 0.337 \text{ V vs. SHE}$$
$$Zn^{2+} + 2\,e^- \rightarrow Zn_{(s)} \qquad E° = -0.762 \text{ V vs. SHE}$$

  - Cell voltage:

$$\Delta V = 0.337 - (-0.762) = 1.099 \text{ V}$$

Use $\Delta V = -\frac{\Delta G}{nF}$ to understand use of e-chem.

- Example $CO_2 \rightarrow CO + \frac{1}{2}O_2$

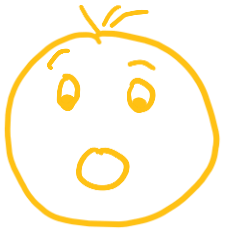
$$\Delta G^\circ = \Delta G_f^\circ(CO) + \frac{1}{2}\Delta G_f^\circ(O_2) - \Delta G_f^\circ(CO_2) = 2.67 \text{ eV}$$

endothermic !

- Changing CO_2 pressure to make this exothermic

$$\Delta G = \Delta G^\circ - k_B T \ln\left(\frac{p_{CO_2}}{p_0}\right)$$

$$\Delta G = 0 \text{ if } p_{CO_2} \approx 10^{46} \text{ atm}$$



Use $\Delta V = -\frac{\Delta G}{nF}$ to understand use of e-chem.

- Example $CO_2 \rightarrow CO + \frac{1}{2}O_2$

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$$\Delta G = 0 \text{ if } p_{CO_2} \approx 10^{46} \text{ atm}$$

- Using an electrochemical cell:
  - $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$
  - $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

$$\Delta V = -1.34\ V$$

Figure reference:CC-BY 3.0: Asim18;
https://commons.wikimedia.org/wiki/File:02_-_Single_Energizer_Battery.jpg

Understanding ΔV

$$nF\Delta V = -\Delta G$$

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  - Measured against the standard hydrogen electrode:

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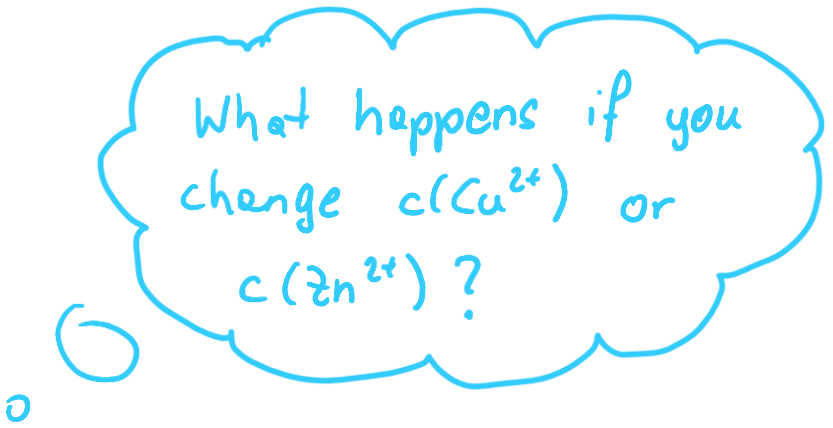
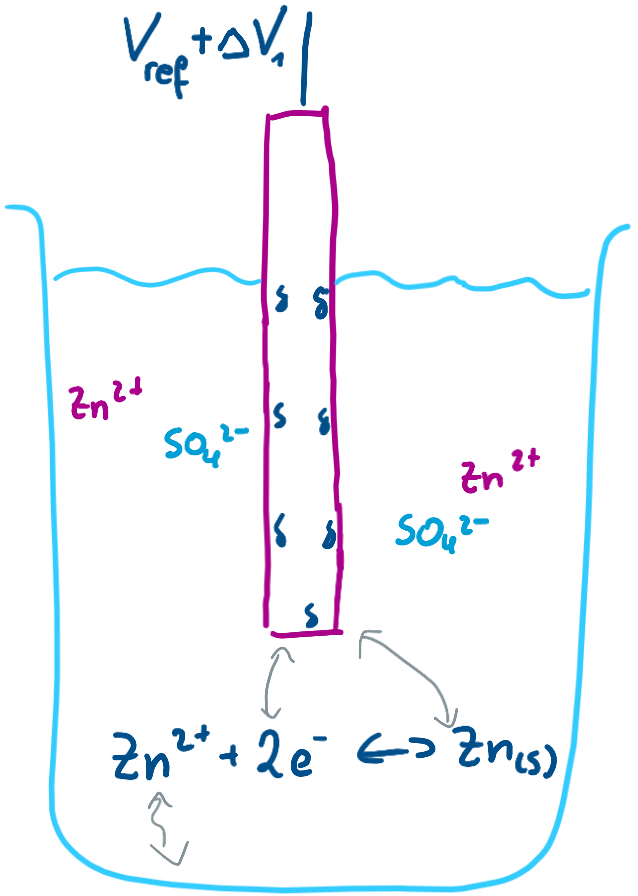


Galvanic cell



changes by $RT\ln\left(\frac{c}{c_0}\right)$

$$Zn^{2+} + 2e^- \rightarrow Zn_{(s)}$$

$$@V^{ref}: \quad \Delta G_1^{ref} = G(Zn_{(s)}) - G(Zn^{2+}) - 2\mu_e^{ref}$$

$$@V^{ref} + \Delta V_1: \quad \Delta G_1^{V_1} = G(Zn_{(s)}) - G(Zn^{2+}) - 2\mu_e^{V_1}$$

half-cell potential:

$$\Delta G^{ref} = -2\,e\,N_A(V - V_{ref})$$

2: # electrons; $(V - V_{ref})$: E

$\Downarrow$

changes!

cell potential ΔV changes!

Take-home messages

Half-cell:

- ΔG requires reference potential!
- A prototypical reference potential is the standard hydrogen electrode (SHE)
  - SHE potential ≙ equilibrium potential for

$$H^+ + e^- \rightarrow \frac{1}{2} H_2 \qquad @\ pH = 0 \text{ and } 1 \text{ bar}$$

Full cell:

- Overall ΔG depends on
  - Reactants
  - Products
  - But not electrons!
- … and determines cell potential ΔV

Reference electrodes

- SHE potential ≙ equilibrium potential for

$$H^+ + e^- \rightarrow \frac{1}{2}H_2 \qquad @\ pH = 0 \text{ and } 1 \text{ bar}$$

- RHE potential ≙ equilibrium potential for

$$H^+ + e^- \rightarrow \frac{1}{2}H_2 \qquad @\ \text{arbitrary pH and } 1 \text{ bar}$$

Electrolysis cell

Turning the working principle around to drive a reaction

- Galvanic cell:

$$Cu^{2+} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}$$

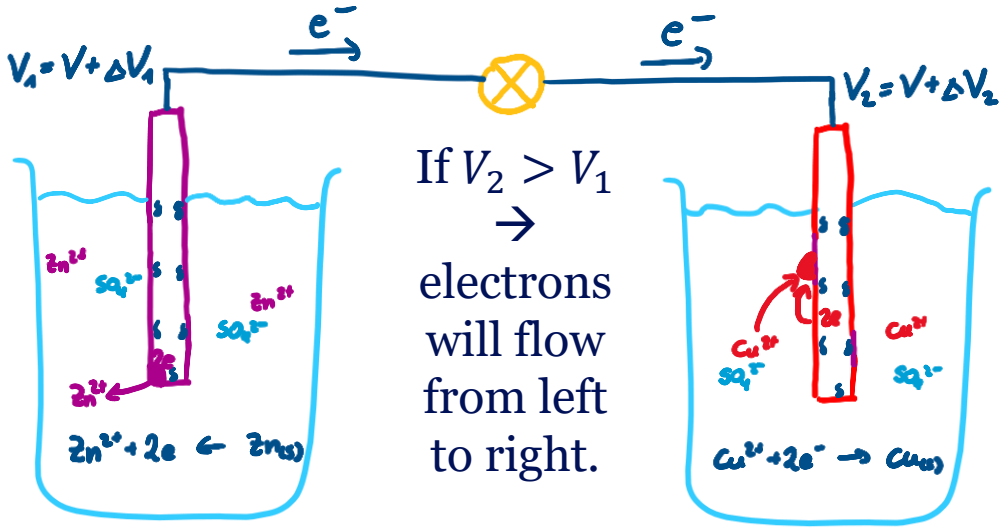
(Cu^{2+} is reduced, $Zn_{(s)}$ is oxidized)

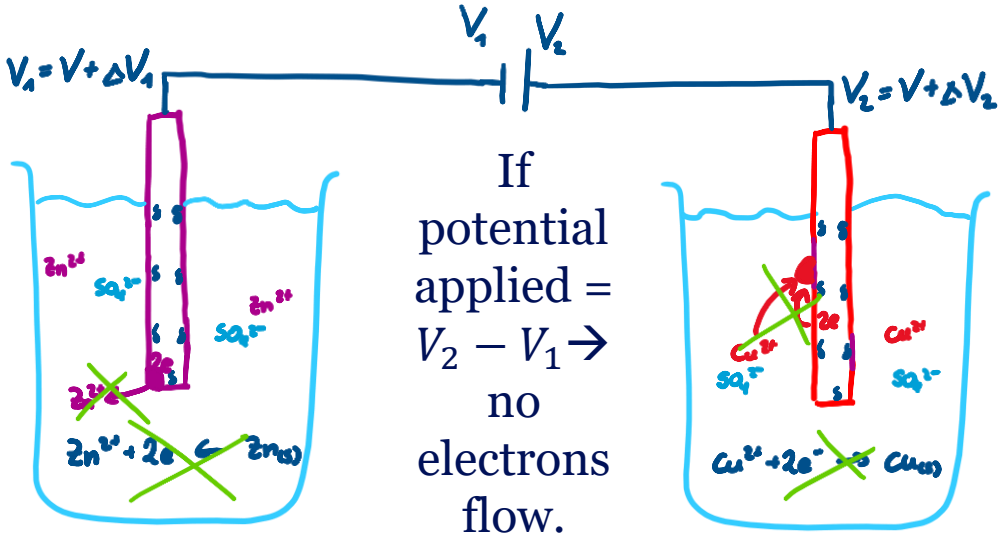
$$\Delta V = 1.099\ \text{V}$$

- Electrolysis cell:

Apply $\Delta V \geq 1.099V$

$$Cu_{(s)} + Zn^{2+} \rightarrow Cu^{2+} + Zn_{(s)}$$





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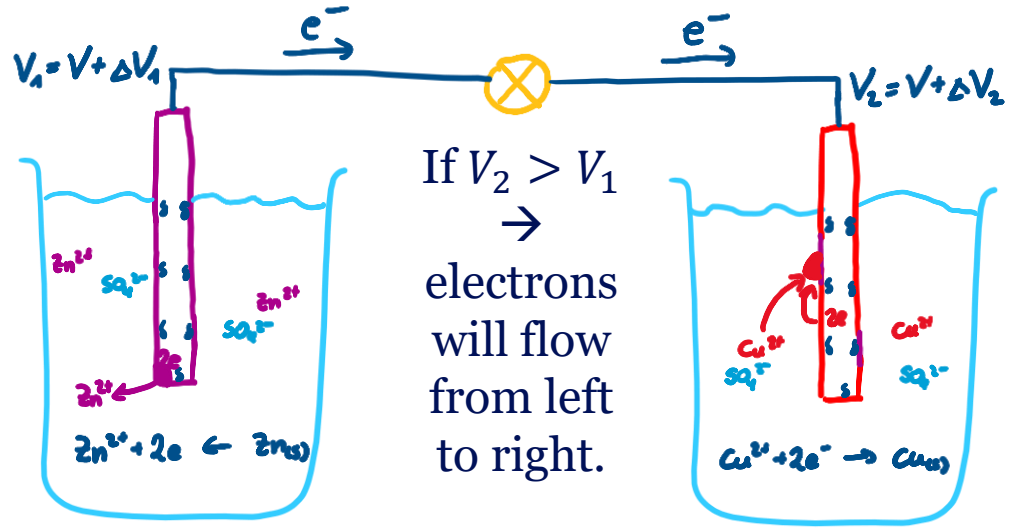
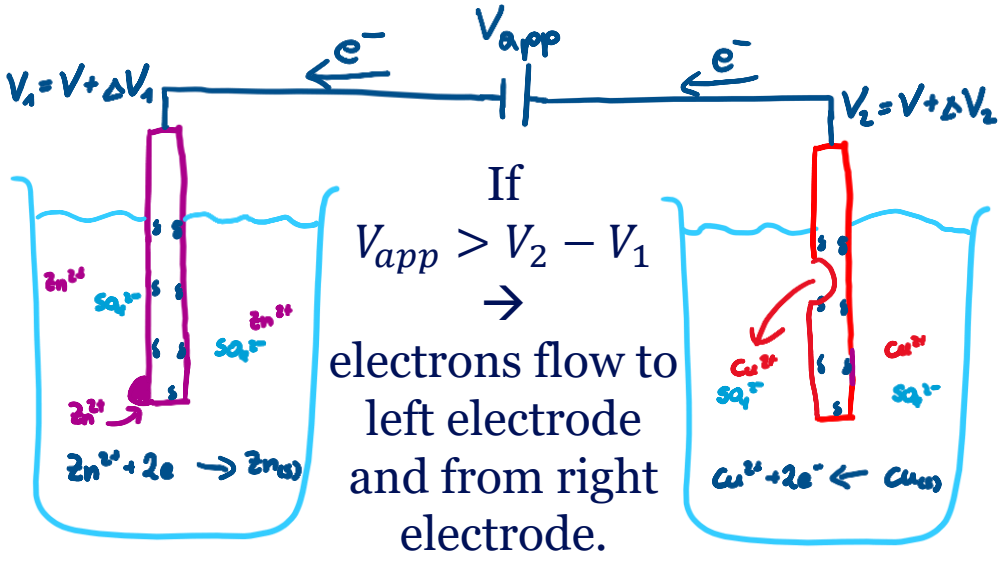
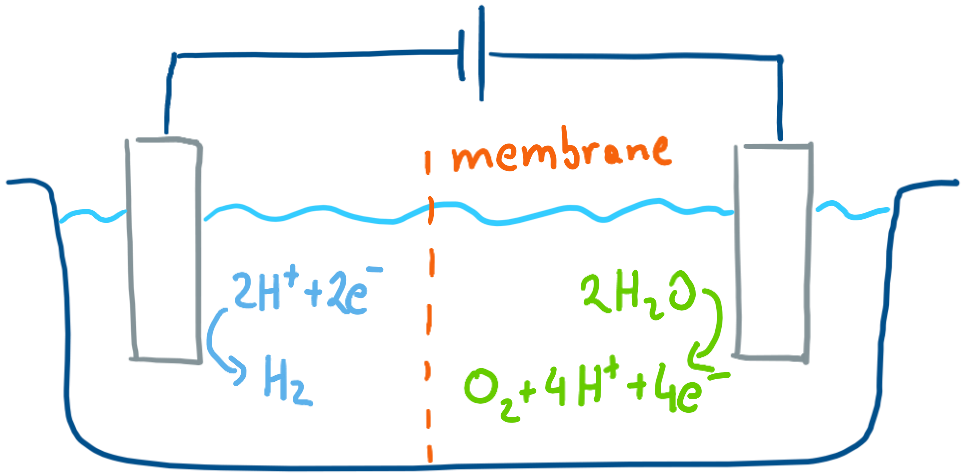


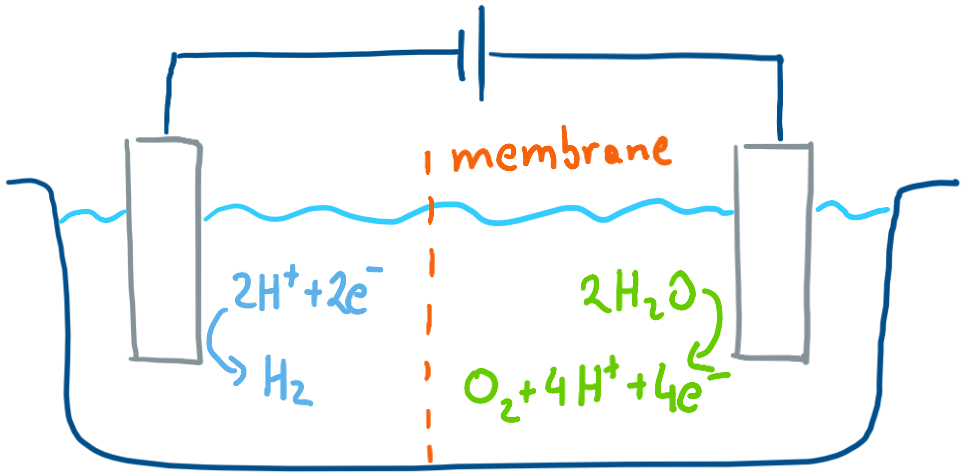


Water electrolysis



- Why?
  - Green hydrogen as fuel
  - Green hydrogen as reducing agent (e.g, steel production)
- What is green/gray/pink hydrogen?
  - Gray: from natural gas through steam reforming
  - Pink hydrogen: water electrolysis + nuclear power
  - Green hydrogen: water electrolysis + renewable energy source

Water electrolysis – test yourself



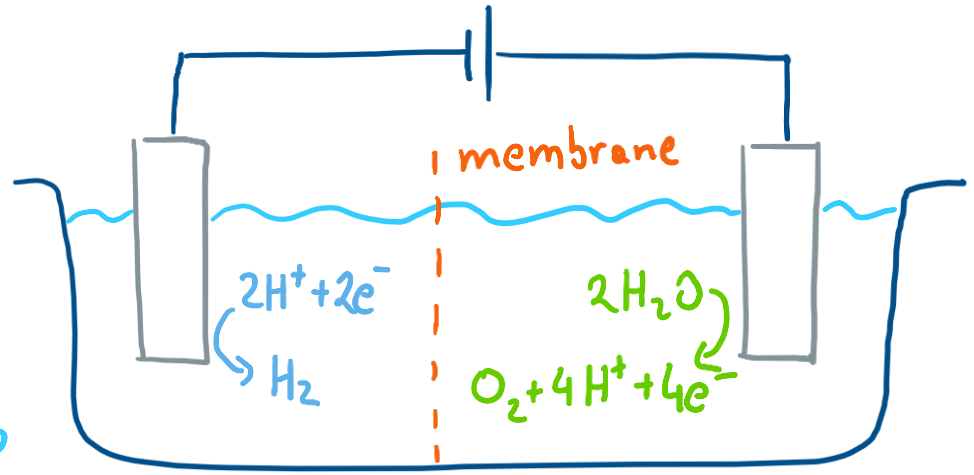
What potential is needed to drive this reaction?

Wikipedia:

O	$O_2(g) + 4H^+ + 4e^-$	⇌	$2H_2O$	1.229	4	[7]
H	$2H^+ + 2e^-$	⇌	$H_2(g)$	0	2	

Water electrolysis – test yourself

Will this potential depend on pH?



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H	$2H^+ + 2e^-$	⇌	$H_2(g)$	0	2	

Water electrolysis – test yourself

- Acidic:
  - $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$
  - $2H^+ + 2e^- \rightarrow H_2$

Overall: $H_2O \rightarrow H_2 + O_2$

- Alkaline
  - $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^-$
  - $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall: $H_2O \rightarrow H_2 + O_2$

Water electrolysis – test yourself

- Acidic:
  - $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$
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  - $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall: $H_2O \rightarrow H_2 + O_2$

Same cell potential, but differing half-cell potentials!
The half-cell potentials (vs. SHE) DO depend on pH!

In practice: Effective cell potentials will differ, but see later…

Water electrolysis – test yourself

- Acidic:
  - $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$
  - $2H^+ + 2e^- \rightarrow H_2$

Overall: $H_2O \rightarrow H_2 + O_2$

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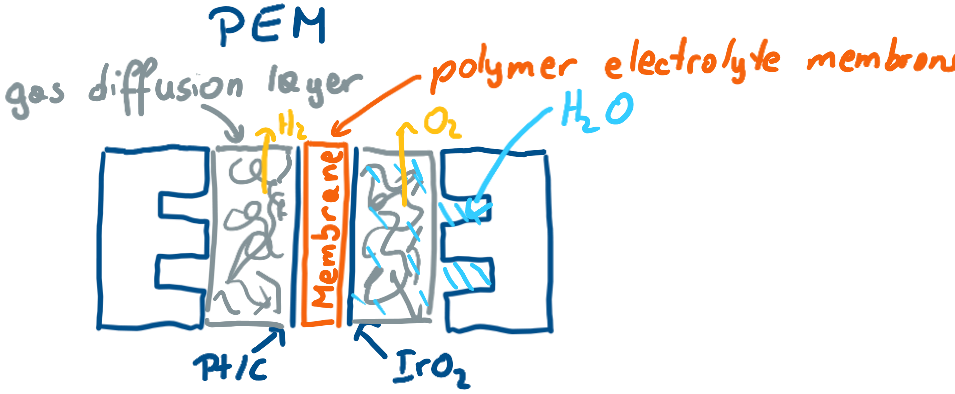
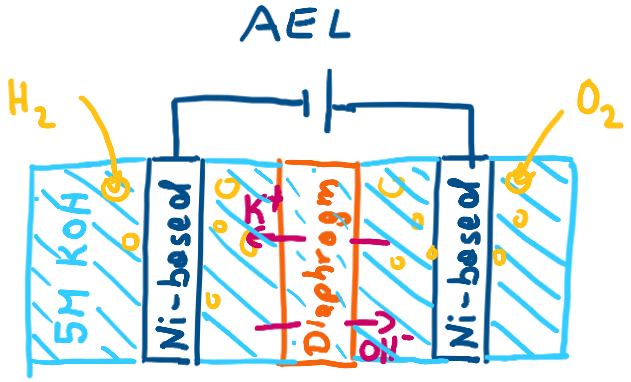




Same cell potential, but differing half-cell potentials!
The half-cell potentials DO depend on pH!

In practice: Effective cell potentials will differ, but see later…

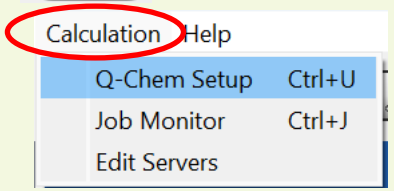
Water electrolysis – computational exercise

- Compute cell potential using DFT:
- water electrolysis
  - Functionals: PBE, M06-2X
  - Basis set: def2-TZVPPD

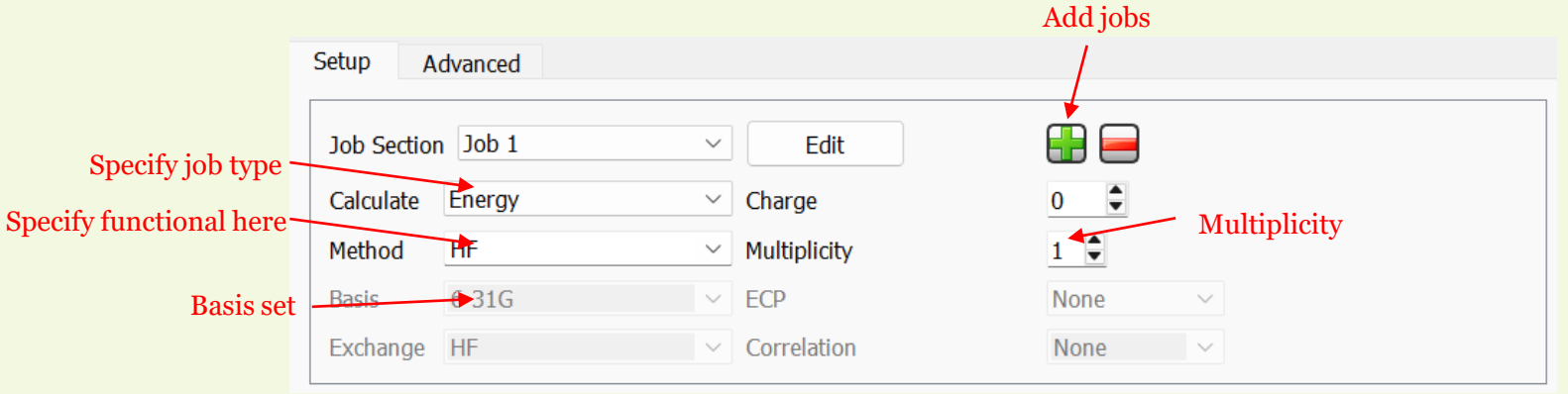
- Iqmol instructions
  - Draw your molecule using the hammer and atom selection: (press for a molecule, drag for a bond)

  - Preoptimize at FF level:

  - Set up the calculation:



  - Specify calculation(s)



  - Submit and download results into a directory

Gas phase corrections for DFT errors in molecules

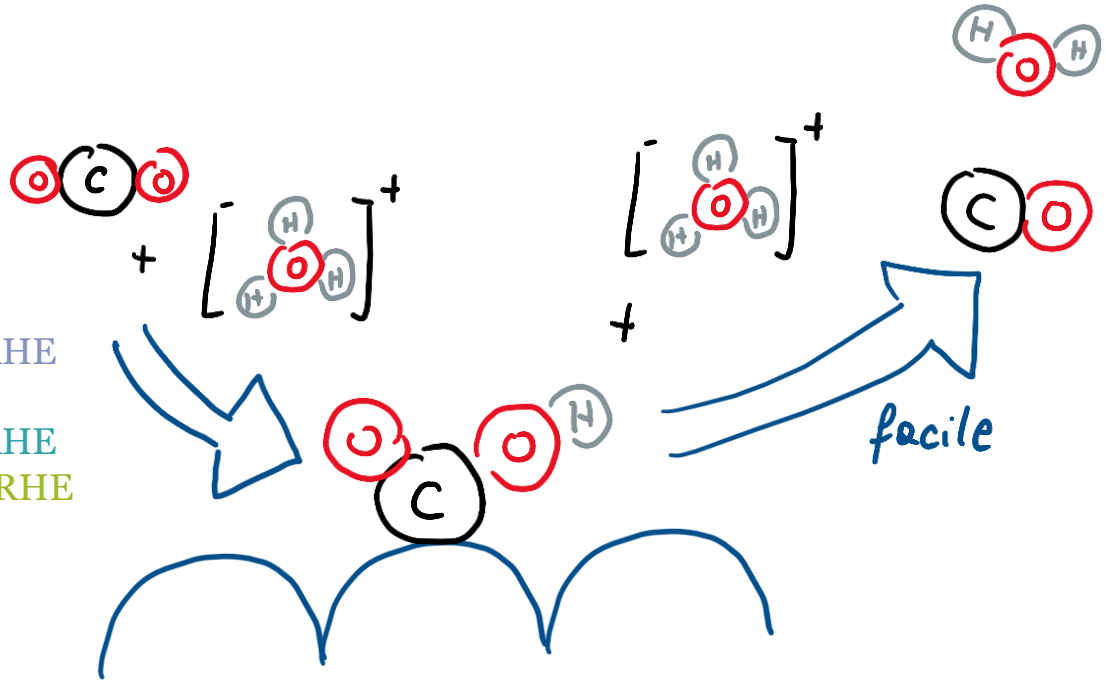
Table 1 DFT errors of molecules and functional groups containing C, N, O, and H, see also Fig. 1c

Molecule or functional group	PBE	PW91	RPBE	BEEF-vdW
O_2 [a]	−0.46	−0.33	−0.74	−0.81
N_2	0.34	0.38	−0.05	−0.32
CO_2 [b]	−0.19	−0.15	−0.46	−0.56
CO [b]	0.24	0.25	−0.07	−0.18
H_2O_2 [c]	−0.26	−0.23	−0.29	−0.34
NO [d]	−0.07	0.05	−0.41	−0.58
NO_2 [d]	−0.80	−0.66	−1.12	−1.27
NO_3 [d]	−1.41	−1.26	−1.72	−1.92
N_2O [d]	−0.50	−0.41	−0.86	−1.10
HNO [d]	−0.05	−0.01	−0.30	−0.43
HNO_2 [d]	−0.54	−0.48	−0.78	−0.95
HNO_3 [d]	−0.96	−0.87	−1.14	−1.35
$NO_{2(aq)}^-$ [de]	−0.54	−0.48	−0.78	−0.95
$NO_{3(aq)}^-$ [de]	−0.96	−0.87	−1.14	−1.35
cis-N_2O_2 [d]	−0.71	−0.55	−1.25	−1.59
N_2O_3 [d]	−1.19	−1.06	−1.66	−2.04

Calle-Vallejo and co-workers, EES Catal., 2024, 2, 157

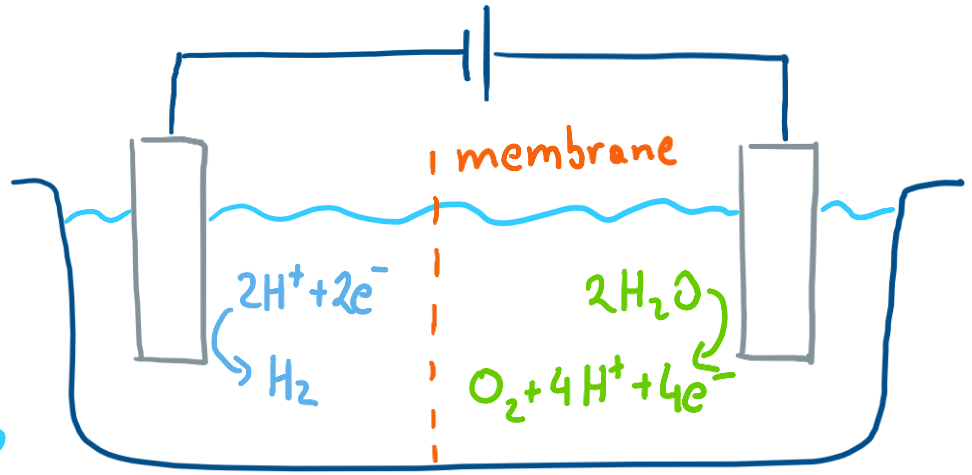
- Similar in spirit to using the cell potential instead of computing O_2 (see later)
- Assumption:
  - Gas phase molecule more affected than adsorbed molecules

$\Delta G^{PBE} = 0.9$ eV
$V_{onset}^{PBE} = -0.9$ V vs. RHE
$\Delta G^{corr} = 0.7$ eV
$V_{onset}^{corr} = -0.7$ V vs. RHE
$V_{onset}^{exp} = -0.66$ V vs. RHE



Water electrolysis – test yourself

Will this potential depend on pH?



What potential is needed to drive this reaction?

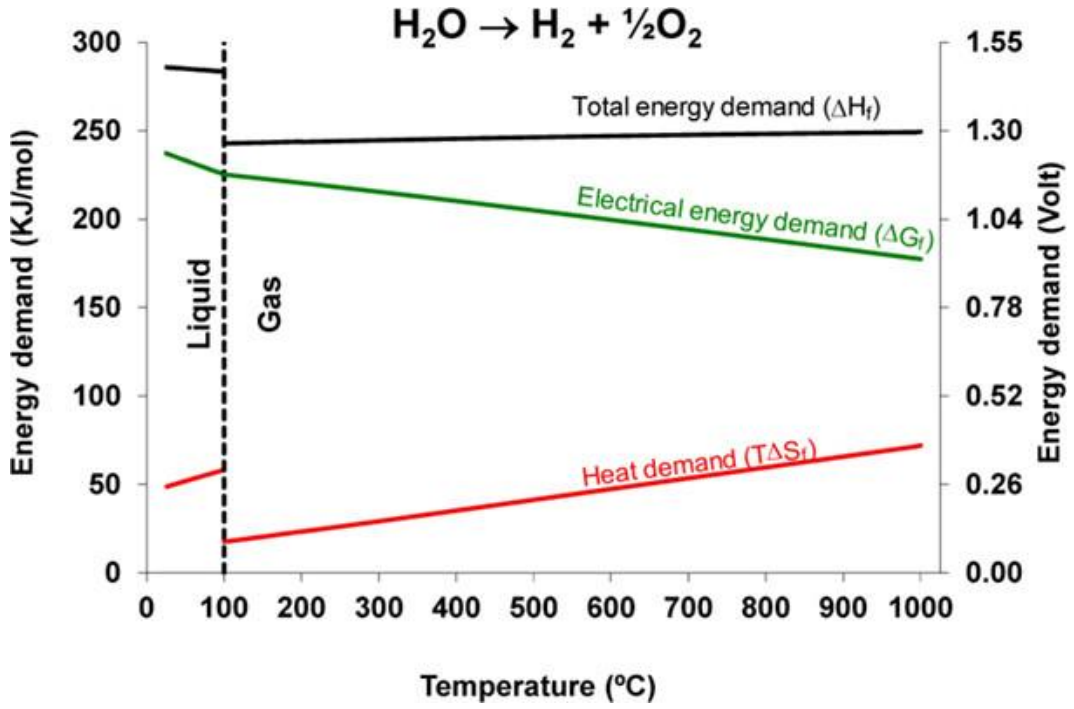
Will this potential depend on temperature?

Wikipedia:

O	$O_2(g) + 4H^+ + 4e^-$	⇌	$2H_2O$	1.229	4	[7]
H	$2H^+ + 2e^-$	⇌	$H_2(g)$	**0**	**2**	

Water electrolysis at higher temperature

$G = H - TS$



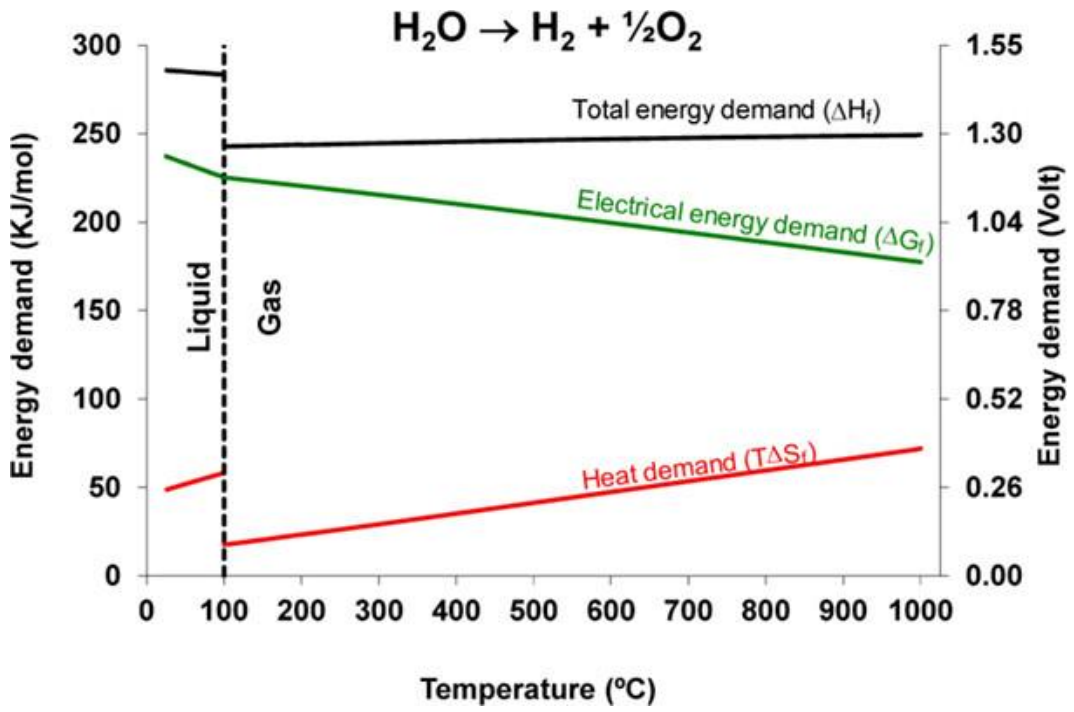
Mueller et al., *Chemie Ingenieur Technik*, 96: 143-166 (2024). https://doi.org/10.1002/cite.202300137

- Thermodynamic corrections in standard DFT codes are based on ideal gas

  - $\Delta H_{trans} = \frac{5}{2} RT$
  - $\Delta H_{rot} = \frac{3}{2} RT$ (nonlinear) or RT (linear molecules)
  - ΔH_{vib} from harmonic oscillator

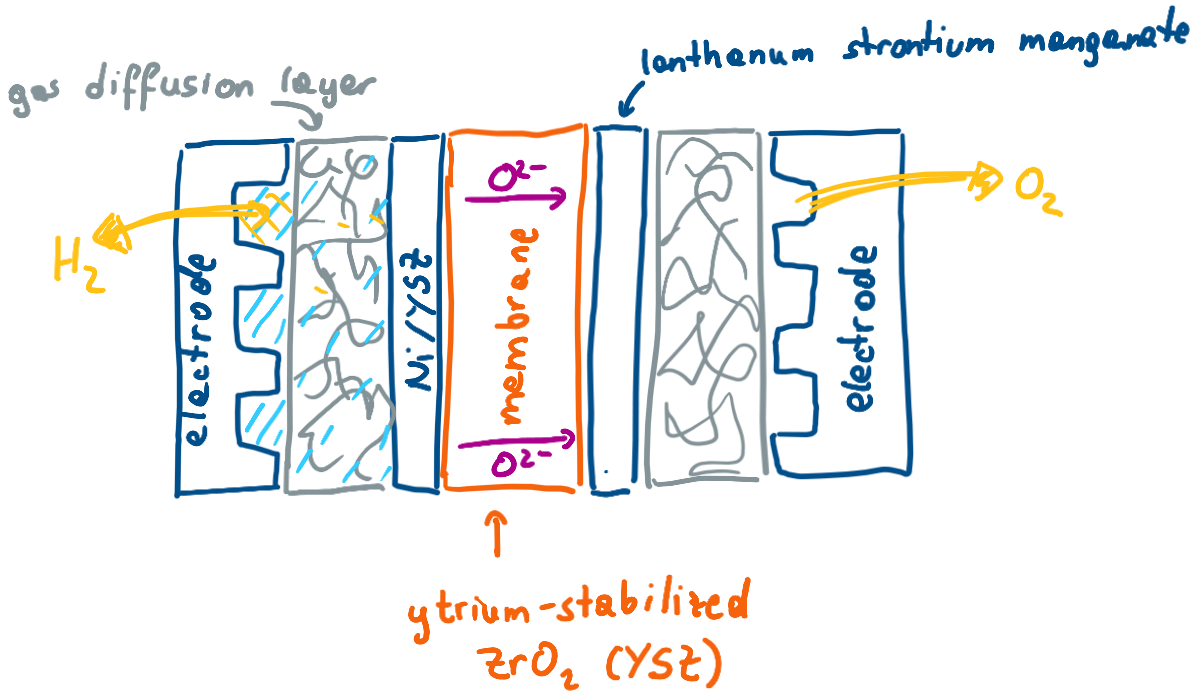
  - $\Delta S_{trans} = k_B \left\{ \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{\frac{3}{2}} \frac{k_B T}{P^\circ} \right] + \frac{5}{2} \right\}$
  - $\Delta S_{rot} = \begin{cases} 0 & \text{if monoatomic} \\ k_B \left[\ln \left(\frac{8\pi^2 I \, k_B T}{\sigma h^2} \right) + 1 \right] & \text{if linear} \\ \text{complicated expression} & \text{otherwise} \end{cases}$
  - ΔS_{vib} from harmonic oscillator

Water electrolysis at higher temperature



Mueller et al., *Chemie Ingenieur Technik*, 96: 143-166 (2024). https://doi.org/10.1002/cite.202300137

- Exploited in solid oxide electrolyzer cells
  - $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$
  - $H_2O + 2e^- \rightarrow H_2 + O^{2-}$



Take home messages

DFT can be used to compute ΔG, but

- Don't forget thermodynamic corrections
- May be erroneous for (certain) (gas phase) species
- Is not particularly suitable to compute energies of (ionic) solution phase species

Part 2: Computational catalysis and electrocatalysis

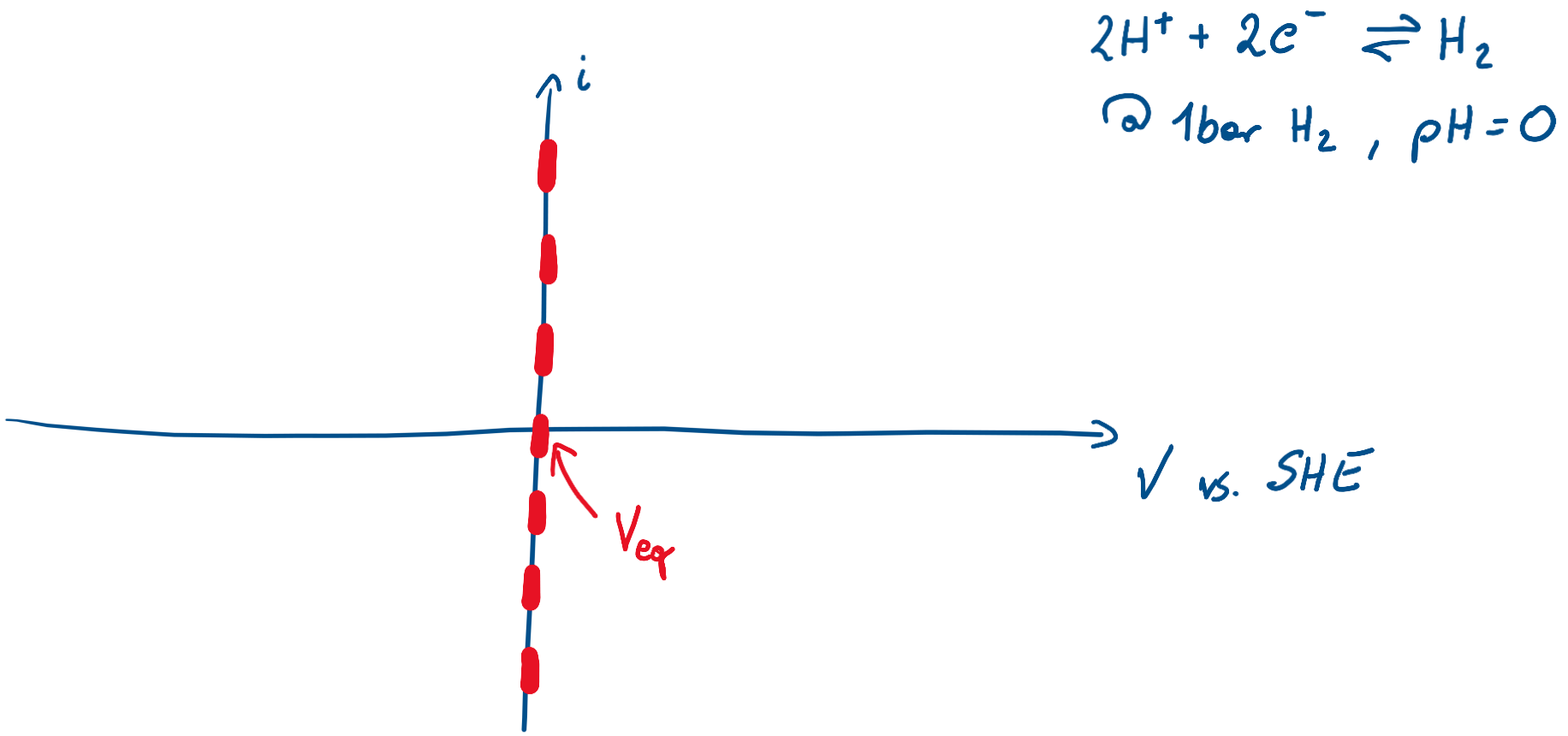
Katharina Doblhoff-Dier| Han-sur-Lesse winterschool 2025

Universiteit Leiden
The Netherlands

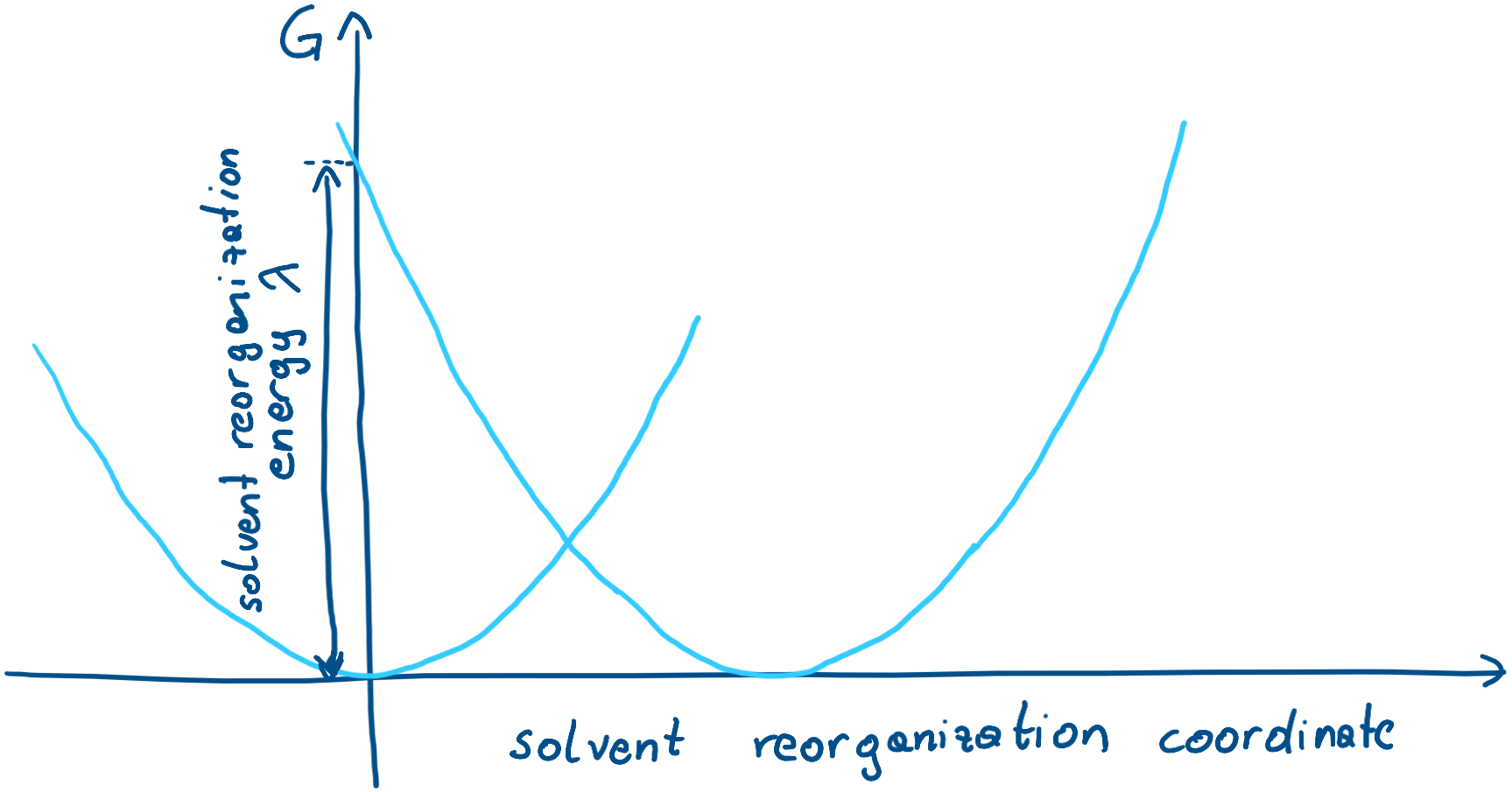
Computational electrochemistry

1. Electrochemistry: The basics
2. **Computational catalysis and computational electrocatalysis**
   - Onset potential
   - Adsorption energies and limiting potential in multi-step reactions
   - Computer exercise: H adsorption on Pt
   - Computational hydrogen electrode method to compute reaction energies for electrochemical reactions
   - Computer exercise: Hydrogen underpotential deposition on Pt
   - Principles of catalysis: Brønsted-Evans-Polanyi relations, Sabatier principle and scaling relations
3. Beyond the computational hydrogen electrode method
4. When the electrolyte is key
5. Mass transport

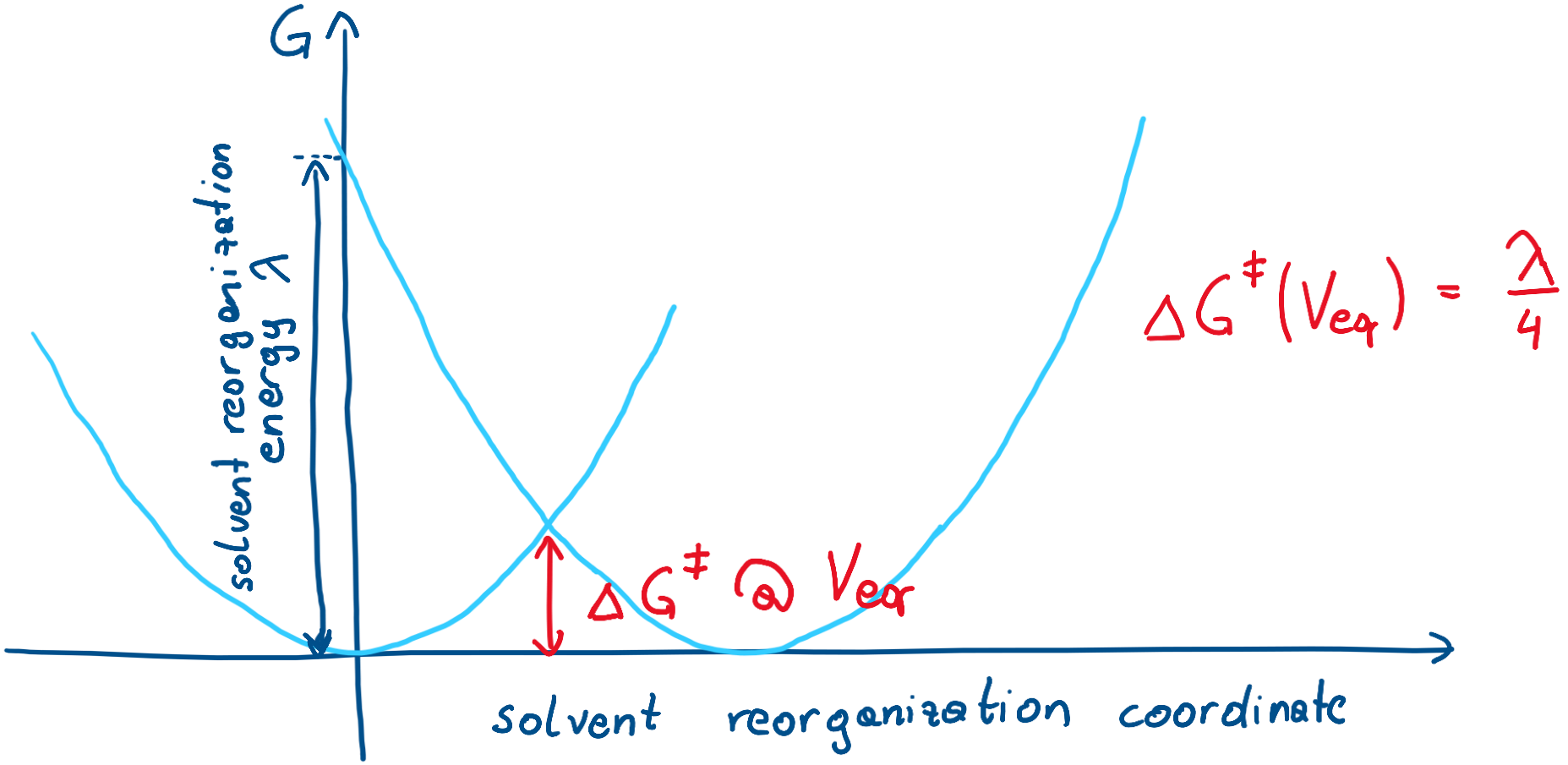
Nominal potential vs. onset potential



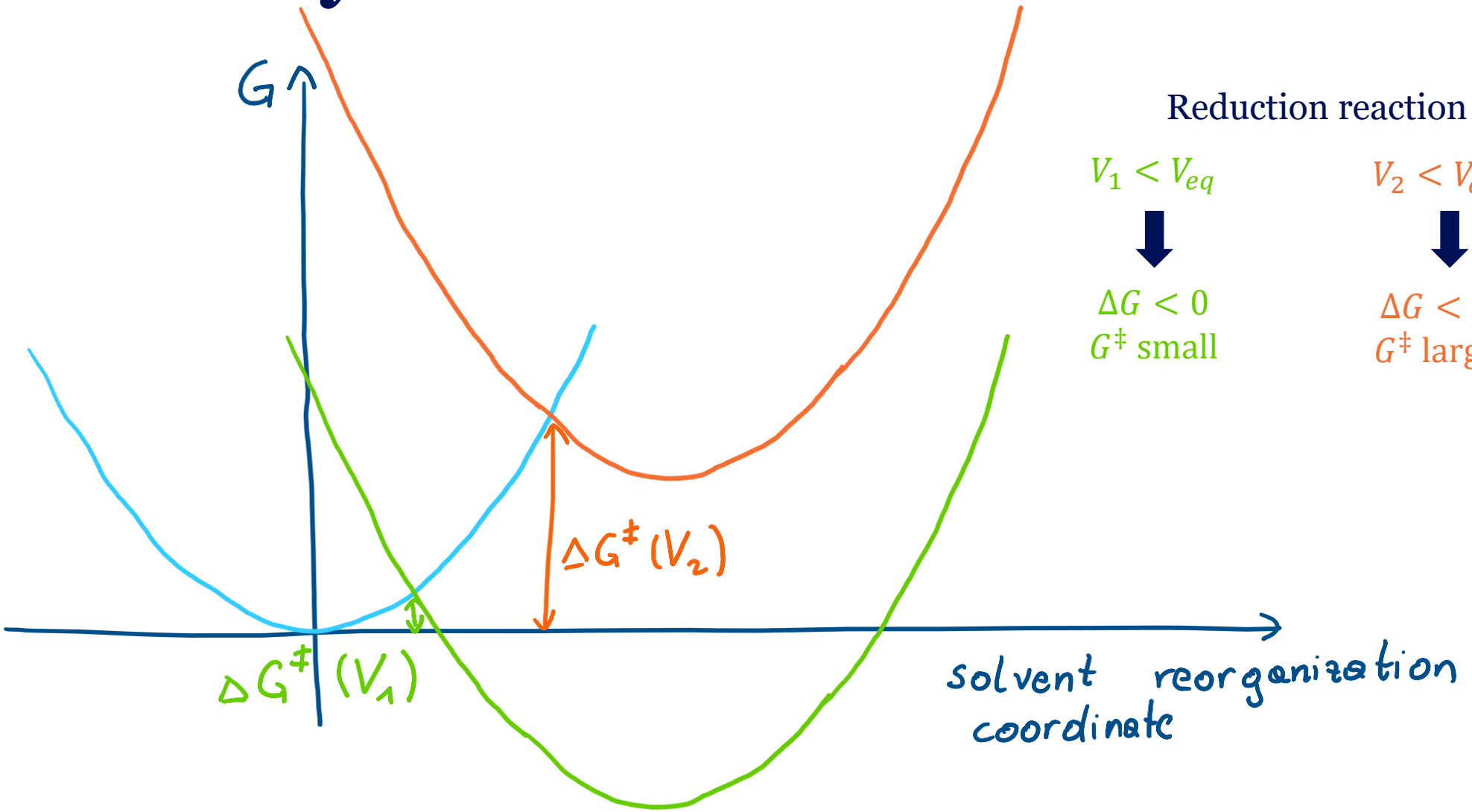
Marcus theory



Marcus theory



Marcus theory



Reduction reaction

$V_1 < V_{eq}$

$\Delta G < 0$

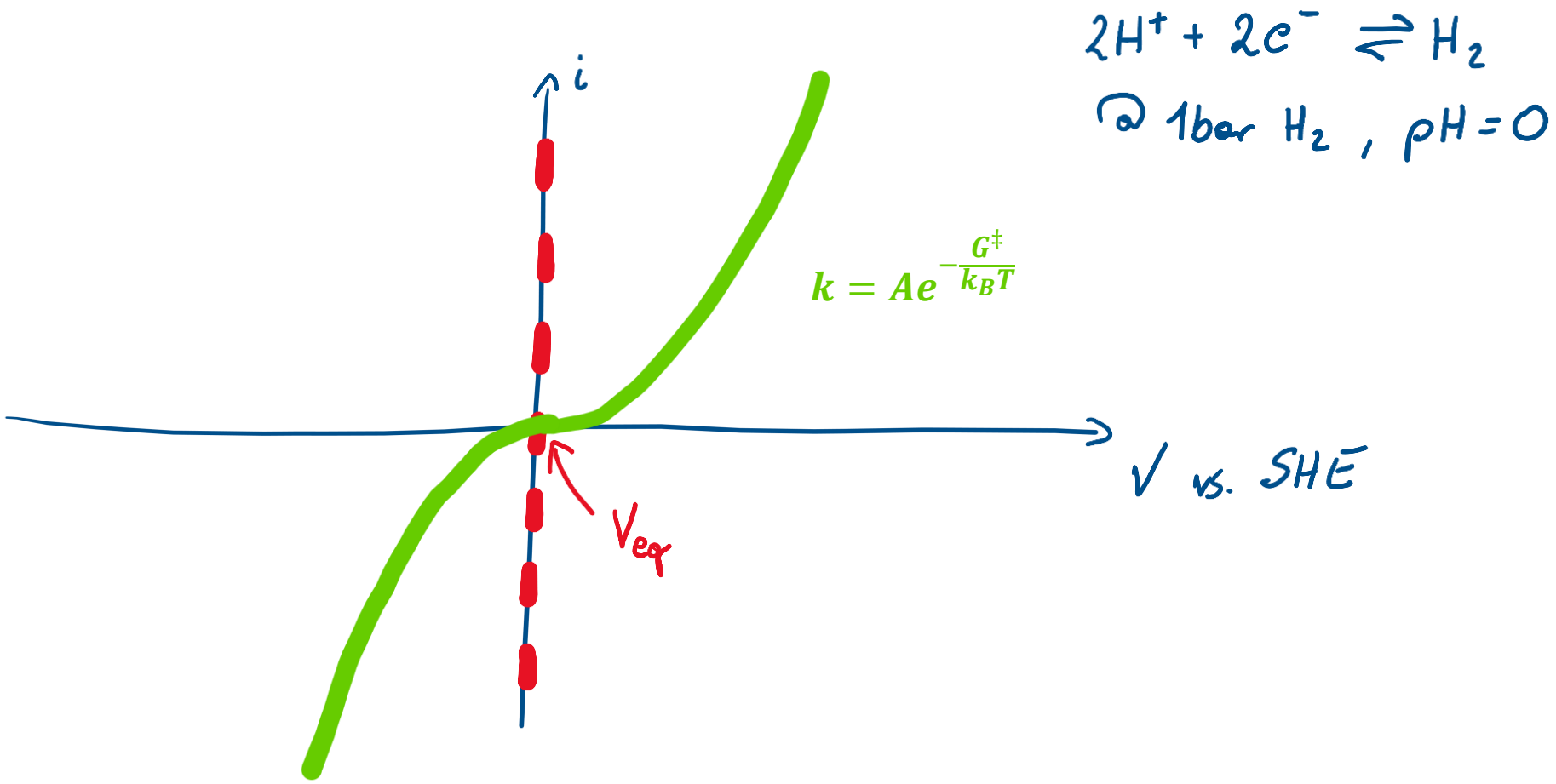
$G^{\ddagger}$ small

$V_2 < V_{eq}$

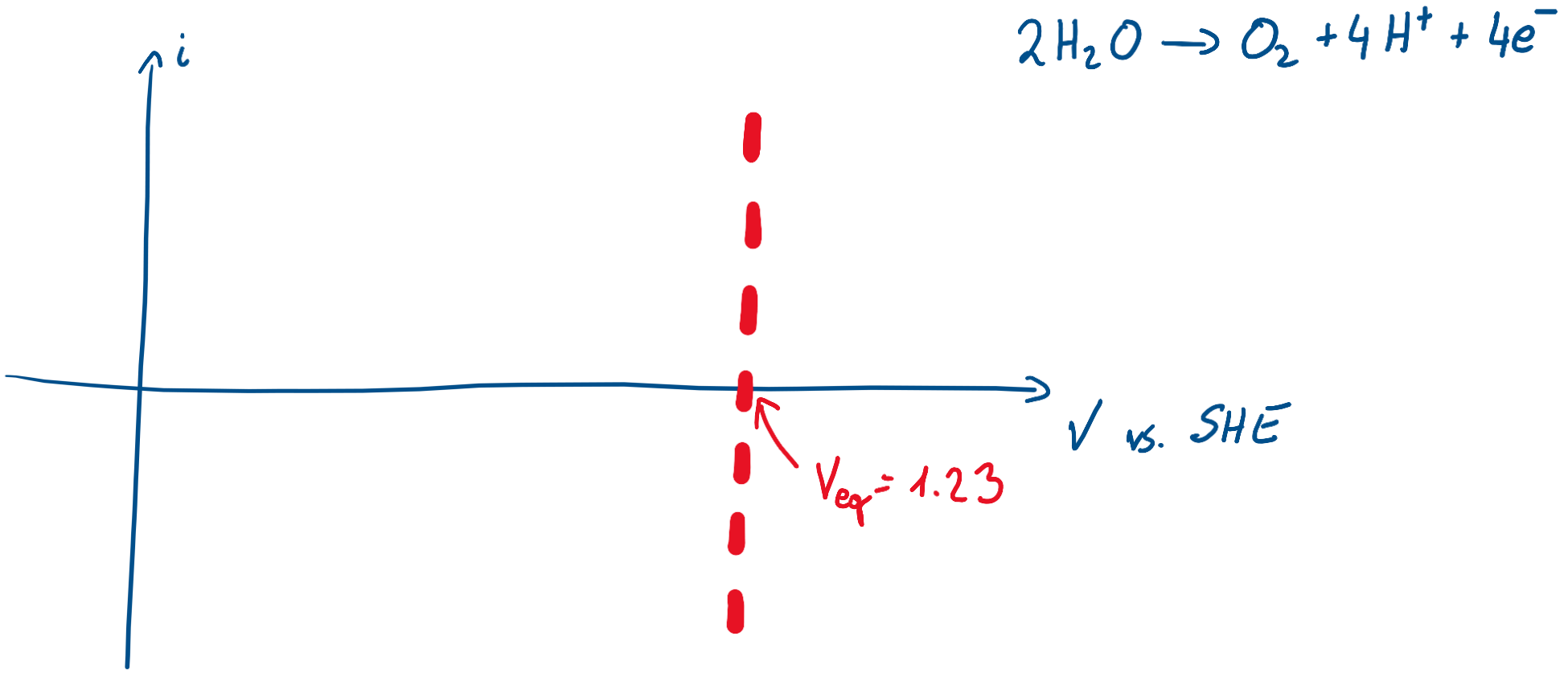
$\Delta G < 0$

$G^{\ddagger}$ large

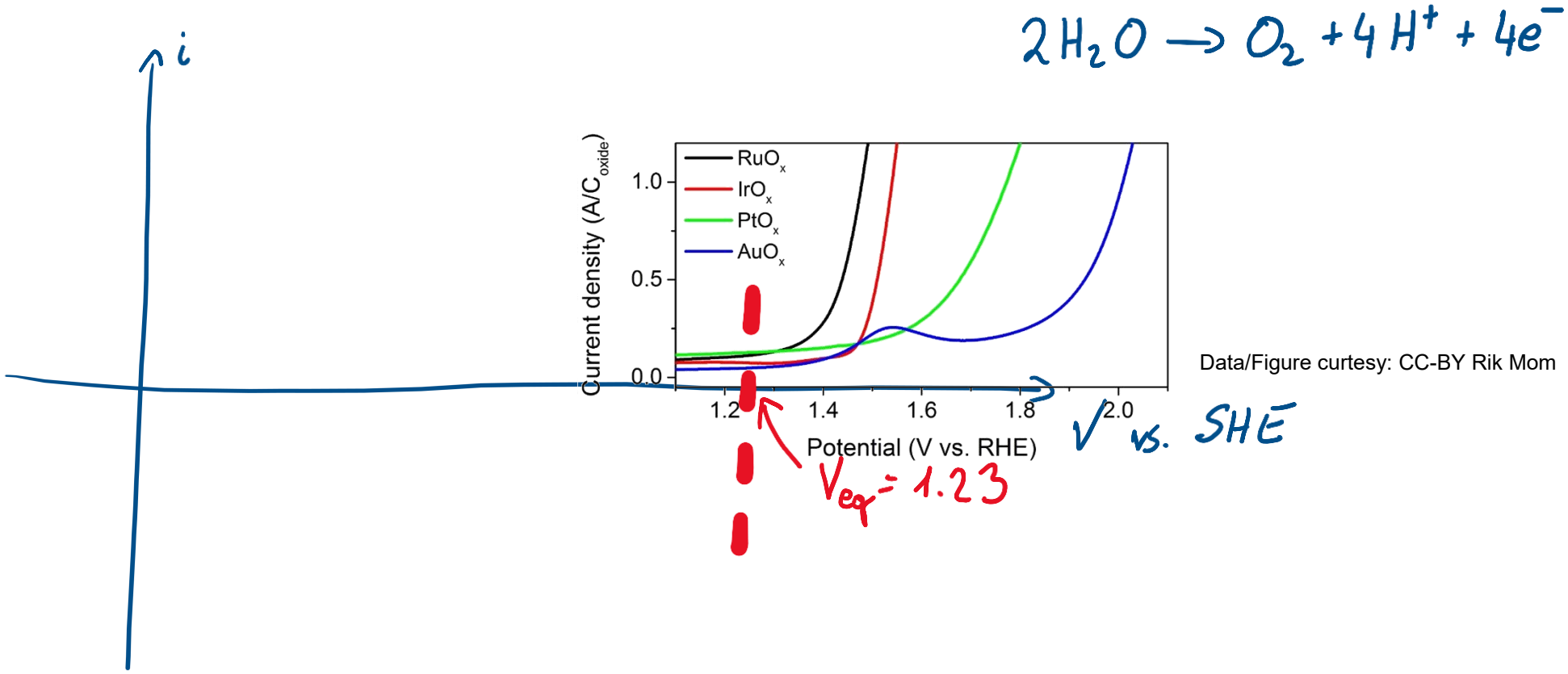
Nominal potential vs. onset potential



Nominal potential vs. onset potential

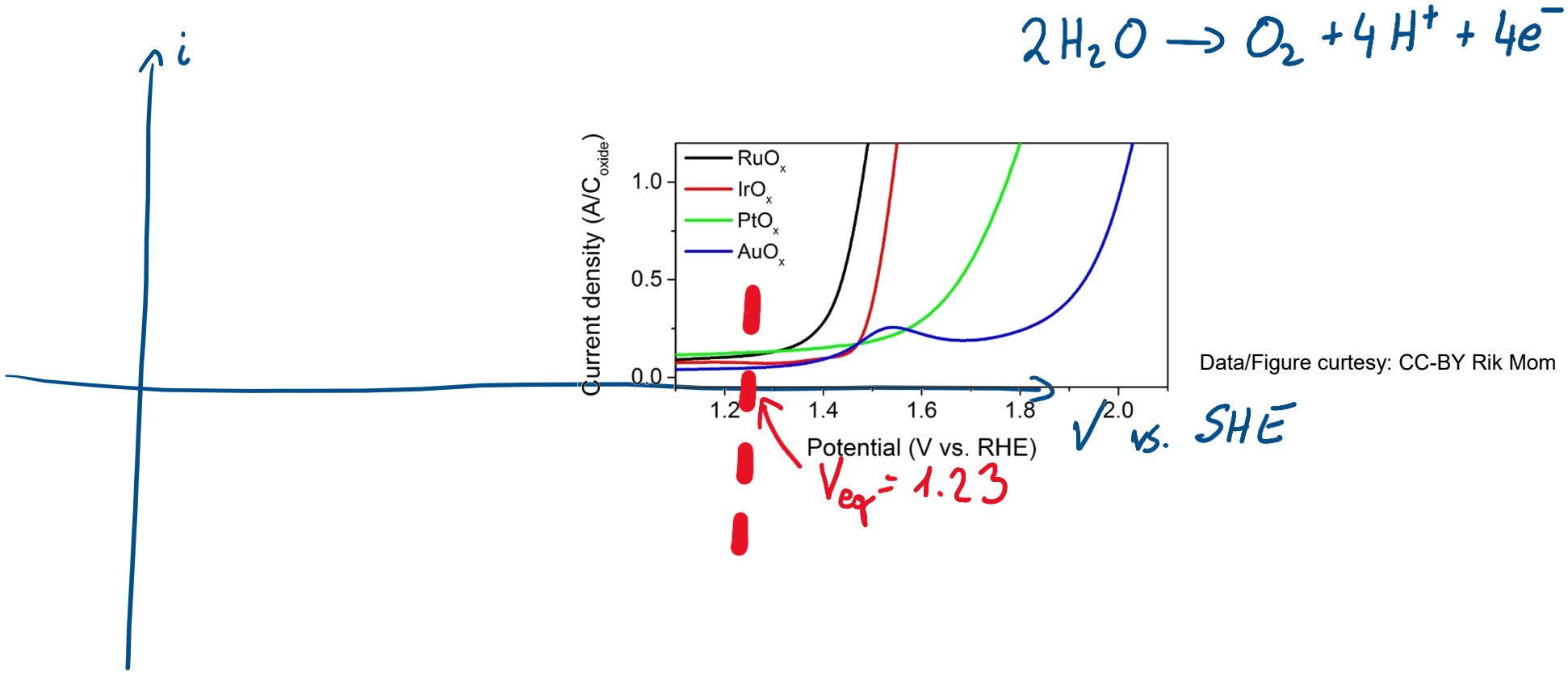


Nominal potential vs. onset potential



Data/Figure curtesy: CC-BY Rik Mom

Nominal potential vs. onset potential



Data/Figure curtesy: CC-BY Rik Mom

- Onset potential strongly delayed compared to equilibrium potential
- Onset potential depends on catalyst material and not only reactants and products!

Multistep reactions

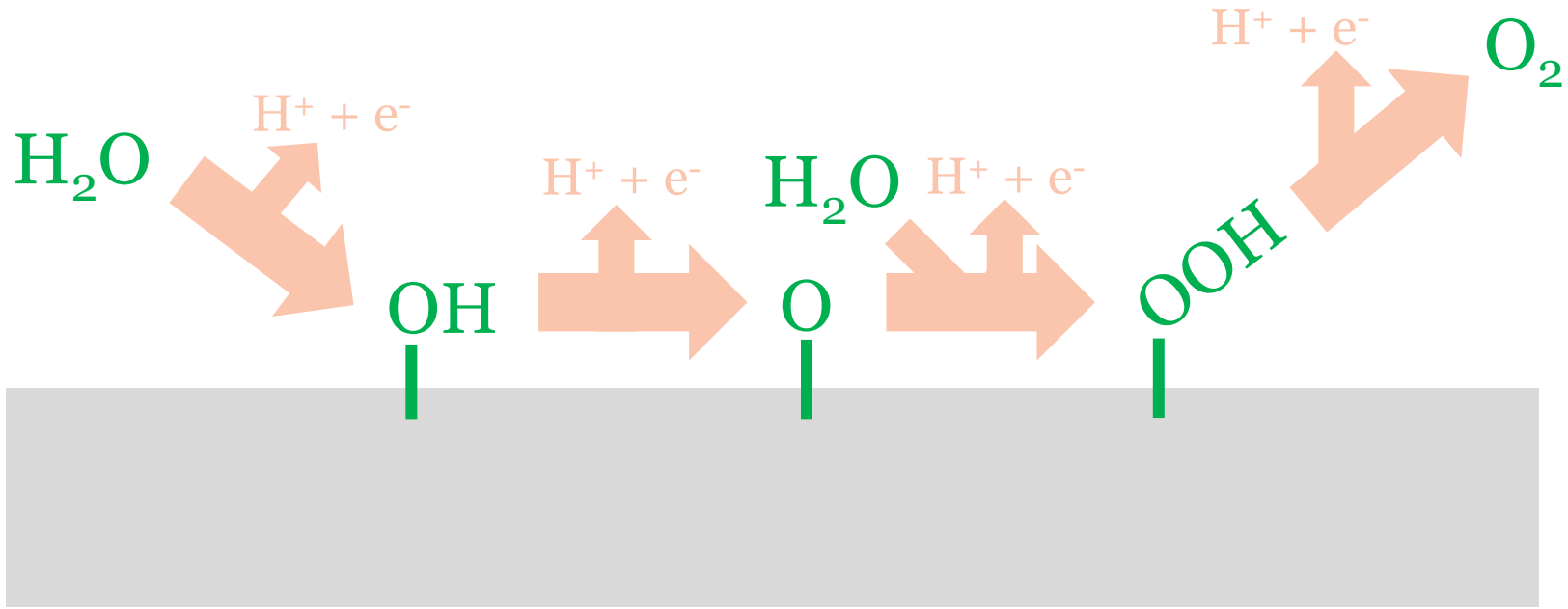


Figure curtesy: adapted with permission from CC-BY Rik Mom

Multistep reactions

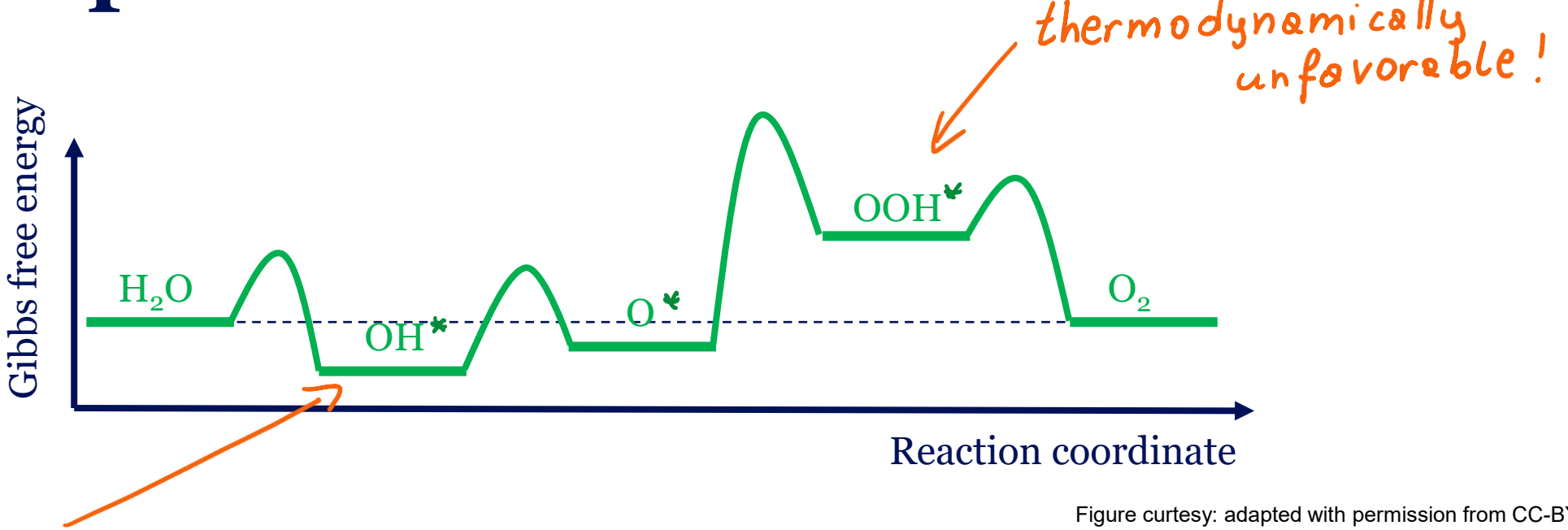
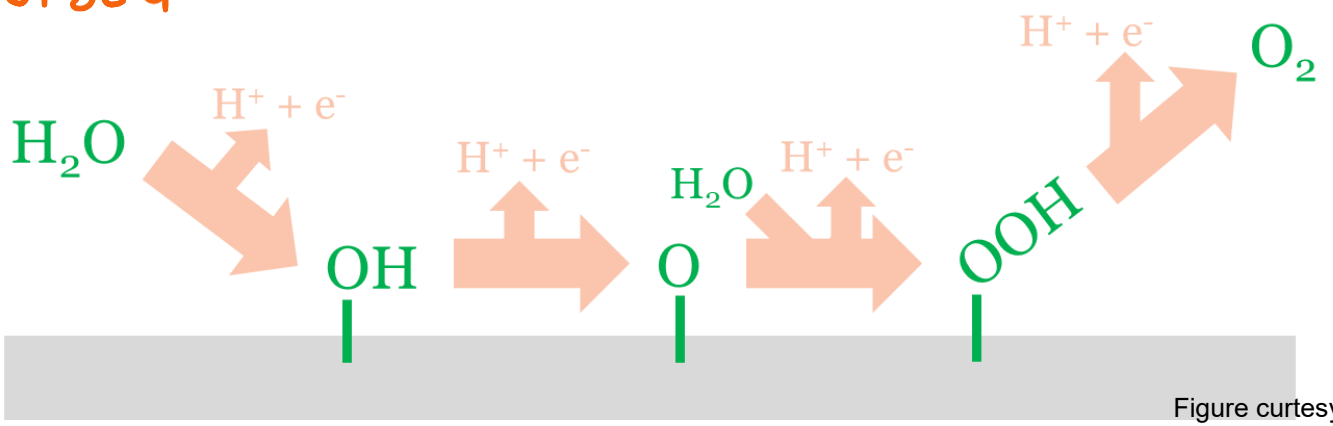


Figure curtesy: adapted with permission from CC-BY Rik Mom

energy of adsorbed species



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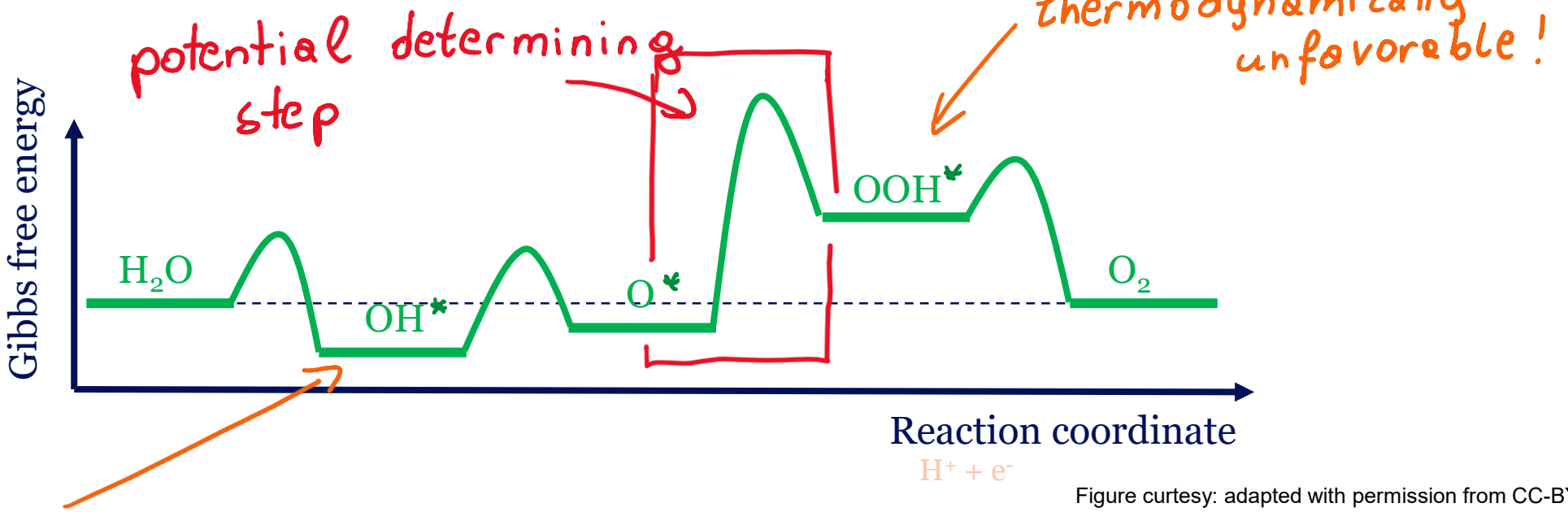
Multistep reactions



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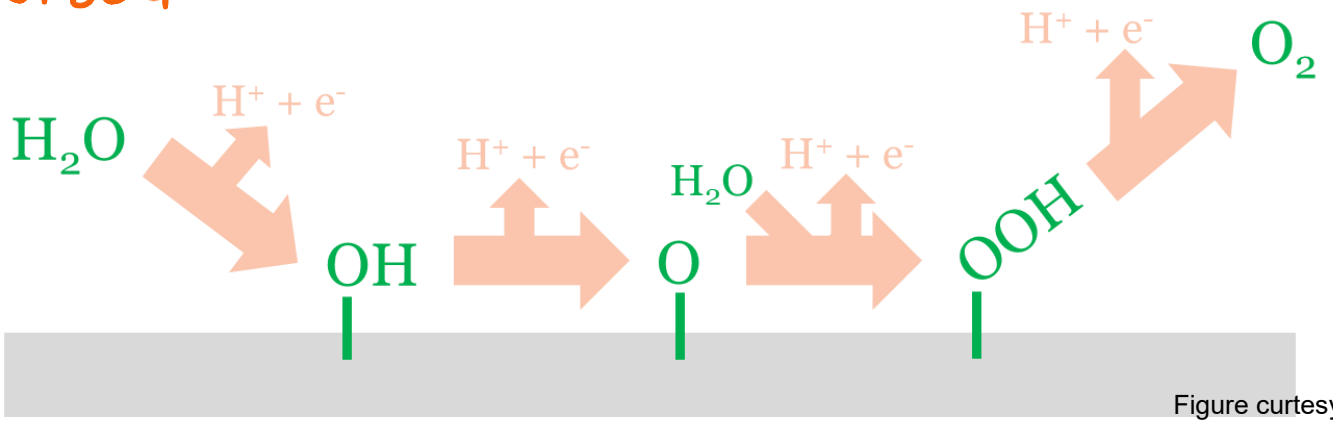

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Multistep reactions

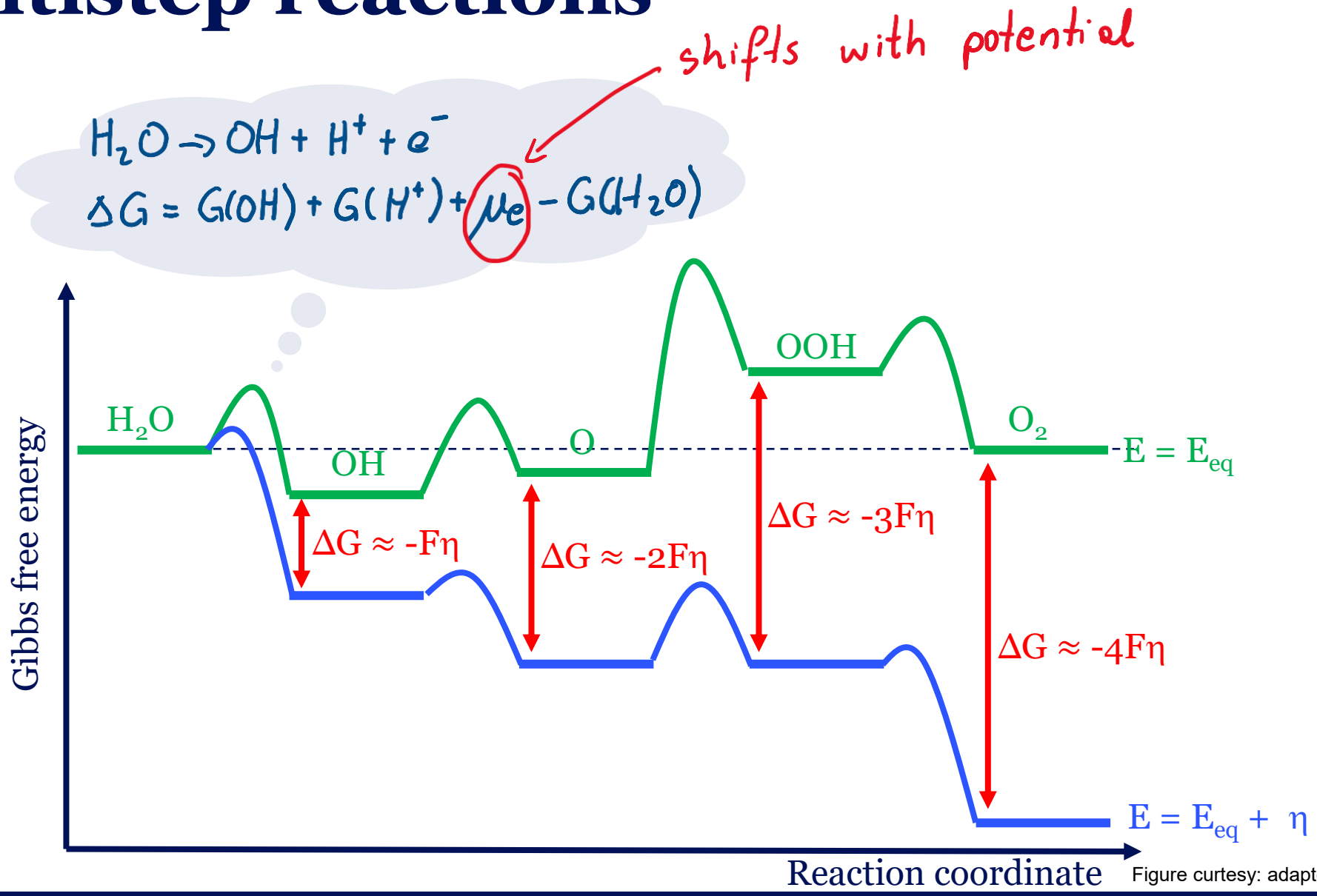


Figure curtesy: adapted with permission from CC-BY Rik Mom

Multistep reactions

All reaction steps energetically downwards!

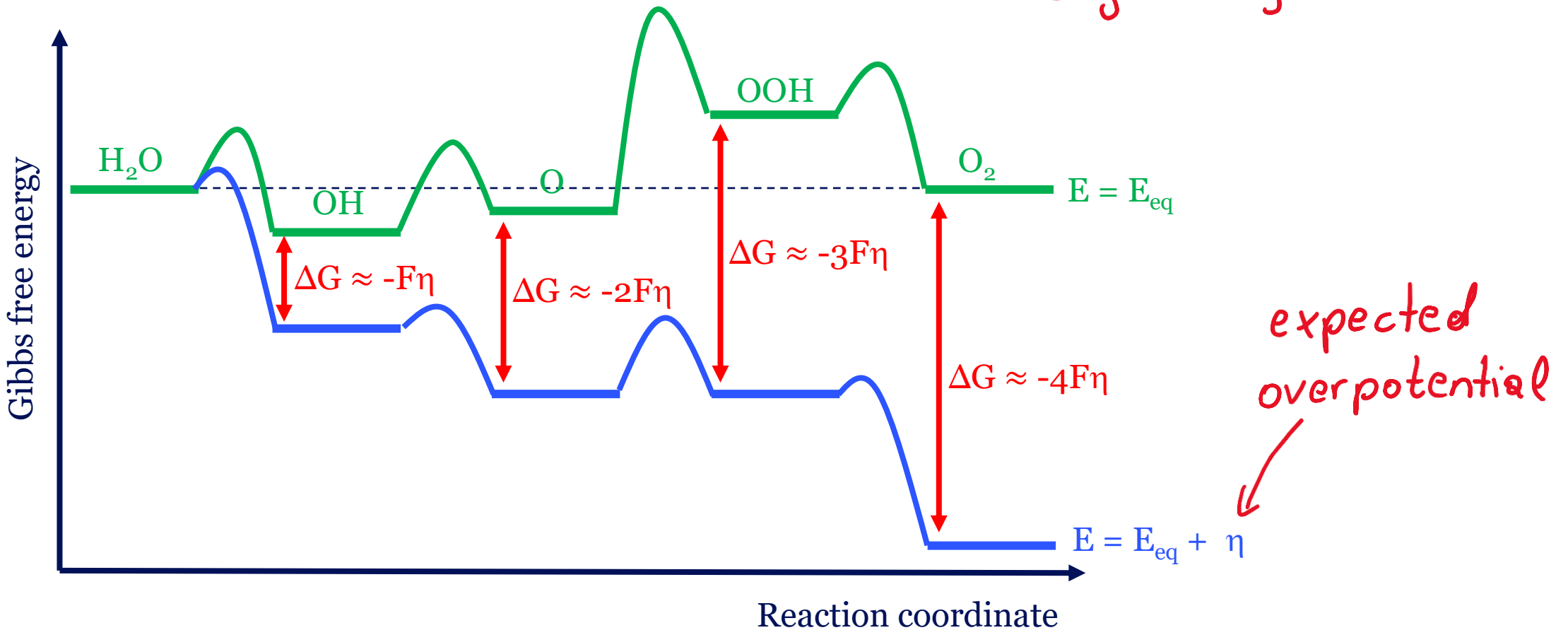


Figure curtesy: adapted with permission from CC-BY Rik Mom

H_{ads} on Pt– computer exercise

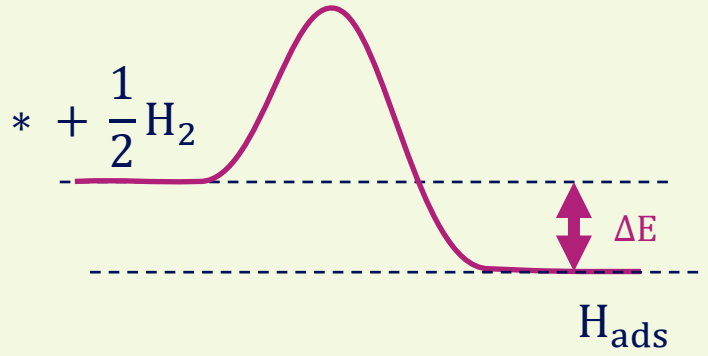
- Instead of

$$2H_2O + * \rightarrow OH^* + H^+ + e^- + H_2O \rightarrow O^* + 2H^+ + 2e^- + H_2O \rightarrow OOH^+ + 3H^+ + 3e^- \rightarrow O_2 + 4H^+ + 4e^-$$

  - Discuss 1 step only
  - Use chemical reaction rather than electrochemical one

$$\frac{n}{2}H_2 + * \rightarrow nH^*$$

  - Will later extend this to $H^+ + e^- + * \rightarrow H^*$



Why study H adsorption on Pt?

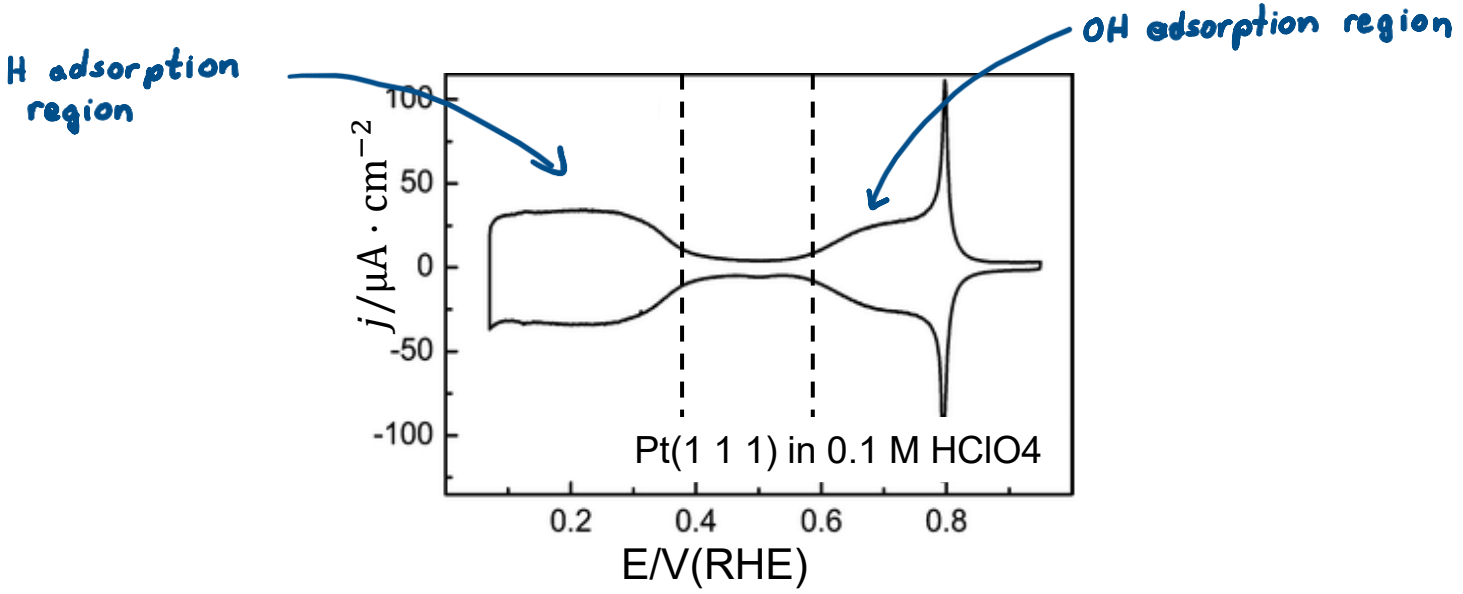
- Based on:

Unraveling the origin of the repulsive interaction between hydrogen adsorbates on platinum single-crystal electrodes

J. Liu, A. Hagopian, I. McCrum, K. Doblhoff-Dier, M.T.M. Koper

DOI: 10.1021/acs.jpcc.4c05193

- From cyclic voltammetry

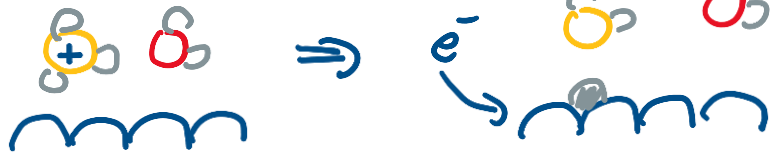


García G, Koper M T M. Phys. Chem. Chem. Phys. **2008**, 10(25): 3802-3811.

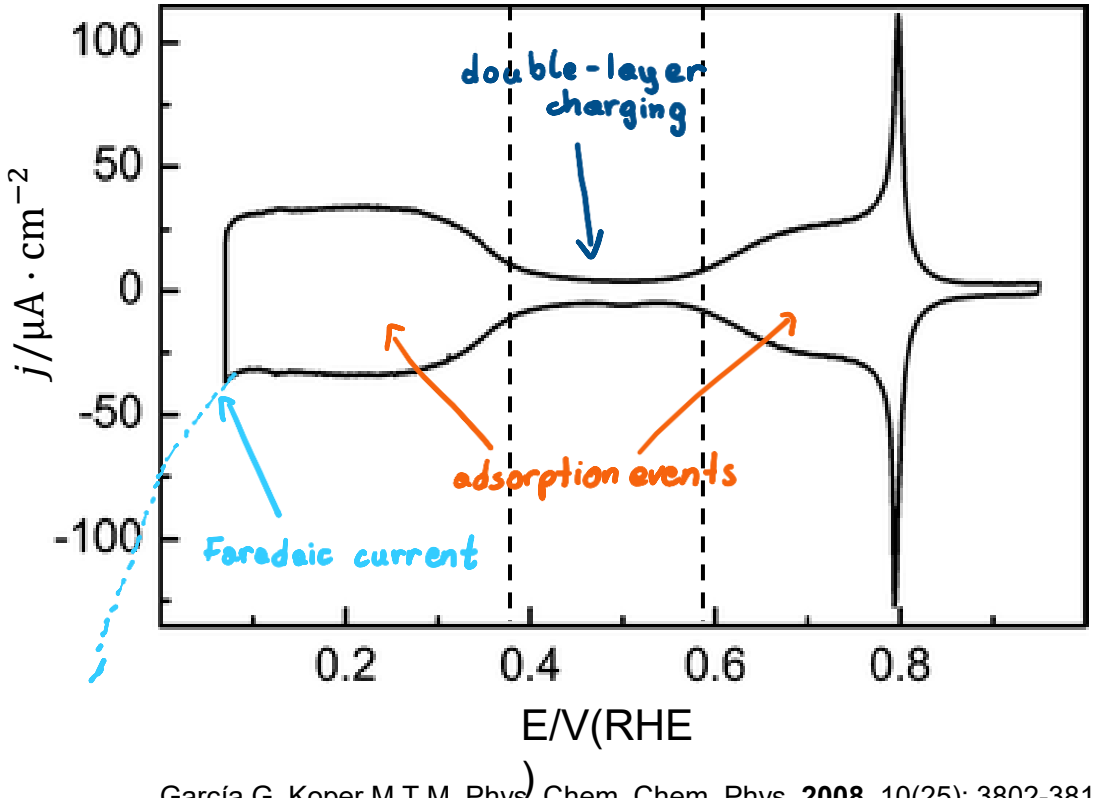
Adsorption and CVs

- Cyclic voltammogram:
  - Sweep potential (often 50 meV/s) and measure current
- Current measured
  - Capacitive charging

  - Adsorption events



  - Faradaic currents



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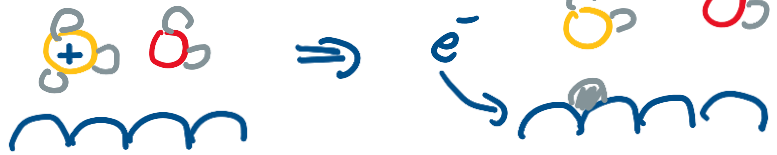

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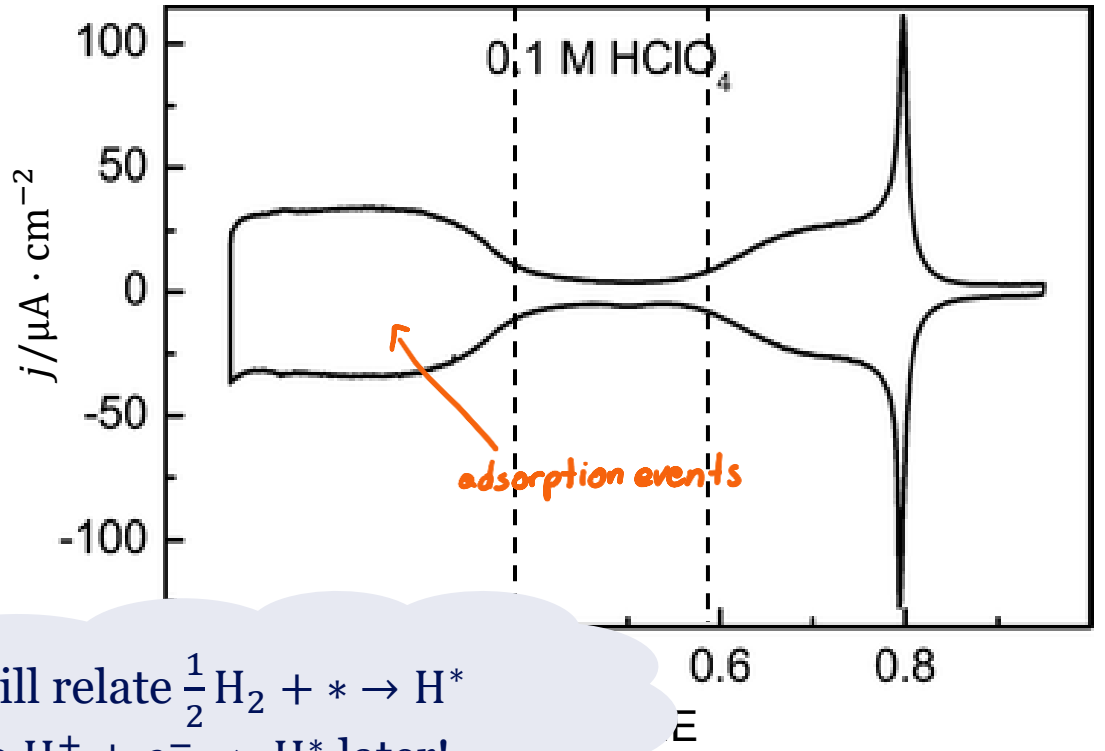


Will relate $\frac{1}{2}H_2 + * \rightarrow H^*$ to $H^+ + e^- \rightarrow H^*$ later!

. Chem. Chem. Phys. **2008**, 10(25): 3802-3811.

Why study H adsorption on Pt?

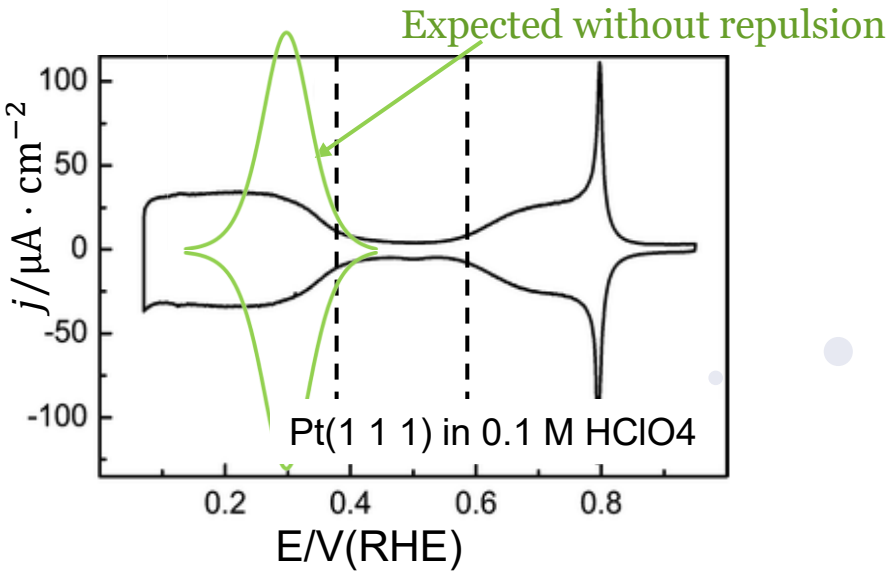
- Based on:

Unraveling the origin of the repulsive interaction between hydrogen adsorbates on platinum single-crystal electrodes

J. Liu, A. Hagopian, I. Mccrum, K. Doblhoff-Dier, M.T.M. Koper

DOI: 10.1021/acs.jpcc.4c05193

- From cyclic voltammetry



What causes the repulsion?

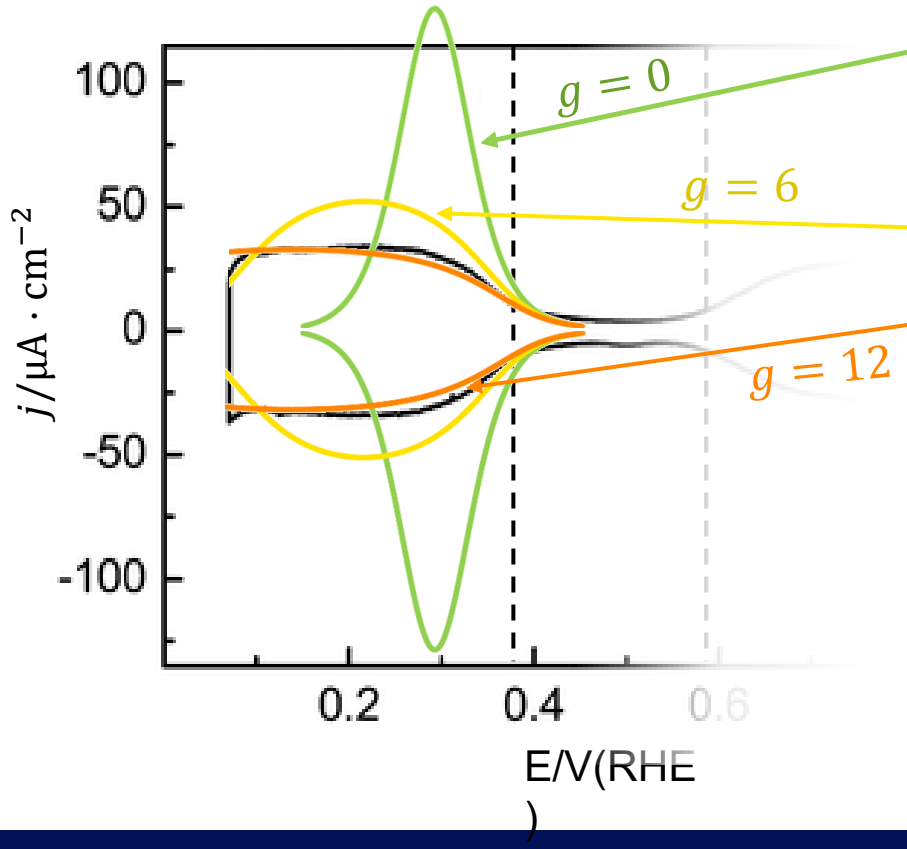
García G, Koper M T M. Phys. Chem. Chem. Phys. **2008**, 10(25): 3802-3811.

Why study H adsorption on Pt?

- From CVs:
  - Weak repulsion between H-atoms

Cyclic voltammetry of Pt(1 1 1) in 0.1 M HClO4

García G, Koper M T M. Phys. Chem. Chem. Phys. **2008**, 10(25): 3802-3811.



Langmuir isotherm

- Constant adsorption energy ΔG_0
- $\ln\left(\frac{\theta}{\theta_{max}-\theta}\right) = -\frac{\Delta G_0 - eU_{RHE}}{k_B T}$

Frumkin isotherm

- Adsorption energy dependent on coverage
- $\Delta G_0(\theta) = \Delta G_0 + k_B T \cdot g \cdot \theta$

H_{ads} on Pt– computer exercise

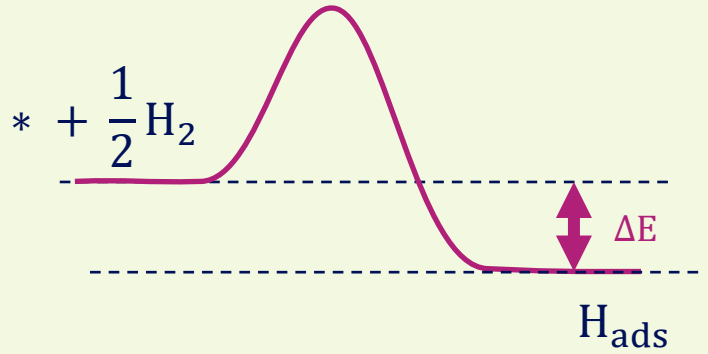
- Instead of

$$2H_2O + * \rightarrow OH^* + H^+ + e^- + H_2O \rightarrow O^* + 2H^+ + 2e^- + H_2O \rightarrow OOH^+ + 3H^+ + 3e^- \rightarrow O_2 + 4H^+ + 4e^-$$

  - Discuss 1 step only
  - Use chemical reaction rather than electrochemical one

$$\frac{n}{2}H_2 + * \rightarrow nH^*$$

  - Will later extend this to $H^+ + e^- + * \rightarrow H^*$



- Use gpaw!
- Lab instructions in folder: Ex1_Hads_chem

The origin of H_{upd} repulsion: surface distortion

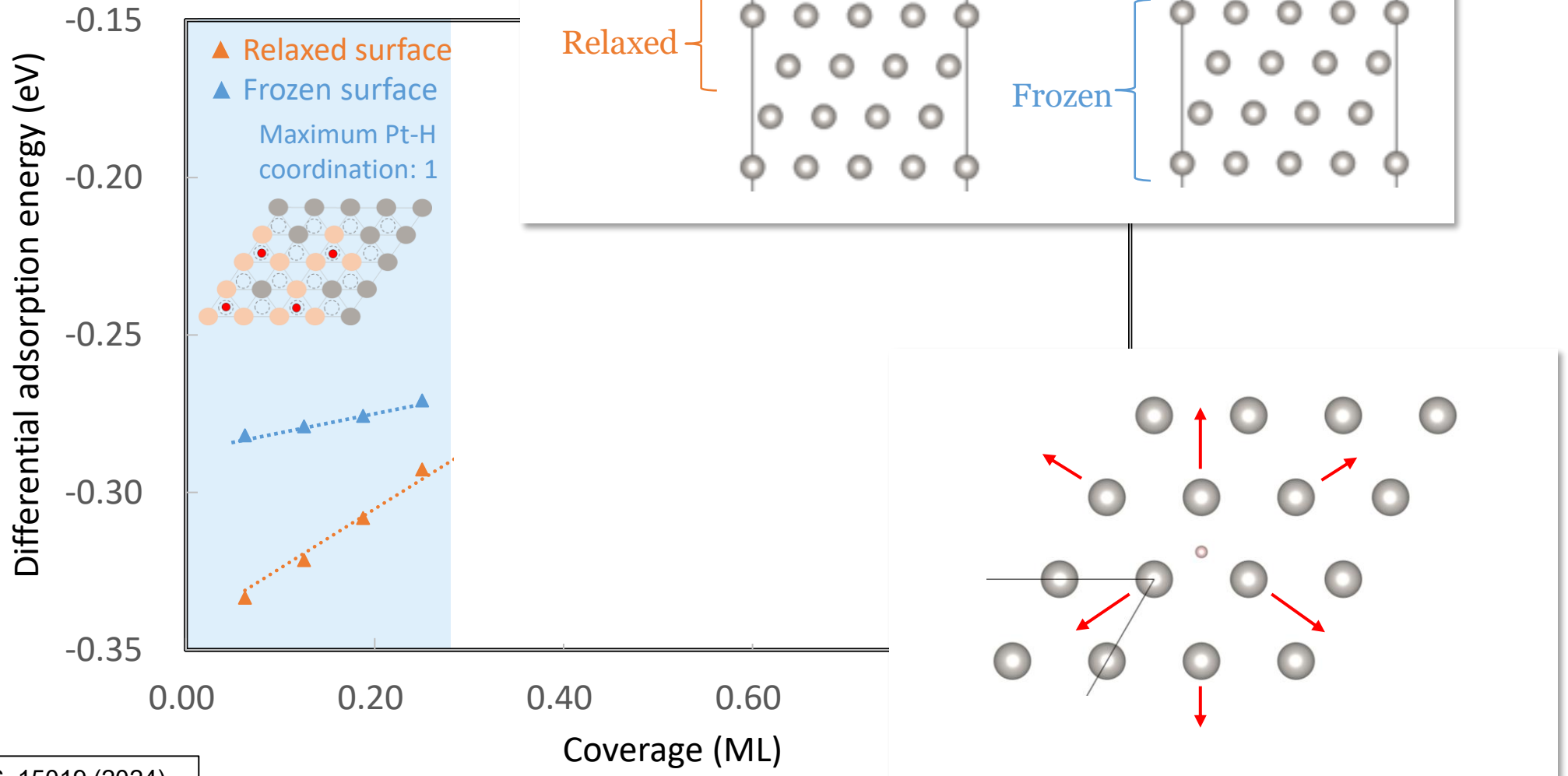
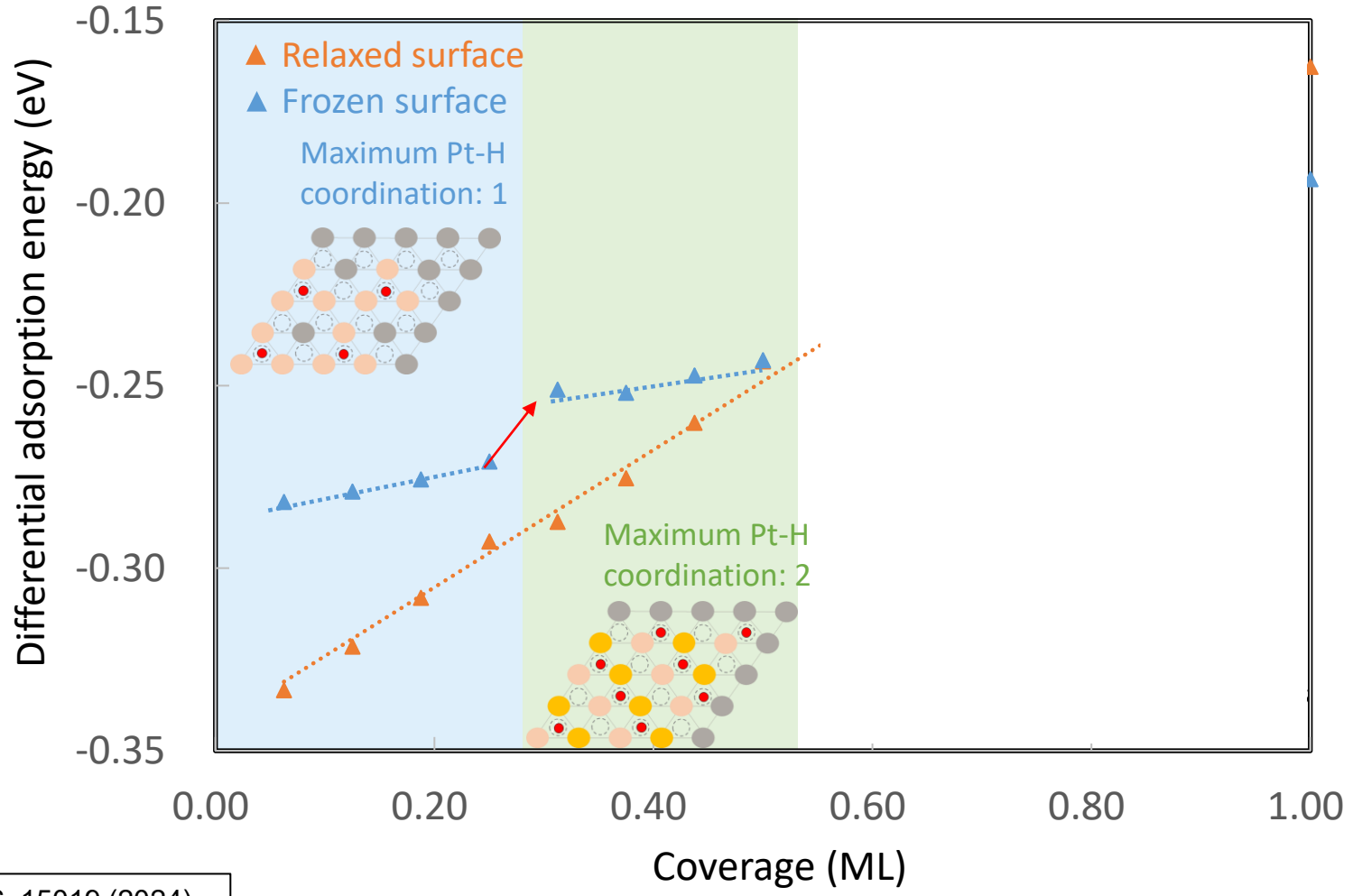


Figure from: JPCC 128,36, 15019 (2024)

The origin of H_{upd} repulsion: surface coordination



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The origin of H_{upd} repulsion: surface coordination

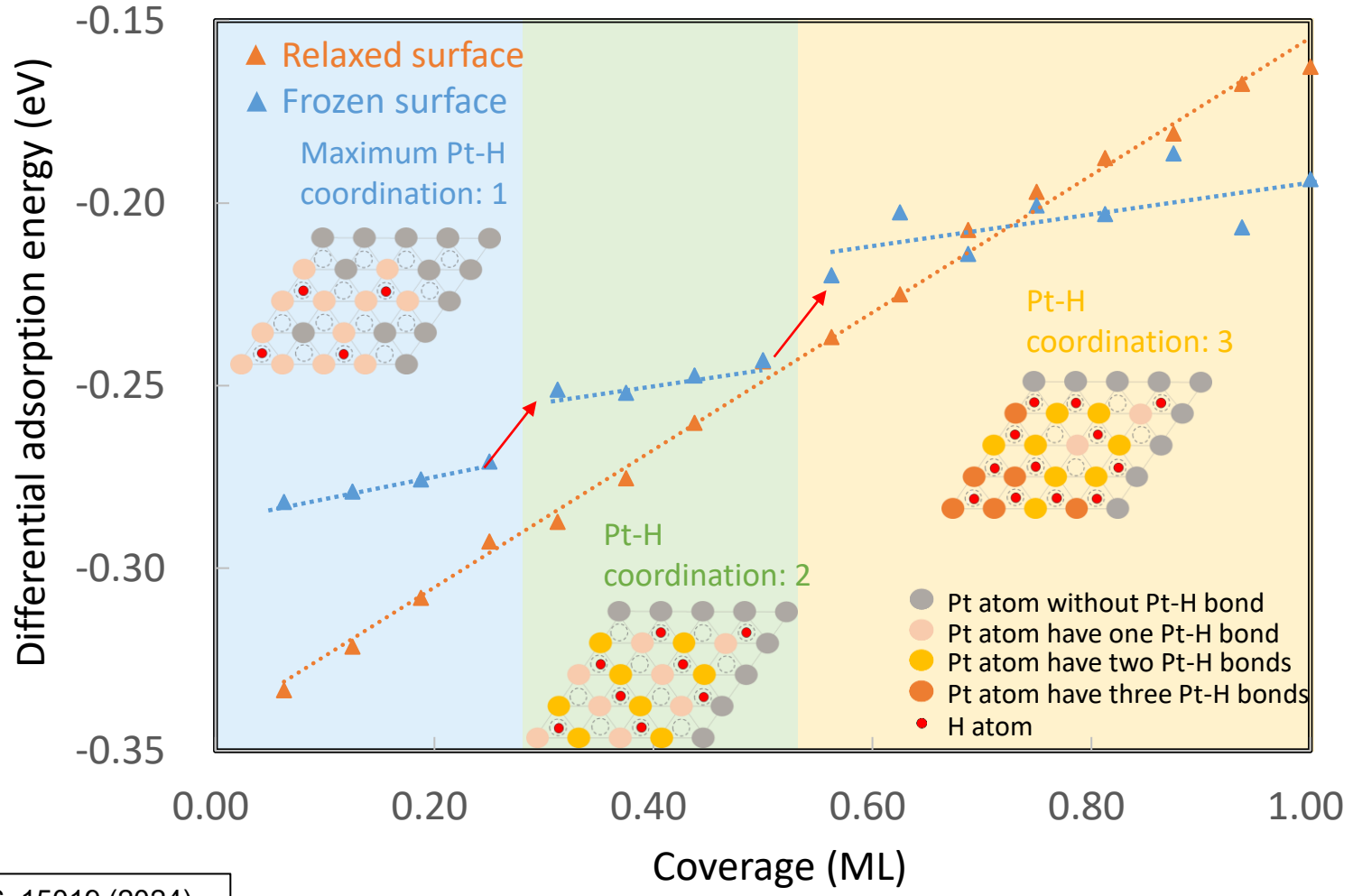
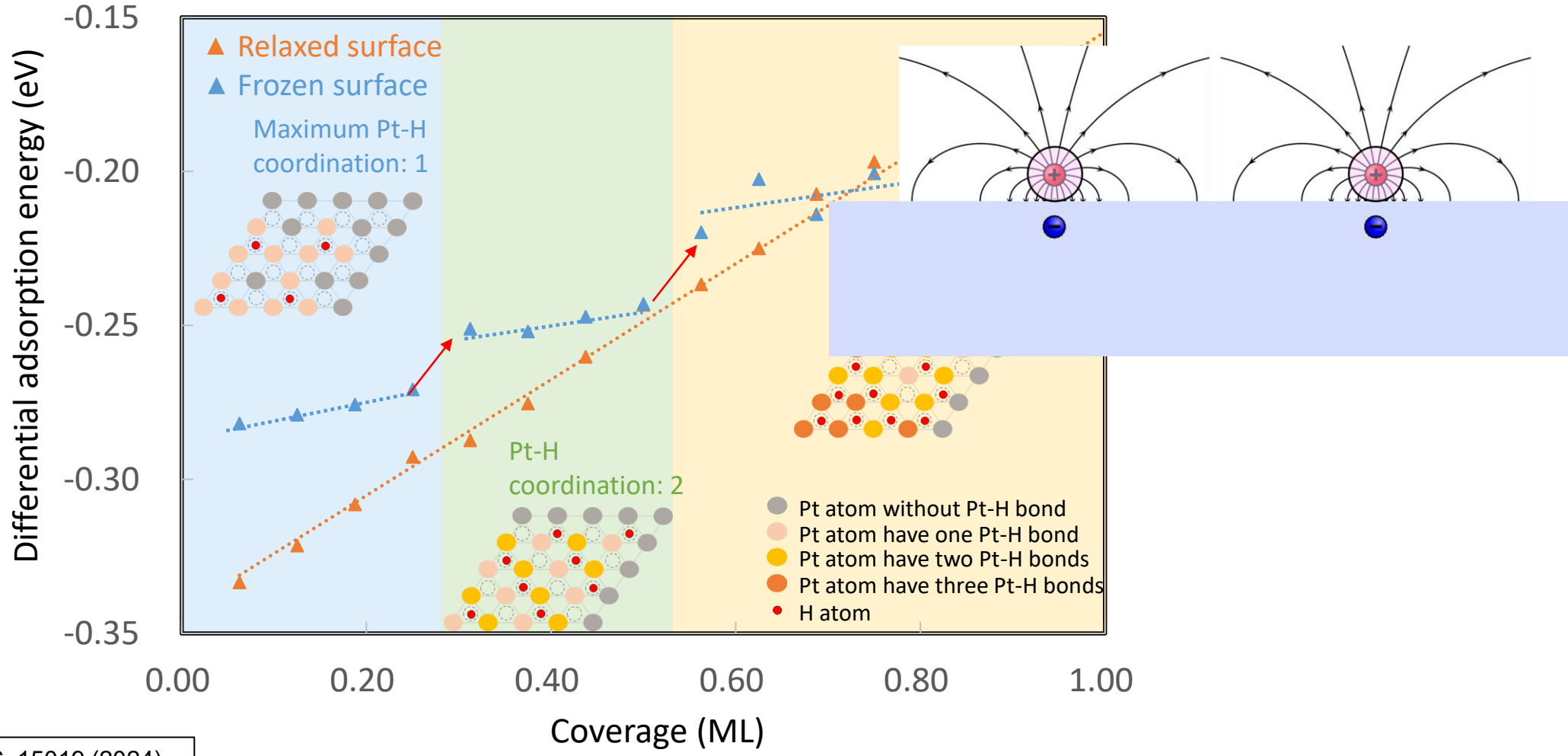


Figure from: JPCC 128,36, 15019 (2024)

The origin of H_{upd} repulsion: electrostatic interaction



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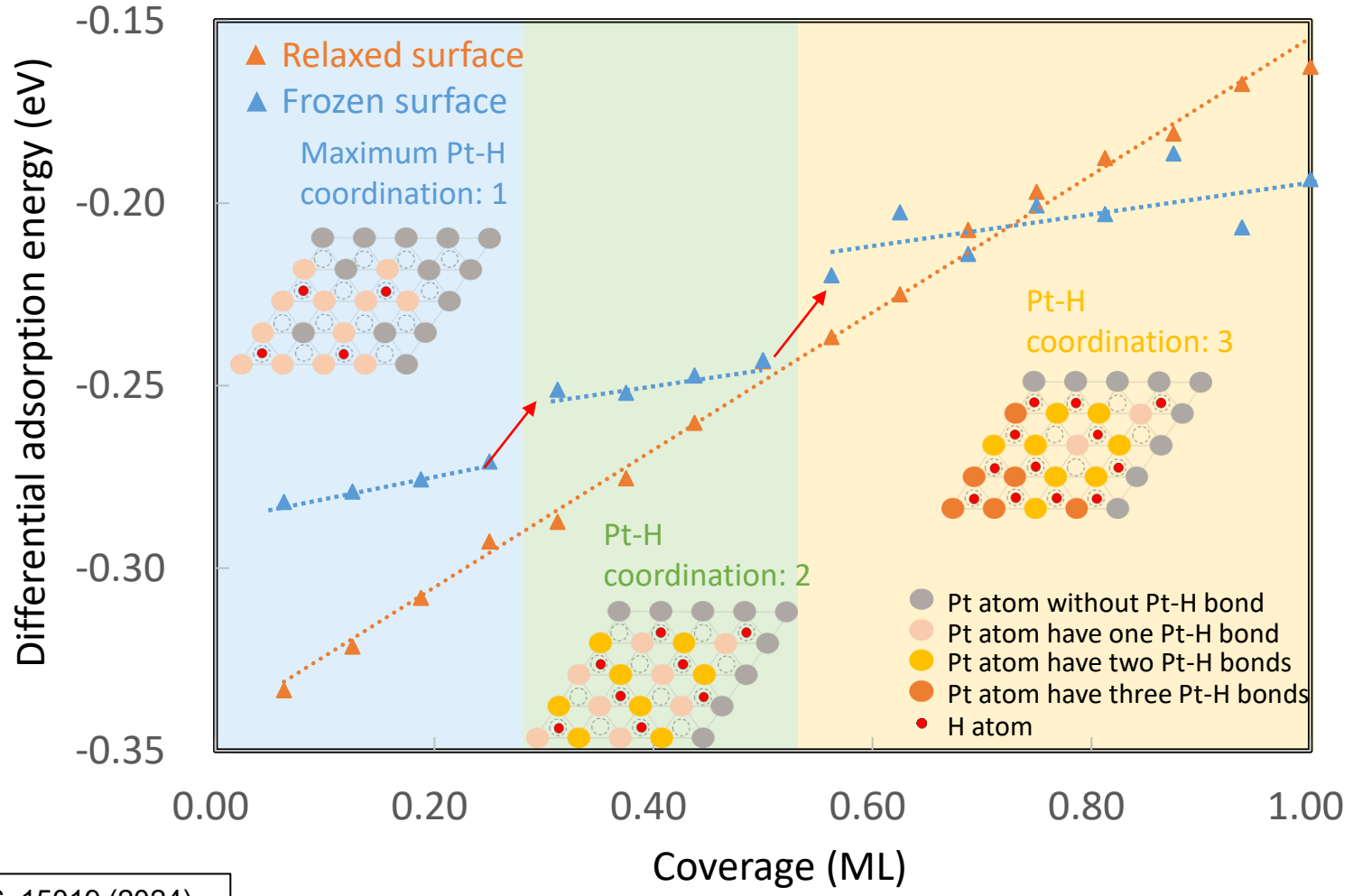


Figure from: JPCC 128,36, 15019 (2024)

Reaction thermodynamics in EC

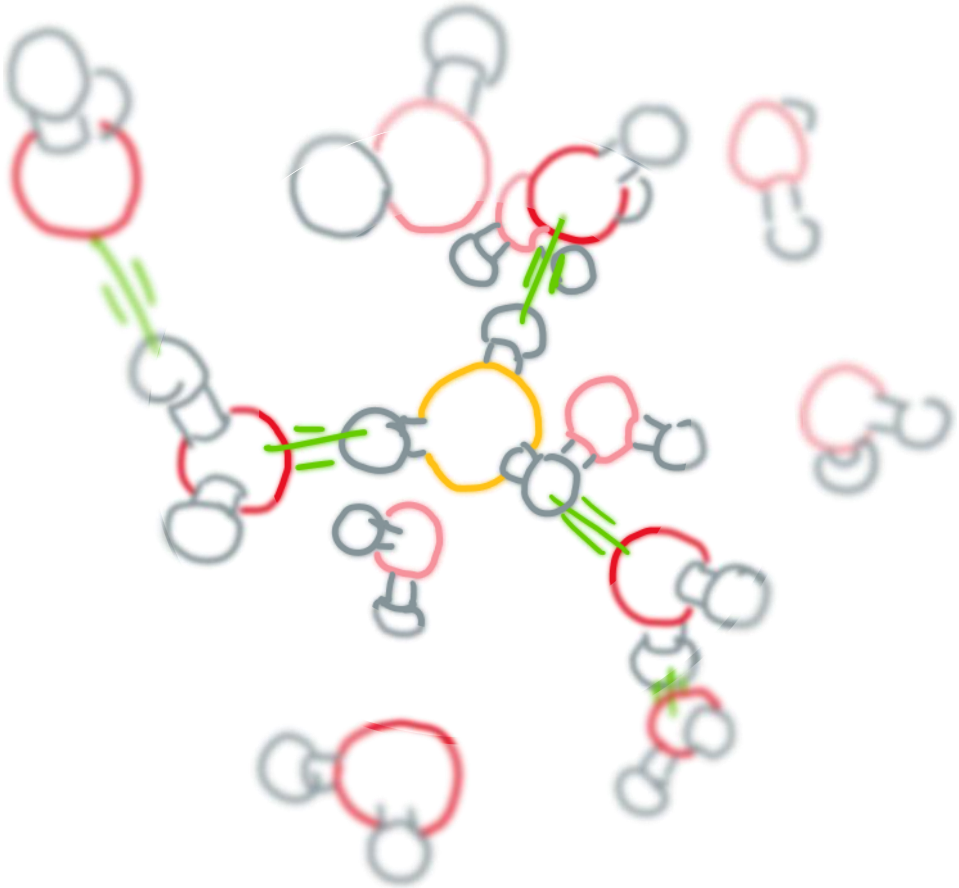
- So far:

$$\frac{1}{2}H_2 + * \rightarrow H^*$$

- But in electrochemistry, we want:

$$H^+ + e^- + * \rightarrow H^*$$

Need energy of a proton!



Adapted from: CC-BY Greg Voth; https://commons.wikimedia.org/wiki/File:ProtonPairs1.jpg

Computational hydrogen electrode method

- Nørskov, Rossmeisl, Jónsson et al, 2024:

@0 V/RHE:

$$\frac{1}{2}H_2 \leftrightarrow H^+ + e^- \quad \Rightarrow \quad \Delta G^{@0V_{RHE}} = G(H^+) + G(e^- @ 0V_{RHE}) - G\left(\frac{1}{2}H_2\right) = 0$$

Computational hydrogen electrode method

- Nørskov, Rossmeisl, Jónsson et al, 2024:

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@0 V/RHE:

$\frac{1}{2}H_2 \leftrightarrow H^+ + e^-$ → $G(H^+) + G(e^- @ 0V_{RHE}) = G\left(\frac{1}{2}H_2\right)$

Change potential → free energy of electron changes!

@ϕ_{RHE} V/RHE: → $G(H^+) + G(e^- @ \phi_{RHE}) = G(H^+) + G(e^- @ 0V_{RHE}) - e\phi_{RHE}$

Computational hydrogen electrode method

- Nørskov, Rossmeisl, Jónsson et al, 2024:

@0 V/RHE:

$$\frac{1}{2}H_2 \leftrightarrow H^+ + e^- \quad \Rightarrow \quad \Delta G = G(H^+) + G(e^- @ 0V_{RHE}) - G\left(\frac{1}{2}H_2\right) = 0$$

Change potential → free energy of electron changes!

@ϕ_{RHE} V/RHE:

$$\Rightarrow \quad G(H^+) + G(e^- @ \phi_{RHE}) = G(H^+) + G(e^- @ 0V_{RHE}) - e\phi_{RHE}$$

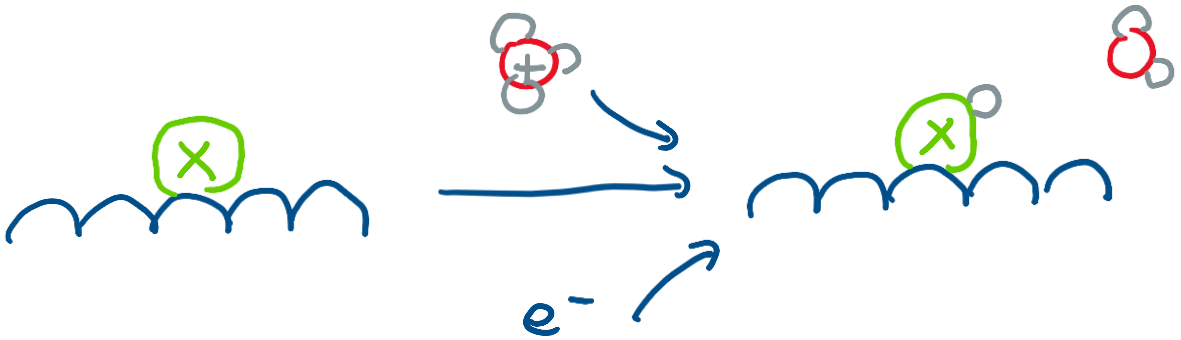
$$G(H^+) + G(e^- @ \phi V_{RHE}) = G\left(\frac{1}{2}H_2\right) - e\phi_{RHE}$$

Energy of proton – electron pair can be computed at any potential!

Computational hydrogen electrode method

As applied to a hydrogenation reaction:

$$X^* + H^+ + e^- \rightarrow XH^*$$

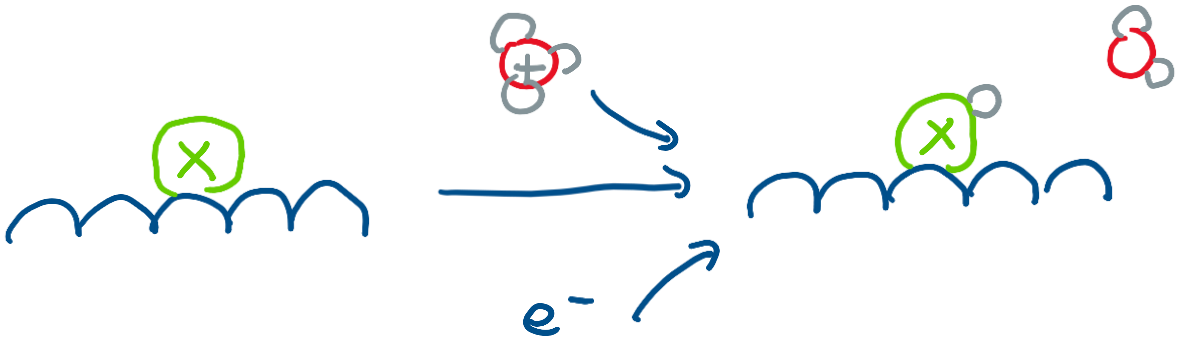


$$\Delta G = G(XH^*) - G(X^*) - G(H^+) - G(e^-)$$

Computational hydrogen electrode method

As applied to a hydrogenation reaction:

$$X^* + H^+ + e^- \rightarrow XH^*$$



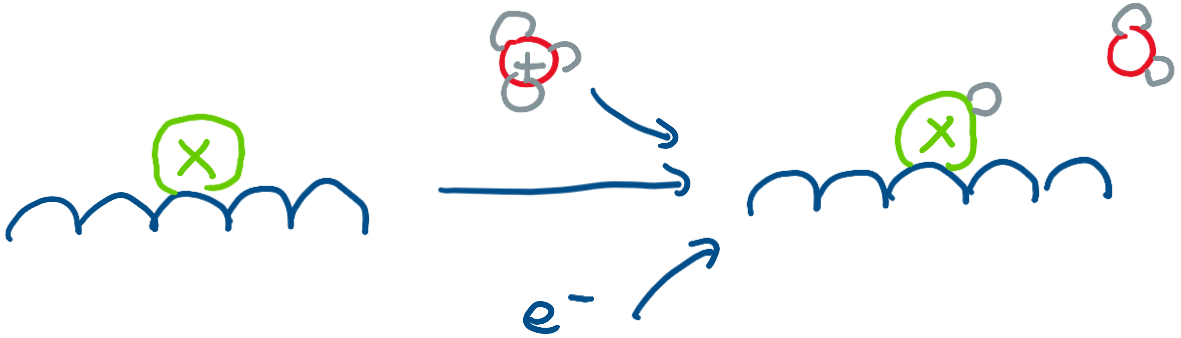
$$\Delta G = G(XH^*) - G(X^*) - G(H^+) - G(e^-)$$

can only be computed for a given potential

Computational hydrogen electrode method

As applied to a hydrogenation reaction:

$$X^* + H^+ + e^- \rightarrow XH^*$$



$$\Delta G(U_{RHE}) = G(XH^*; U_{RHE}) - G(X^*; U_{RHE}) - G(H^+) - G(e^-; U_{RHE})$$

Applying a potential

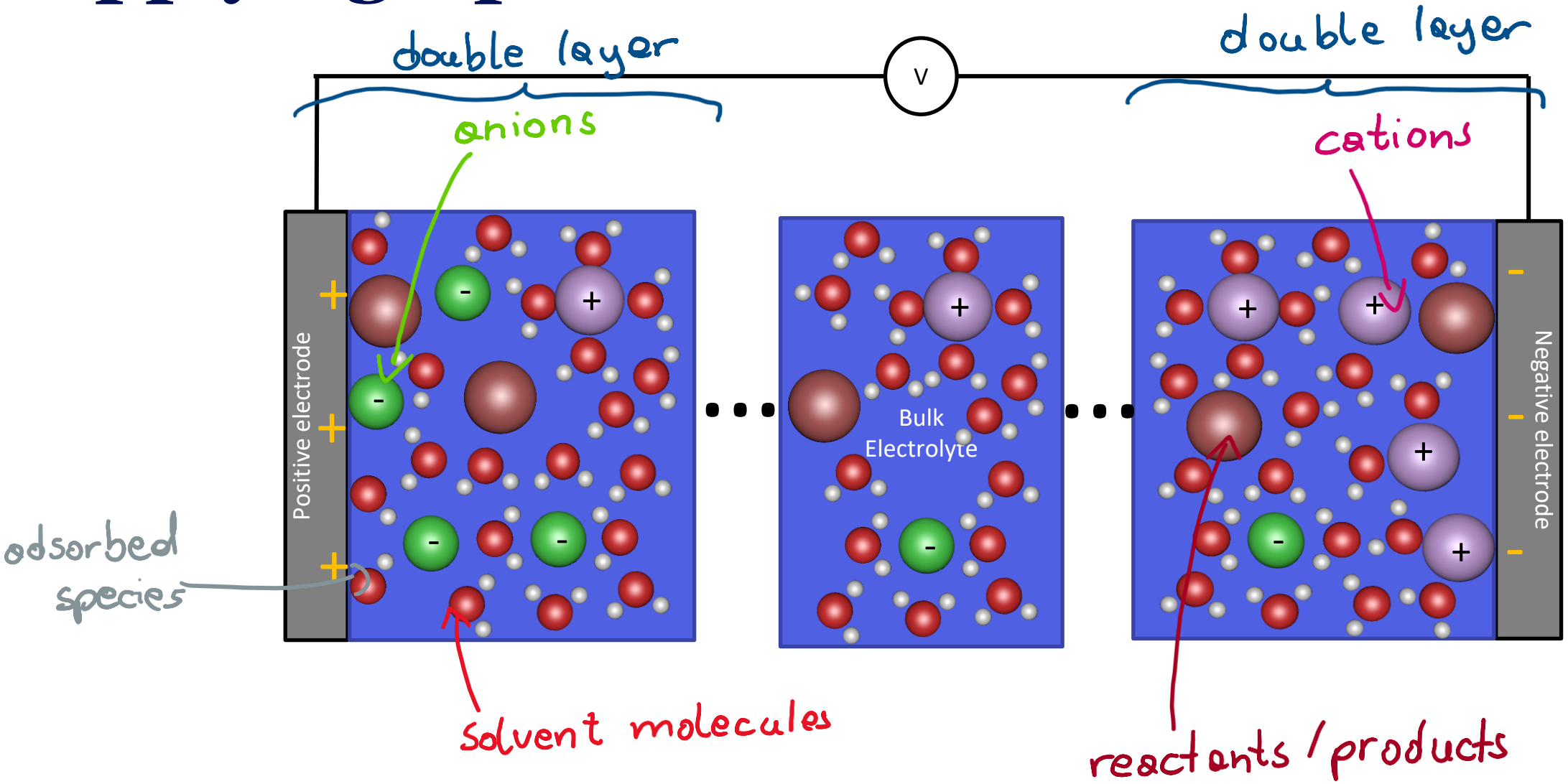
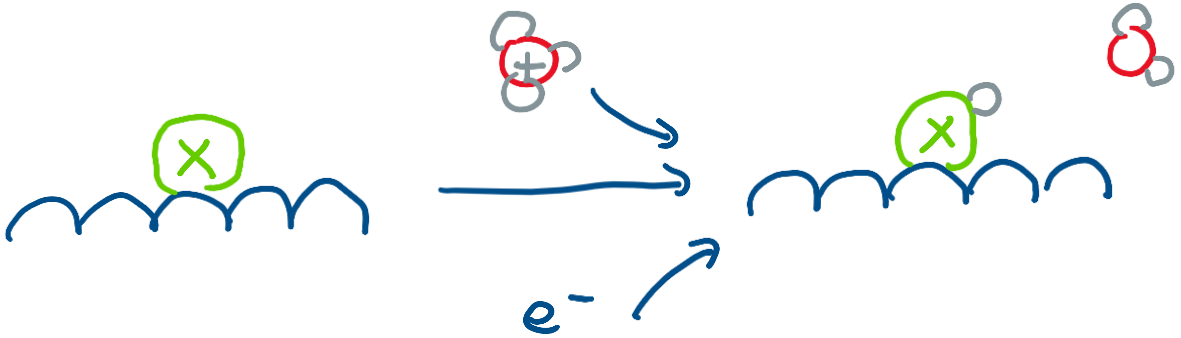


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Computational hydrogen electrode method

As applied to a hydrogenation reaction:

$$X^* + H^+ + e^- \rightarrow XH^*$$



$$\Delta G(U_{RHE}) = G(XH^*; U_{RHE}) - G(X^*; U_{RHE}) - G(H^+) - G(e^-; U_{RHE})$$

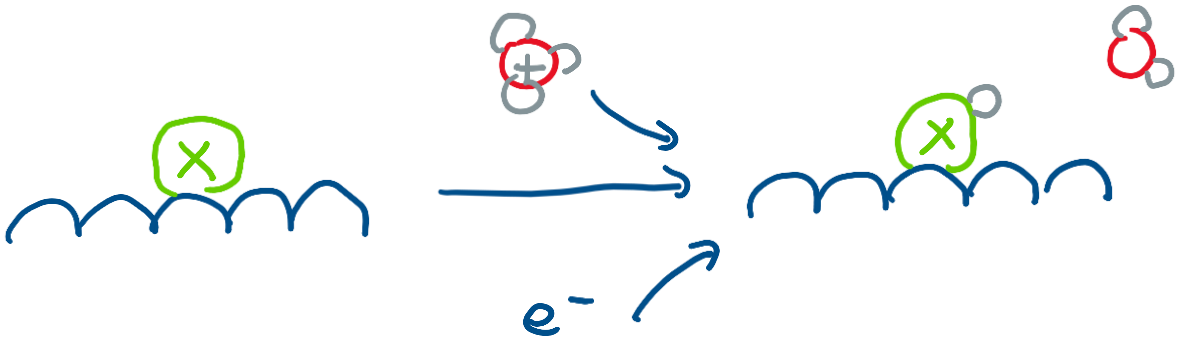
assumption: independent of potential

$$\Delta G(U_{RHE}) \approx G(XH^*) - G(X^*) - G(H^+) - G(e^-; U_{RHE})$$

Computational hydrogen electrode method

As applied to a hydrogenation reaction:

$$X^* + H^+ + e^- \rightarrow XH^*$$



$$\Delta G(U_{RHE}) \approx G(\mathrm{XH^*}) - G(\mathrm{X^*}) - G(\mathrm{H^+}) - \mathrm{G}(e^-; \mathrm{U_{RHE}})$$

use SHE:

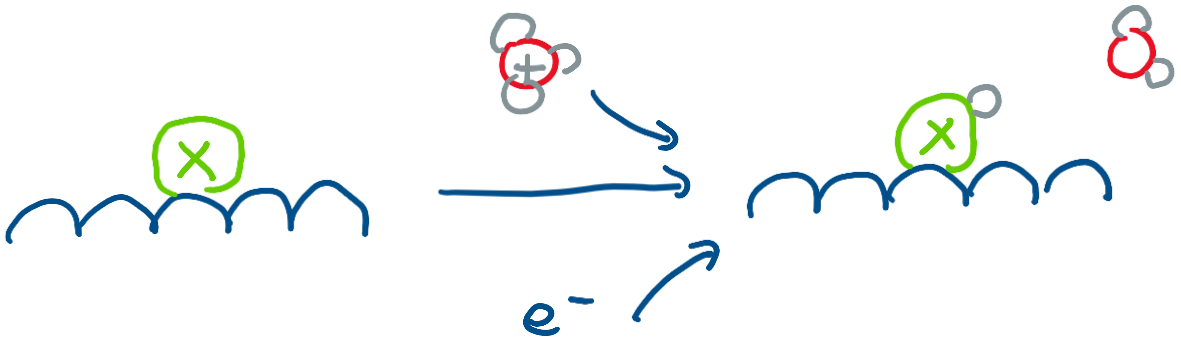
$$G(H^+) + G(e^- @ U_{RHE}) = G\left(\frac{1}{2}H_2\right) - eU_{RHE}$$

$$\Delta G(U_{RHE}) \approx G(\mathrm{XH^*}) - G(\mathrm{X^*}) - \frac{1}{2}H_2 + eU_{RHE}$$

Computational hydrogen electrode method

As applied to a hydrogenation reaction:

$$X^* + H^+ + e^- \rightarrow XH^*$$



$$\Delta G(U_{RHE}) \approx G(XH^*) - G(X^*) - \frac{1}{2}H_2 + eU_{RHE}$$

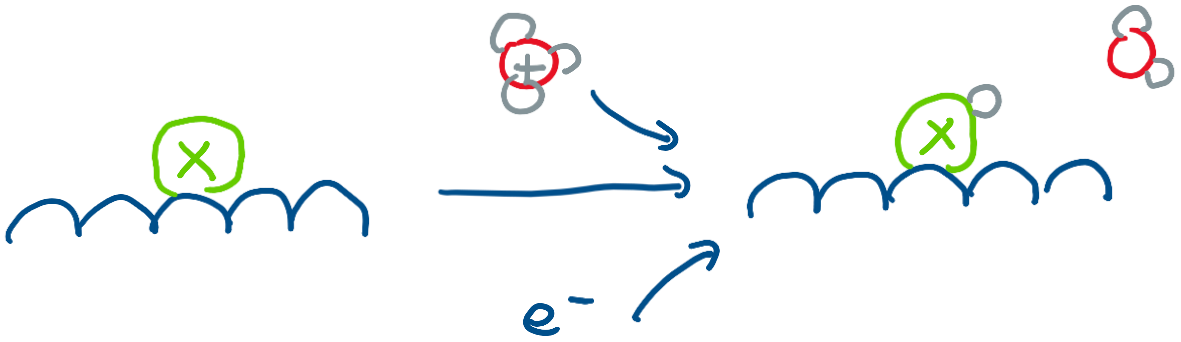
compute energy of
- XH^*
- X^*
- H_2

No potential needed during calculation! Only features in a posteriori correction!

Computational hydrogen electrode method

As applied to a hydrogenation reaction:

$$X^* + H^+ + e^- \rightarrow XH^*$$



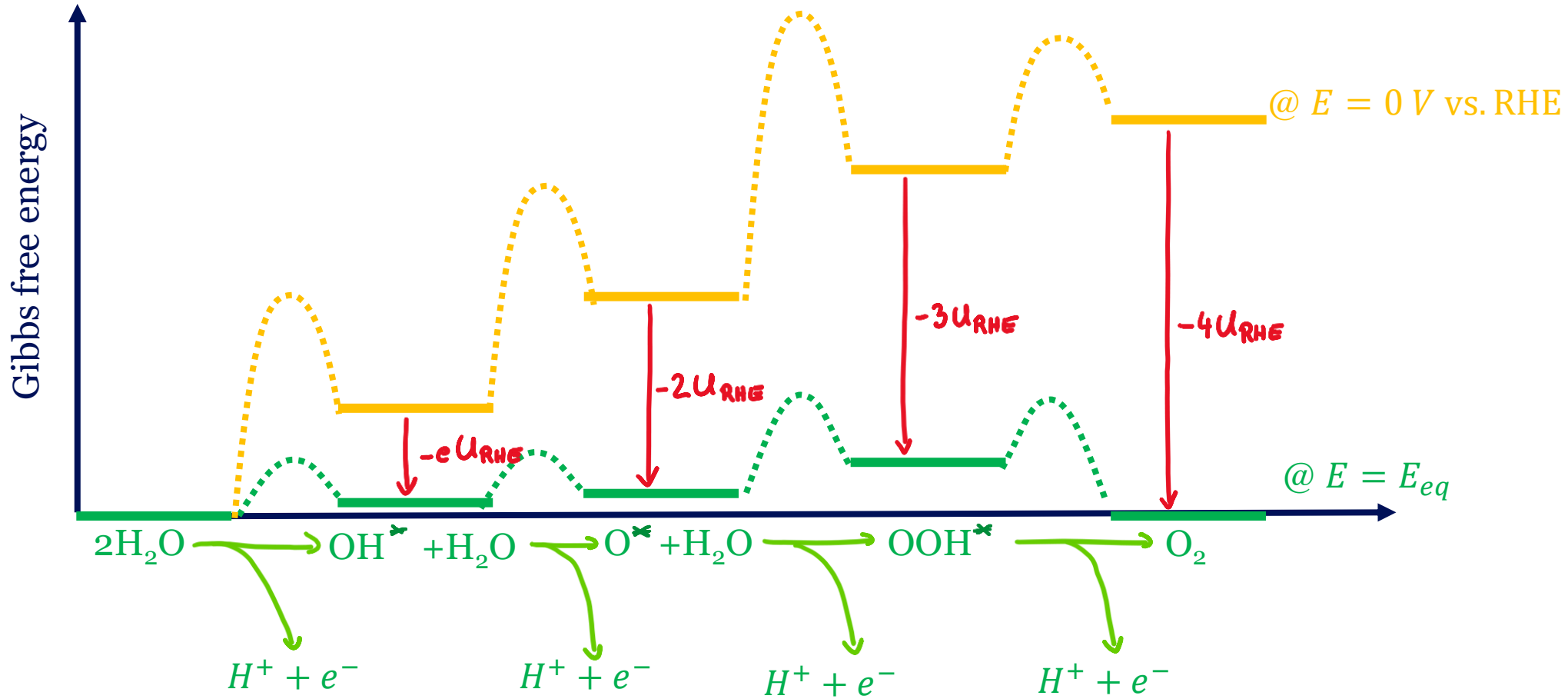
$$\Delta G(U_{RHE}) \approx G(XH^*) - G(X^*) - \frac{1}{2}H_2 + eU_{RHE}$$

compute energy of
- XH^*
- X^*
- H_2

Why do we need to compute this? Isn't that known?!

Computational hydrogen electrode method

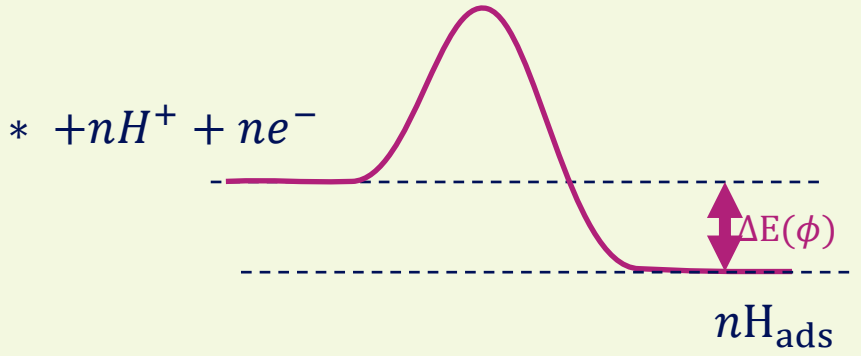
$$\Delta G(U_{RHE}) \approx G(X^*) + \frac{1}{2}H_2 - eU_{RHE} - G(\mathrm{XH}^*)$$



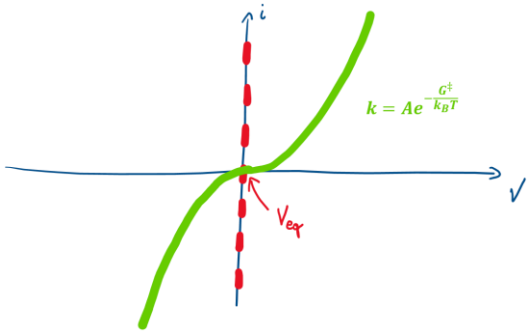
EC Adsorption energies – computer exercise

- $nH^+ + ne^- + * \rightarrow n\mathrm{H}_{\mathrm{ads}}$

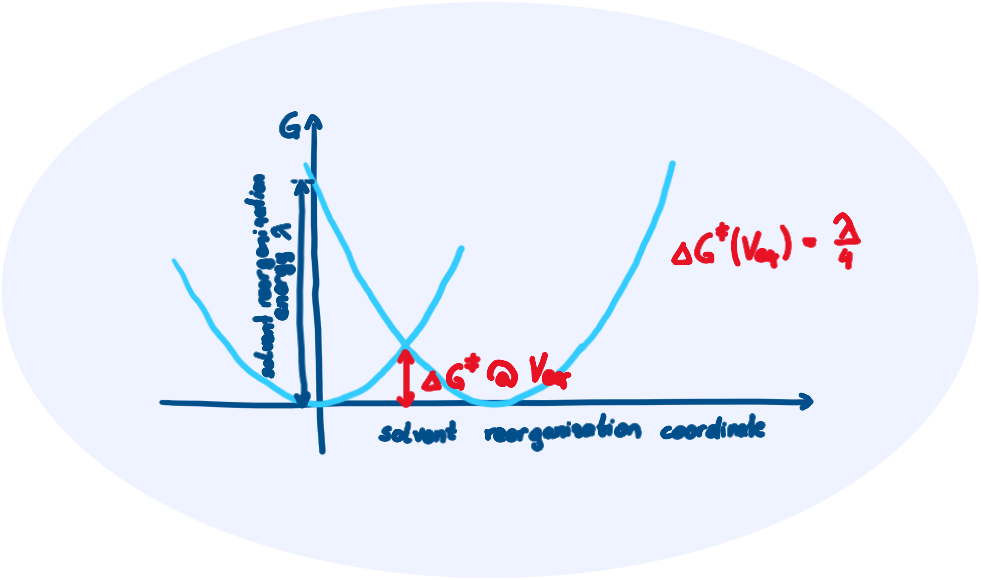
- Use gpaw!
- Lab instructions in folder: Ex2_Hads_e-chem



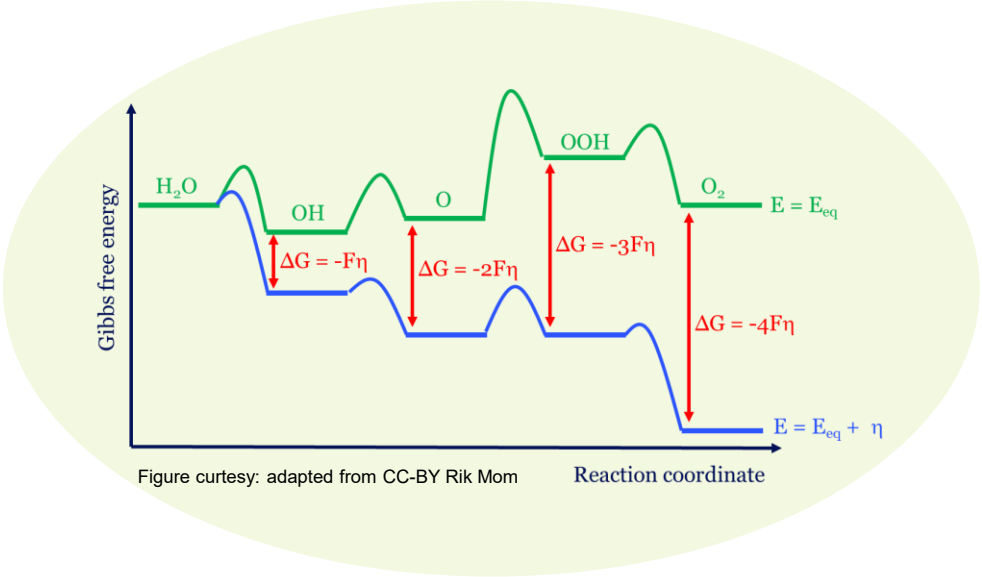
Computational hydrogen electrode



Barriers vs. reaction energies?!

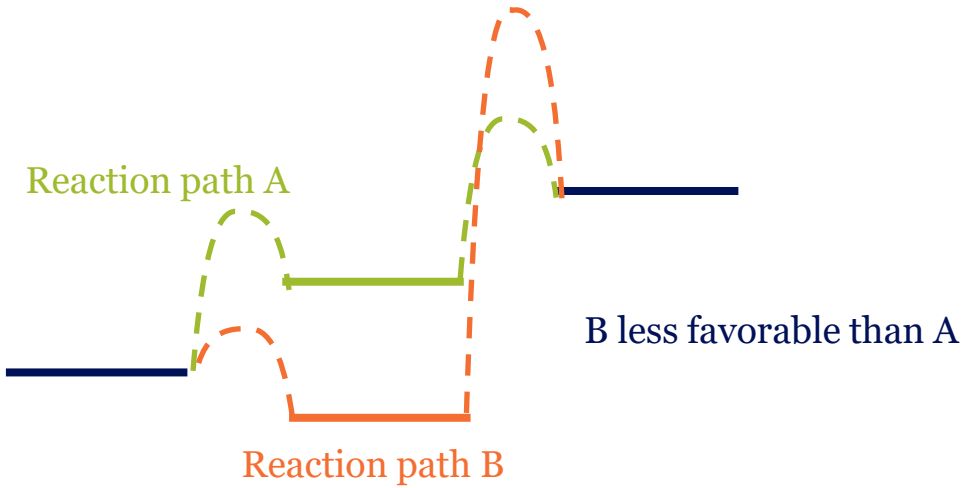


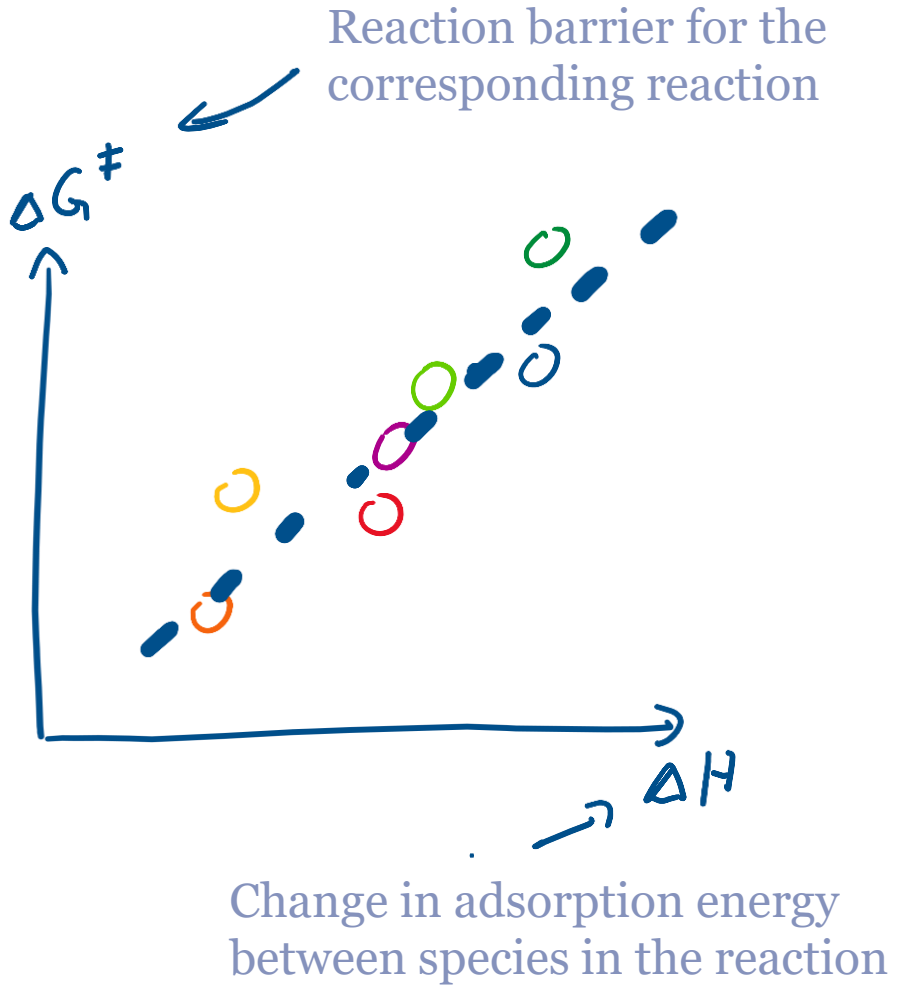
versus



Brønsted-Evans-Polanyi (BEP) relations

- Assumes that barrier scales with reaction enthalpy





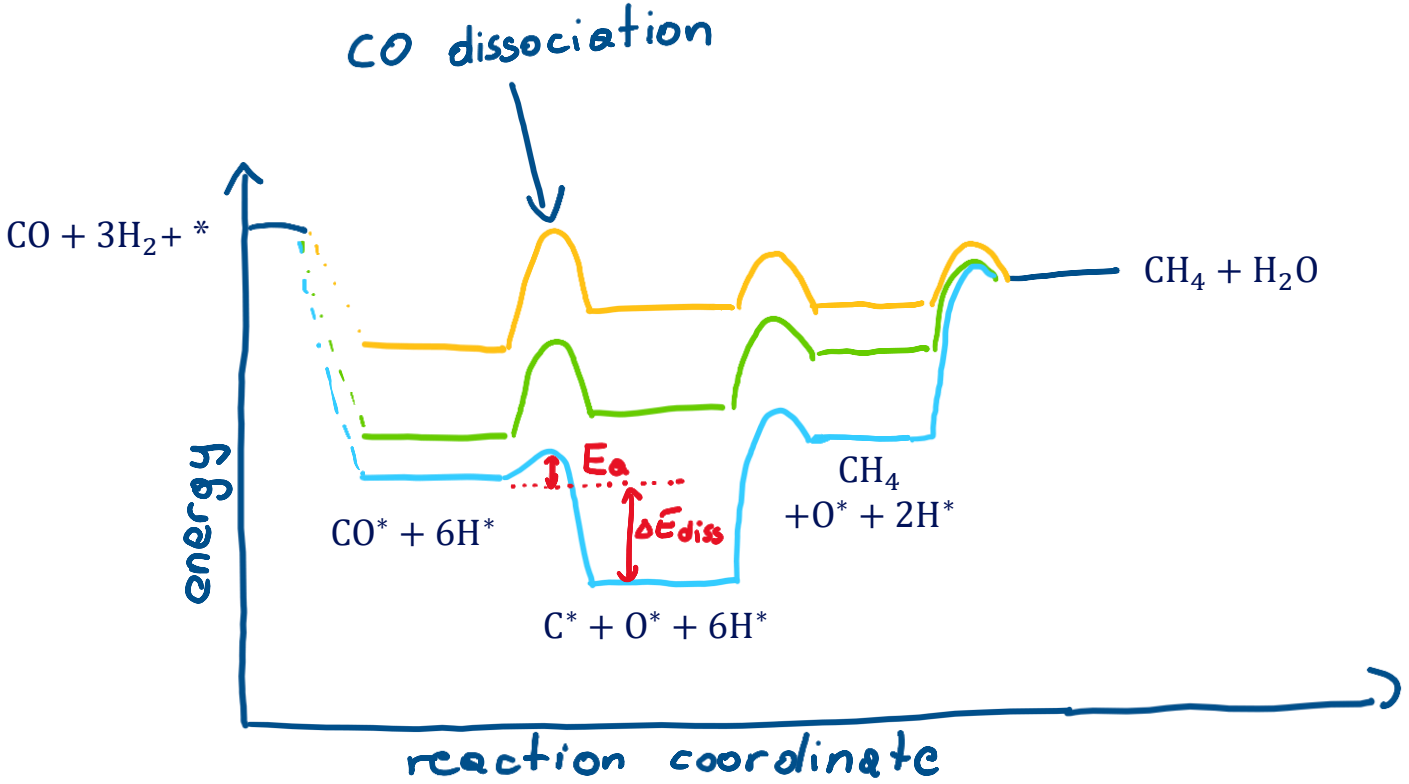
$$E_a \approx E_0 + \alpha \Delta H$$

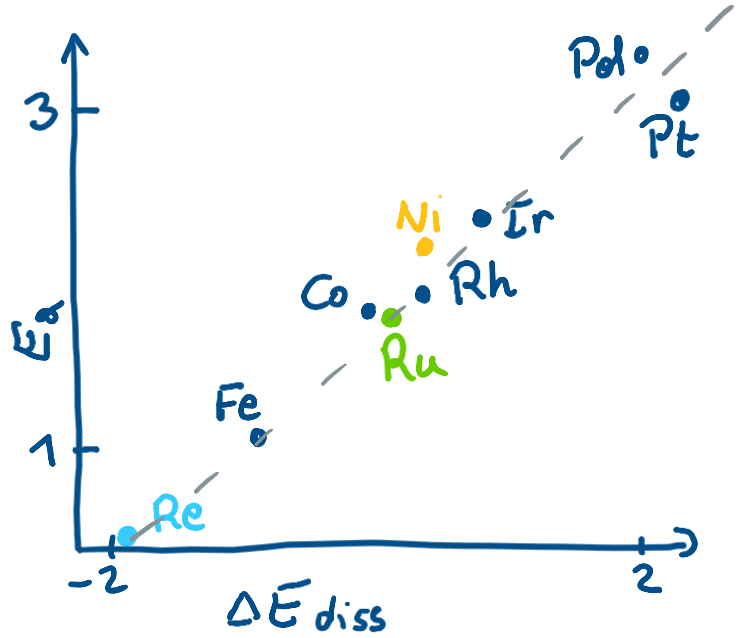
Brønsted-Evans-Polanyi (BEP) relations

- Example: Heterogeneous catalysis

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

Example taken from: Nørskov, J. et al. (2009). *Nat Chem.* 1(1), 37–46



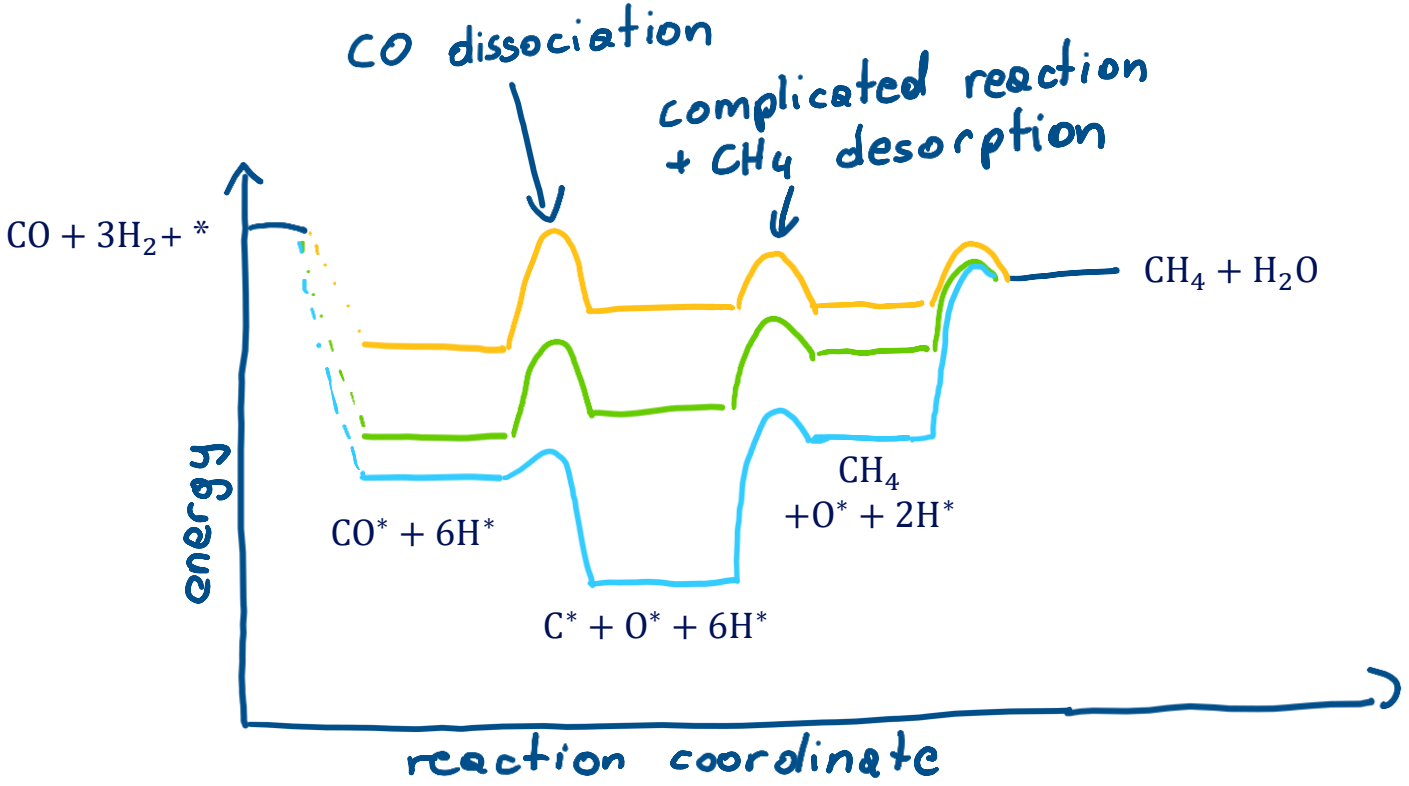


Sabatier principle

- Example: Heterogeneous catalysis

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

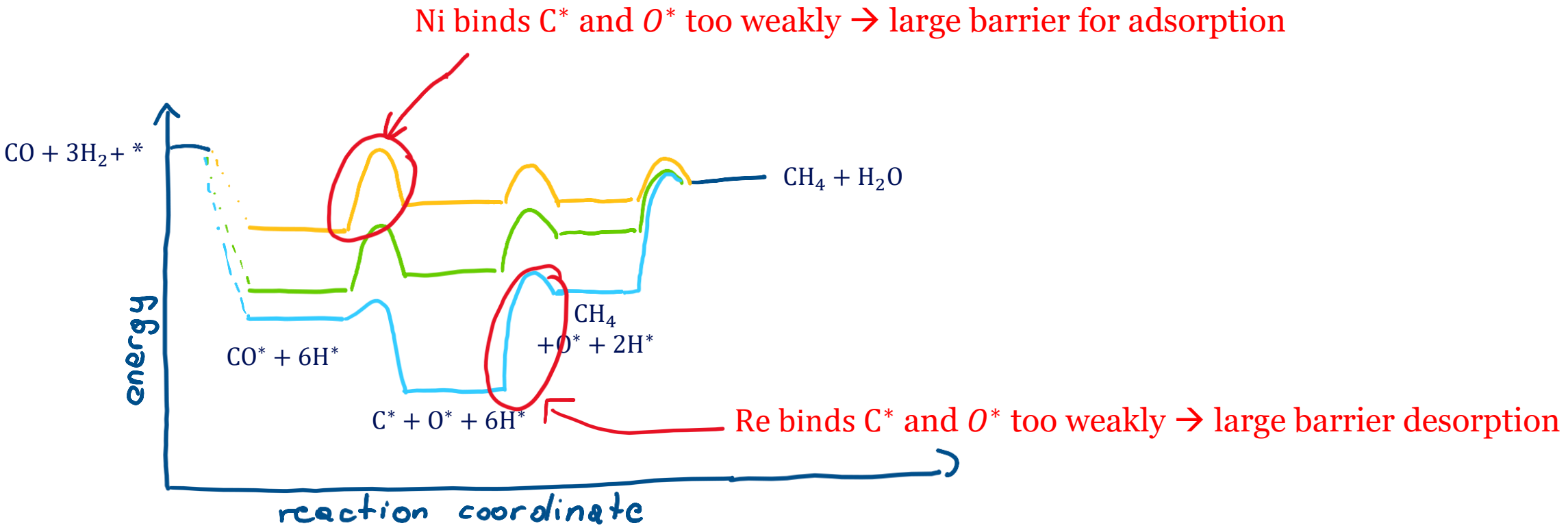
Example taken from: Nørskov, J. et al. (2009). *Nat Chem.* 1(1), 37–46



Sabatier principle

- $CO + 3H_2 \rightarrow CH_4 + H_2O$

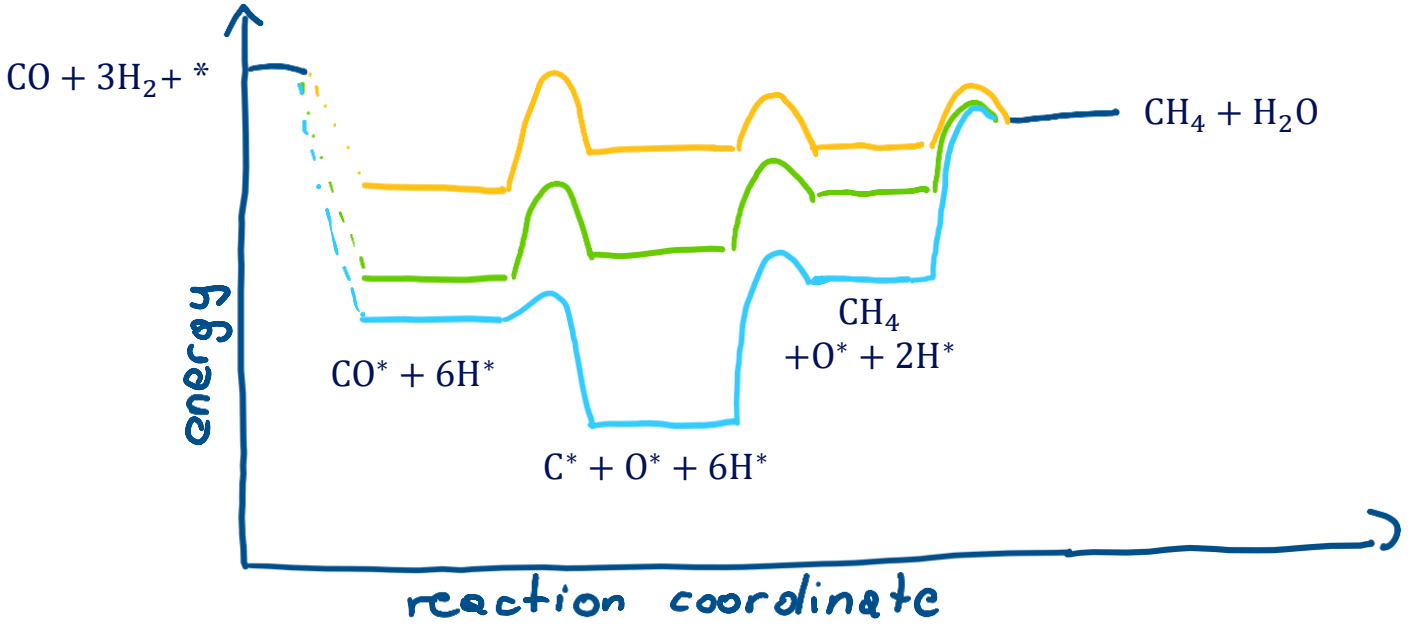
Example taken from: Nørskov, J. et al. (2009). *Nat Chem.* 1(1), 37–46

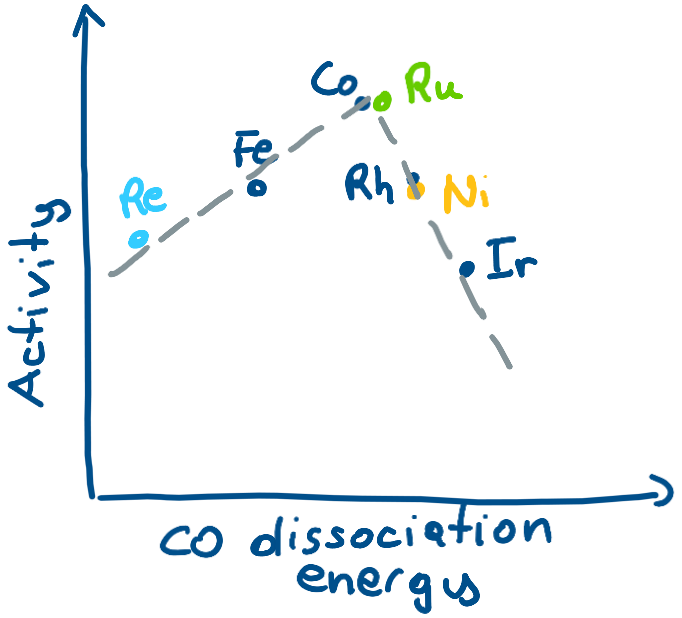


Sabatier principle and volcano plots

- $CO + 3H_2 \rightarrow CH_4 + H_2O$

Example taken from: Nørskov, J. et al. (2009). *Nat Chem.* 1(1), 37–46





Ideal catalyst and scaling relations

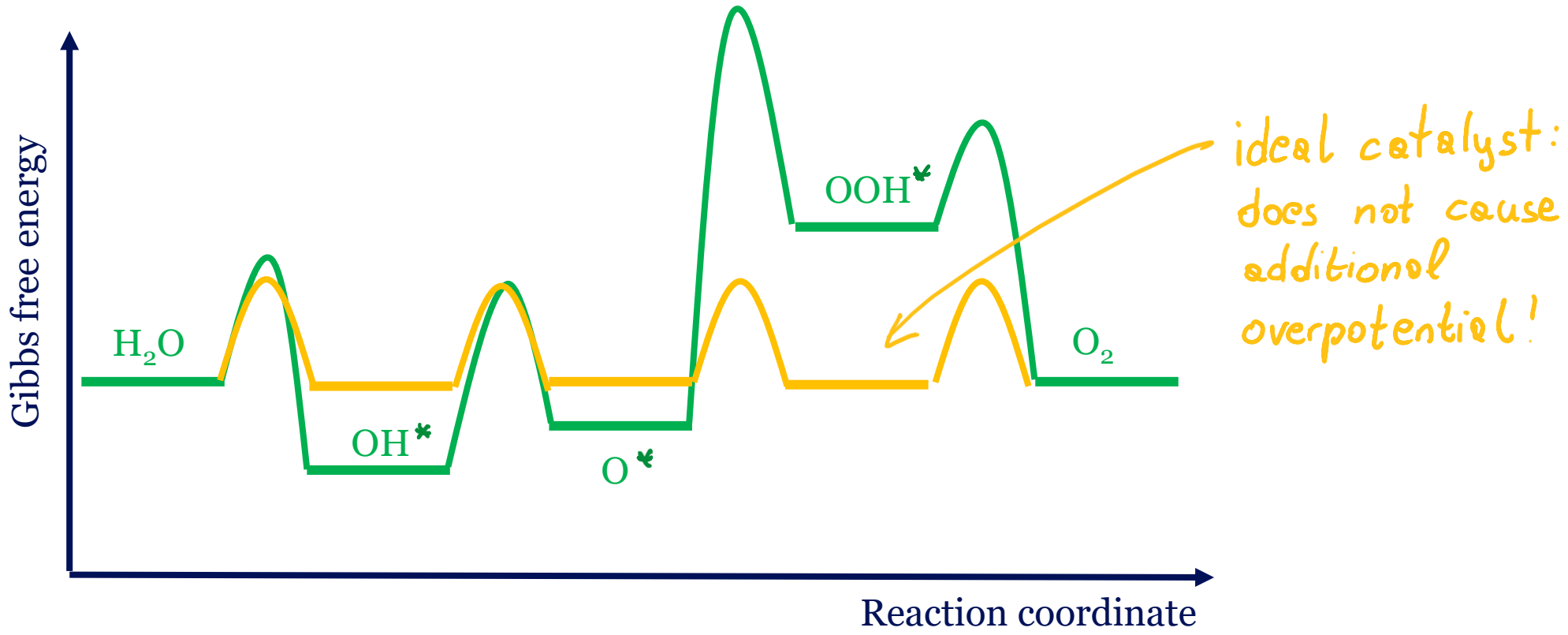


Figure curtesy: adapted with permission from CC-BY Rik Mom

Ideal catalyst and scaling relations

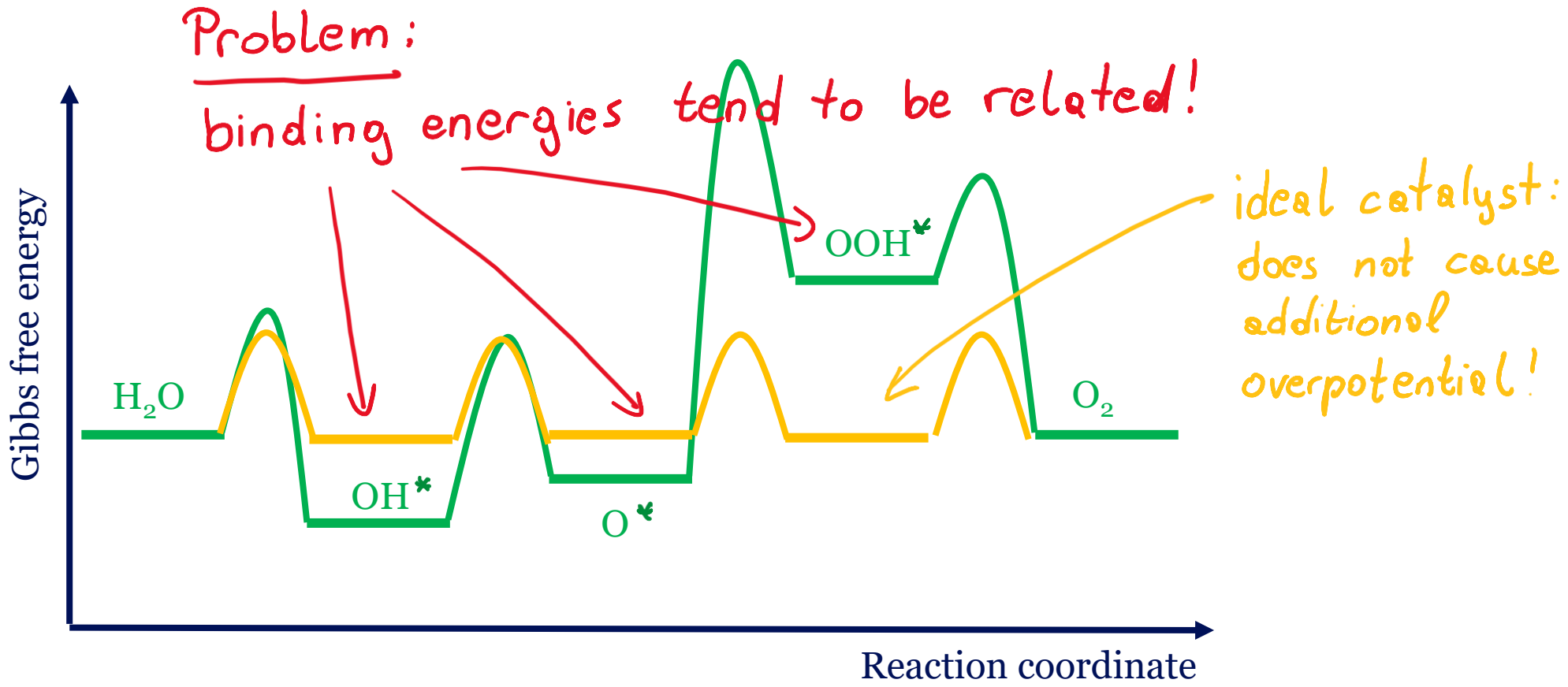
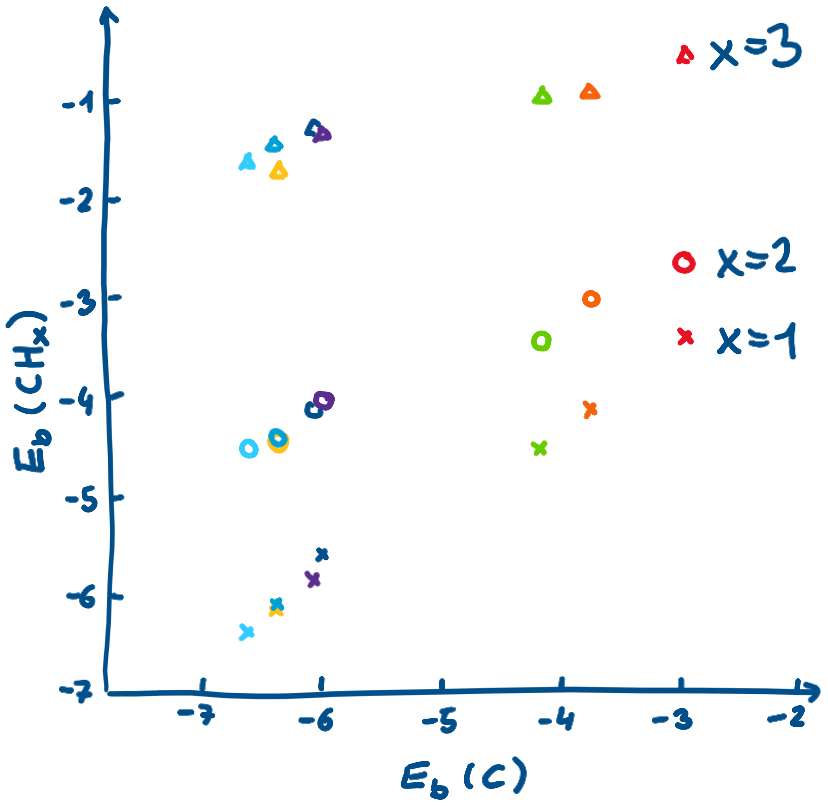
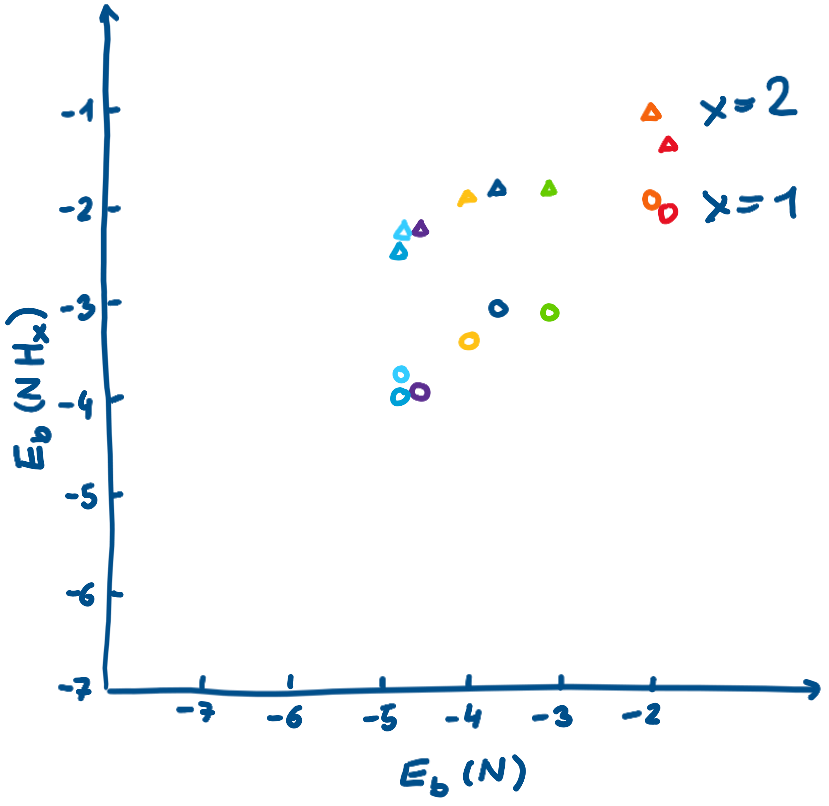
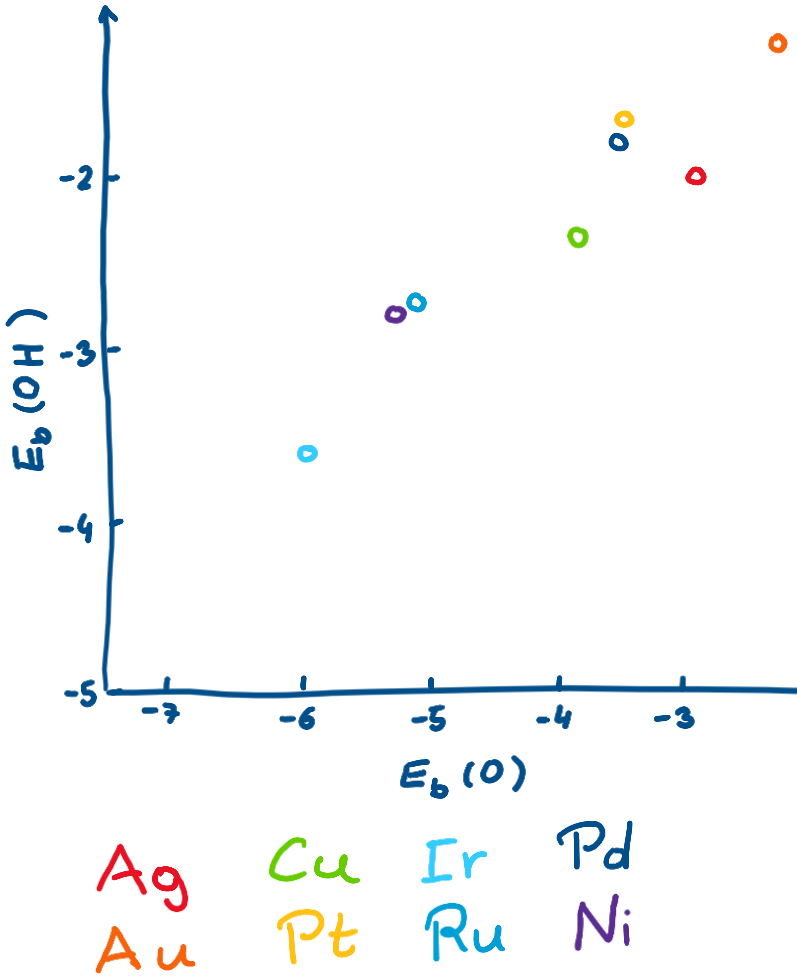


Figure curtesy: adapted with permission from CC-BY Rik Mom

Scaling relations

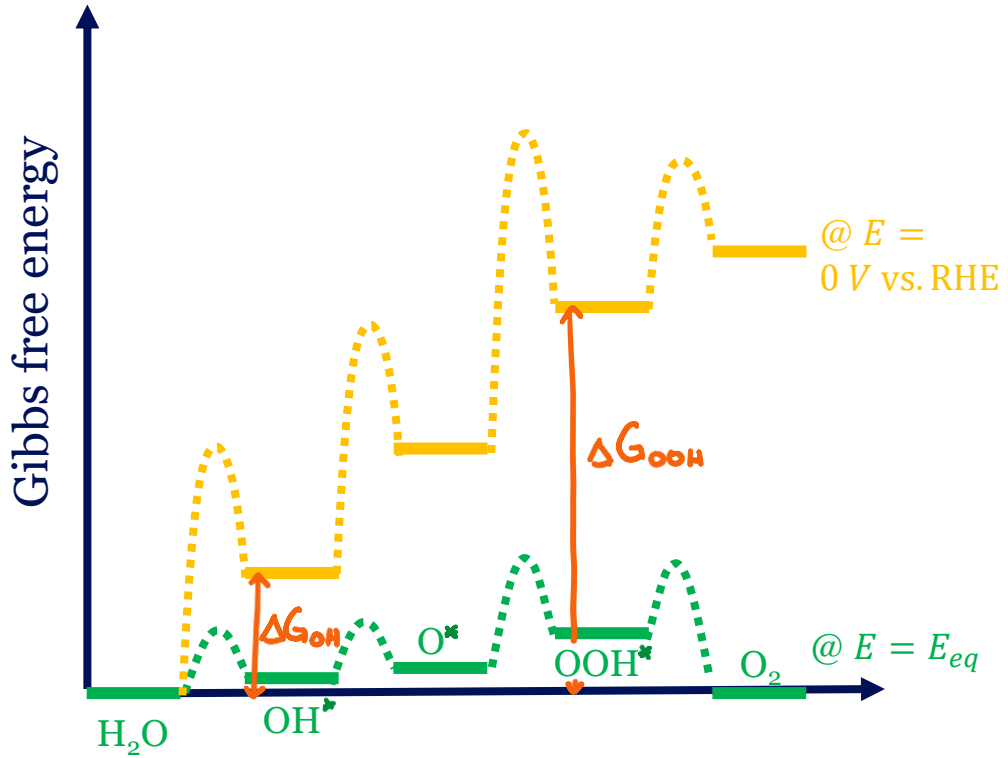


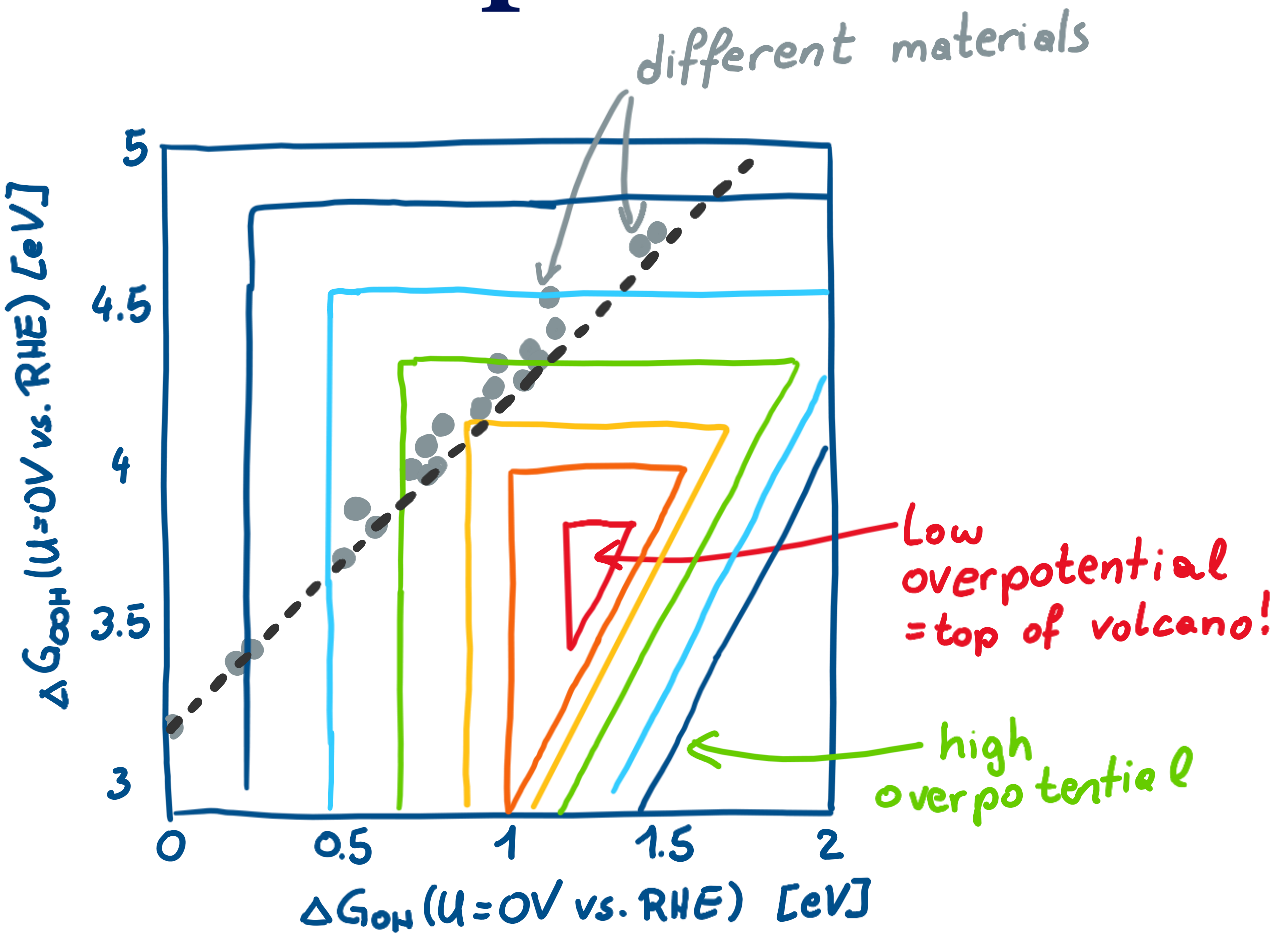




Data from: Abid-Pedersen et al., Phys. Rev. Lett. 99, 016105

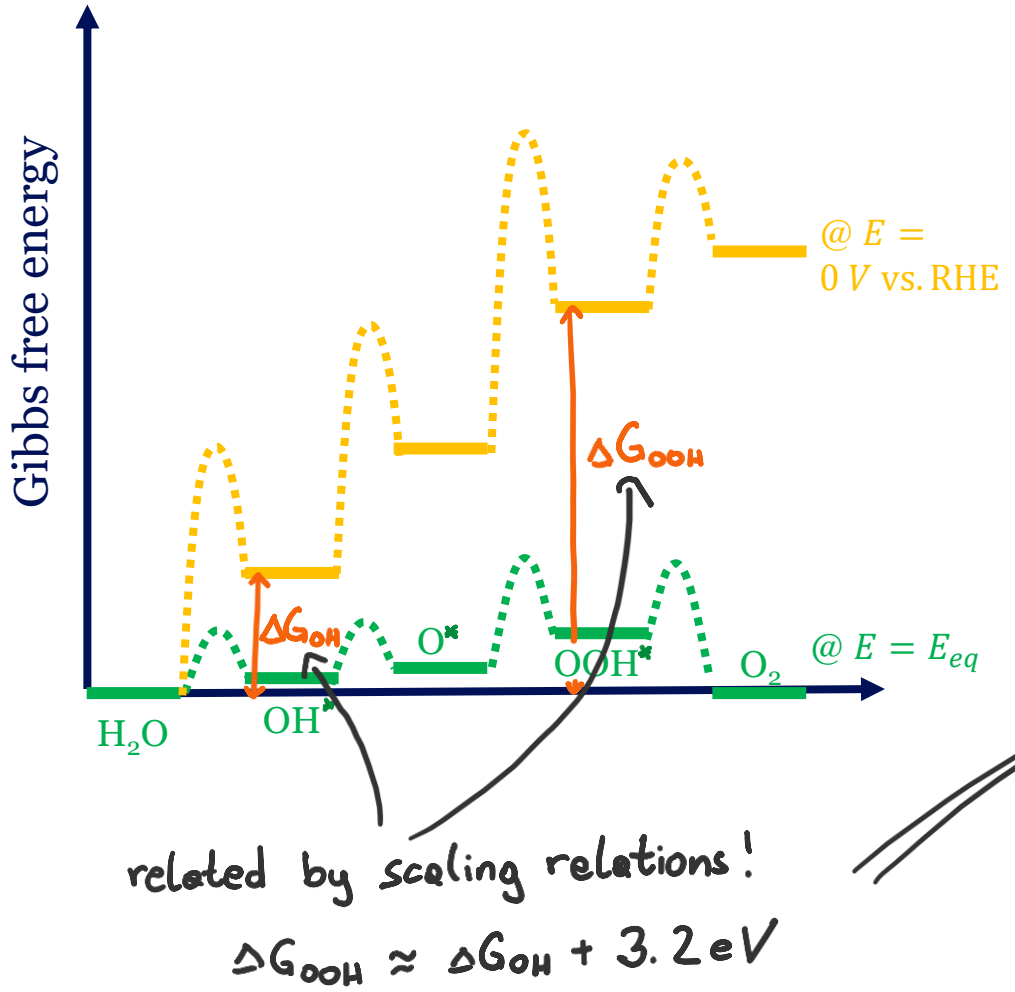
Scaling relations and volcano plots

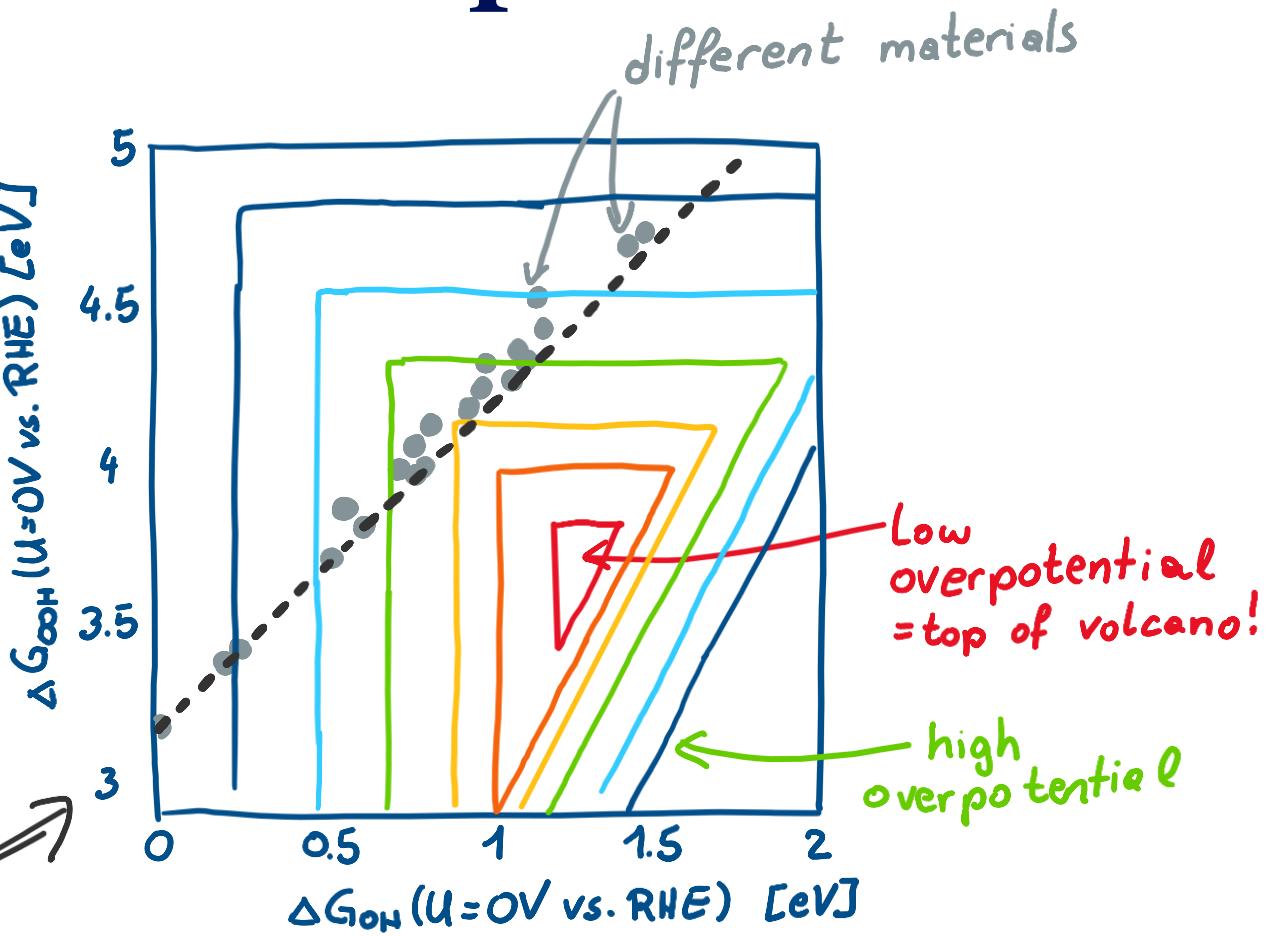




Data from: Chem. Rev. 2018, 118, 5, 2302–2312

Scaling relations and volcano plots



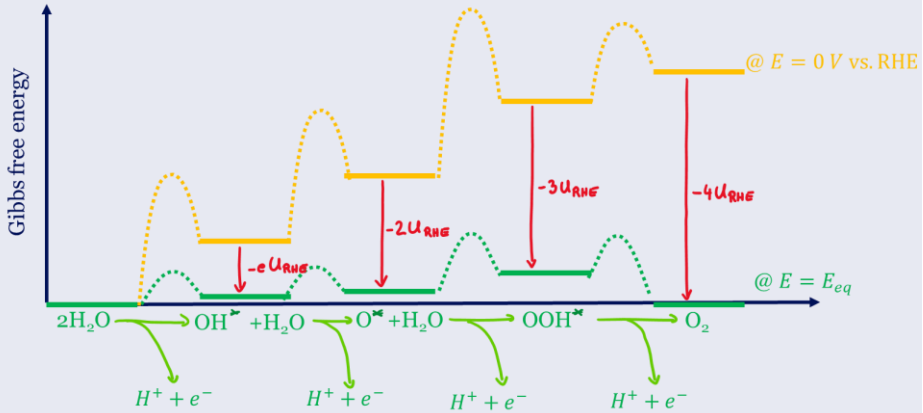


Data from: Chem. Rev. 2018, 118, 5, 2302–2312

Take home messages

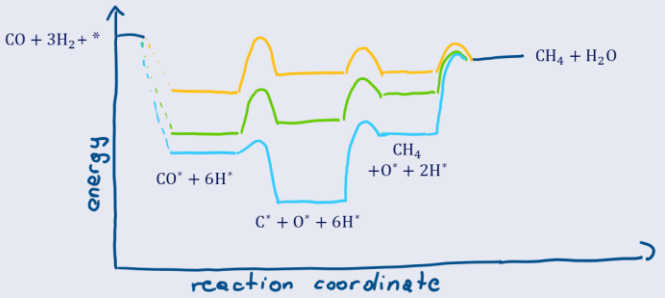
Computational hydrogen electrode method

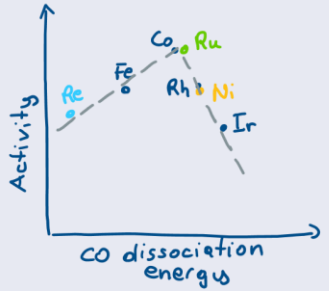
- allows electrochemical reaction energies
  - for hydrogenation/dehydrogenatin reactions
  - (Can be extended to other species in a similar fashion exploiting equilibrium potentials.)
- No good for dipolar species/partial charge transfer/transition states



Simple reaction energetics are relevant for

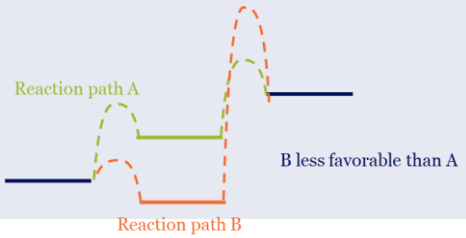
- Determining potential limiting step
- Volcano relations





The success of this approach is based on

- The Brønsted-Evans-Polanyi (BEP) relations



Part 3: Beyond the computational hydrogen electrode method

Katharina Doblhoff-Dier| Han-sur-Lesse winterschool 2025

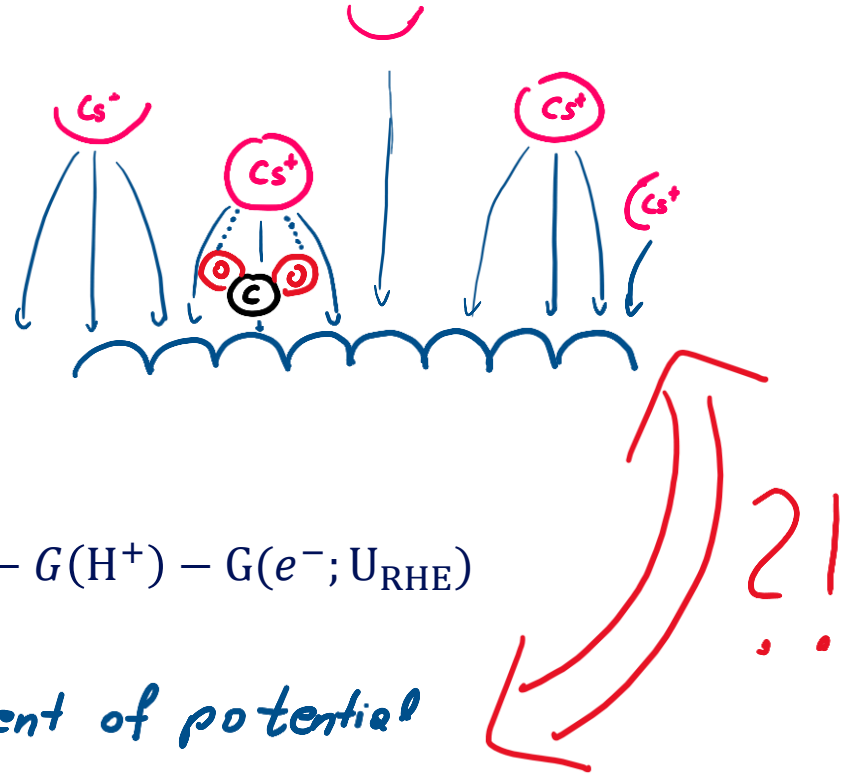
Universiteit Leiden
The Netherlands

Computational electrochemistry

1. Electrochemistry: The basics
2. Computational catalysis and computational electrocatalysis
3. **Beyond the computational hydrogen electrode method**
   - Half-cell simulations
   - Constant potential DFT
   - Computer exercise: Volmer reaction
4. When the electrolyte is key
5. Mass transport

Computational hydrogen electrode – limitations (1)

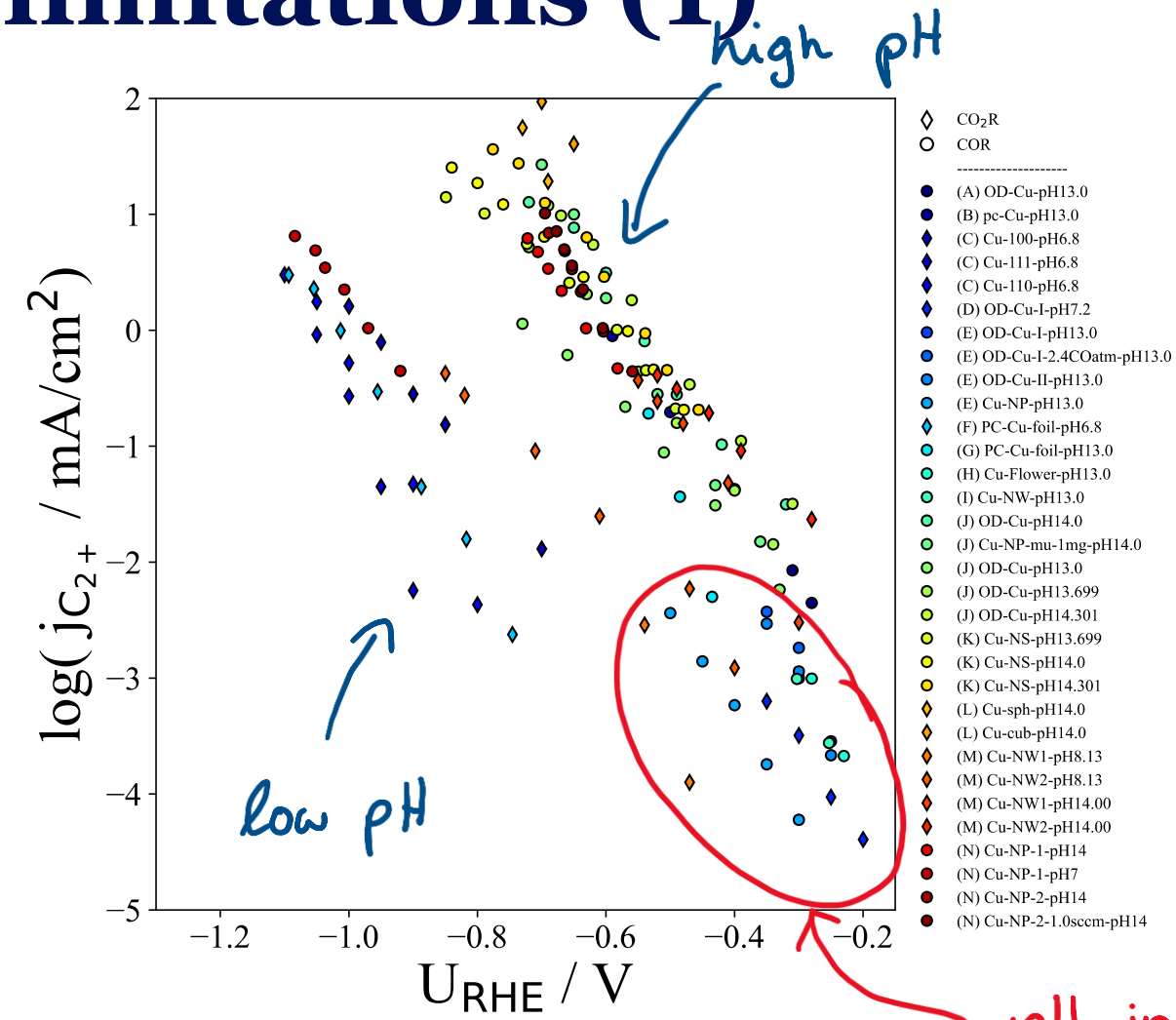
- Assumes adsorbate energy is independent of potential
  - No electric field effects
  - Incorrect description of partial charge transfer



$$\Delta G(U_{RHE}) = G(\mathrm{XH}^*; U_{RHE}) - G(\mathrm{X}^*; \mathrm{U_{RHE}}) - G(\mathrm{H}^+) - \mathrm{G}(e^-; \mathrm{U_{RHE}})$$

assumption: independent of potential

Computational hydrogen electrode – limitations (1)



CO_2 (CO) reduction to C_2 products:

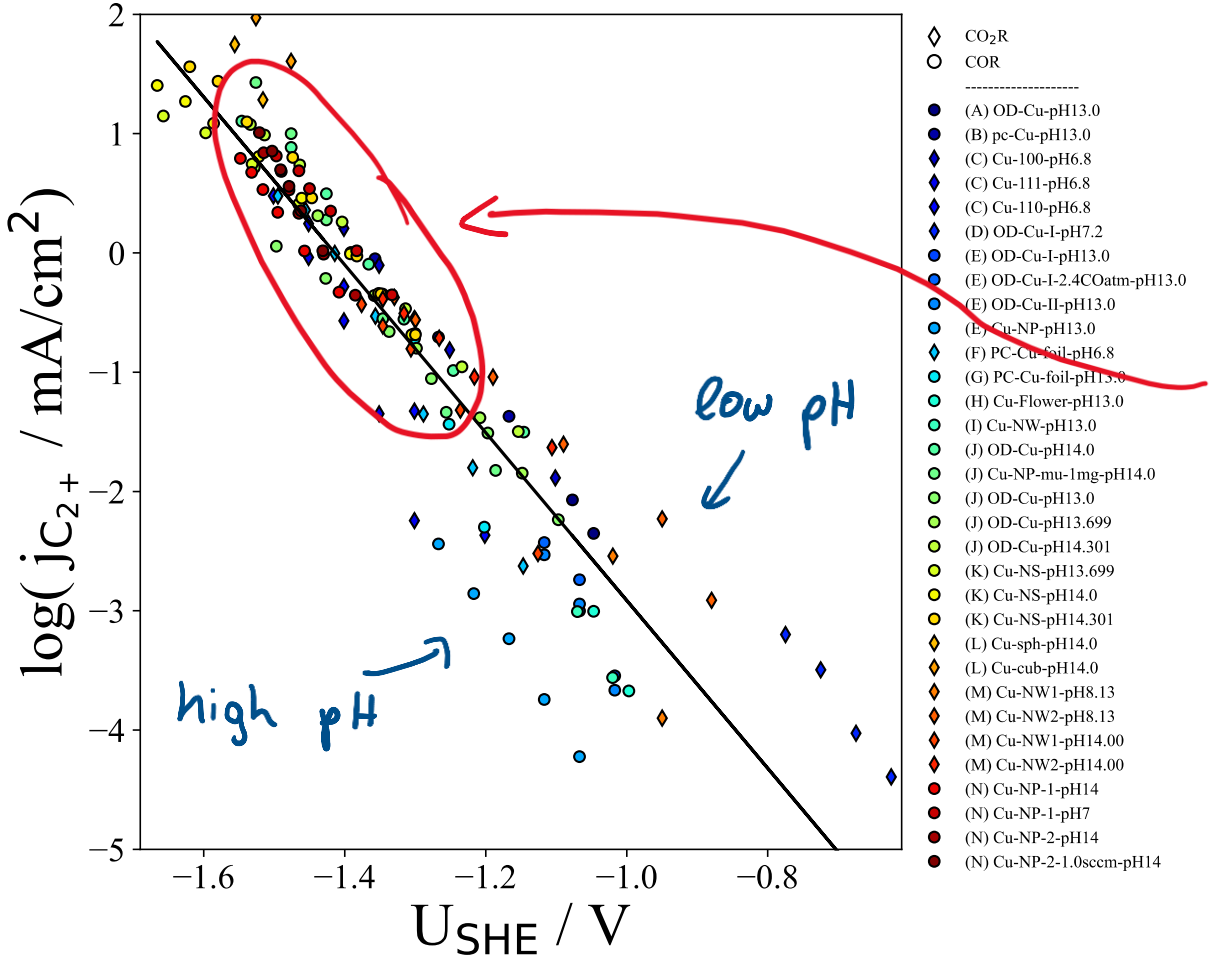
$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$$

(A) Bertheussen et al, Angew.Chem. Int.Ed. 55 (2016)
(B) Betheussen et al, ACS Energy Lett. 3, 3 (2018)
(C) Huang, et al, ACS Catal. 7 (2017)
(D) Li and Kanan, J. Am. Chem. Soc. 134, 17 (2012)
(E) Li et al, Nature 508 (2014)
(F) Kuhl et al., Energy Environ. Sci. 5 (2012)
(G) Wang et al., ACS Catal. 8, 8 (2018)
(H) Wang et al., Nature Catalysis 2 (2019)
(I) Raciti et al., ACS Catal. 7, 7 (2017)
(J) Jouny et al, Nature Catalysis 1 (2018)
(K) Luc et al, Nature Catalysis 2 (2019)
(L) De Gregorio ACS Catal. 10, 9 (2020)
(M) Zhang et al., J. Mater. Chem. A, 7 (2019)
(N) Ripatti et al., Joule 3 (2019)

pH independent on RHE scale ⇔ comp. hydrogen electrode

Figure curtesy: CC-BY Georg Kastlunger

Computational hydrogen electrode – limitations (1)



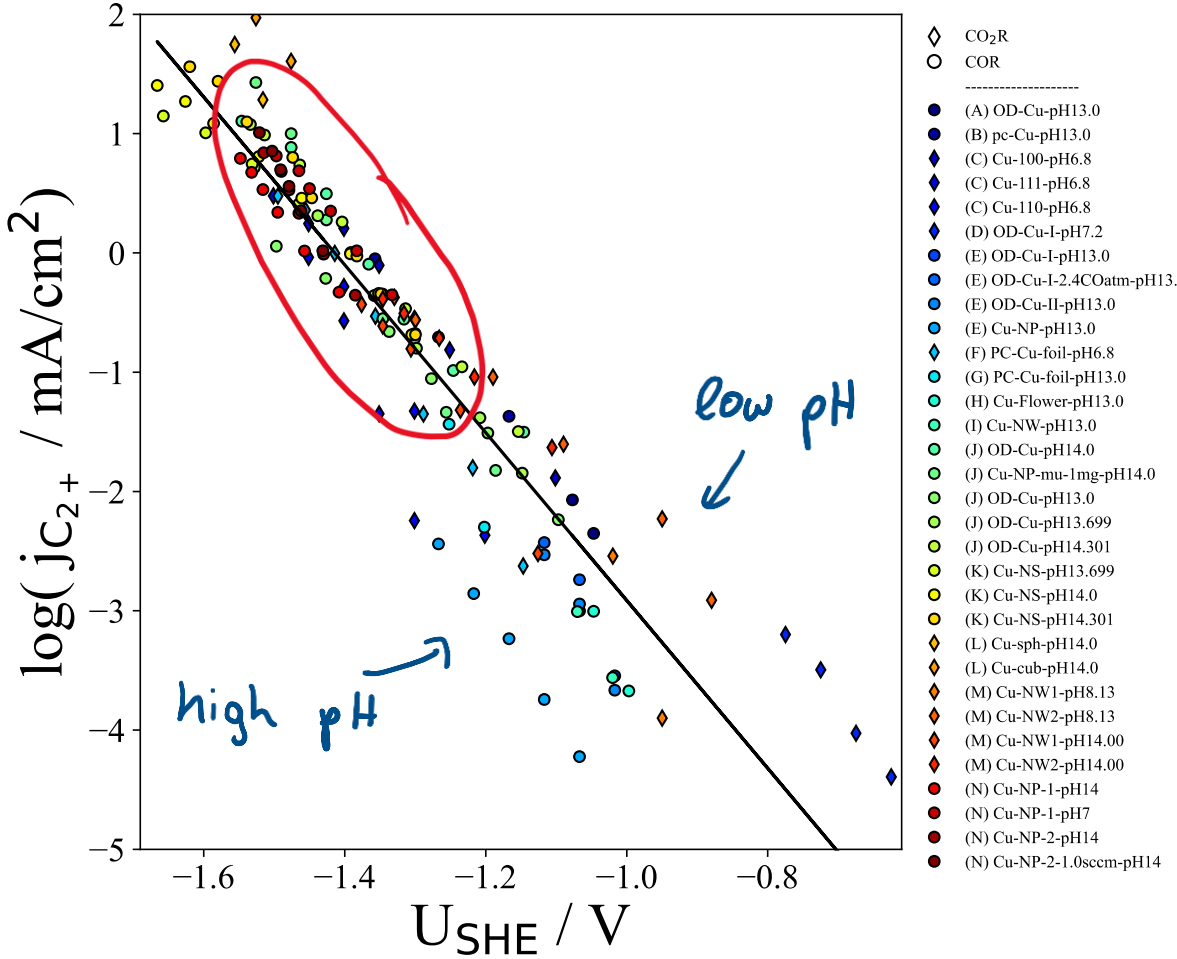
CO_2 (CO) reduction to C_2 products:

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$$

pH independent on SHE scale

Figure curtesy: CC-BY Georg Kastlunger

Computational hydrogen electrode – limitations (1)



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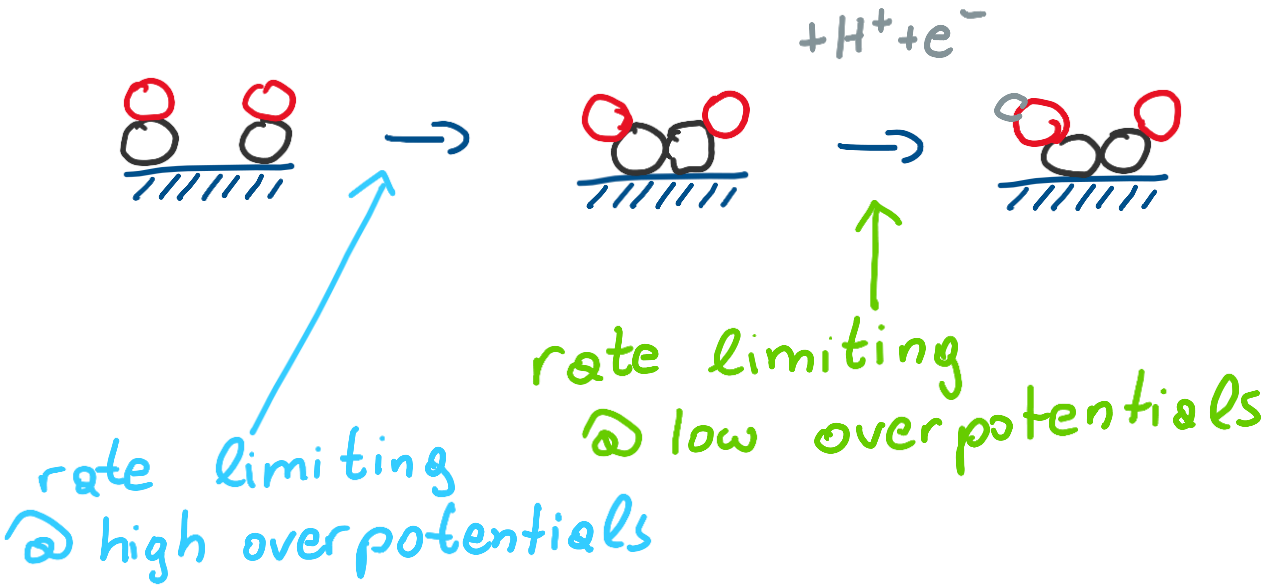

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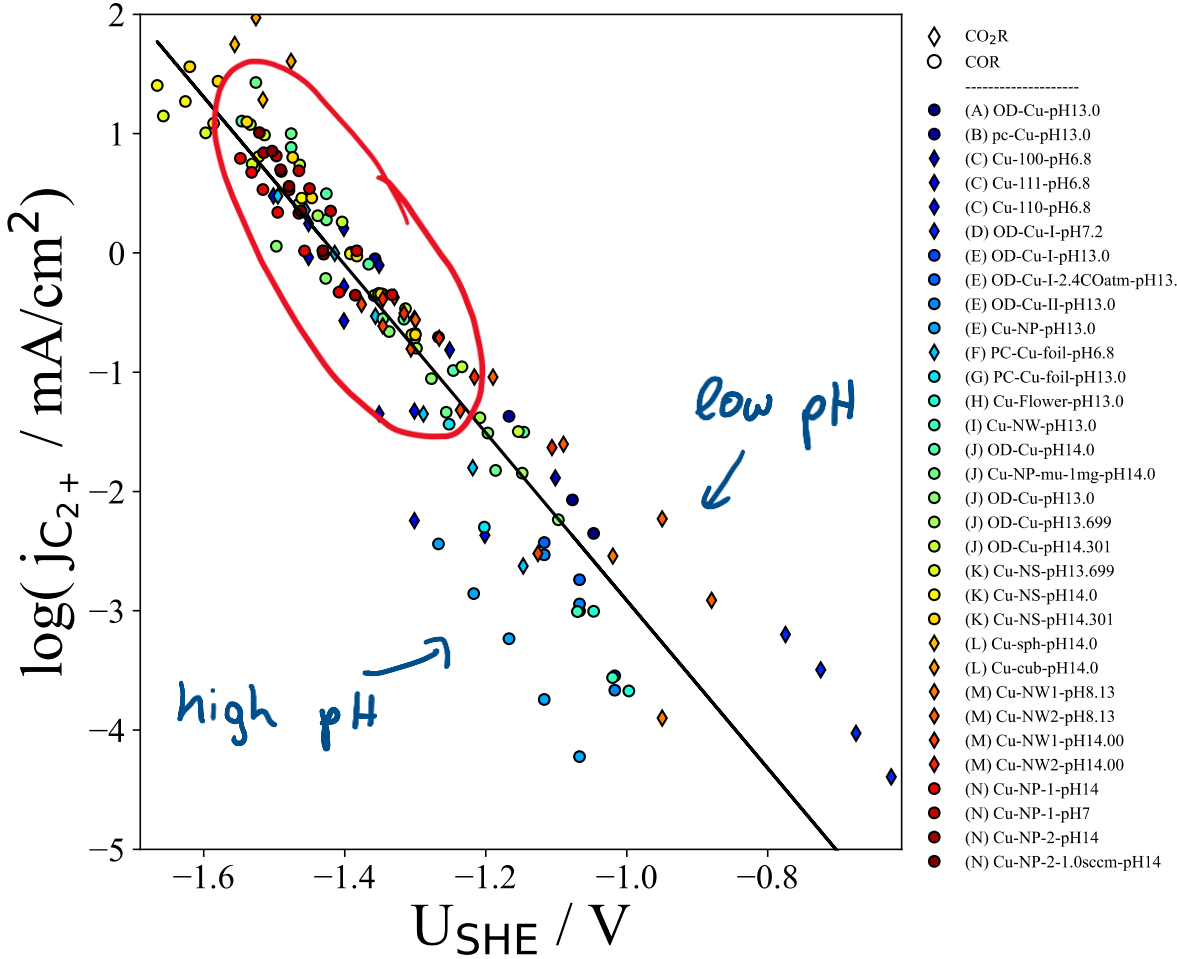
Computational hydrogen electrode – limitations (1)



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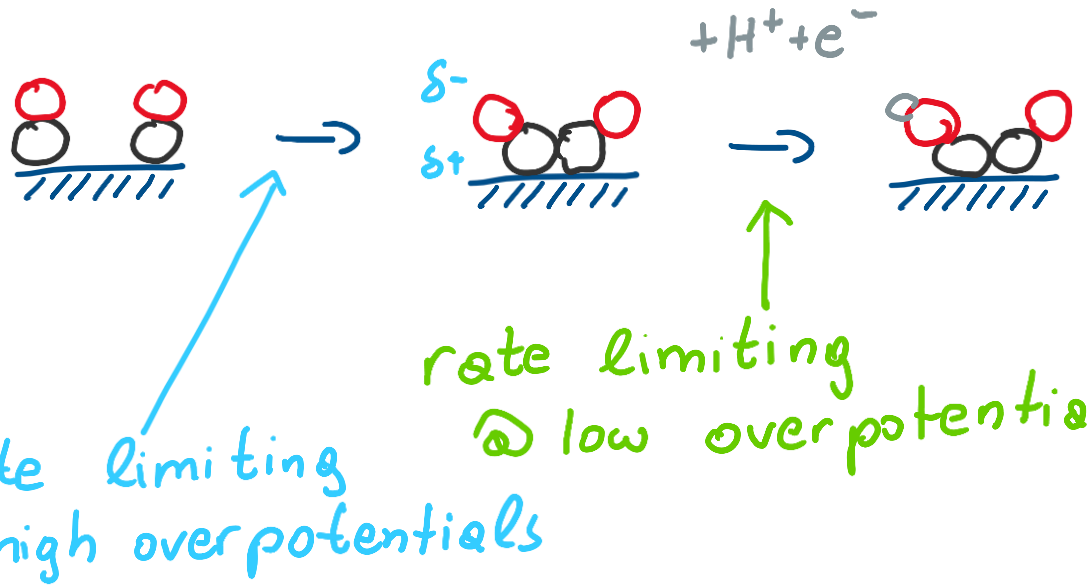

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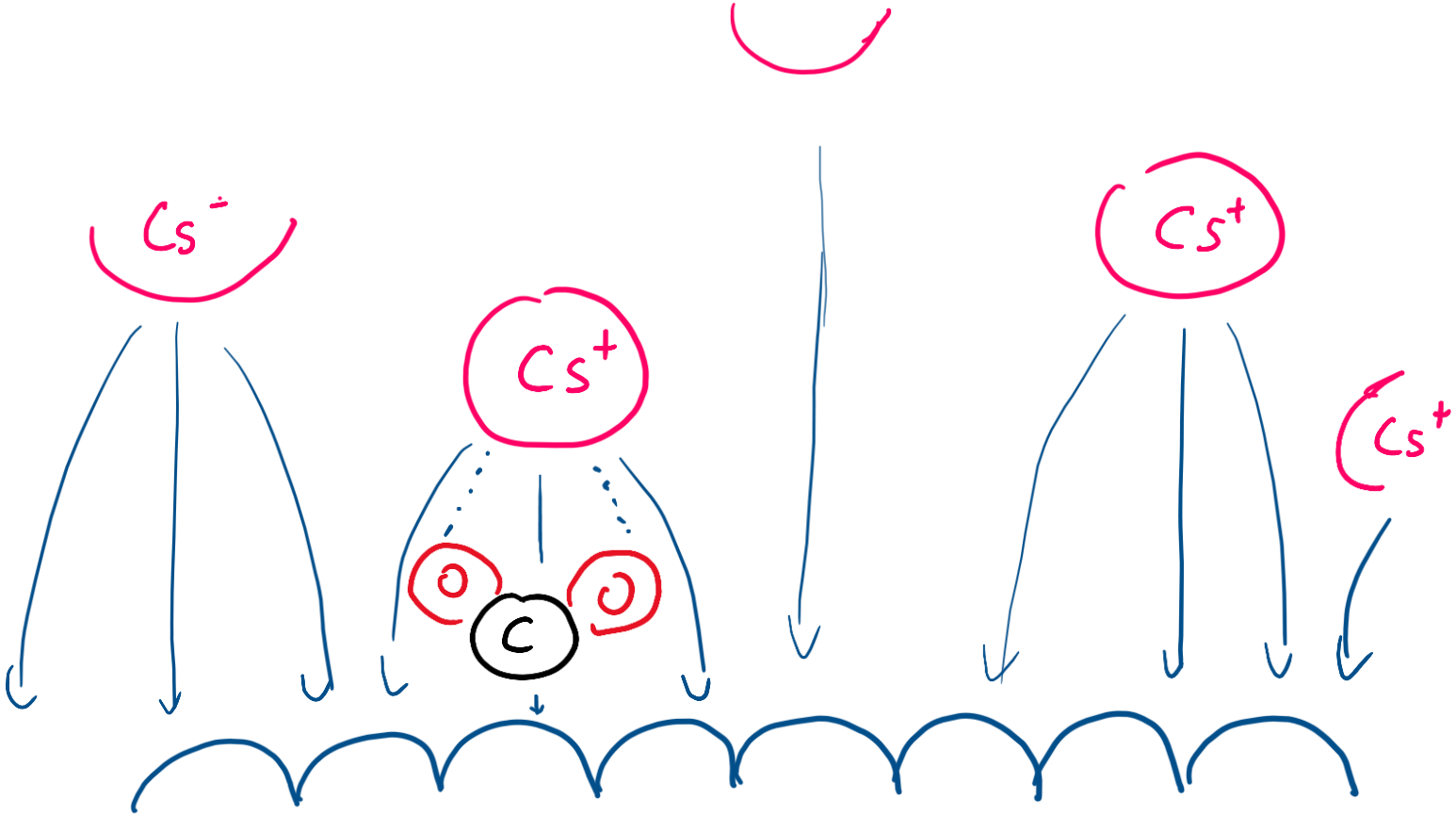
Computational hydrogen electrode – limitations (1)



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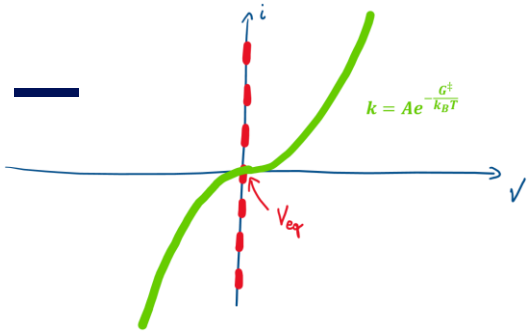
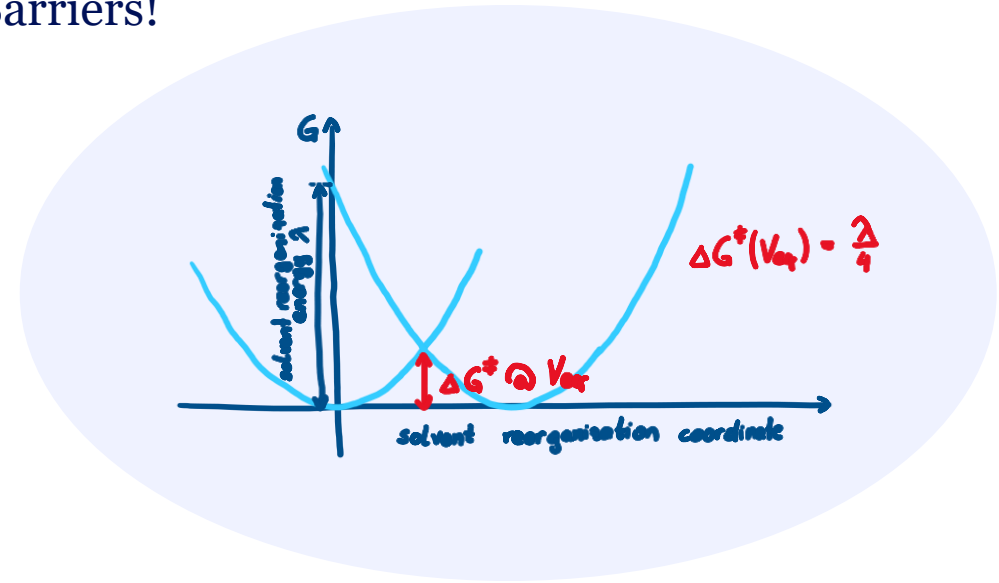
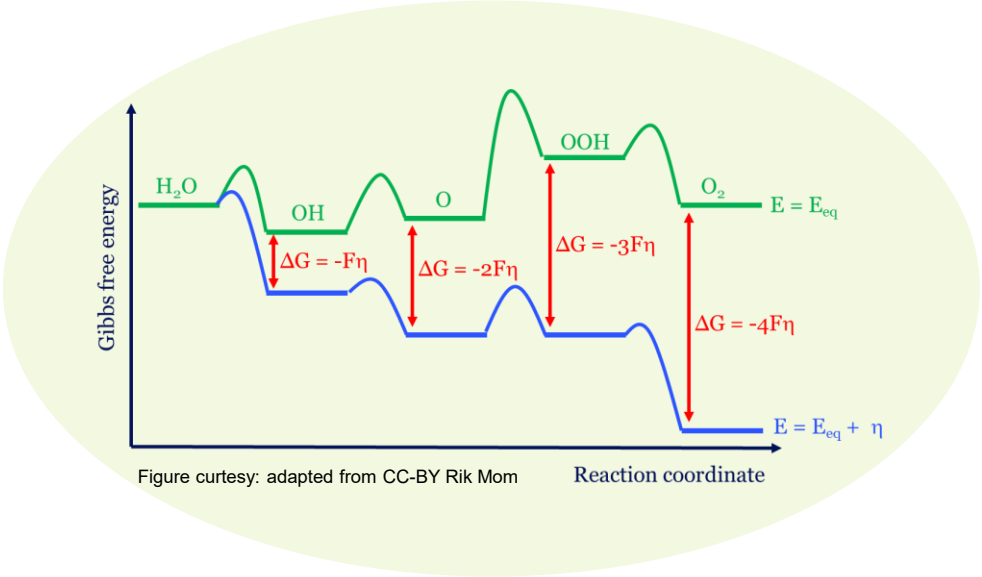
Computational hydrogen electrode – limitations (2)



- Barriers!



versus



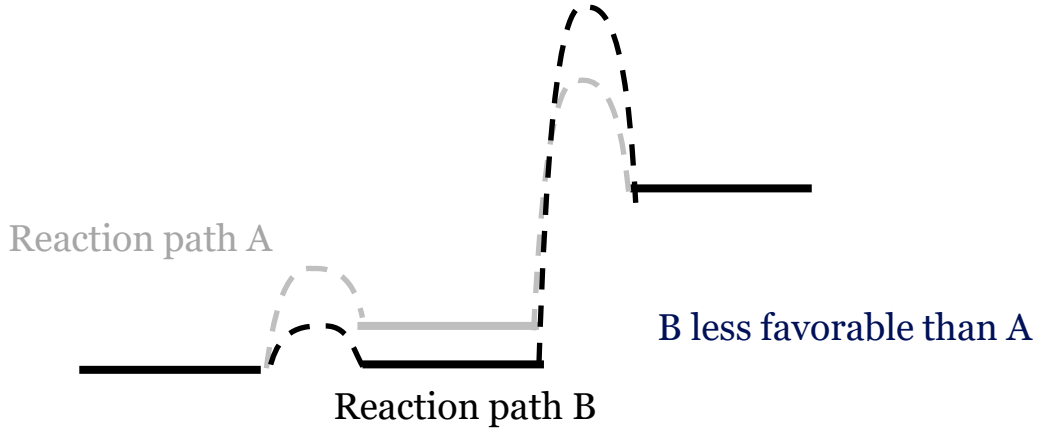
Barriers – When BEP fails

Brønsted-Evans-Polanyi

- Assumes perfect scaling between E_a and ΔE

\+ Reduces computational cost!
  - No transition state search needed!
  - No EC barriers → can often use CHE method

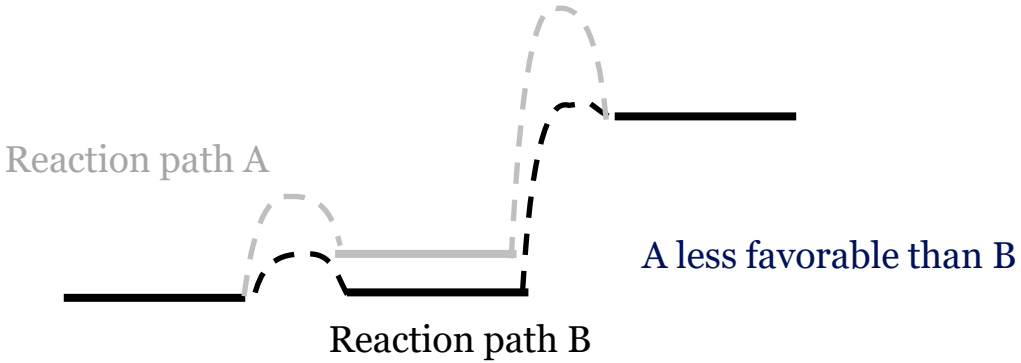
– Approximation!



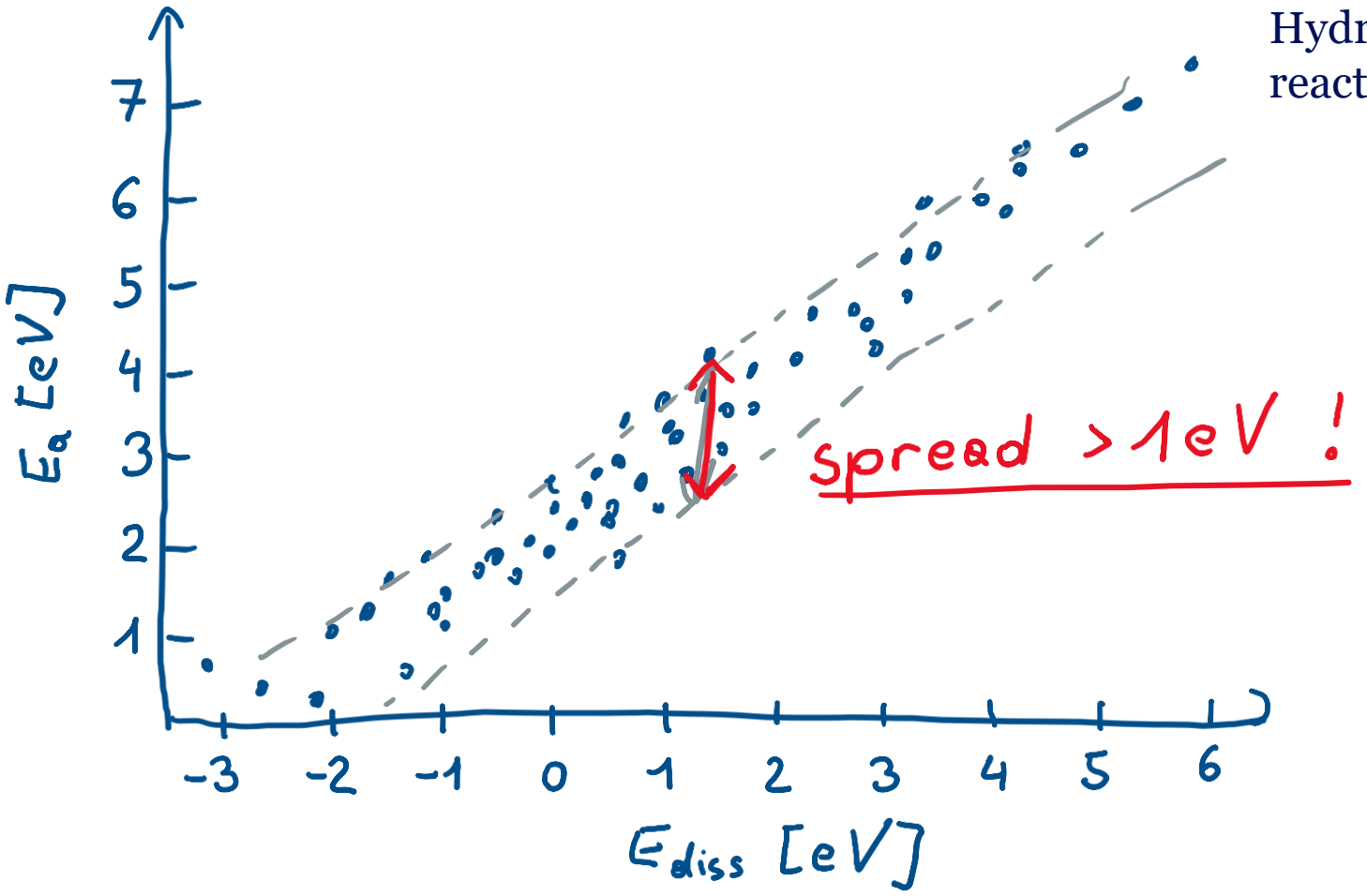
Computing Barriers

- Assumes perfect scaling between E_a and ΔE

\+ More accurate!
– High computational cost!
– CHE fails!



Barriers – when BEP fails



Data from: Wang et al. PCCP 2011, 13, 20760–20765

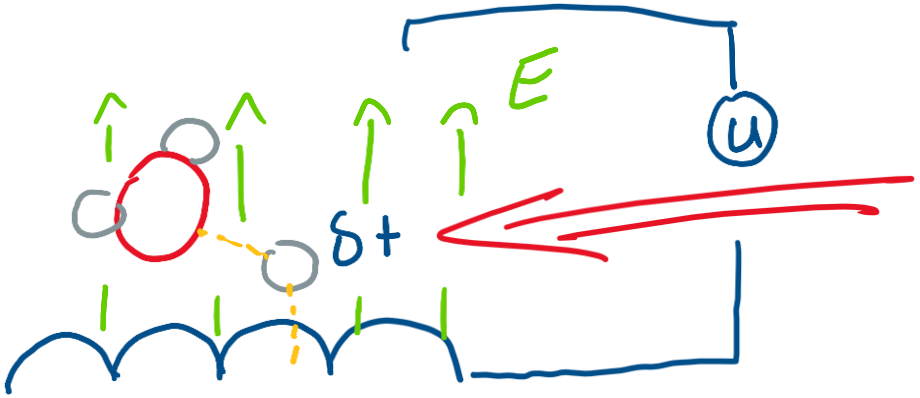
Computing barriers in EC

- E.g., Volmer reaction:

$$H_3O^+ + e^- + * \rightarrow H^* + H_2O$$

  - Final state from DFT
  - Initial state from CHE

  - How about transition state



CHE ☹!!!
- Electron not transported through entire *U*
- TS is typically dipolar!

Applying a potential

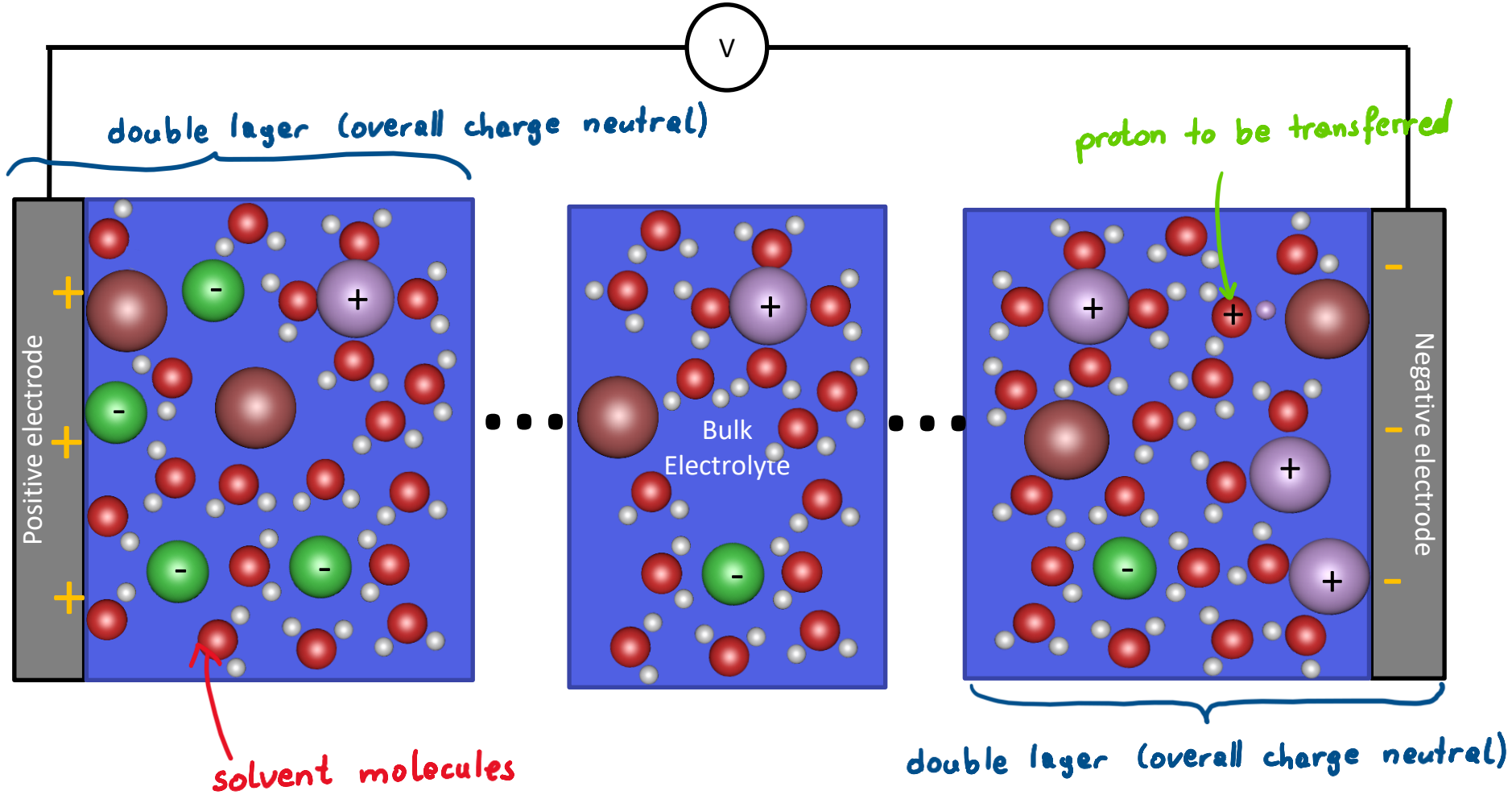


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Applying a potential

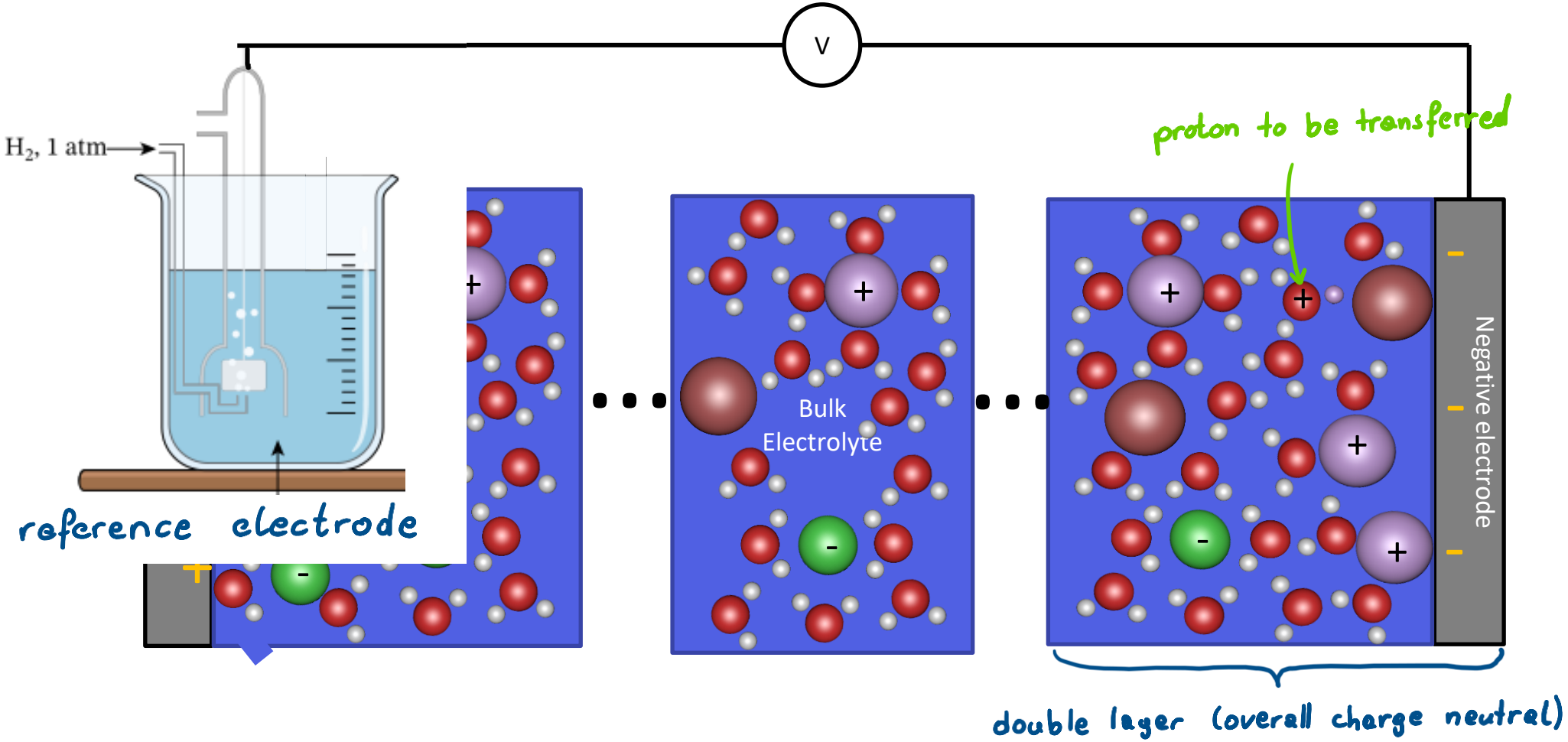


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Applying a potential

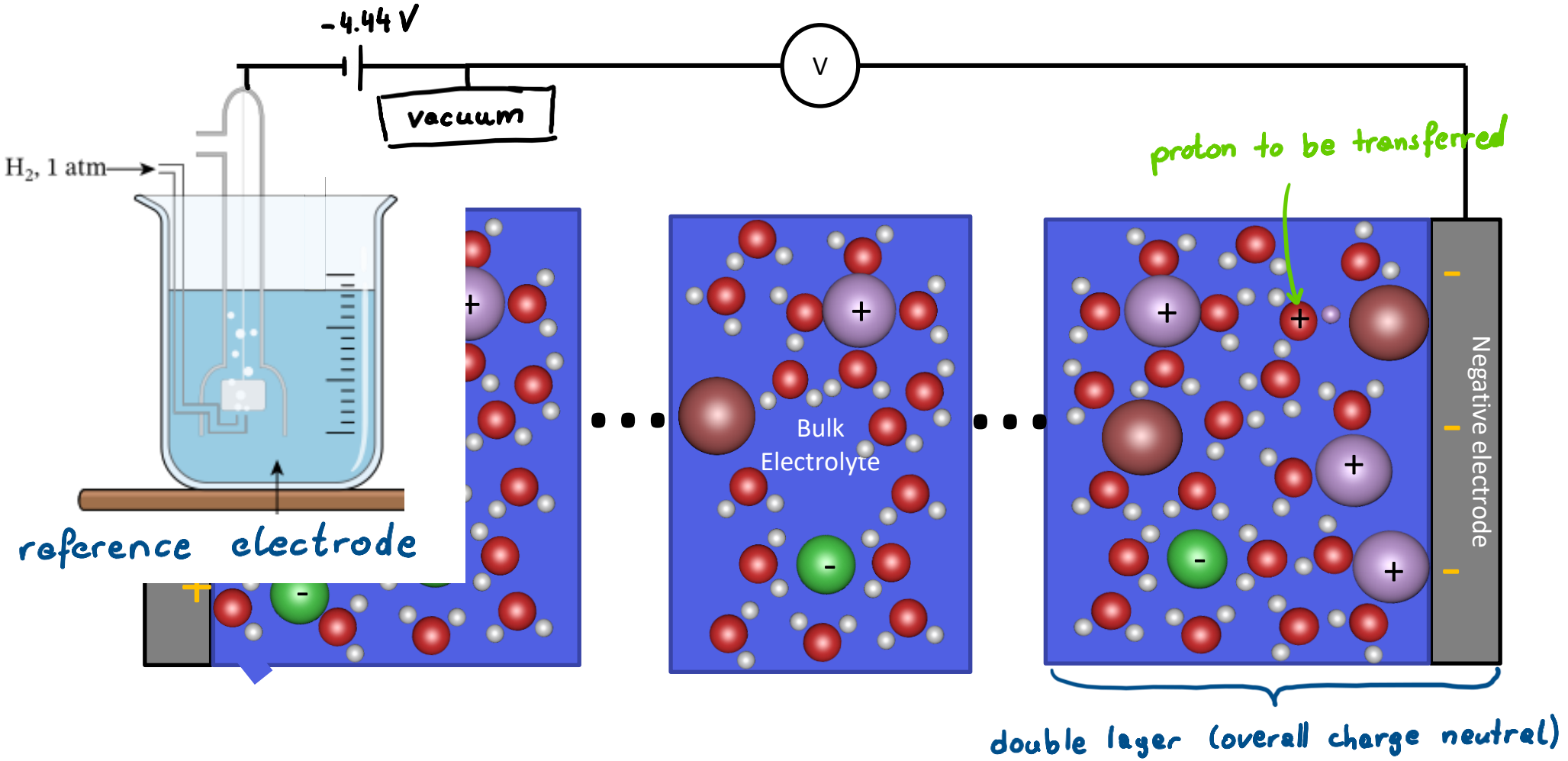


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Applying a potential

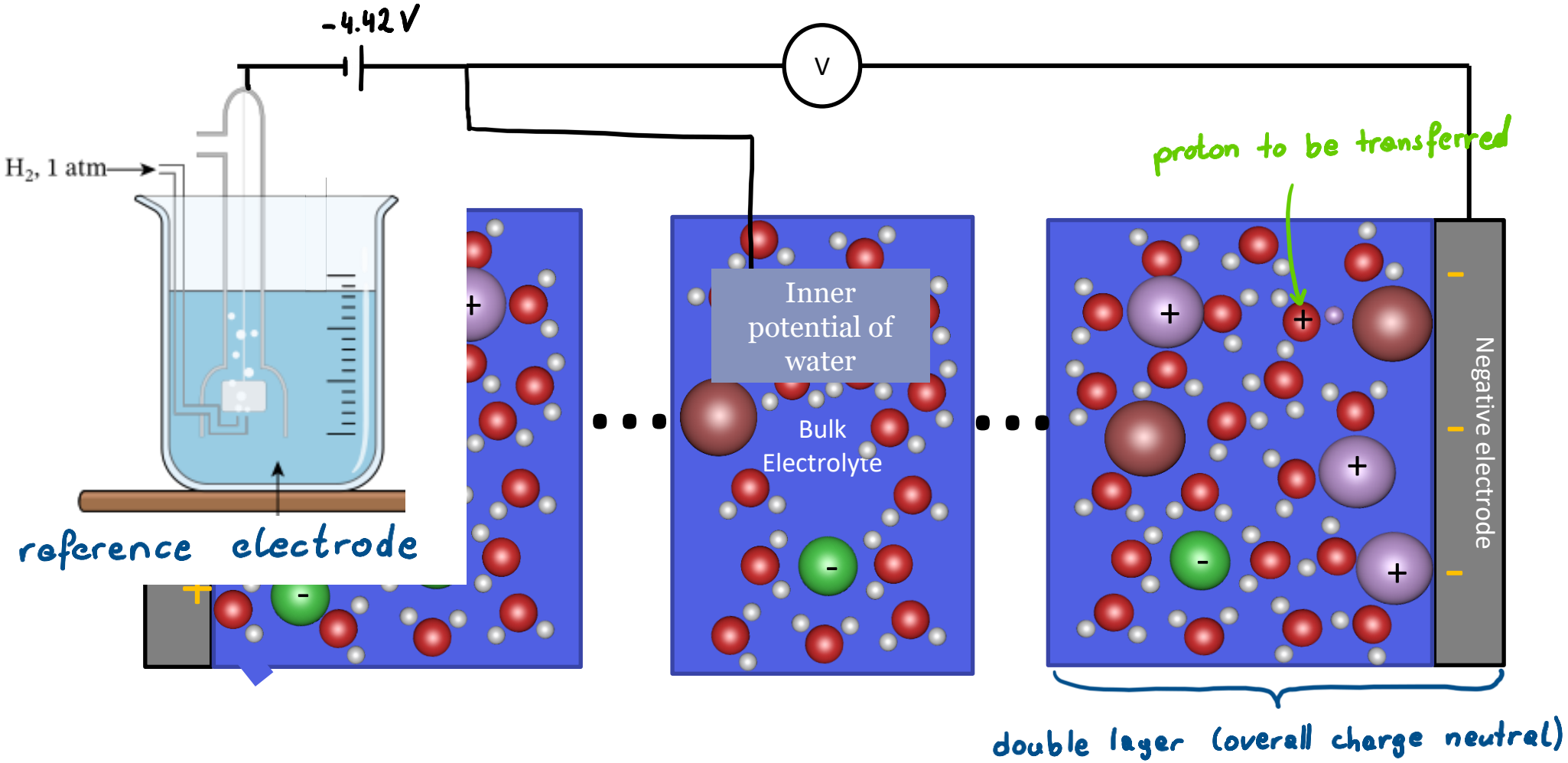


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Applying a potential

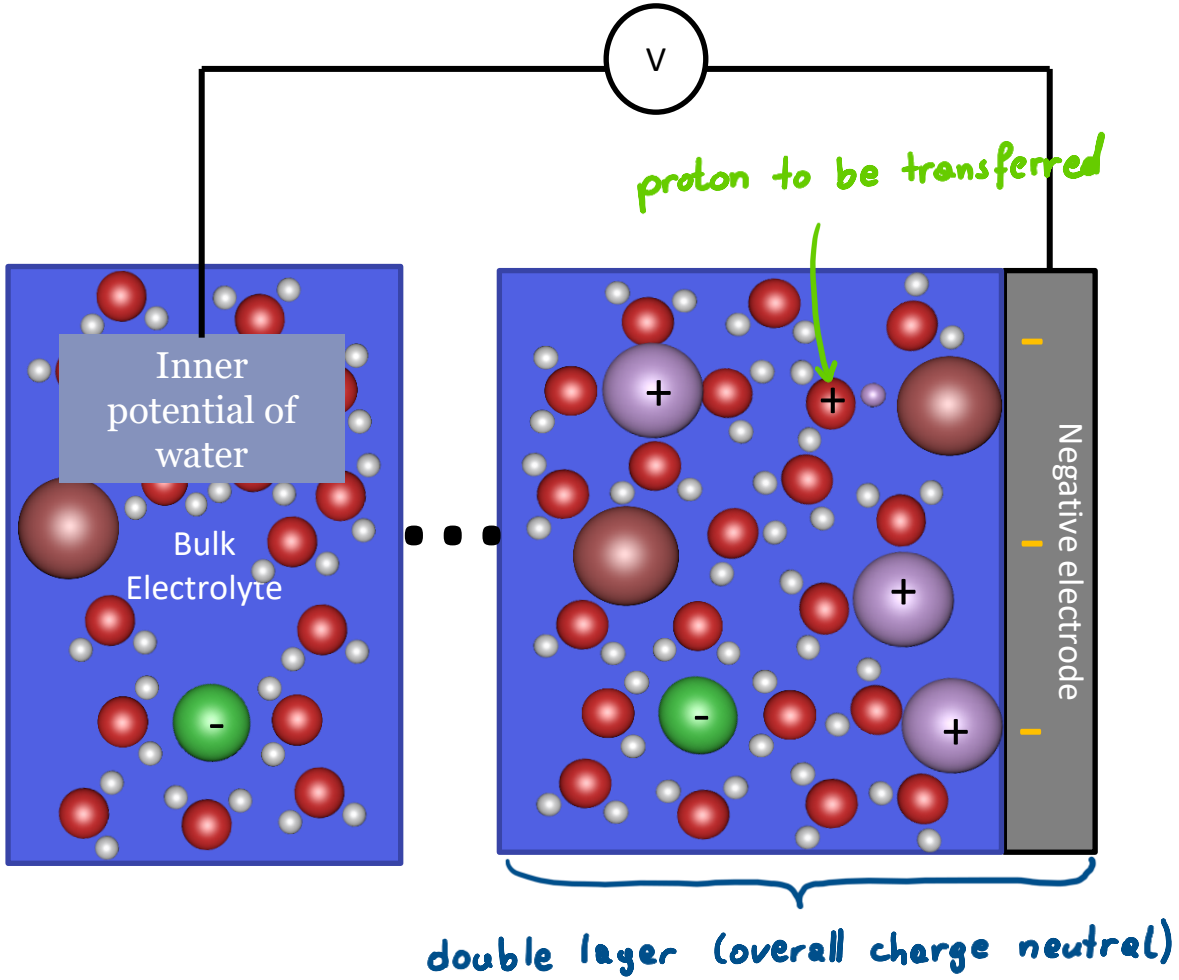


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Applying a potential

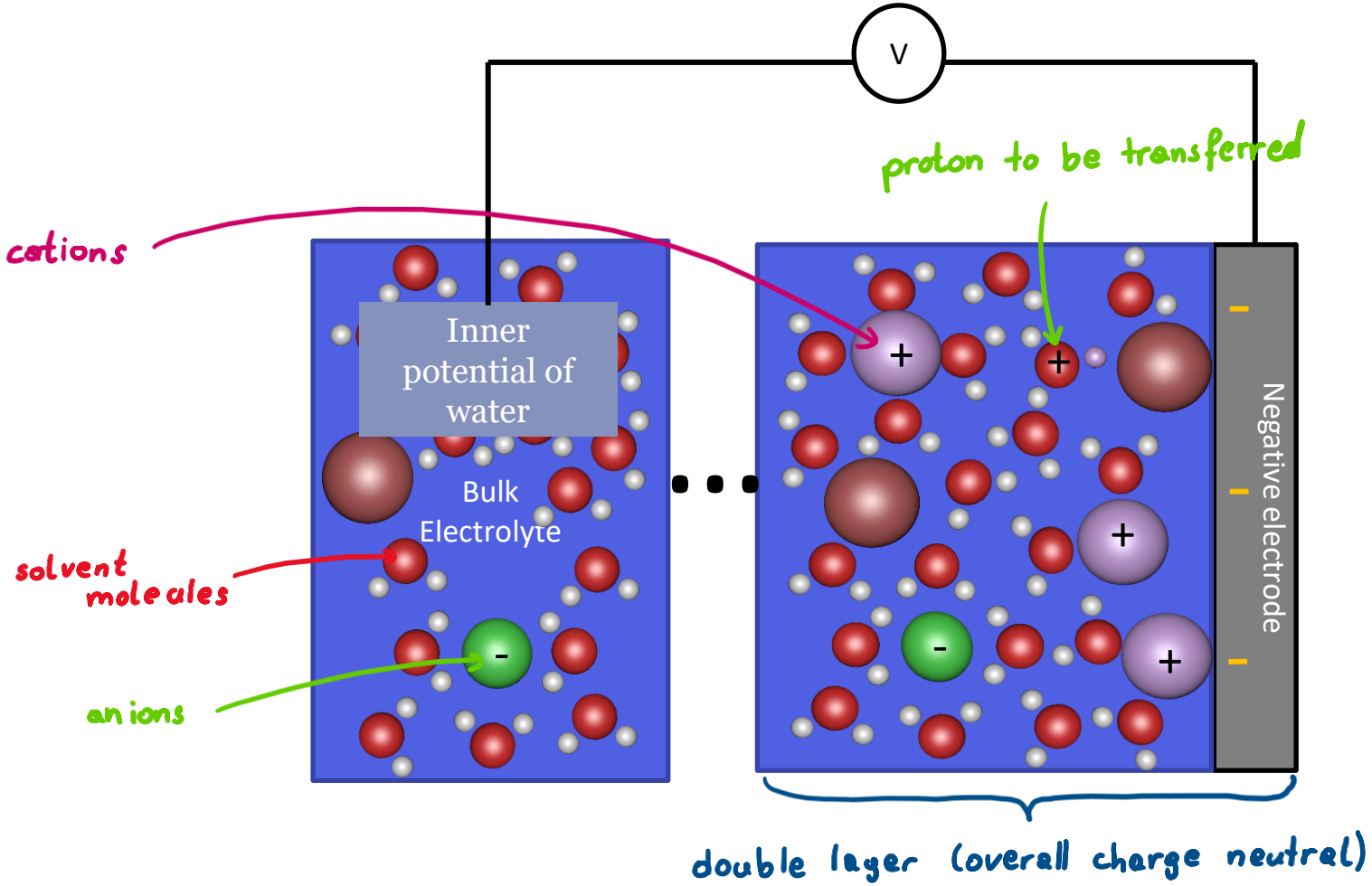


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Applying a potential

- **Constant potential DFT**
  - Implicit electrolyte
  - Mean-field charges

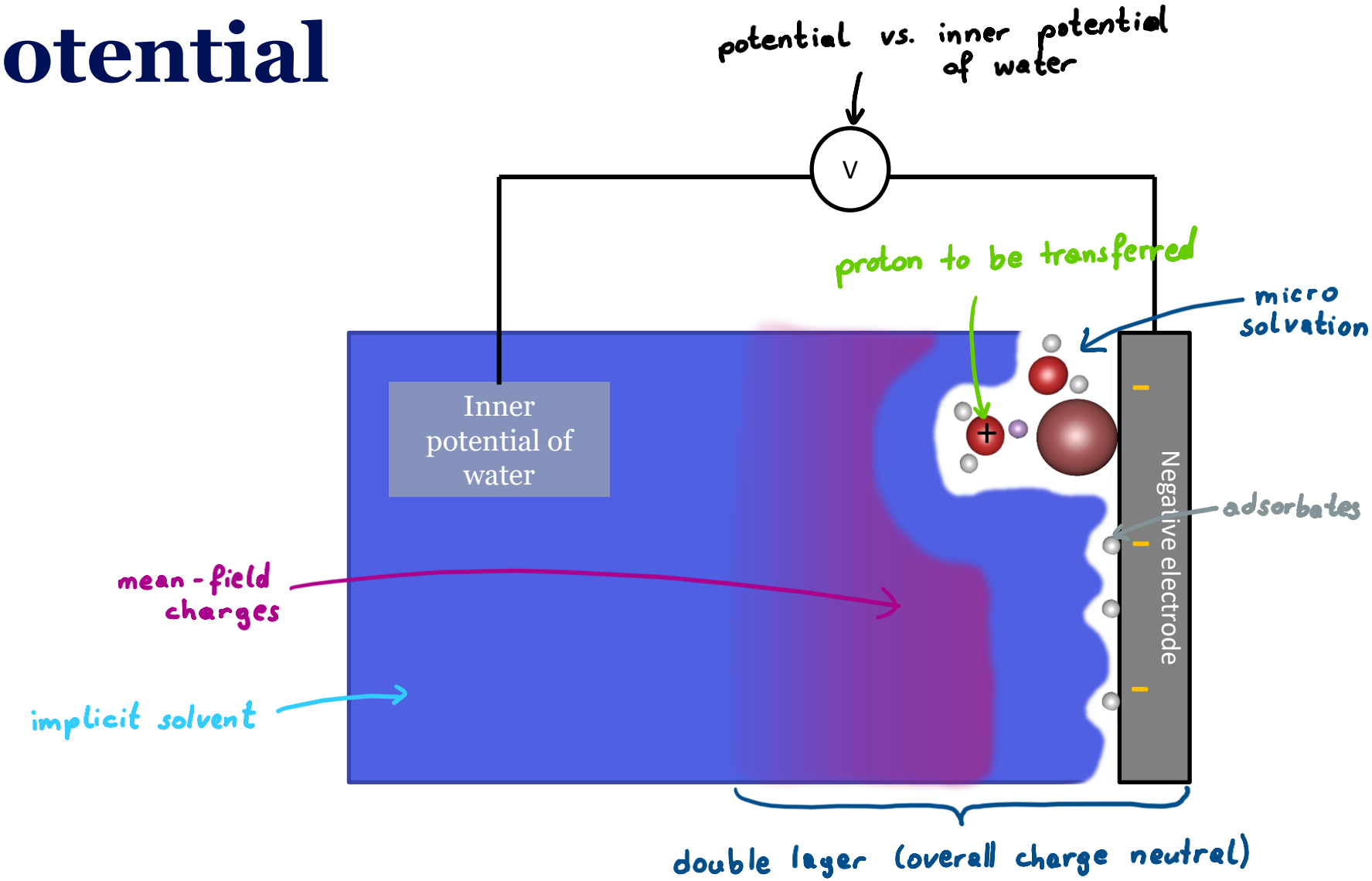


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger

Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Constant potential DFT: changed ensemble

- DFT
  - Microcanonical in # of electrons
- Contant potential DFT
  - Grand-canonical in # of electrons (# of electrons changes!)

⇓

  - Usually returns a potential that is grand canonical in the electrons

$$\Omega(U) = G - n_e \mu_e$$

⇓

$$\Omega(U) = G + neU$$

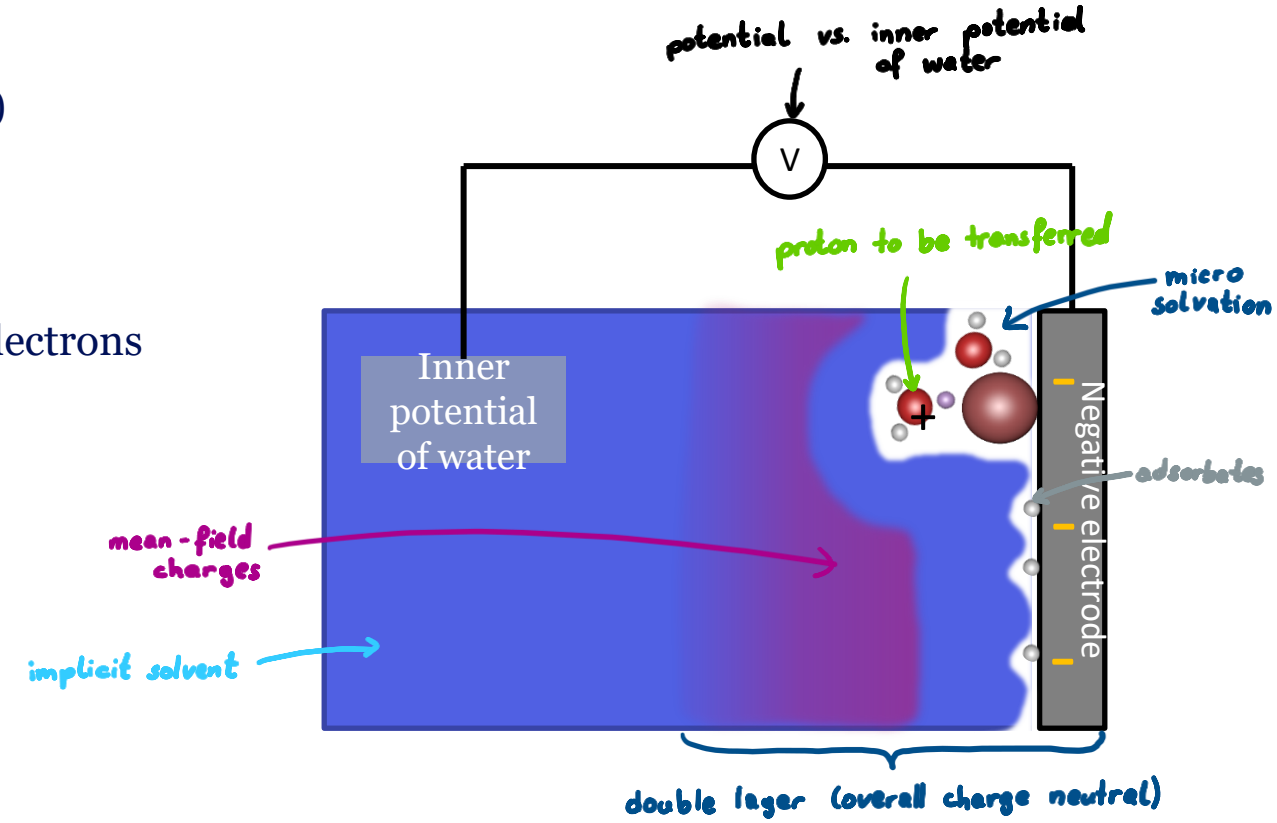
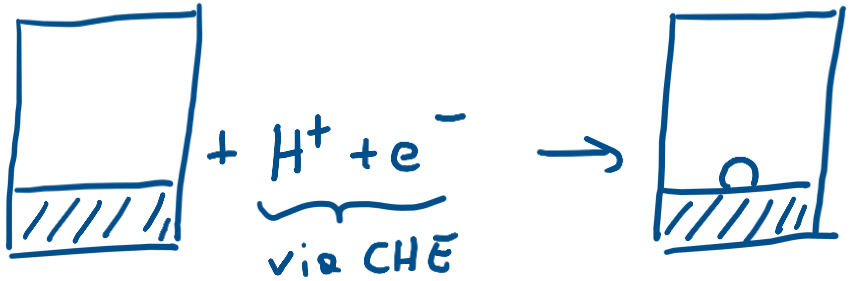


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger
Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Constant potential DFT: change in ensemble

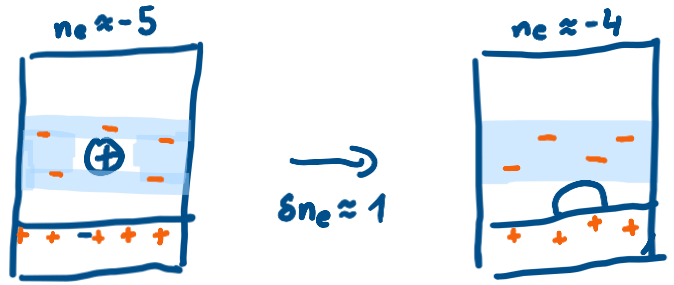
- $\Delta\Omega$ is compatible with the ΔG computed in the CHE, if
  - CHE is valid
  - Constant potential DFT can correctly describe the H^+

CHE:



$$\Delta G = G(H^*) - G(*) - G(H^+) + eU_{vac}$$

constant potential DFT



$$\Omega_1 = G_1 + ne\,U_{vac}$$

$$\approx G(*) + E_{el}^1 + G(H^+) + ne\,U_{vac}$$

$$\Omega_2 = G_2 + (n+\delta)e\,U_{vac}$$

$$\approx G(H^*) + E_{el}^2 + (n+1)e\,U_{vac}$$

$$\Delta\Omega \approx G(H^*) - G(*) - G(H^+) + eU_{vac}$$

Wishlist for electrochemical simulations

- Interaction between electrode and molecules
- Electrons: feel the correct potential
- Electron transfer should not lead to a change in surface charge/potential
- Molecules: feel the correct electric field
- Solvation
- Explicit interaction with electrolyte species

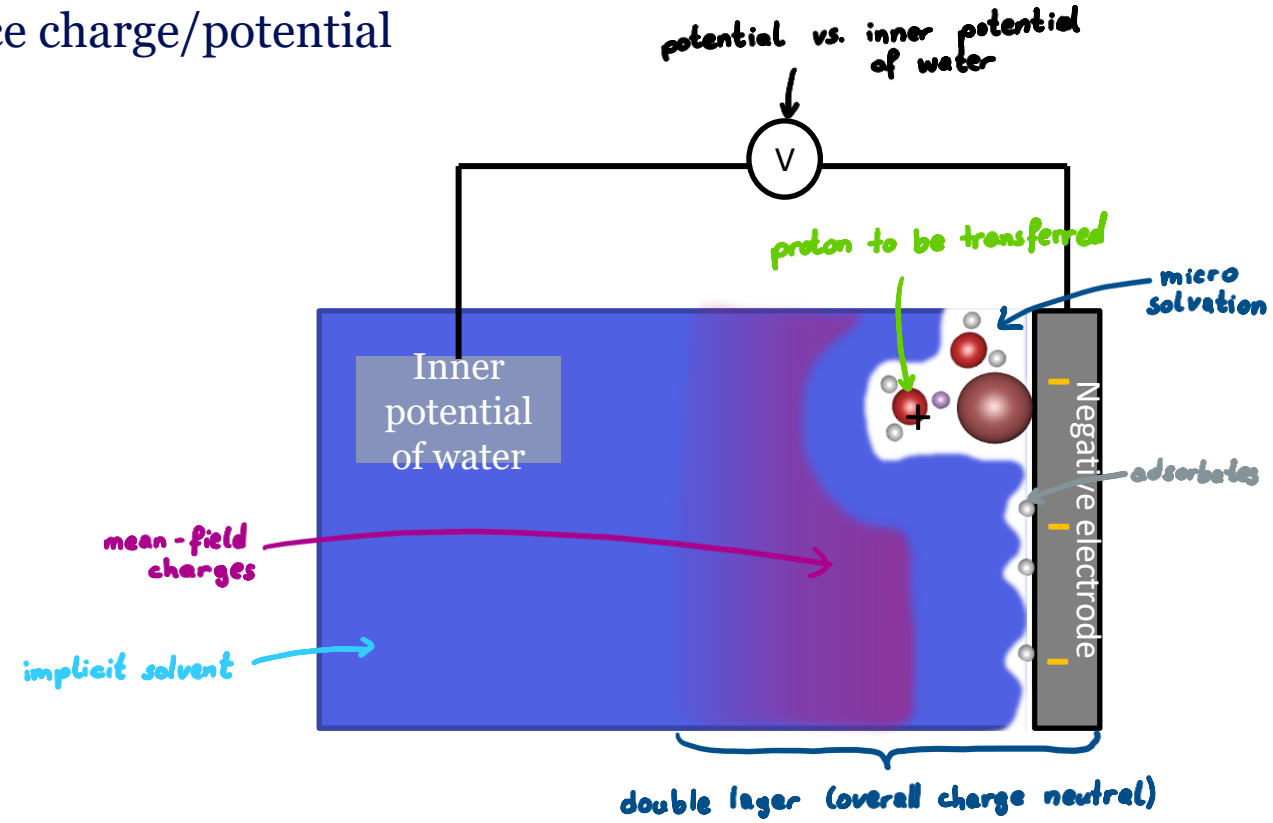


Figure curtesy: adapted with permission from CC-BY Georg Kastlunger
Figure reference: reference electrode: CC-By-SA lulu61; https://commons.wikimedia.org/wiki/File:Electrode_ENH.svg

Constant potential DFT

- Interaction between electrode and molecules
- Electrons: feel the correct potential
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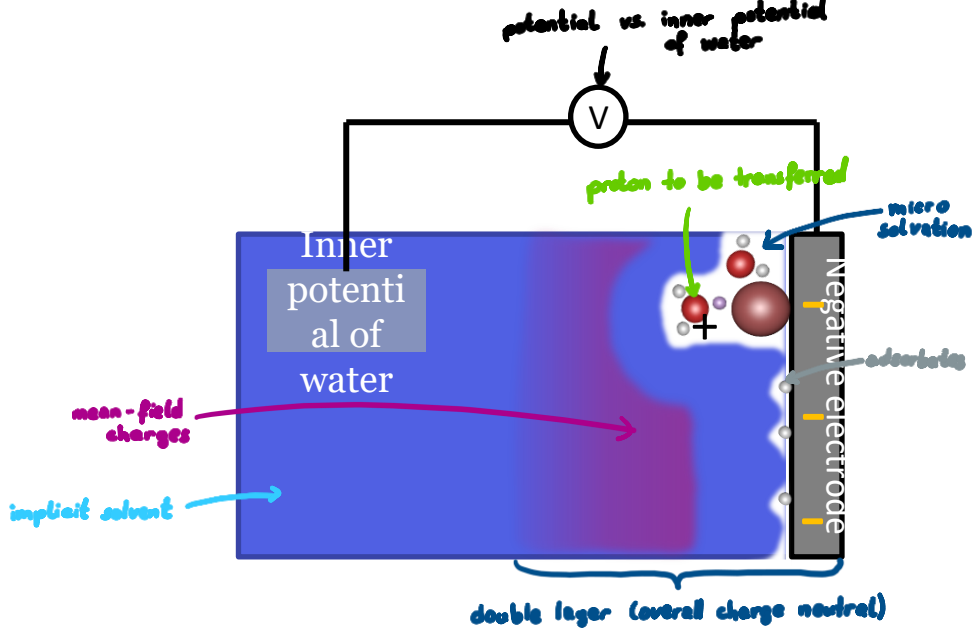

Figure curtesy: adapted with permission from CC-BY Georg Kastlunger
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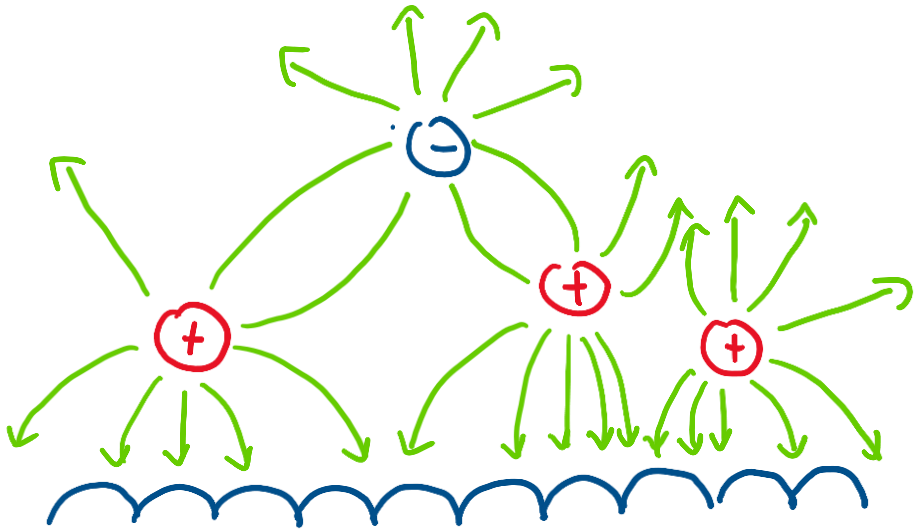
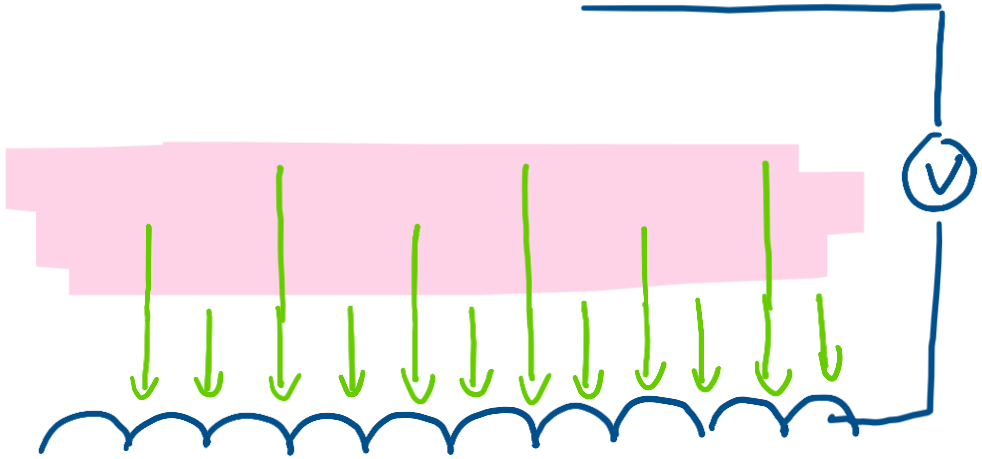
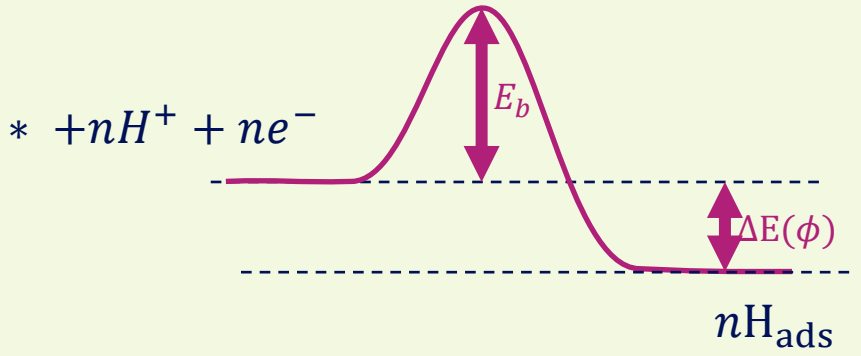




Volmer reaction in constant potential DFT

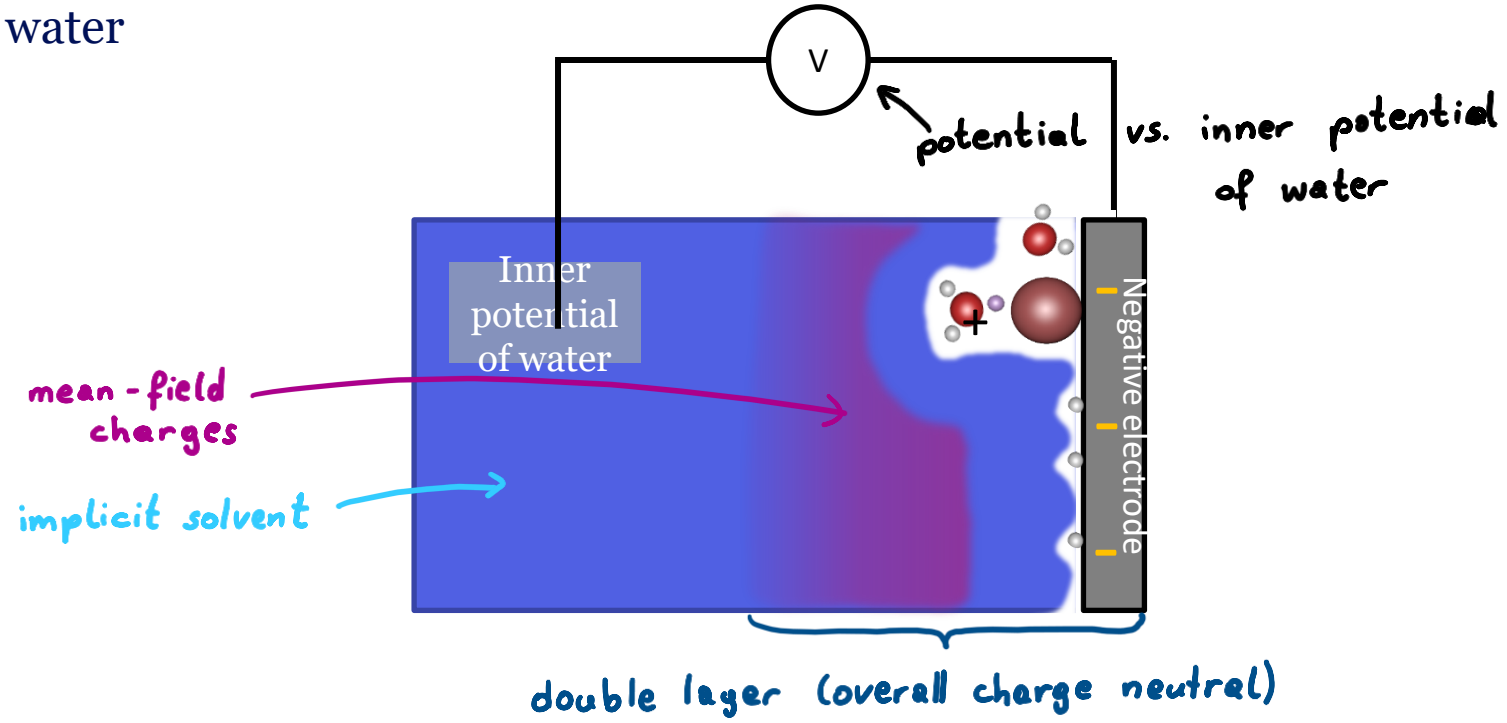
- $H^+ + e^- + * \rightarrow \mathrm{H_{ads}}$
- Include transition state!

- Use constant potential DFT in gpaw!
- Lab instructions in folder: Ex3_Volmer-barrier



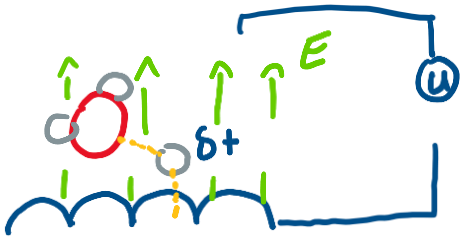
Take-home messages: Constant potential DFT 1

- Electronically grand canonical
  - Changes number of electrons in the system depending on potential and surface structure
- Makes use of mean field solvation and simplified, mean-field charge distributions distributions
- References potential to inner potential of water

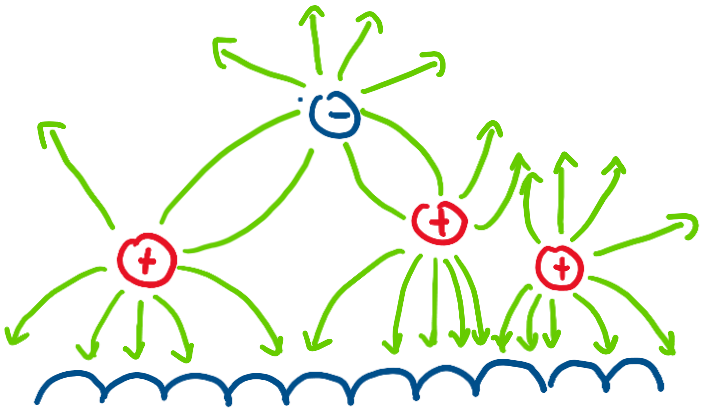


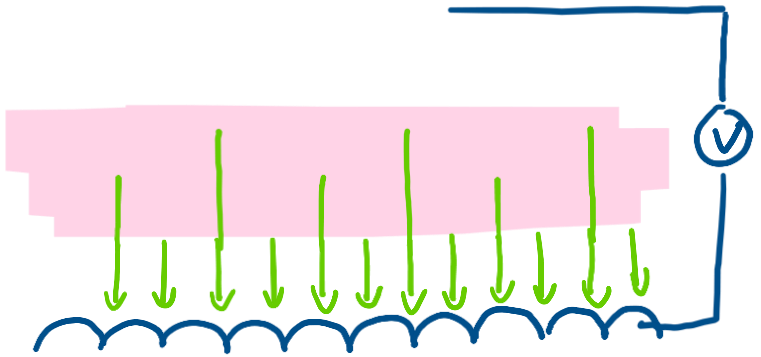
Take-home messages: Constant potential DFT 2

- Allows computing
  - electrochemical barriers
  - Energetics for polar species



- Does not resolve all issues! Errors remain due to
  - Incorrect Q/U relation
  - Incorrect potential profile
  - Missing local electric field effects/explicit solvent interaction





Part 4: Modeling electrochem. double layers

Katharina Doblhoff-Dier| Han-sur-Lesse winterschool 2025

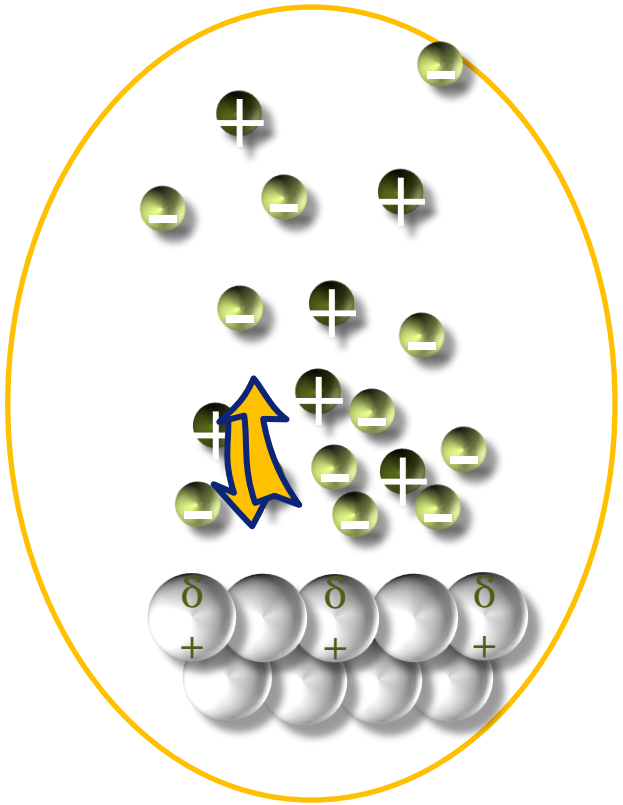
Universiteit Leiden
The Netherlands

Computational electrochemistry

1. Electrochemistry: The basics
2. Computational catalysis and computational electrocatalysis
3. Beyond the computational hydrogen electrode method
4. **Modeling electrochemical double layers**
   - Simulating double layers in simplified models
   - Simulating double layers in ab initio molecular dynamics
   - Example: pzc of stepped Pt
   - Simulating double layers in force field molecular dynamics
   - Example: ion crowding
   - Simulating double layers using machine learned force fields
5. Mass transport

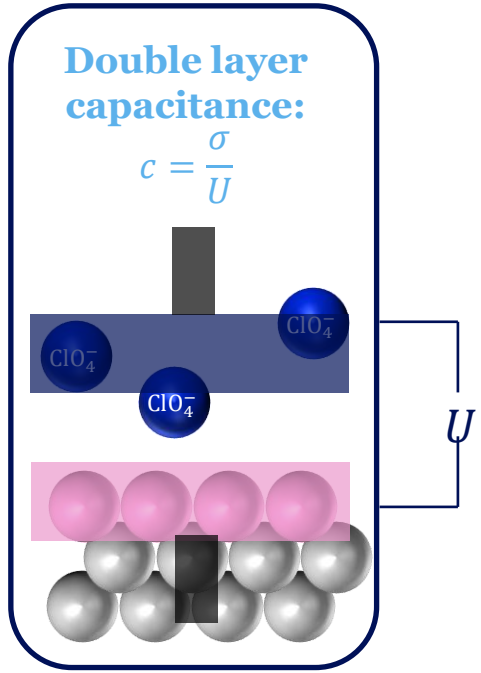
Simulating double layers using (analytic) models

- Gouy-Chapman-Stern model



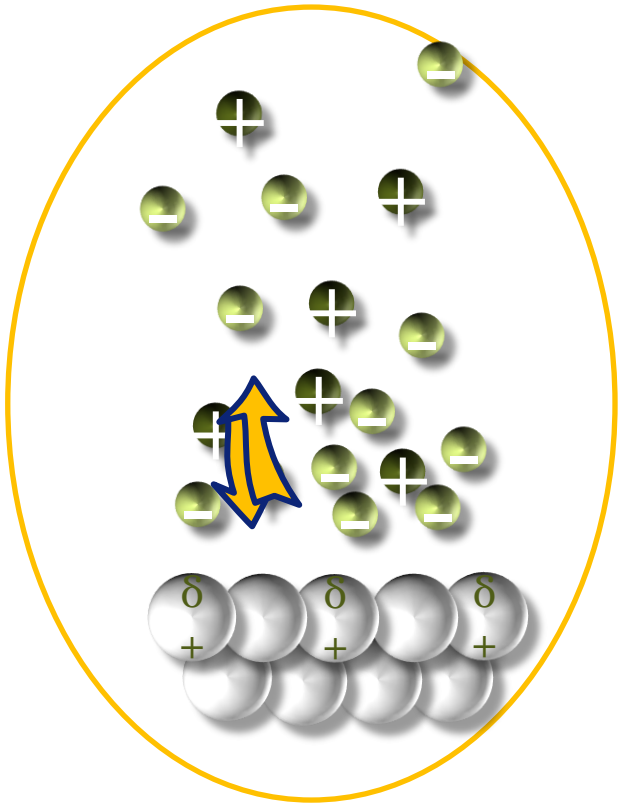
Entropic push

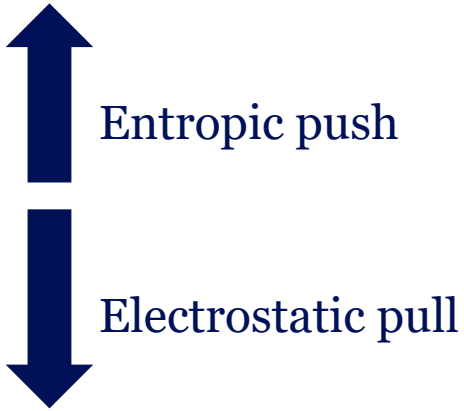
Electrostatic pull

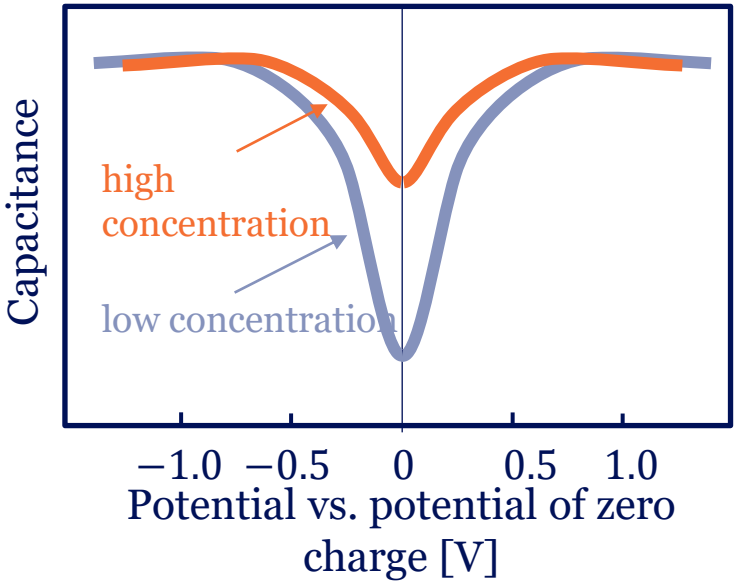


Simulating double layers using (analytic) models

- Gouy-Chapman-Stern model

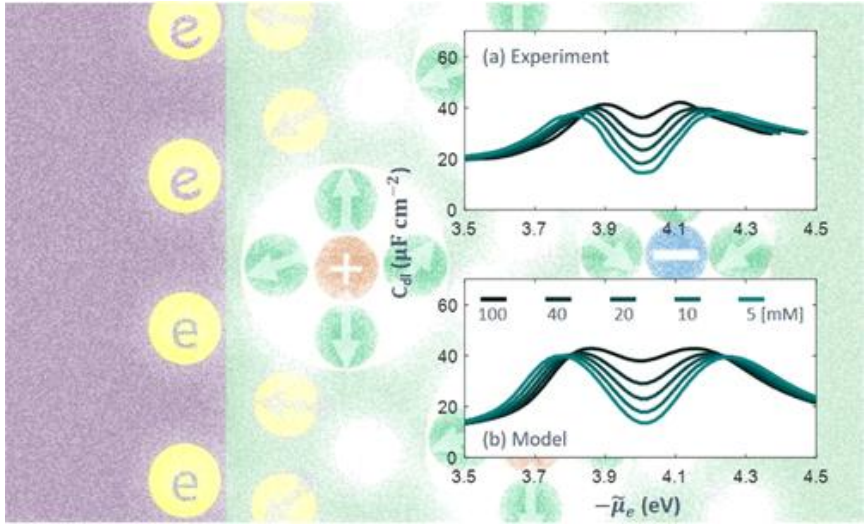




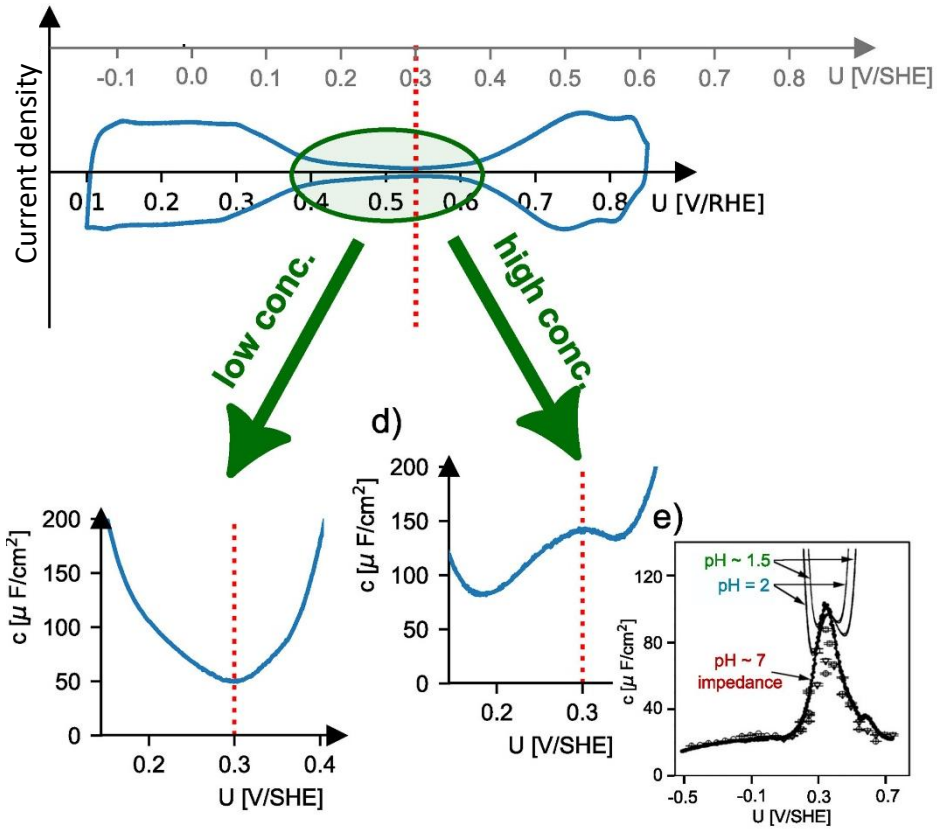


Simulating double layers using (analytic) models

- Gouy-Chapman-Stern model
- … and beyond
  - Add ion size/“bound” solvent molecules
  - Add field dependent polarizability
  - Add solvent/metal interaction
  - Treat metal as actual metal

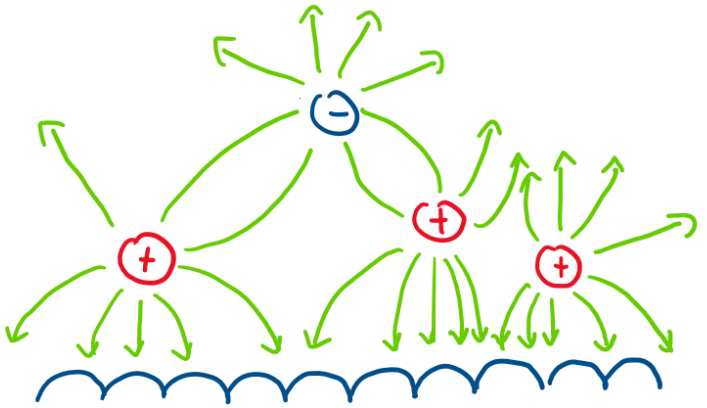


Beyond mean field models



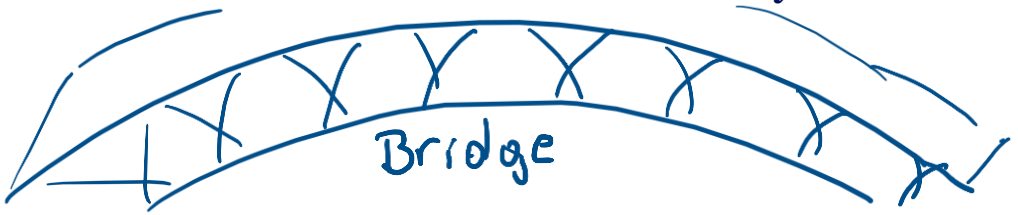
K. Doblhoff-Dier, M.T.M Koper, Cur. Op. in Electrochem., 39, 101258 (2023); doi: 10.1016/j.coelec.2023.101258

- Interaction between electrode and molecules
- Electrons: feel the correct potential
- Electron transfer should not lead to a change in potential
- Molecules: feel the correct electric field
- Solvation
- Explicit interaction with electrolyte species

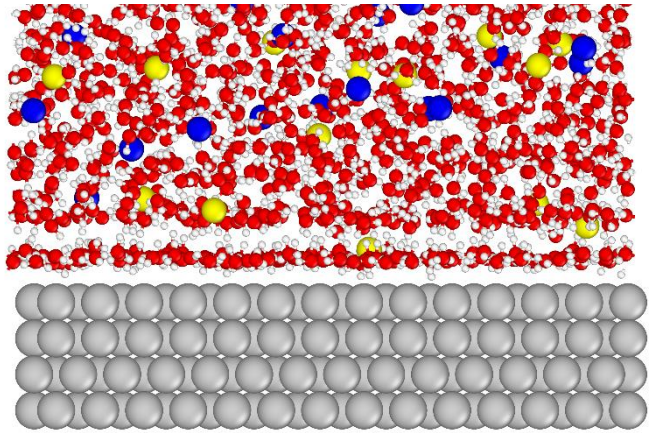


Molecular dynamics simulations

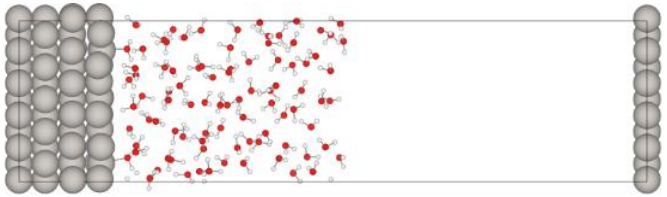
- Machine-learned molecular dynamics



- Force-field molecular dynamics



- Ab-initio molecular dynamics

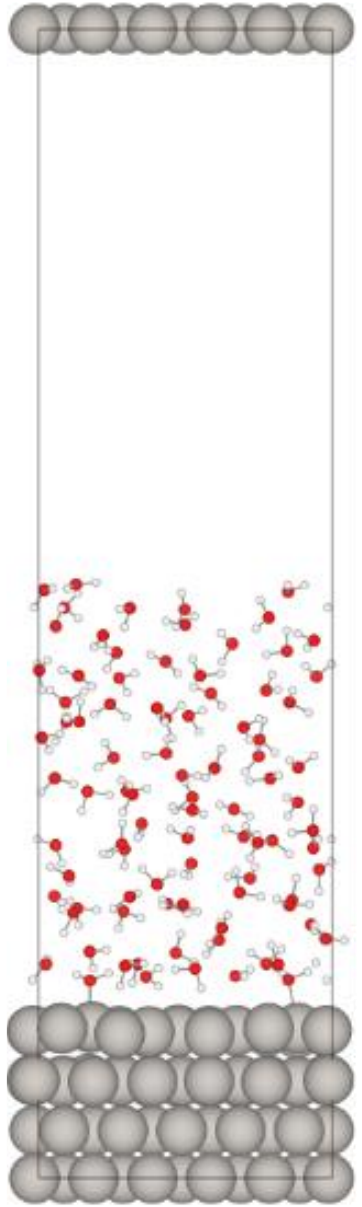


Molecular dynamics simulations

Ab-initio molecular dynamics

- Simulation sizes
  - ~6x6 supercells
  - ~100 ps

} For metals

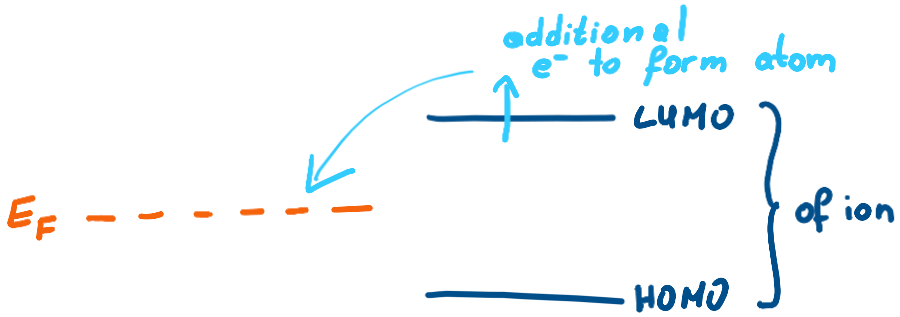


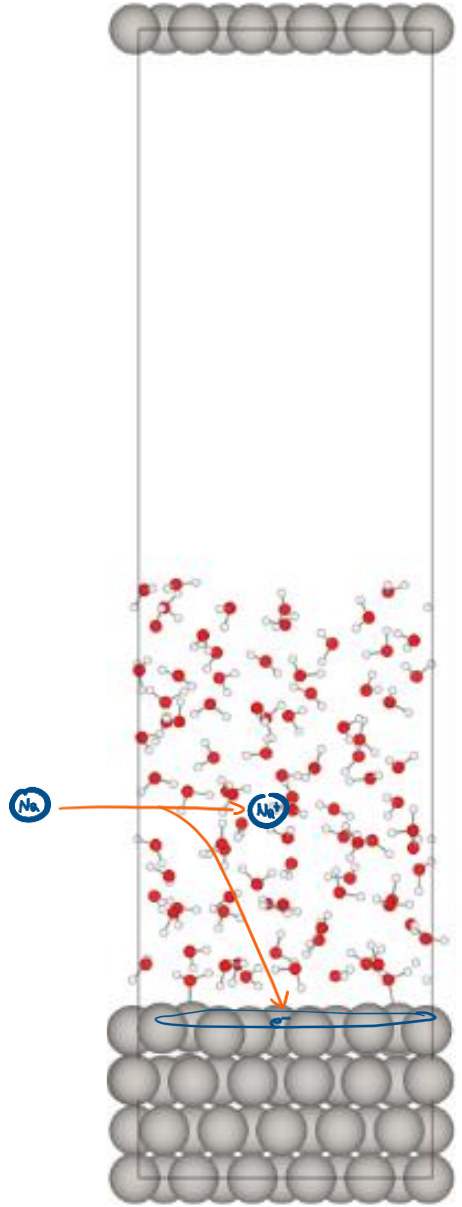
Molecular dynamics simulations

Ab-initio molecular dynamics

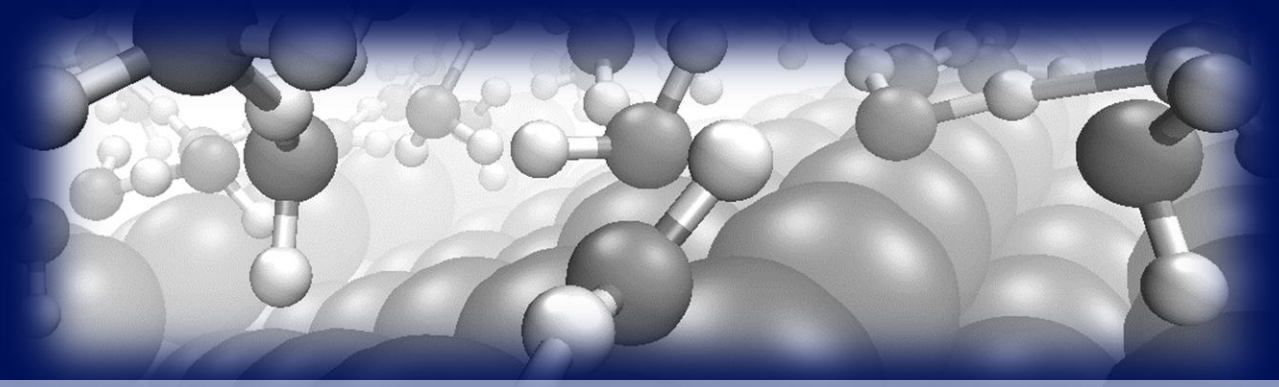
- Simulation sizes
  - ~6x6 supercells
  - ~100 ps

  } For metals
- Charging via ion imbalance





Example: Potential of zero charge of stepped Pt



Katharina Doblhoff-Dier| 2025 – Predictor meeting

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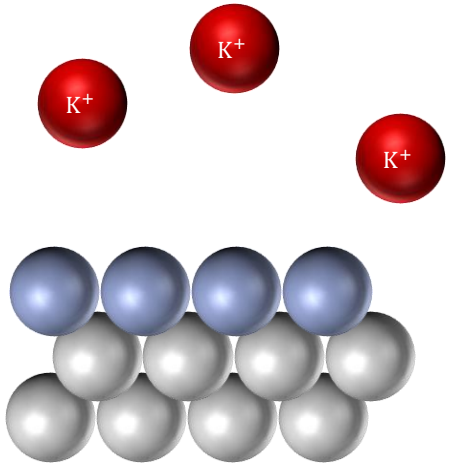
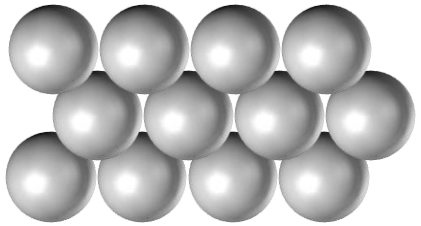
Potential of zero charge

Excess of positive ions at the surface



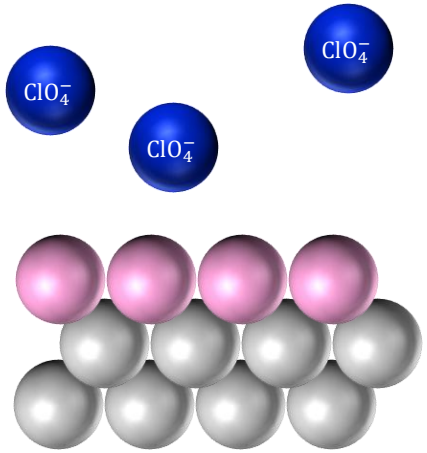
$U <$ pzc
σ negative

No excess of ionic charges



Potential of zero charge (pzc)
$\sigma = 0$

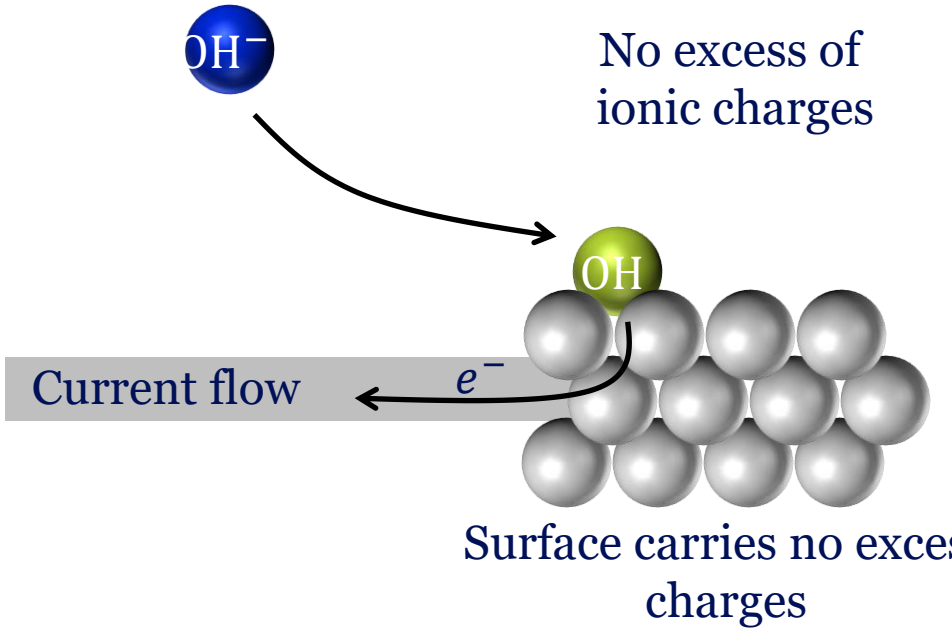
Excess of negative ions at the surface



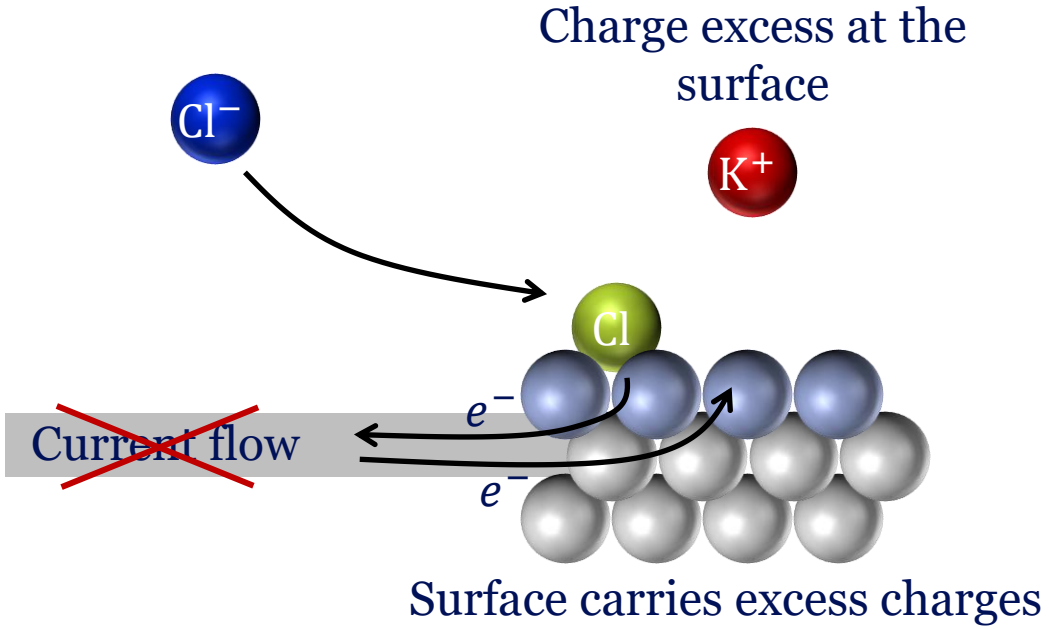
$U >$ pzc
σ positive

Potential of zero charge with adsorbates

- Potential of zero **free** charge (pzfc)
  - Pzfc may differ for surface with and without adsorbates
  - Pzfc may not be observable

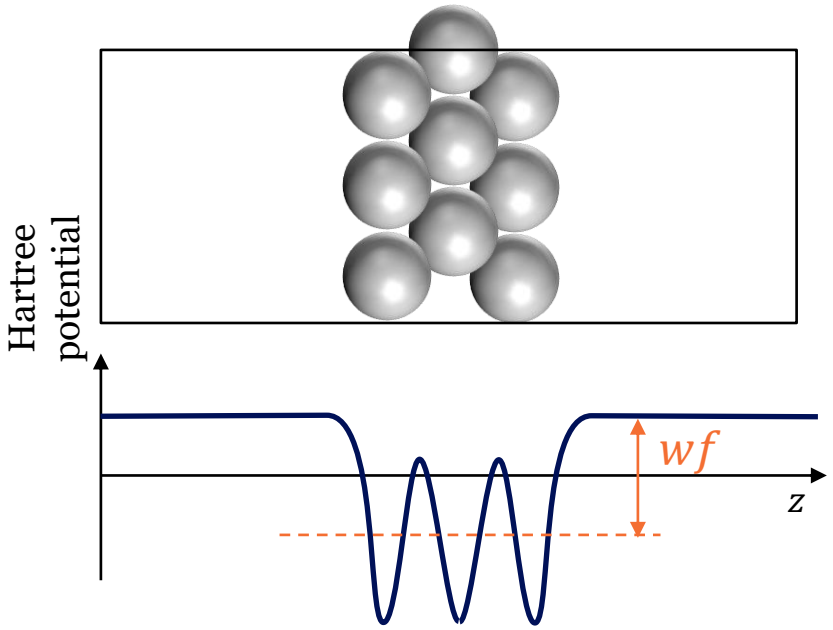


- Potential of zero **total** charge (pztc)

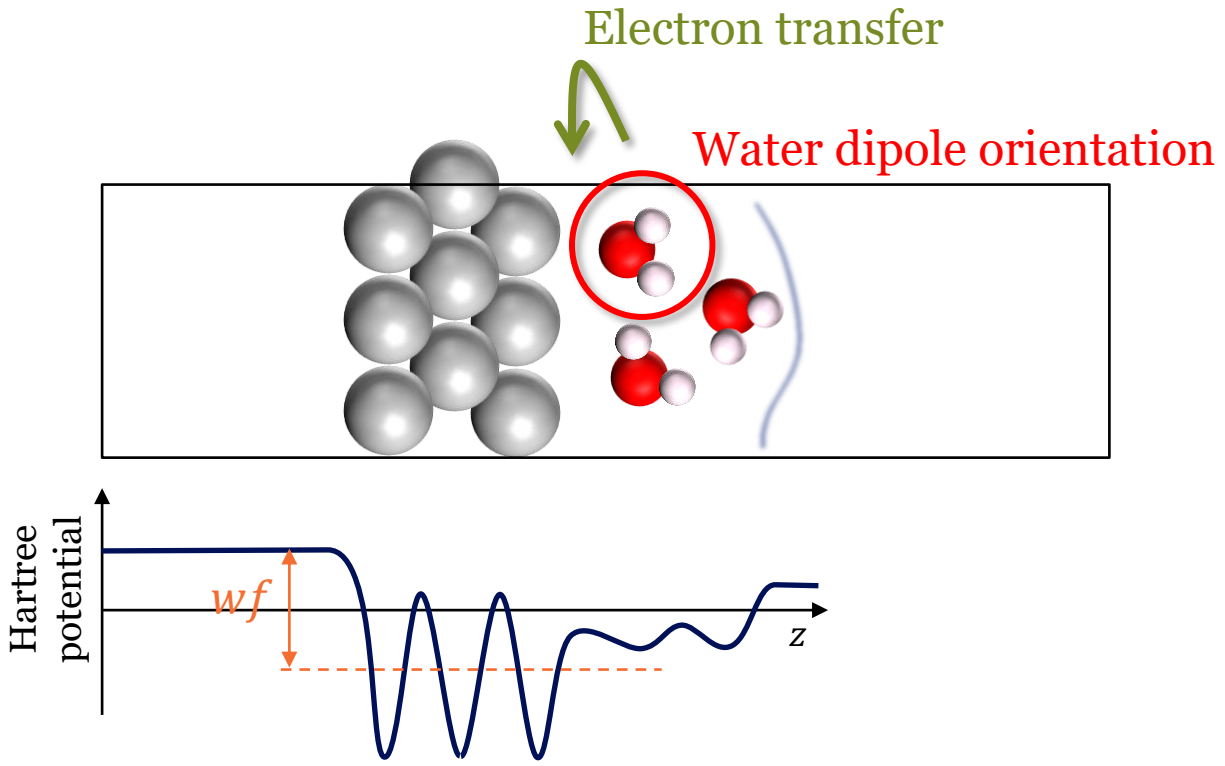


Work function vs. potential of zero charge

- **Work function**

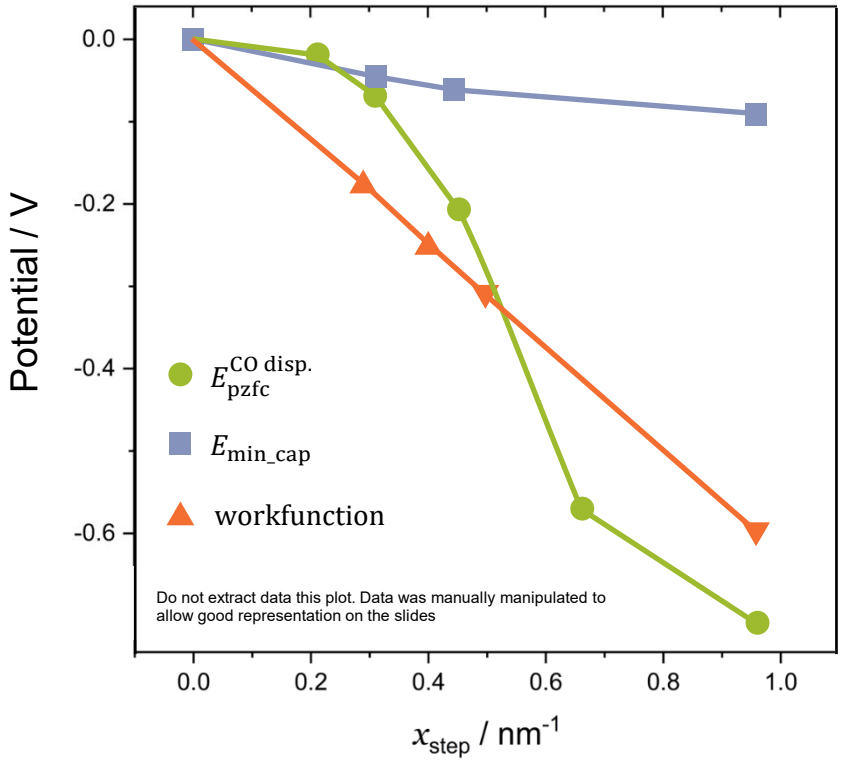


- **Potential of zero charge**

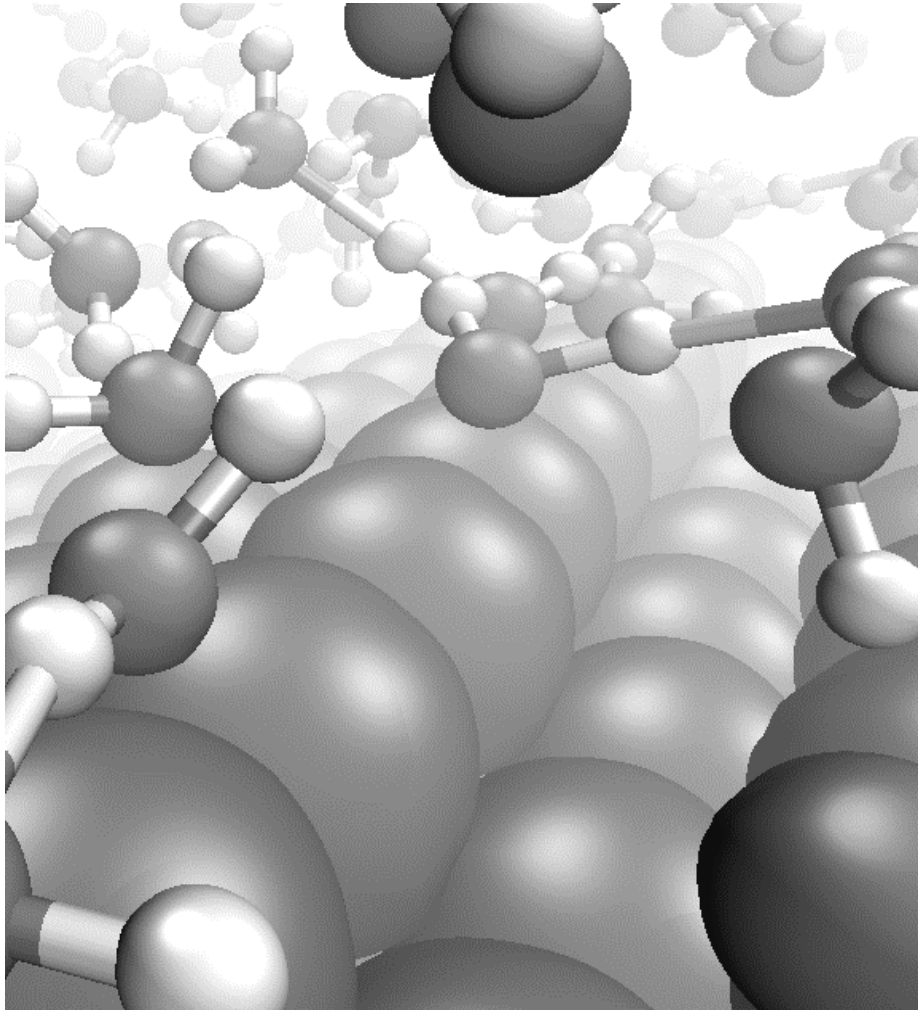


Stepped Pt: pzfc

- pzfc from CO displacement measurements
- Gouy-Chapman minimum

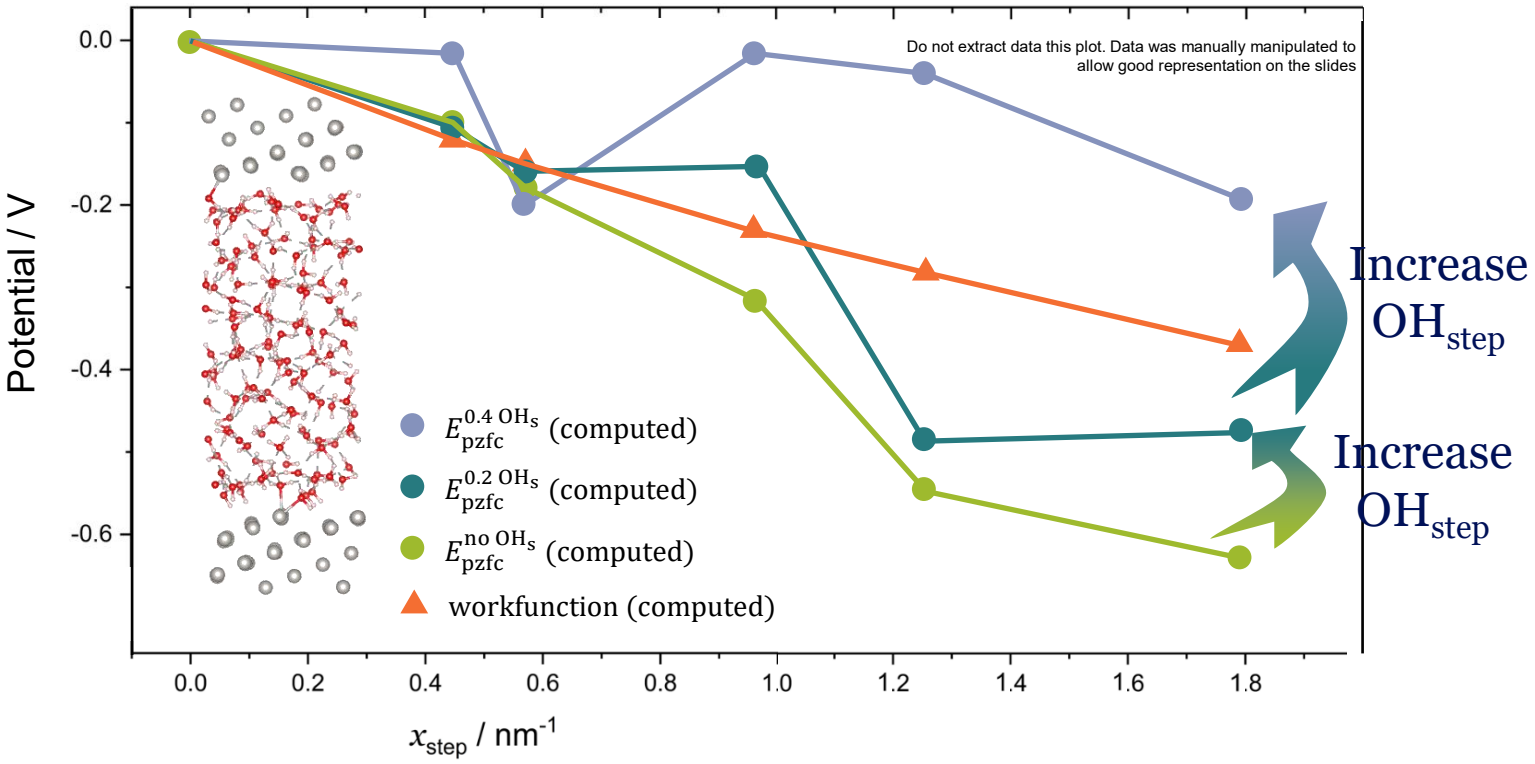


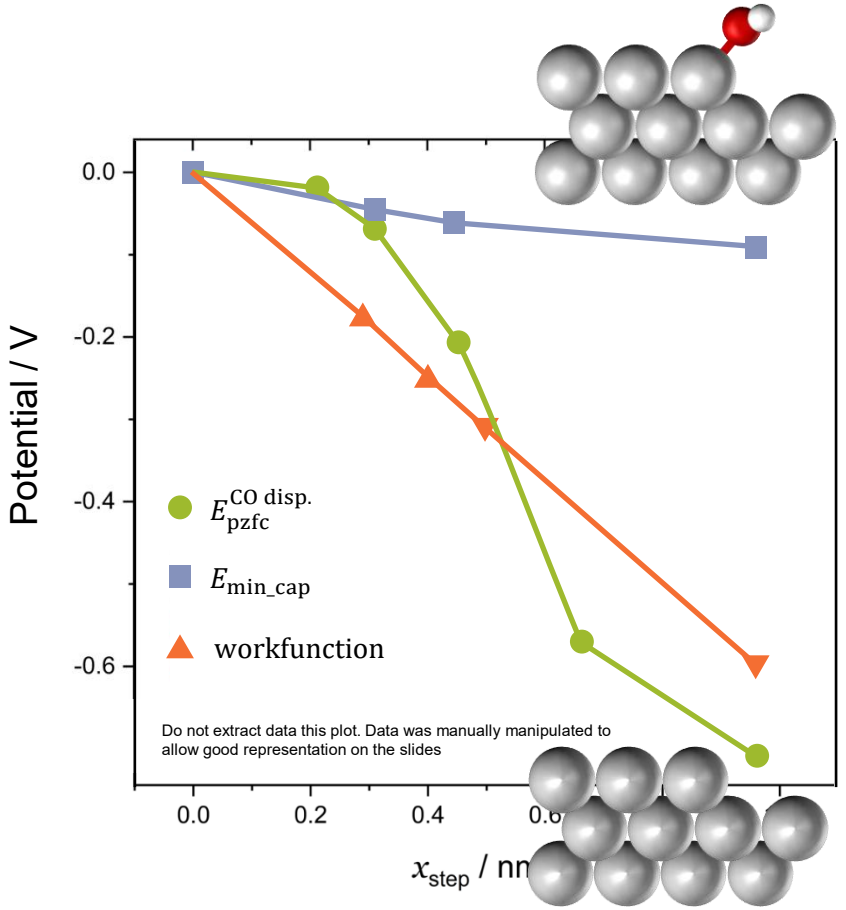
CO displacement: Gomez et al., *J. Phys. Chem. B* **2000**, 104, 3, 597–605
$E_{\mathrm{min\_cap}}$: Nicci Fröhlich; Koper group; Leiden University
wf: Ross, PN & Jr. *J. Chim. Phys.* **88**, 1353–1380 (1991); Besocke et al, *Surf Sci* **68**, 39–46 (1977).



Fröhlich, Liu, Ojha, Hagopian, Doblhoff-Dier, Koper, under submission

Computational pzfc for Pt





CO displacement: Gomez et al., *J. Phys. Chem. B* **2000**, 104, 3, 597–605
E_{min_cap}: Nicci Fröhlich; Koper group; Leiden University
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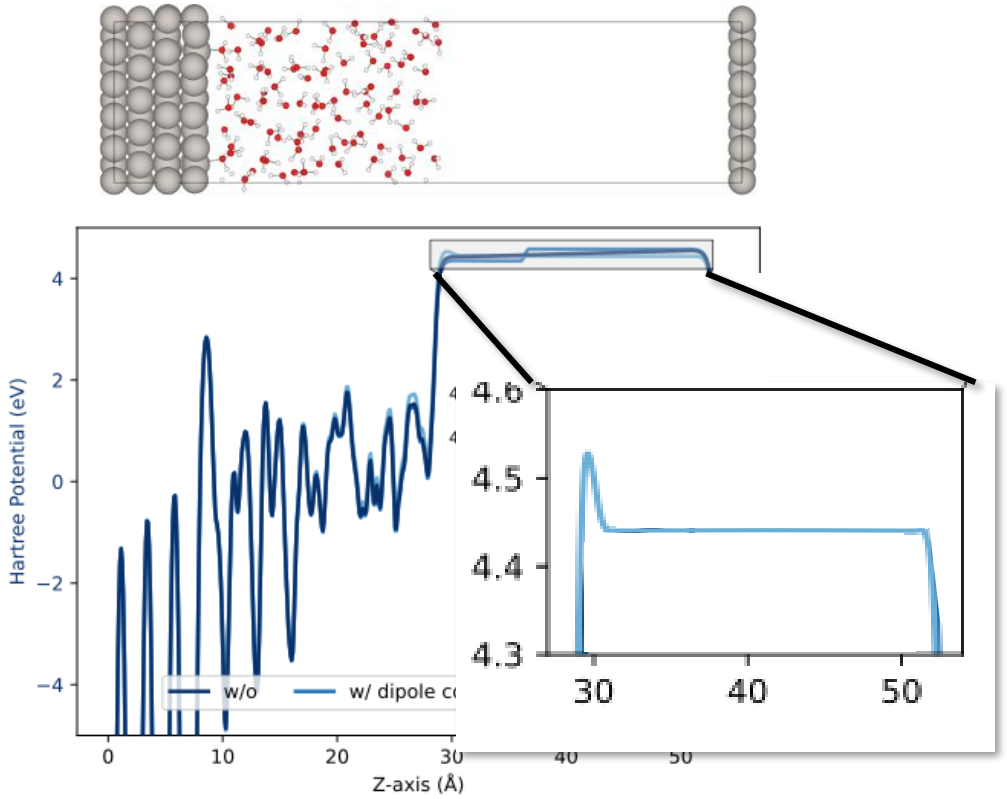
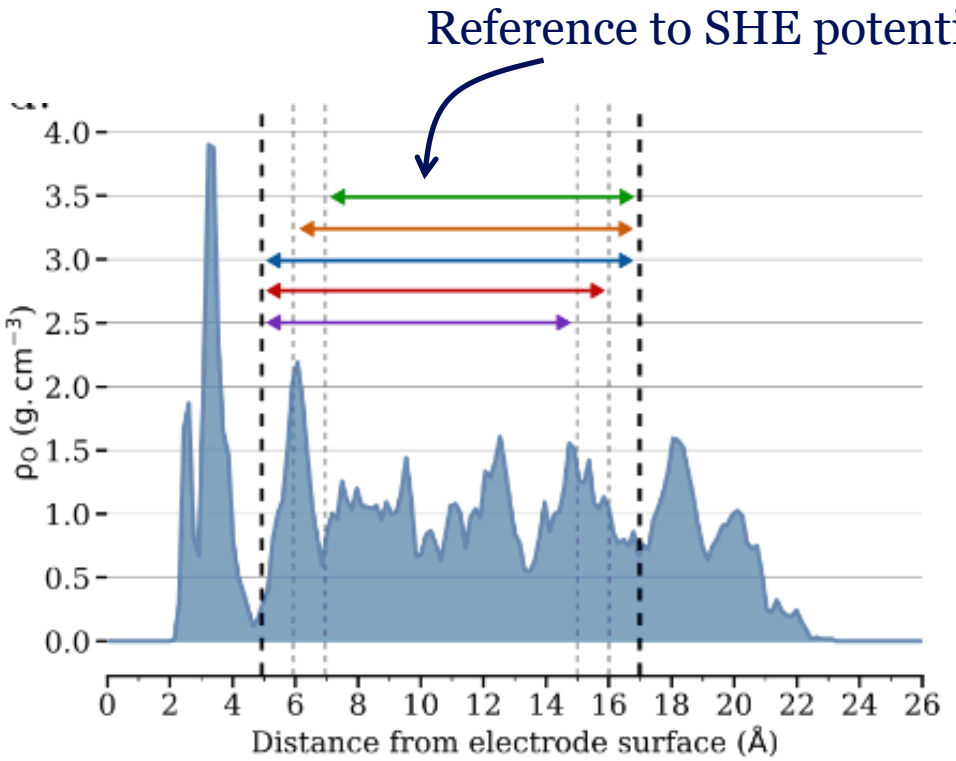
Fröhlich, Liu, Ojha, Hagopian, Doblhoff-Dier, Koper, under submission

Computing the potential of zero charge

Work function method

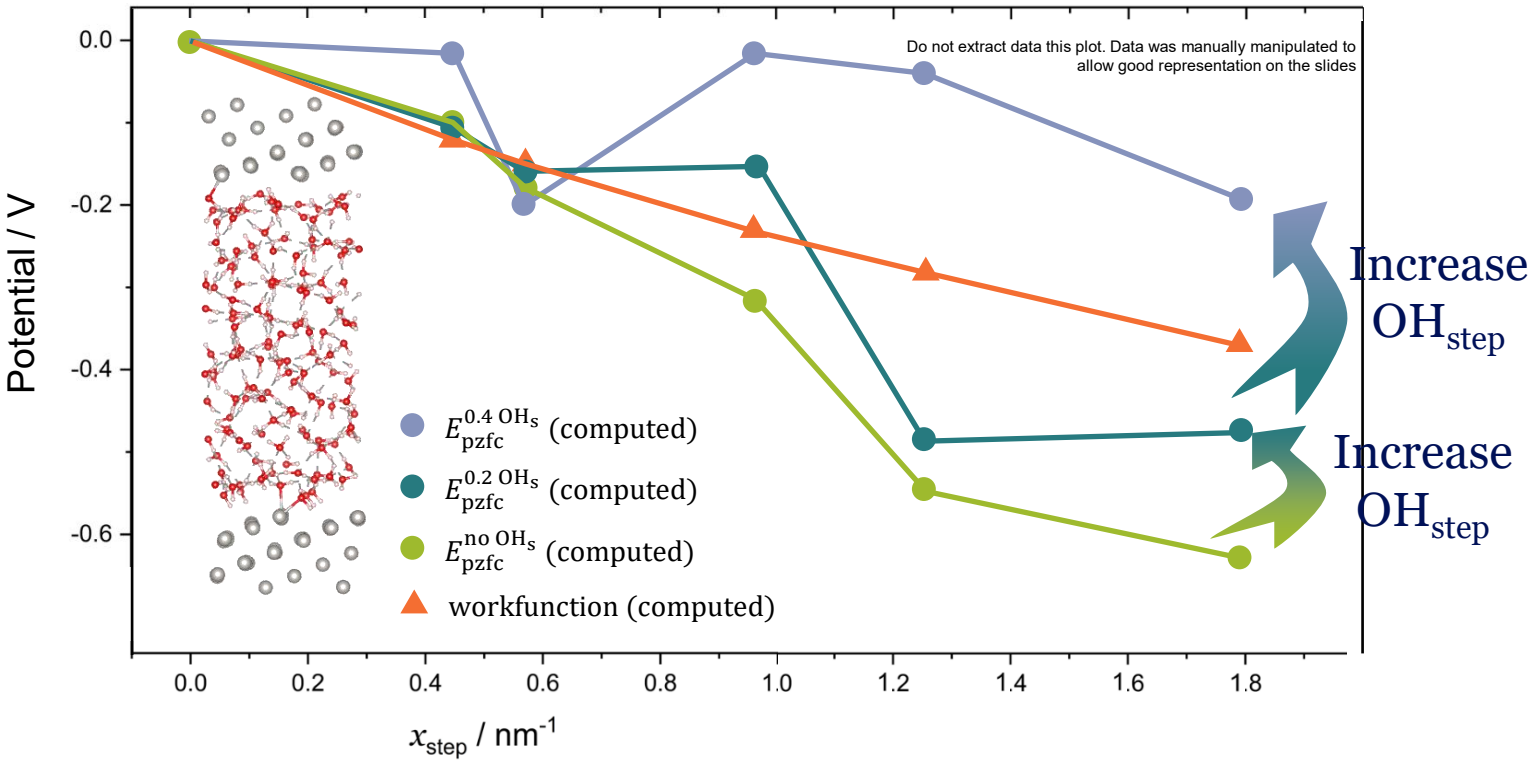


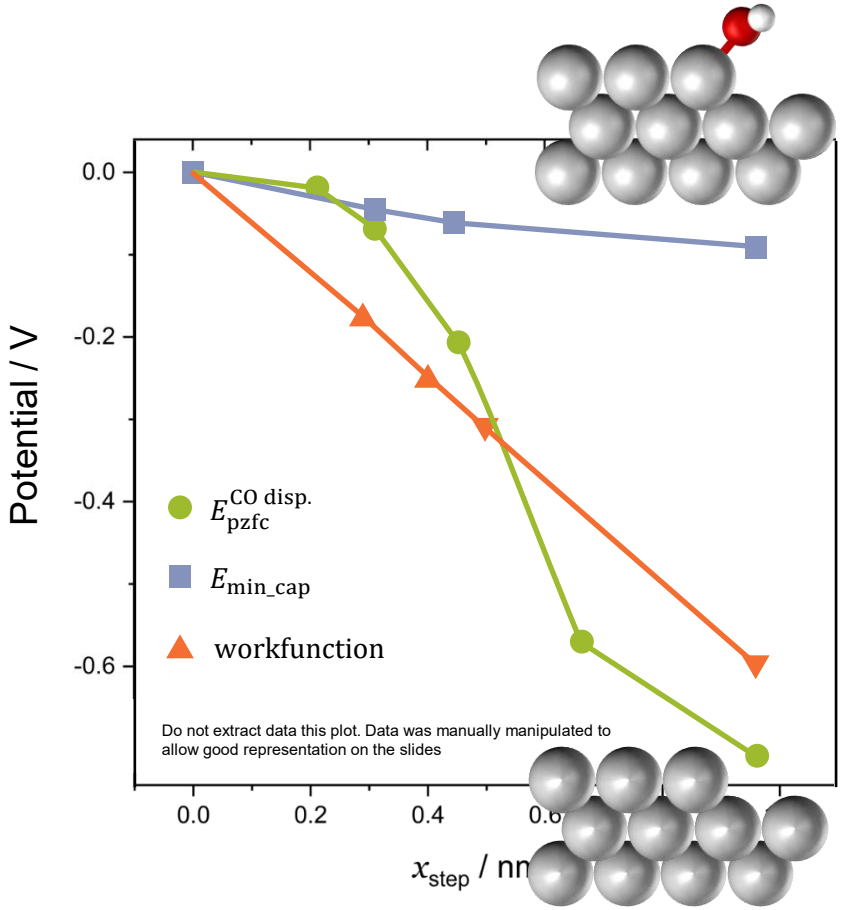
Computational standard hydrogen electrode method



Figures: Hagopian, Koper, and Doblhoff-Dier, in preparation

Computational pzfc for Pt





CO displacement: Gomez et al., *J. Phys. Chem. B* **2000**, 104, 3, 597–605
E_{min_cap}: Nicci Fröhlich; Koper group; Leiden University
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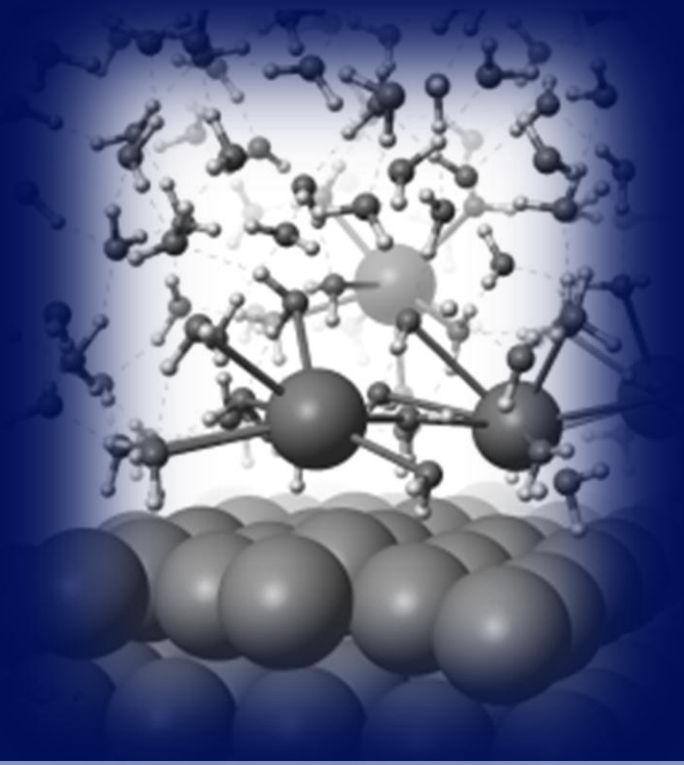
Fröhlich, Liu, Ojha, Hagopian, Doblhoff-Dier, Koper, under submission

Example:
Ion where are you?

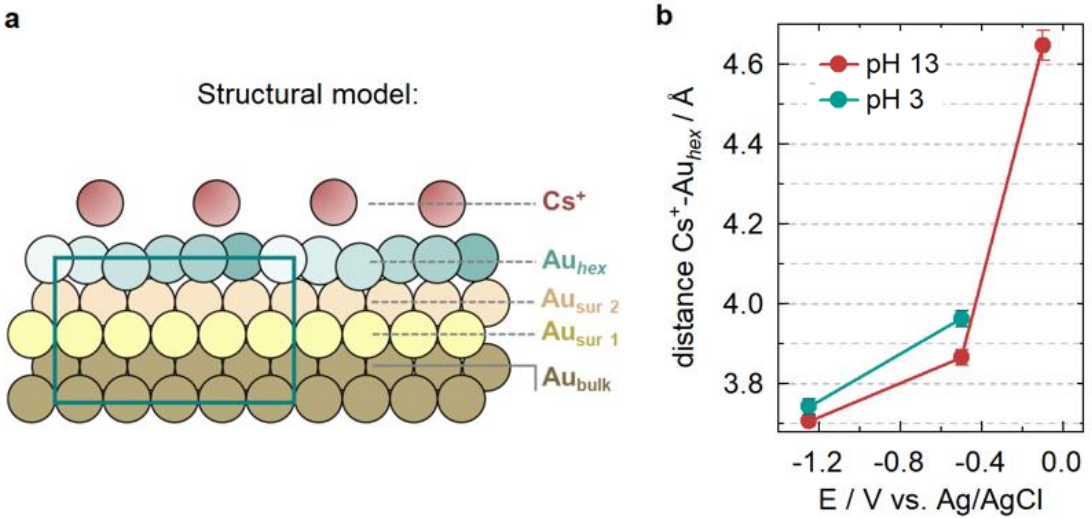


Katharina Doblhoff-Dier| 2025 – Predictor meeting

Universiteit Leiden
The Netherlands

Cs on Au(100)-hex: ion – surface distance

- Experiments Mariana C.O. Monteiro
  - Specular crystal truncation rod measurements



Ions reside close to the surface.

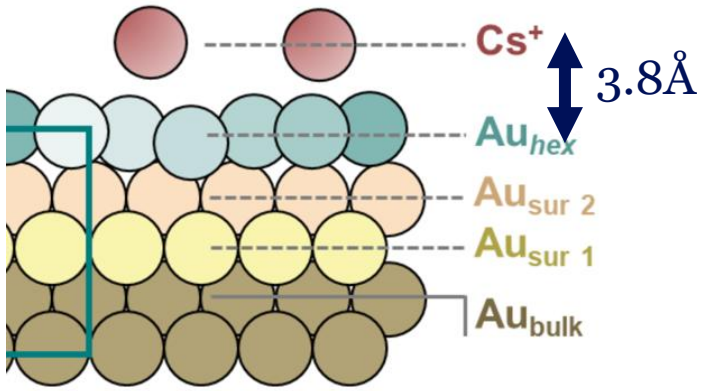
M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

Where do the ions reside?

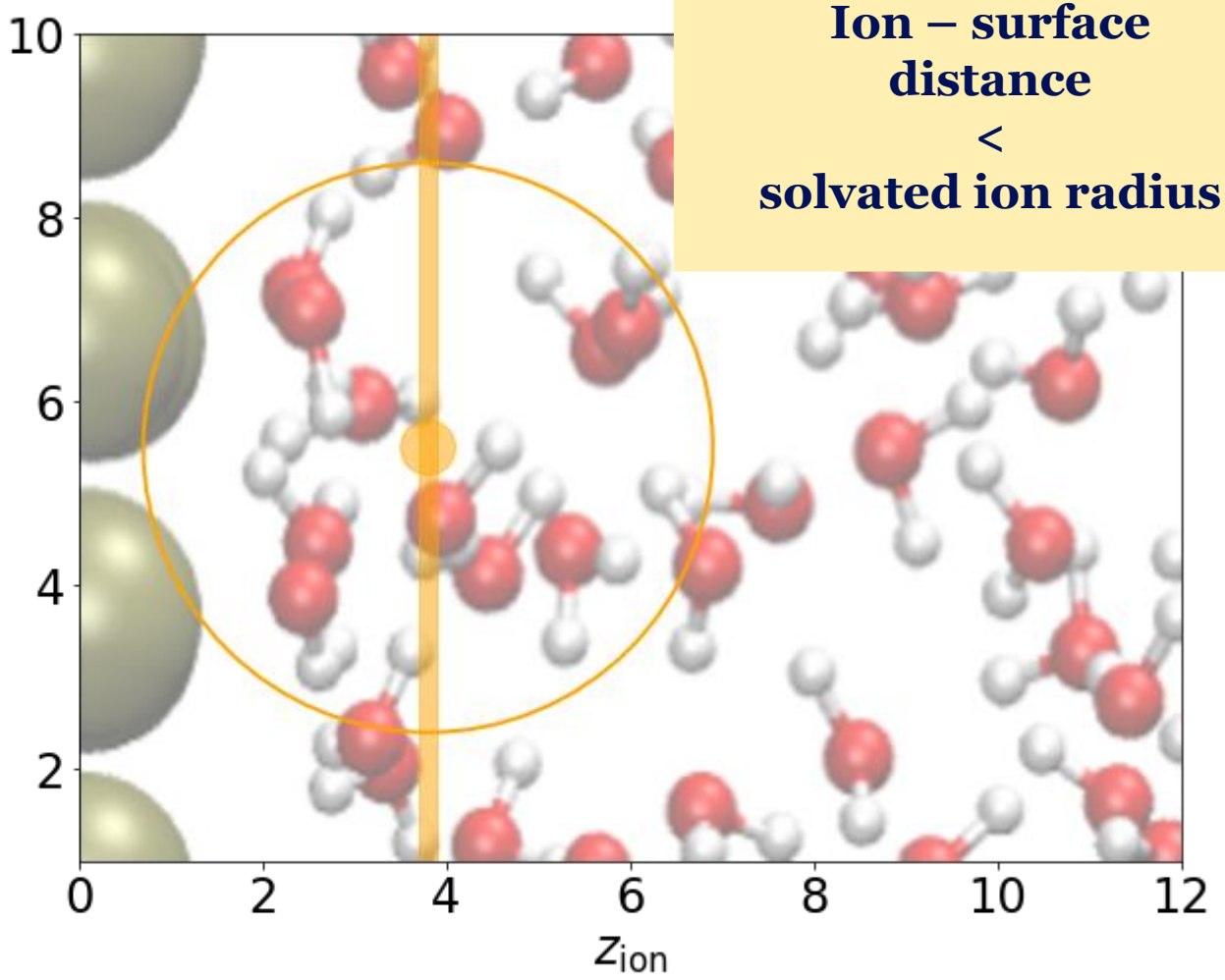
Collaboration with Mariana Monteiro

Publication in preparation

- Experiments



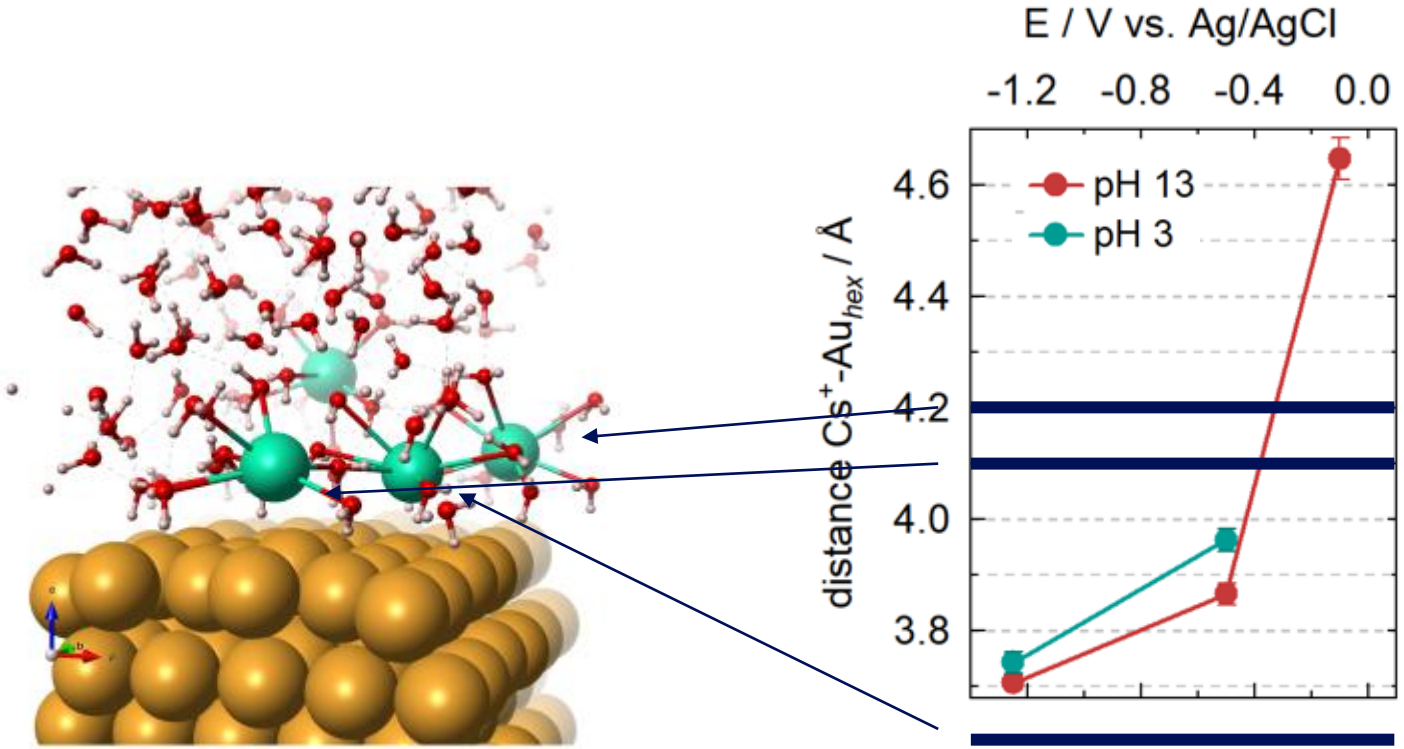
Ion – surface distance < solvated ion radius



M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

How solvated are ions at the interface?

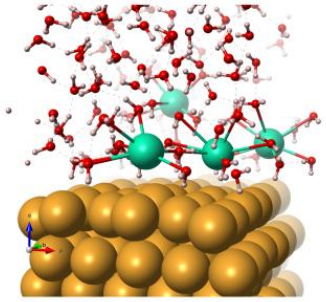
- Ab-initio molecular dynamics simulations

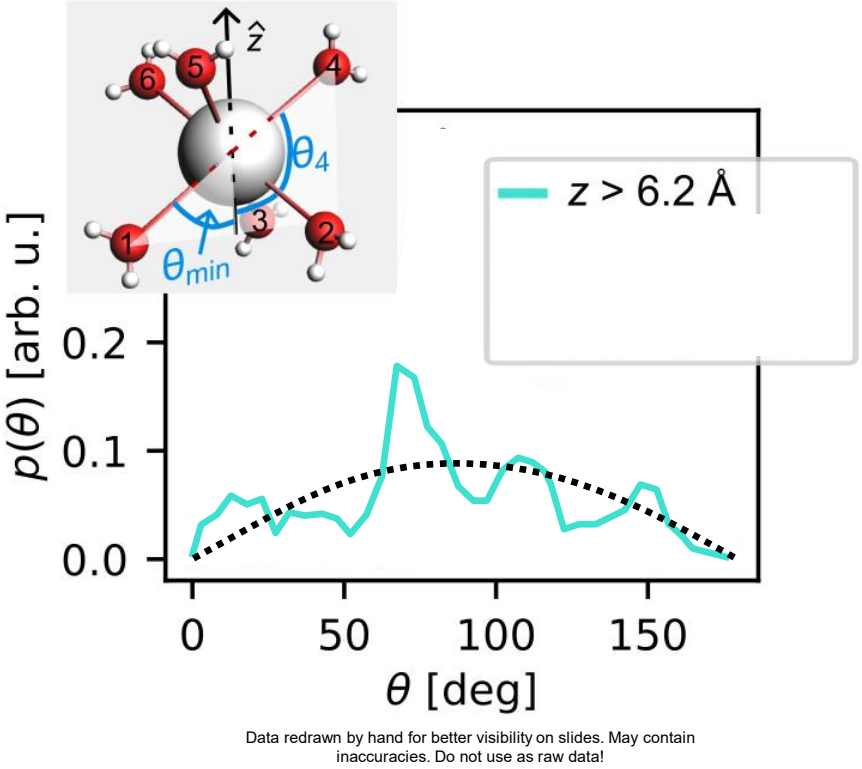


No water below the Cs^+ for experimental Cs^+ – surface distances!

M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

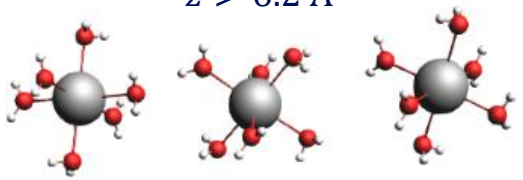
How solvated are ions at the interface?





Data redrawn by hand for better visibility on slides. May contain inaccuracies. Do not use as raw data!

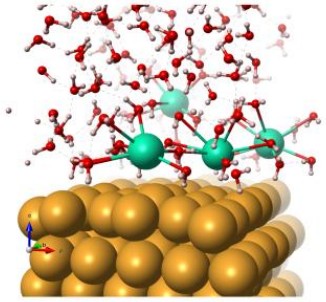
$z > 6.2$ Å

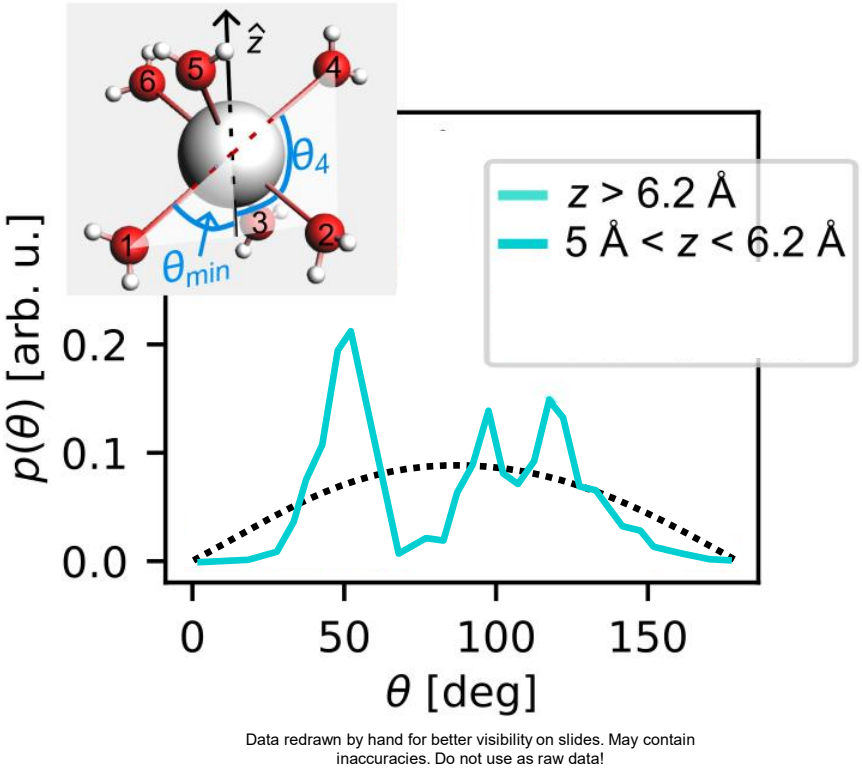


Random orientation
→ $\theta_{min} = 0$

M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

How solvated are ions at the interface?





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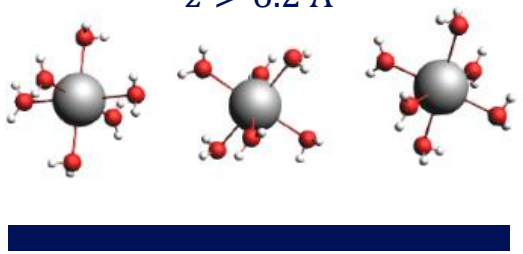
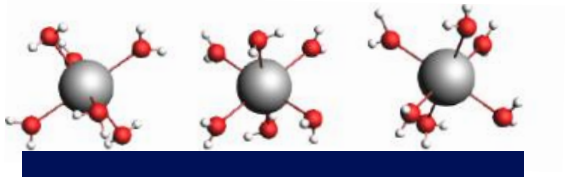
$z > 6.2$ Å



Random orientation
→ $\theta_{min} = 0$

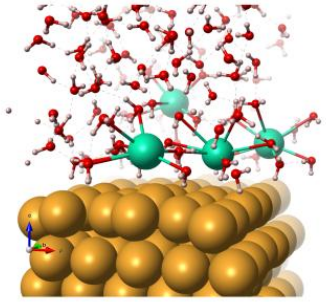
5 Å $< z <$ 6.2 Å

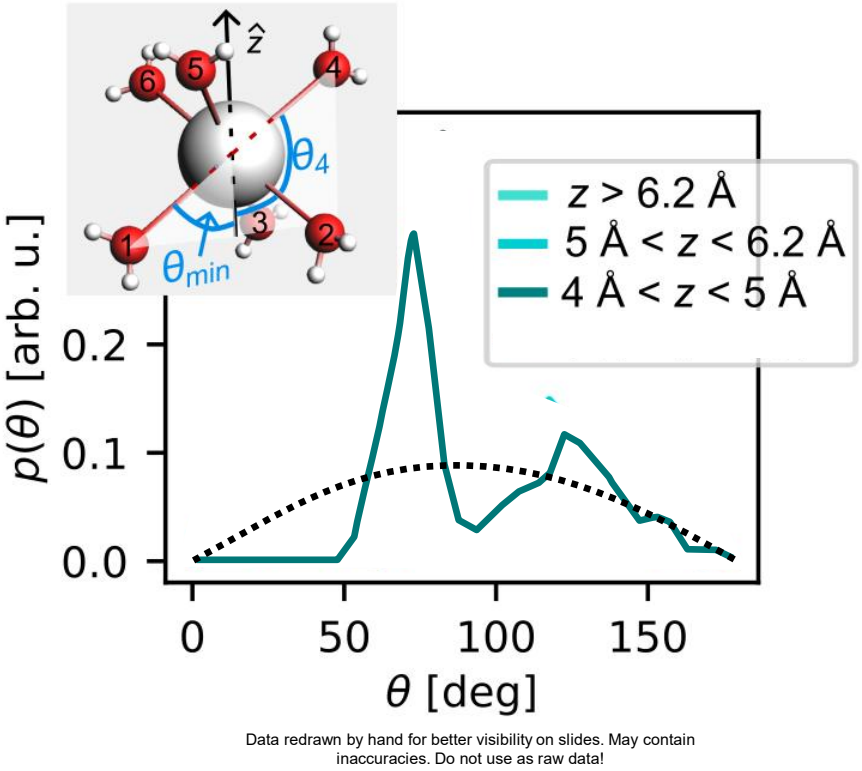


Solvation shell oriented
→ $\theta_{min} \rightarrow 55°$

M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

How solvated are ions at the interface?





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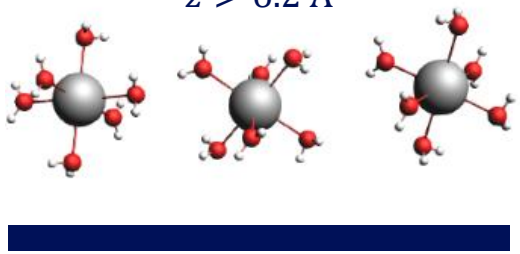
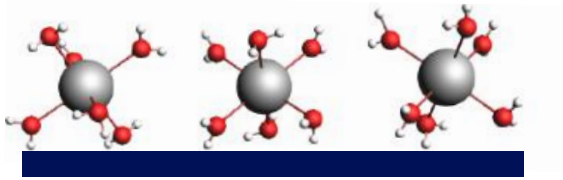
$z > 6.2$ Å



Random orientation
→ $\theta_{min} = 0$

5 Å < z < 6.2 Å



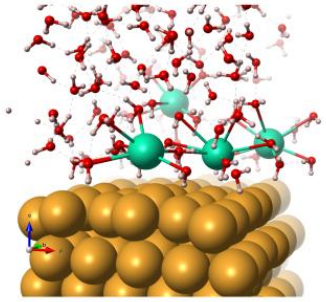
Solvation shell oriented
→ $\theta_{min} \rightarrow 55°$

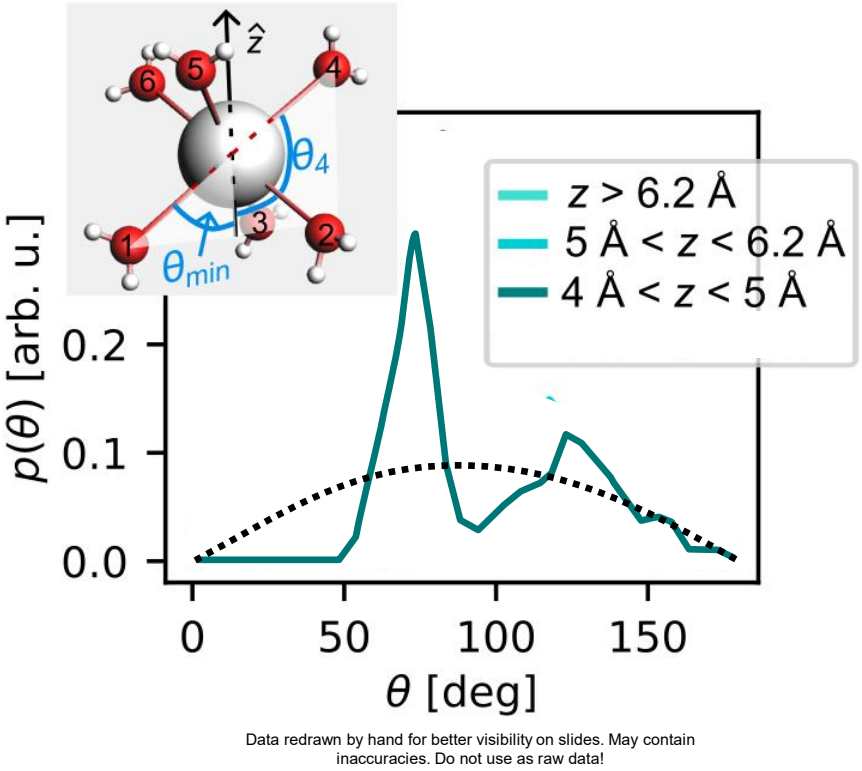
4 Å < z < 5 Å

+ Distortion of solvation shell

M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

How solvated are ions at the interface?





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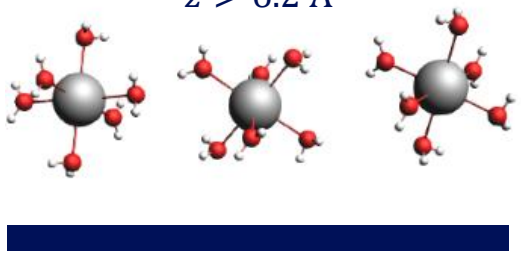
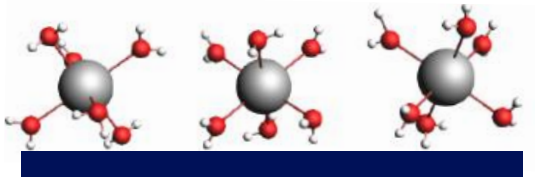
$z > 6.2$ Å



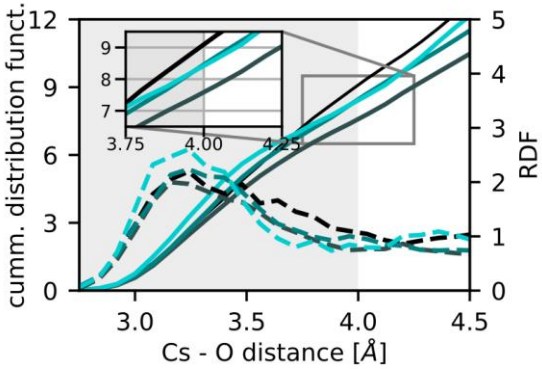
Random orientation
→ $\theta_{min} = 0$

5 Å $< z <$ 6.2 Å



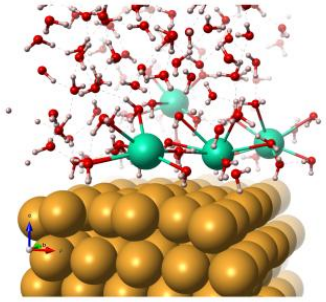
Solvation shell oriented
→ $\theta_{min} \rightarrow 55°$

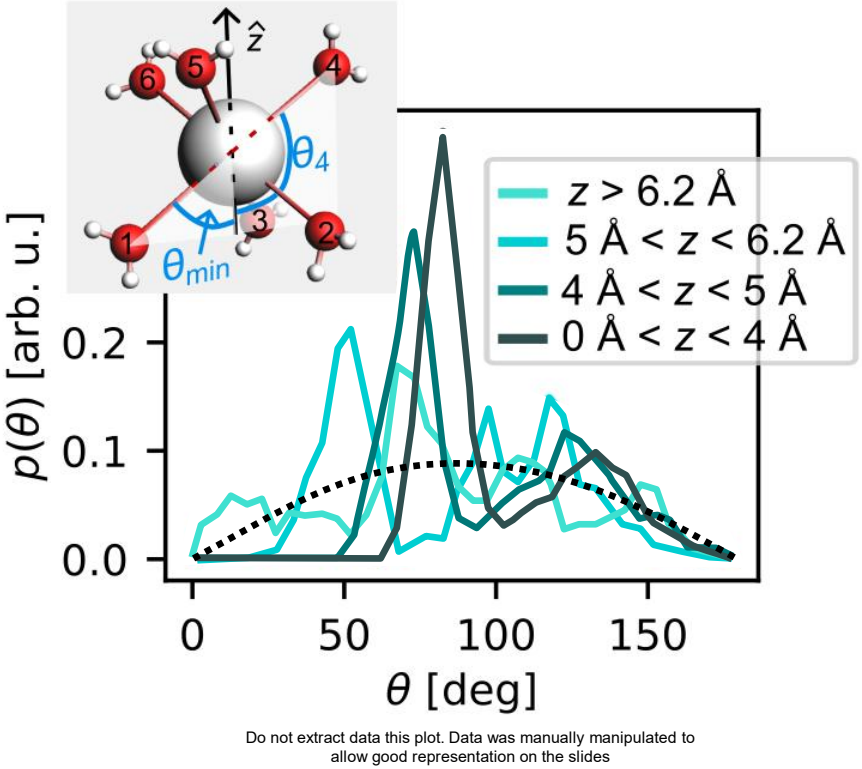
4 Å $< z <$ 5 Å



M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

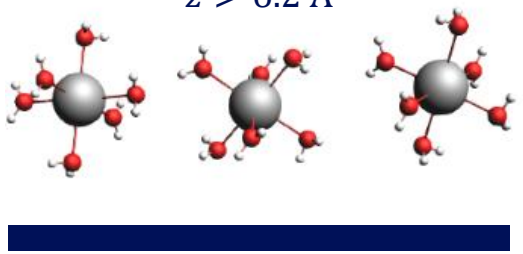
How solvated are ions at the interface?





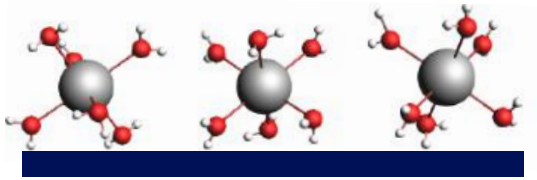
Do not extract data this plot. Data was manually manipulated to allow good representation on the slides

$z > 6.2$ Å



Random orientation
→ $\theta_{min} = 0$

5 Å < z < 6.2 Å

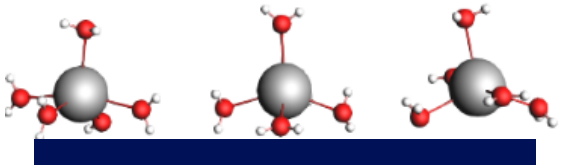


Solvation shell oriented
→ $\theta_{min} \rightarrow 55°$

4 Å < z < 5 Å

+ Distortion of solvation shell

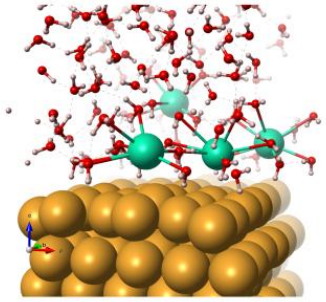
$z < 4$ Å

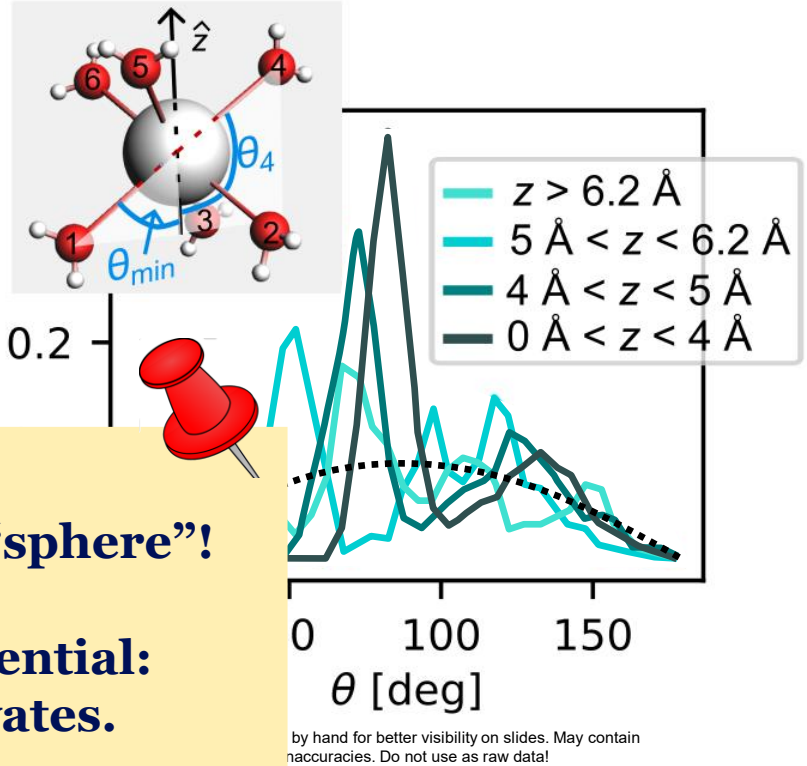


10% desolvation

M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

How solvated are ions at the interface?

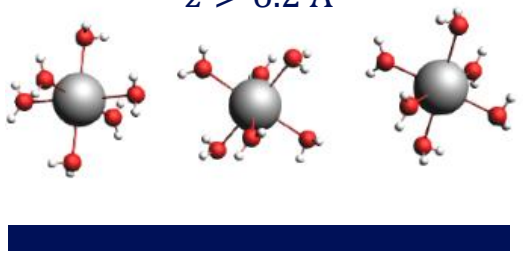




- **Solvation shell ≠ "sphere"!**

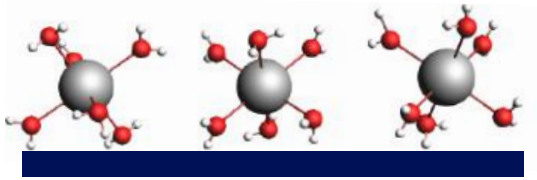
- **Depending on potential: Cs partially desolvates.**

$z > 6.2$ Å



Random orientation
→ $\theta_{min} = 0$

5 Å $< z <$ 6.2 Å

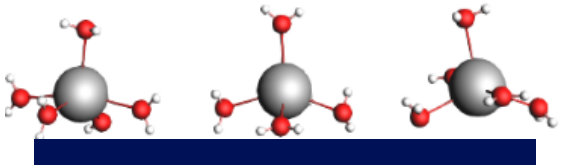


Solvation shell oriented
→ $\theta_{min} \rightarrow 55°$

4 Å $< z <$ 5 Å

+ Distortion of solvation shell

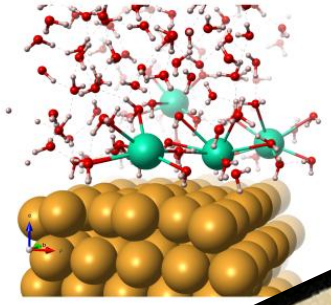
$z < 4$ Å



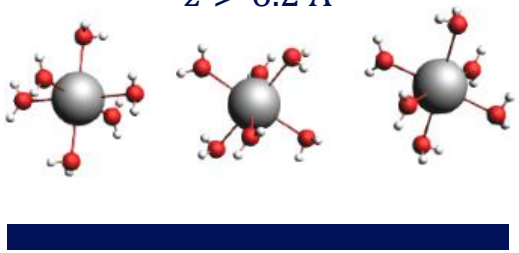
10% desolvation

M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

How solvated are ions at the interface?

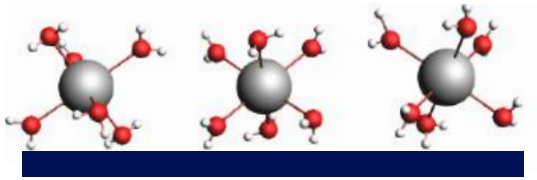


$z > 6.2$ Å



Random orientation
→ $\theta_{min} = 0$

5 Å $< z <$ 6.2 Å

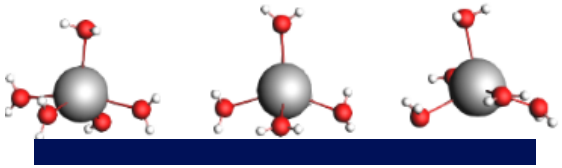


Solvation shell oriented
→ $\theta_{min} \rightarrow 55°$

4 Å $< z <$ 5 Å

+ Distortion of solvation shell

$z <$ 4 Å



10% desolvation

M.C.O Monteiro, K. Doblhoff-Dier and co-workers; under submission

Example:
When AIMD is no good:
Ion clustering

Katharina Doblhoff-Dier| 2025 – Predictor meeting

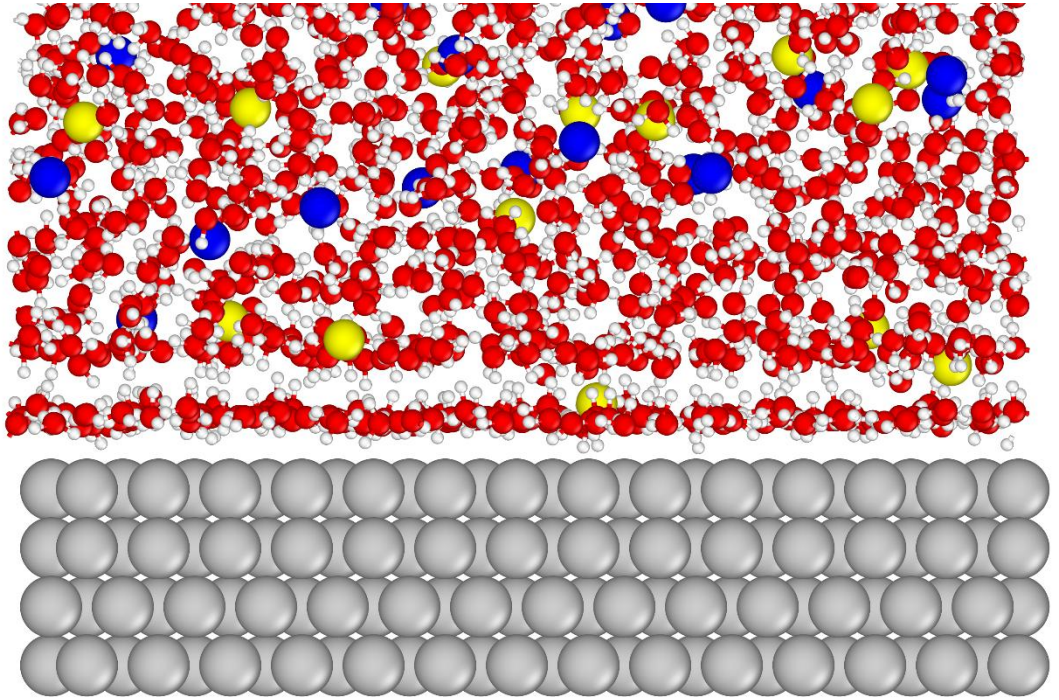
Universiteit
Leiden
The Netherlands

Molecular dynamics simulations

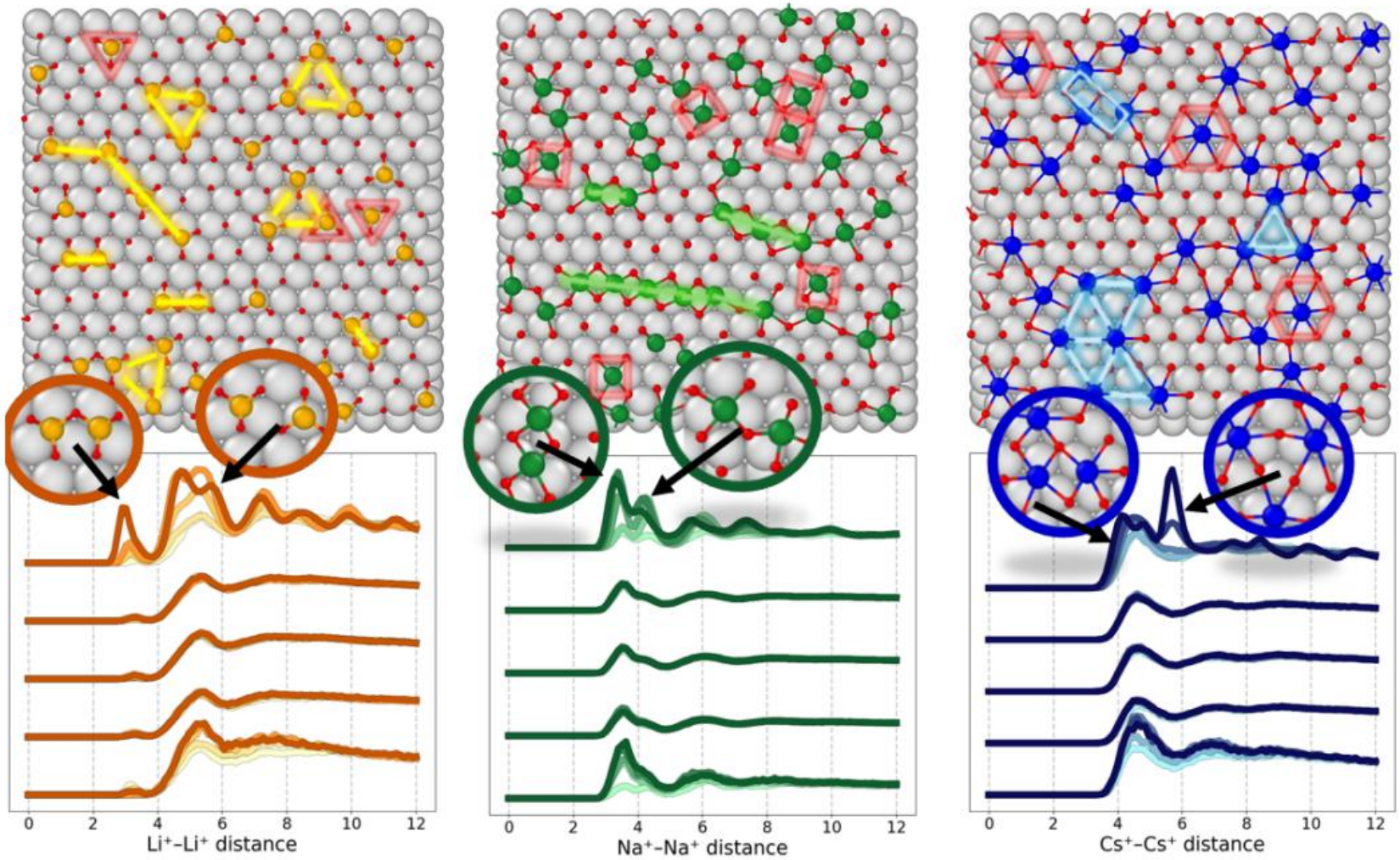
Force-field molecular dynamics

- Simulation sizes
  - ~15x15 supercells
  - ~ns
- Charging via Siepmann-Sprik method

- Interface force-fields poorly parameterized
- No electronic dielectric response



Ions @ charged interface share solvation shell



Ion packing defined by

- **3D ion hydration**
- **Metal structure**

Moss and Doblhoff-Dier, DOI: 10.26434/chemrxiv-2025-cw68k

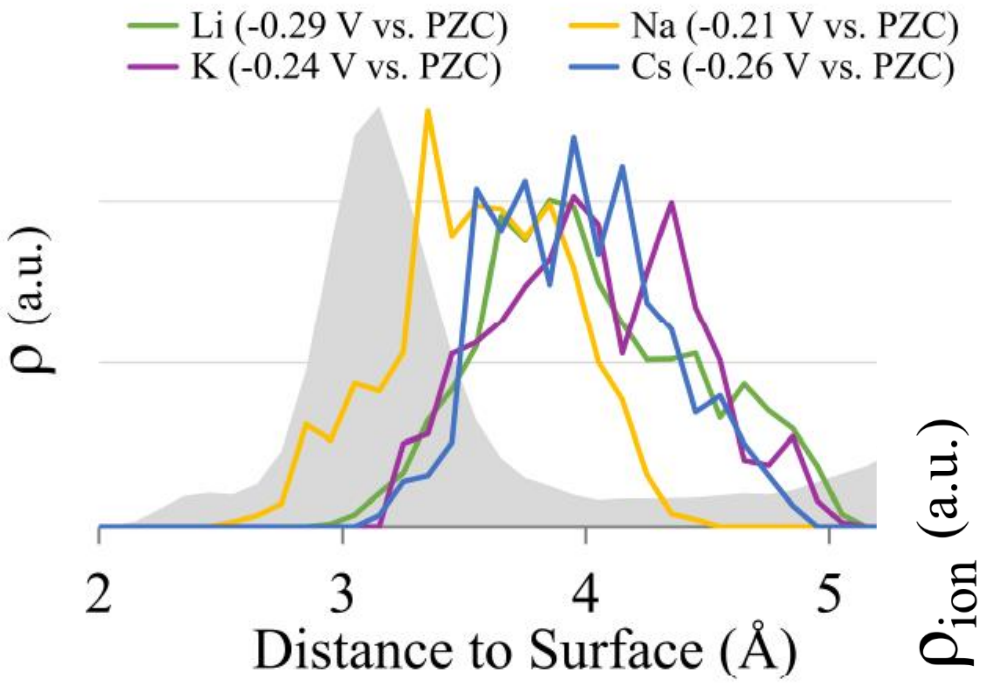
Example: When AIMD is no good2: Ion positions

Katharina Doblhoff-Dier| 2025 – Predictor meeting

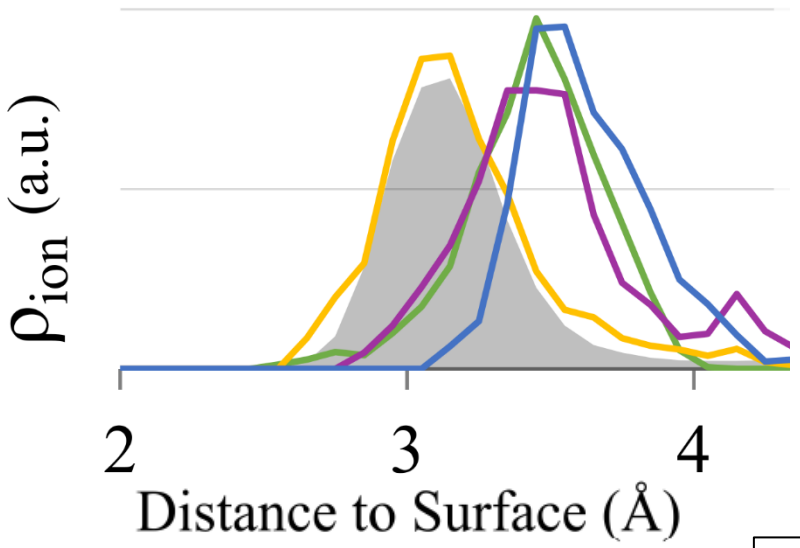
Universiteit Leiden
The Netherlands

Ions @ Pt(111): ion size influence

- Ab-initio molecular dynamics simulations
  - Position of the closest ions



Lower potentials (4 ions)



Na < Li ~ K ~ Cs

Ion – surface distance follows neither
- **Ion size nor**
- **Solvated ion size**

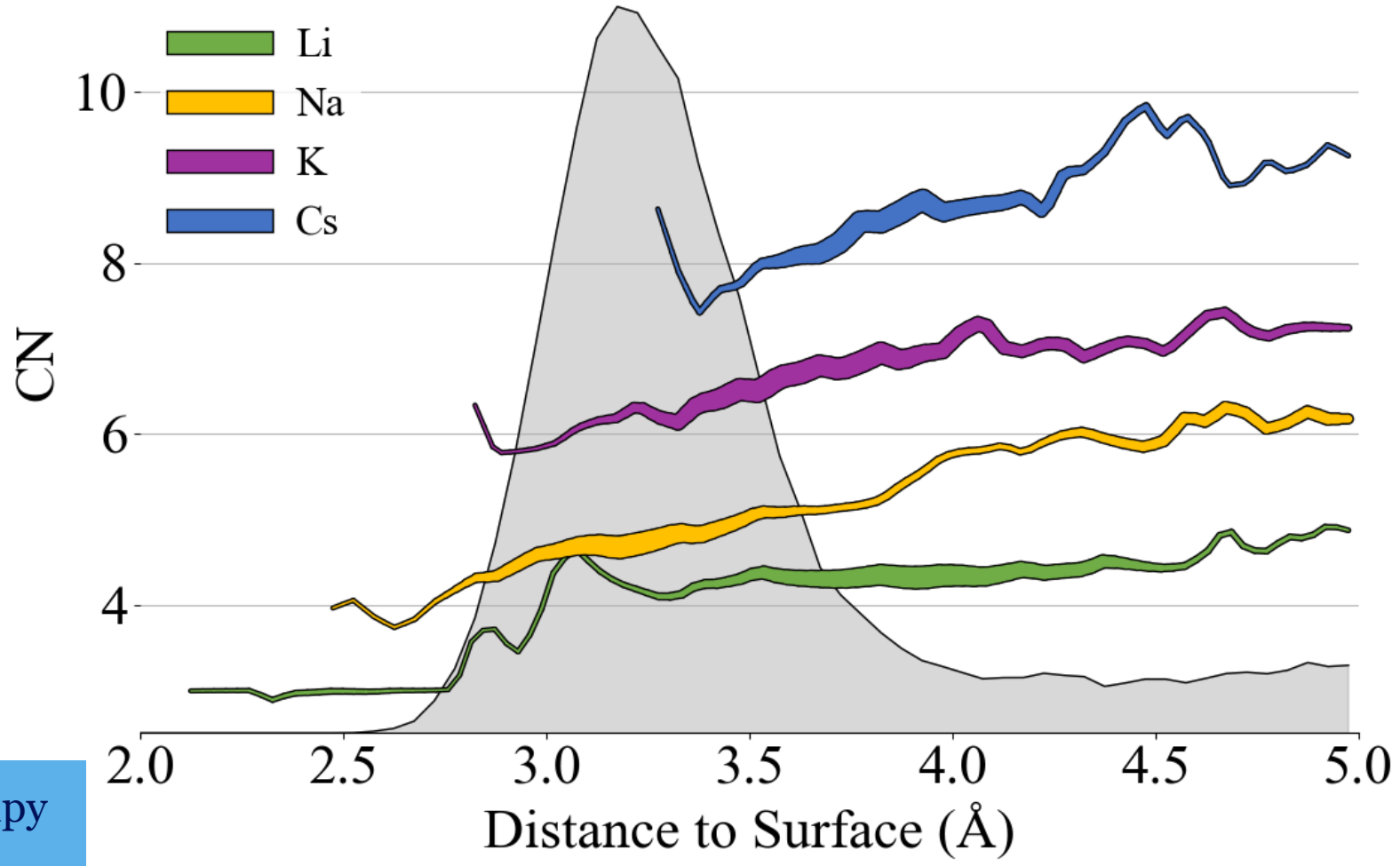
Hydrated ion radii [A]

Li+	Na+	K+	Cs+
3.8	3.6	3.3	3.3

Master thesis Rick Kort; Supervisor: K. Doblhoff-Dier

How solvated are ions at the interface?

- DFT-MD simulations:
  - all alkali cations can/will partially desolvate
  - Some will only desolvate at high enough potential



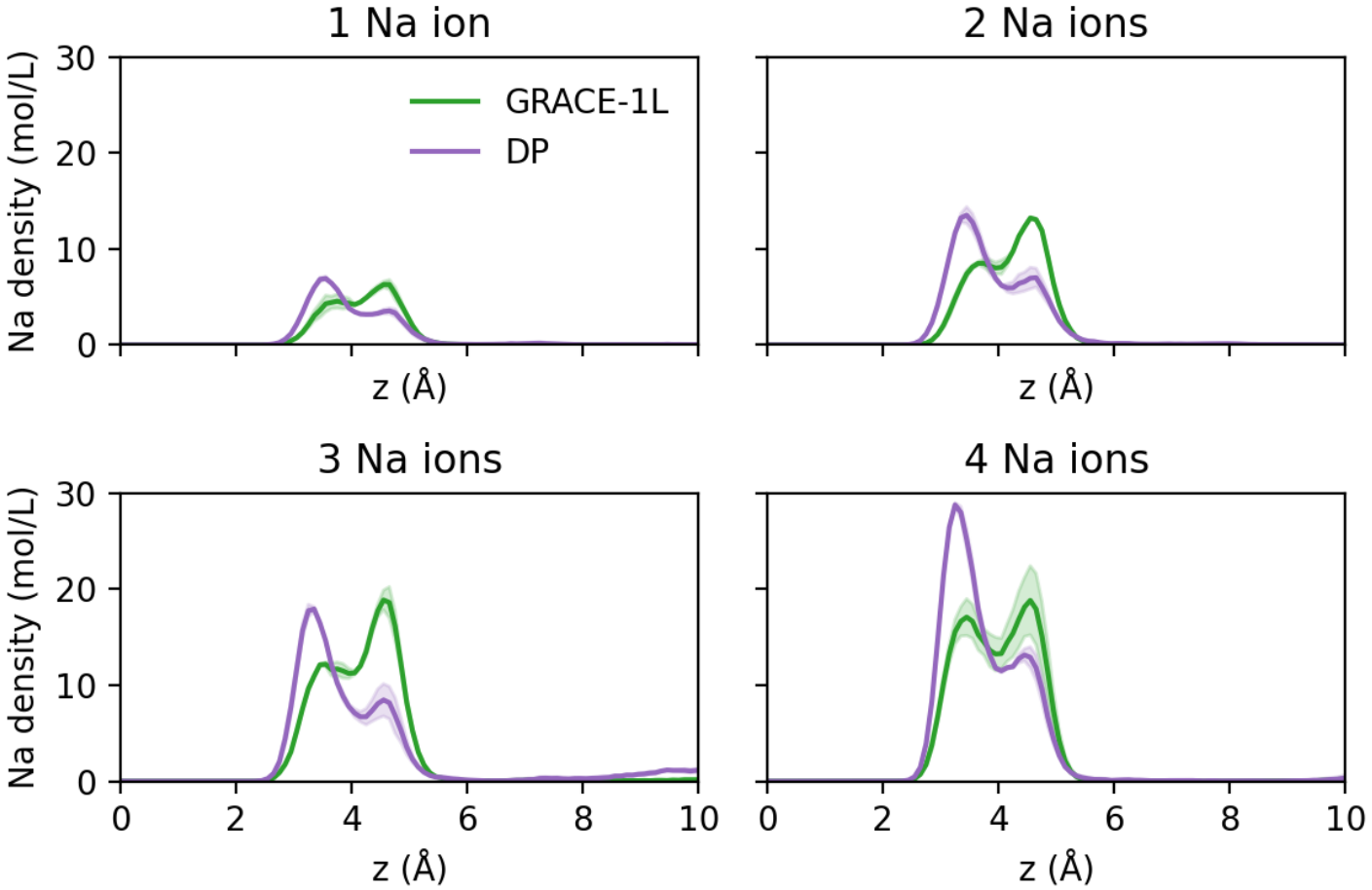
- **All ions can partially shed their solvation shell.**

Solvation enthalpy
$\Delta H_{Li} \sim 2\ \Delta H_{Cs}$

Master thesis Rick Kort; Supervisor: K. Doblhoff-Dier

Ions @ Pt(111): extending the timescales

- Using machine learned potentials

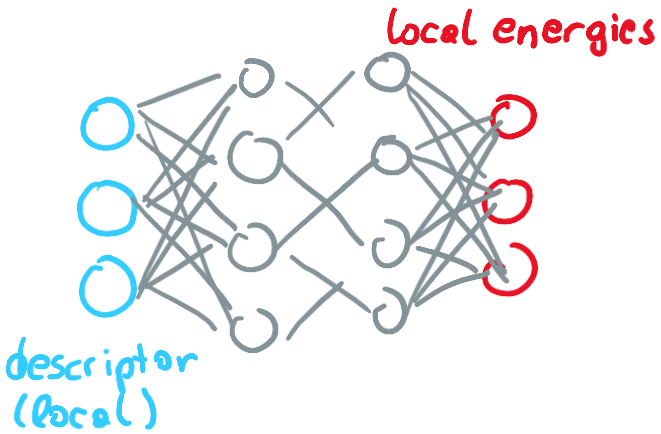


Different models give different results.

$$\Delta F(20\ meV) \gg RMSE_{test\ set}\ (1\ \text{meV/atom})$$

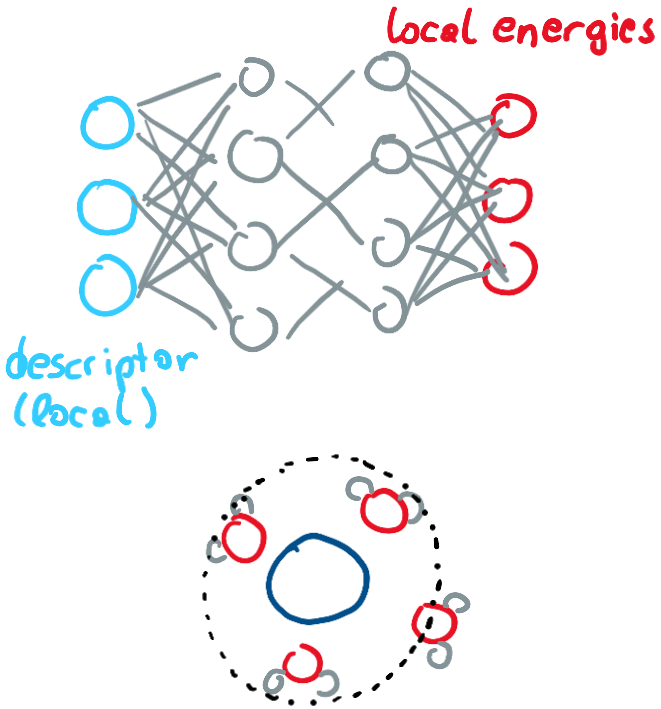
Lucas de Kam, Nitish Govindarajan, K. Doblhoff-Dier and co-workers; in preparation

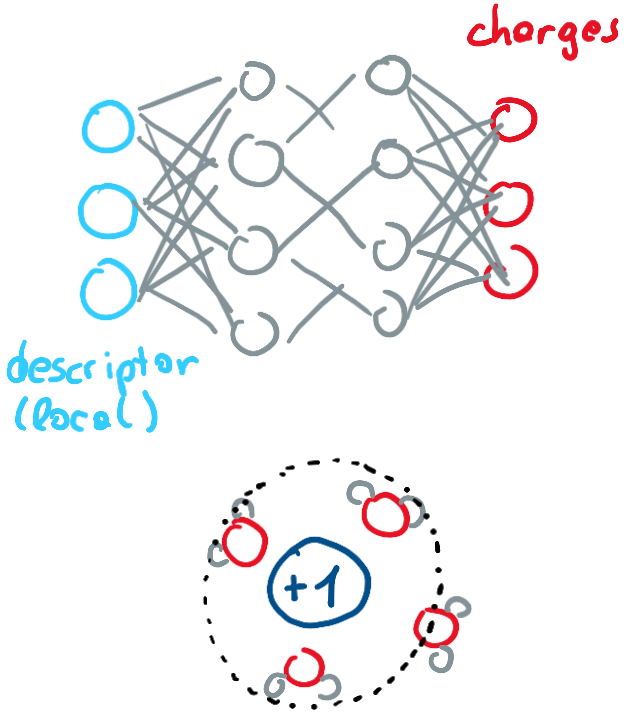
The difficulty of ML potentials for electrochemistry



- No long-range electrostatic interactions
- Can lead to charged regions in an electrolyte

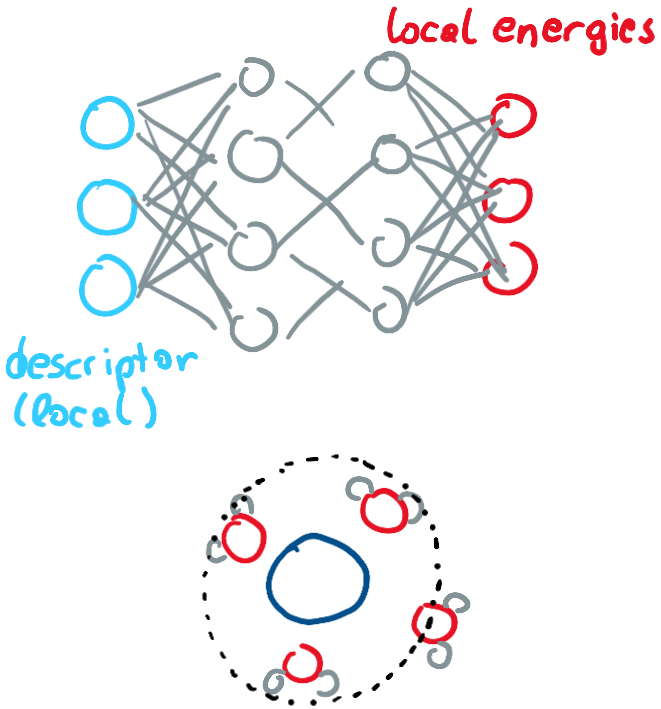
The difficulty of ML potentials for electrochemistry

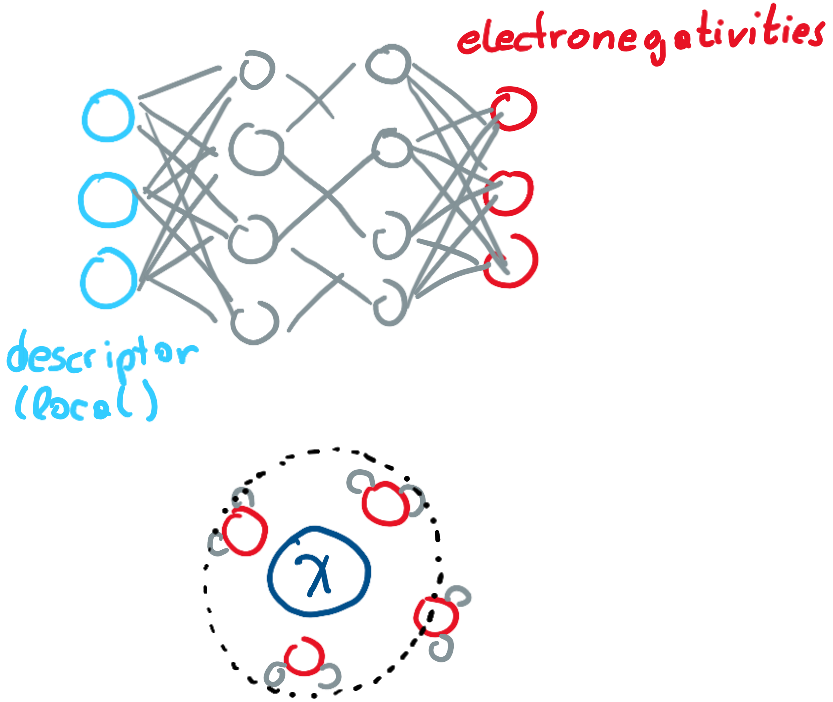




- Long-range charge transfer through insulator allowed

The difficulty of ML potentials for electrochemistry

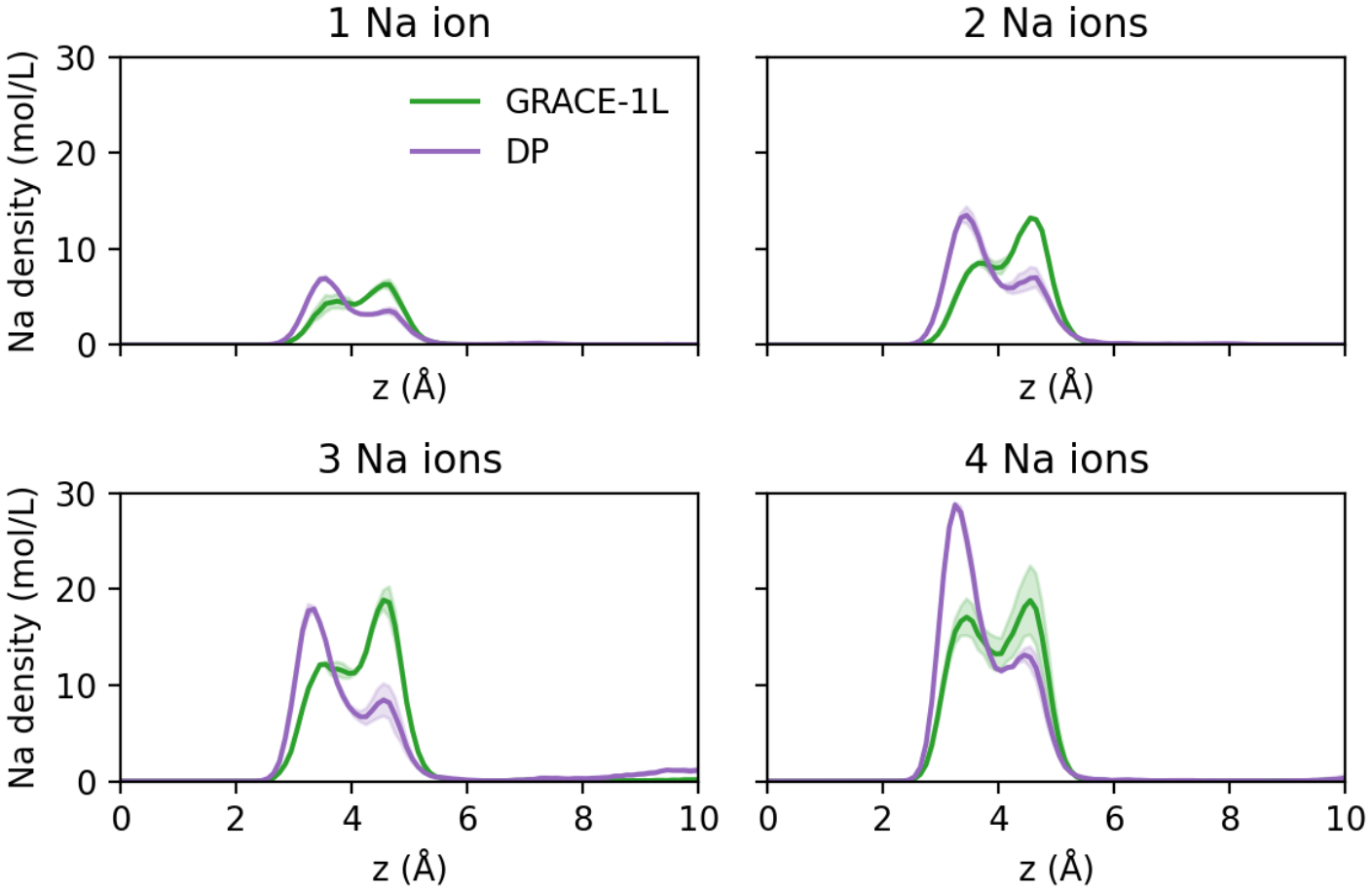




- No long-range charge transfer
- How to get the metal charged?

Ions @ Pt(111): extending the timescales

- Using machine learned potentials



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Lucas de Kam, Nitish Govindarajan, K. Doblhoff-Dier and co-workers; in preparation

Take-home messages: Double layer modeling

- Simplified (mean-field) models
  - may capture interfacial capacitance (trends) reasonably well
  - but depend heavily on parameterization
- Ab-initio molecular dynamics
  - Small simulation boxes
  - No real “bulk”/only reasonable at high concentrations
- Force-field molecular dynamics
  - Larger boxes,
  - But badly prameterised interfacial force-field + tricks for metal
- Machine learned molecular dynamics
  - Challenge to describe short + long range charge transfer correctly

Part 4: Modeling electrochem. double layers

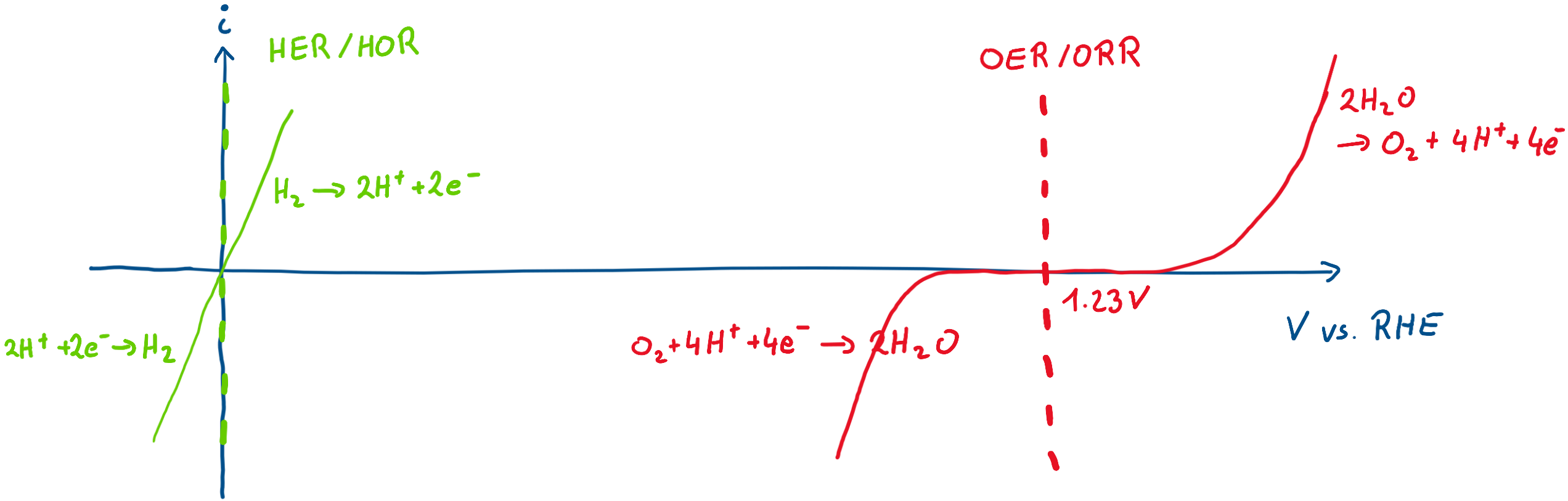
Katharina Doblhoff-Dier| Han-sur-Lesse winterschool 2025

Universiteit Leiden
The Netherlands

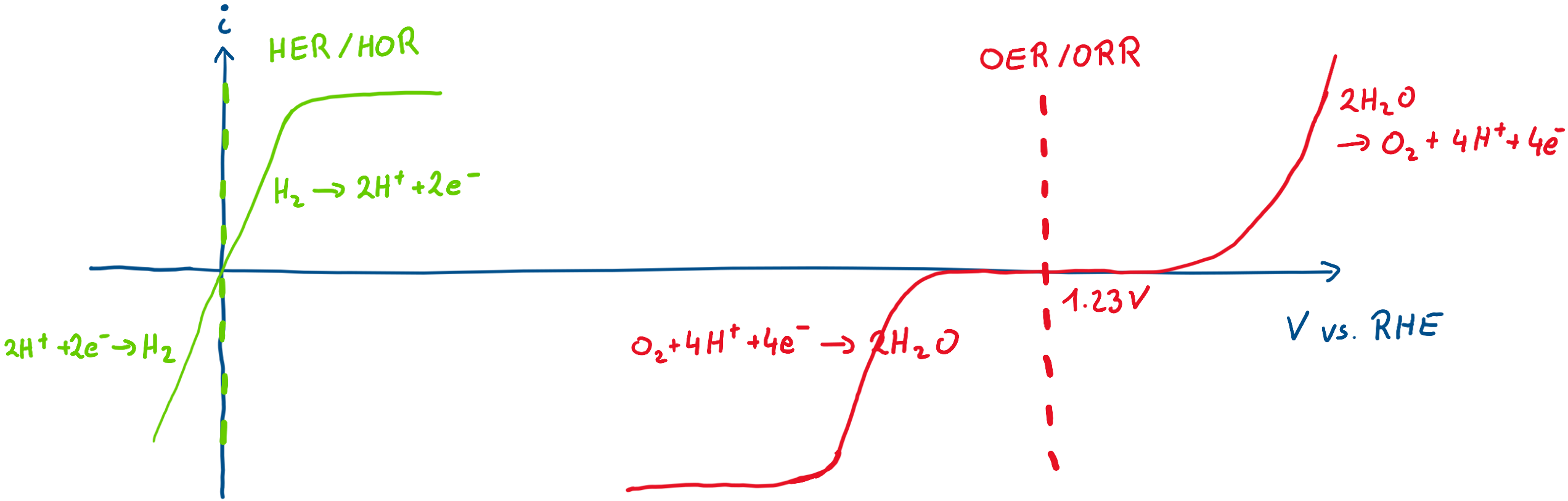
Computational electrochemistry

1. Electrochemistry: The basics
2. Computational catalysis and computational electrocatalysis
3. Beyond the computational hydrogen electrode method
4. Modeling electrochemical double layers
5. **Mass transport**
   - Mass transport limitations in electrochemistry
   - Fickian diffusion
   - Simulating diffusion and diffusion layers
   - Poisson-Nernst-Planck
   - Working examples

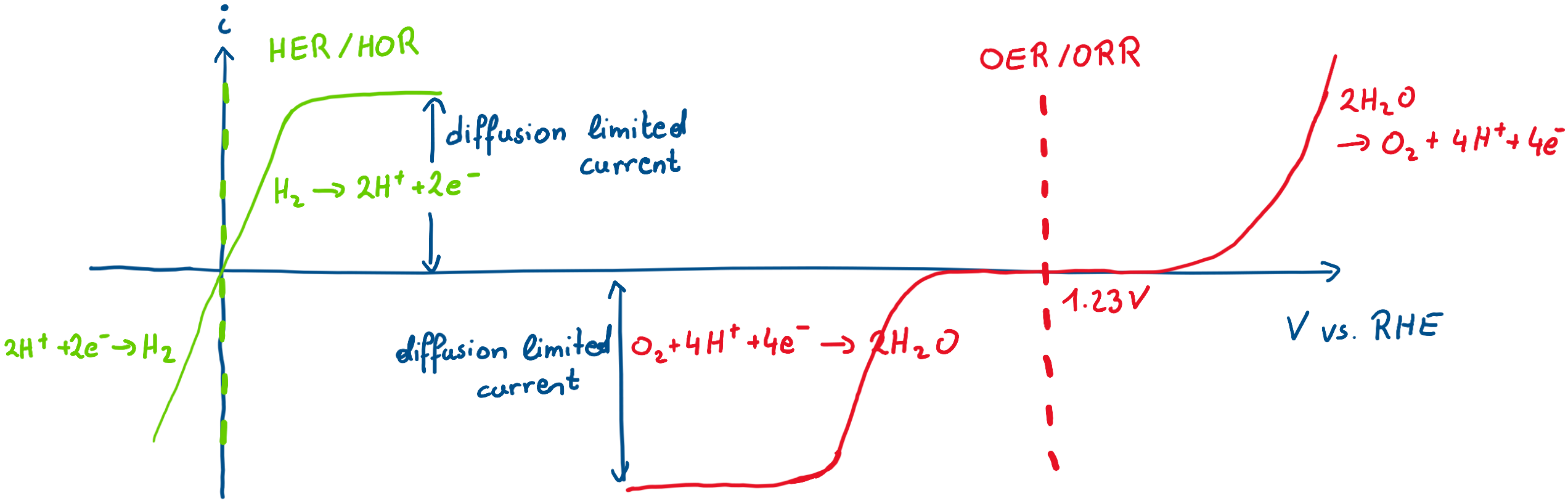
Reaction kinetics



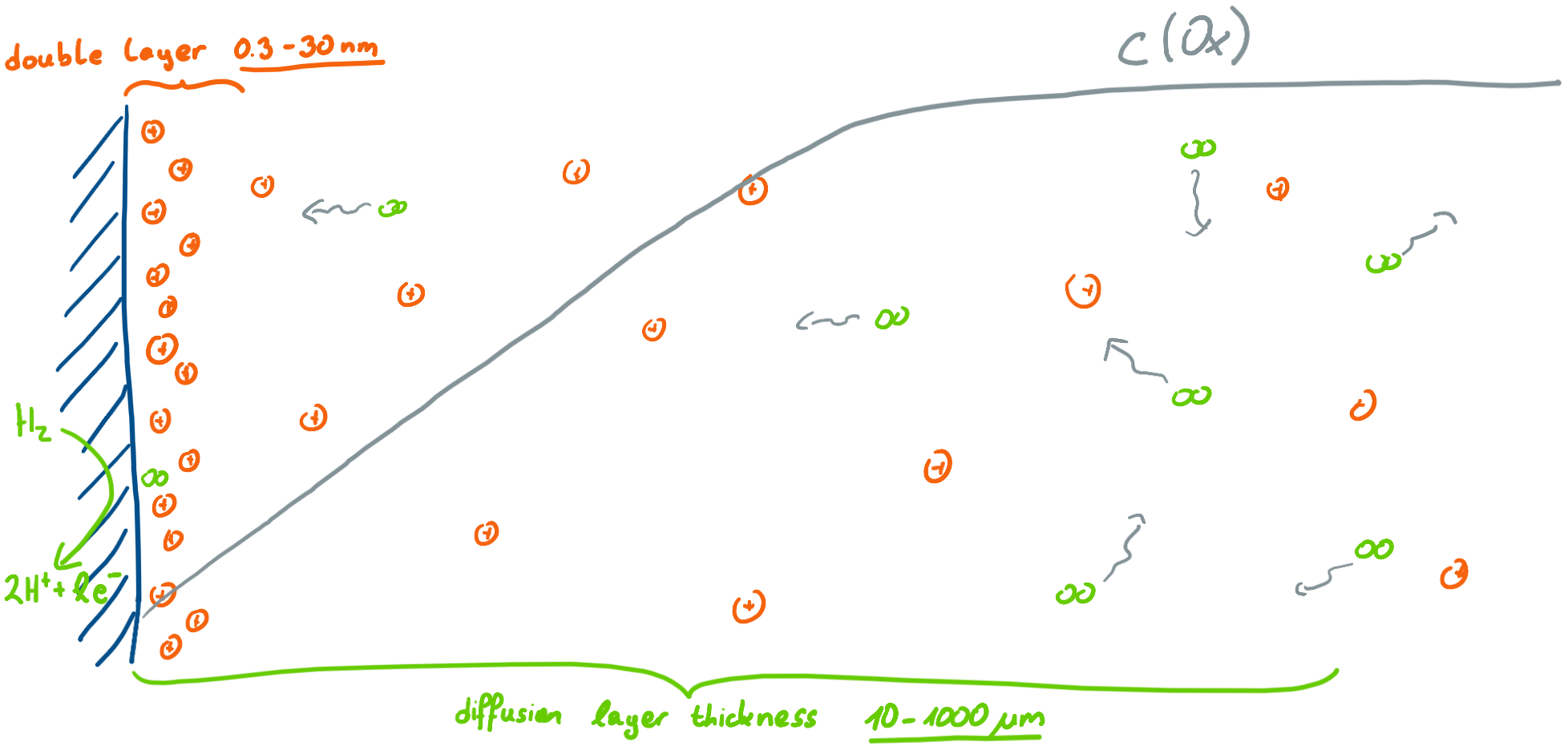
Reaction kinetics and mass transport



Reaction kinetics and mass transport



Diffusion layer



Mass transport – Fickian diffusion

- Flux of particles: proportional to concentration gradient

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}x}$$

J: Flux; D: Diffusion coefficient; $\frac{\mathrm{d}c}{\mathrm{d}x}$: Concentration

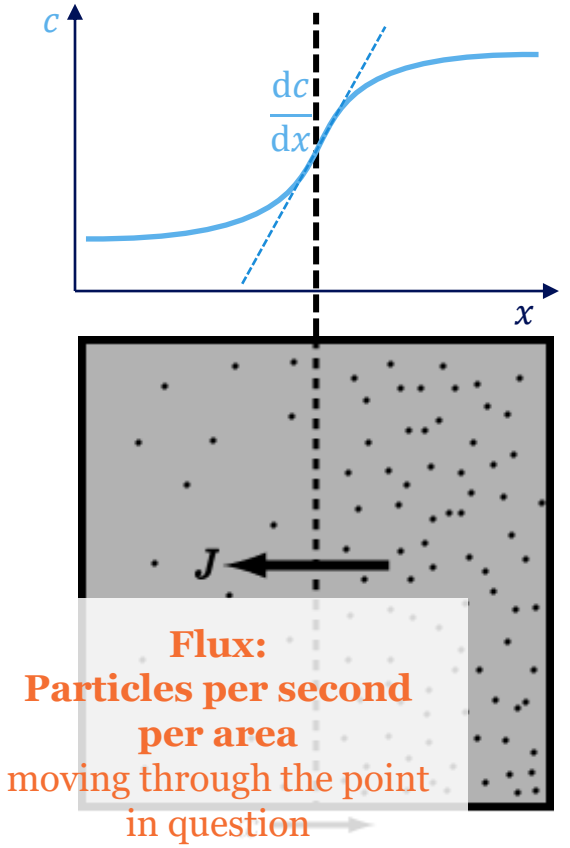
Values from: www.aqion.de/site/diffusion-coefficients

Diffusion coefficient

$H^+ : 9.3 \times 10^{-9}$ m²/s
$Li^+ : 1.0 \times 10^{-9}$ m²/s
$Na^+ : 1.3 \times 10^{-9}$ m²/s
$K^+ : 1.9 \times 10^{-9}$ m²/s
$Al^{3+} : 0.6 \times 10^{-9}$ m²/s
$F^- : 1.4 \times 10^{-9}$ m²/s
$Cl^- : 2.0 \times 10^{-9}$ m²/s
$HCO_3^- : 1.2 \times 10^{-9}$ m²/s

- Due to mass conservation →

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$



Adapted from: StarLight(CC-BY-SA)
commons.wikimedia.org/wiki/File:Fick_law_01.png

Mass transport – Fickian diffusion

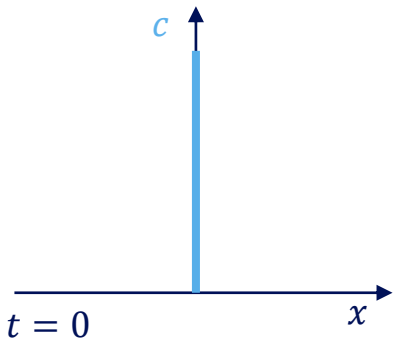
- How to solve?
  - Analytical

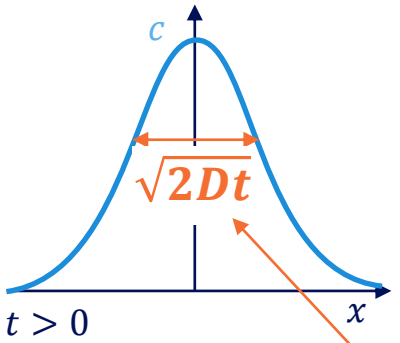
$$c(x, t = 0) = \delta(x)$$

time

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

$$c(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$





Diffusion layer thickness!!!

Mass transport – Fickian diffusion

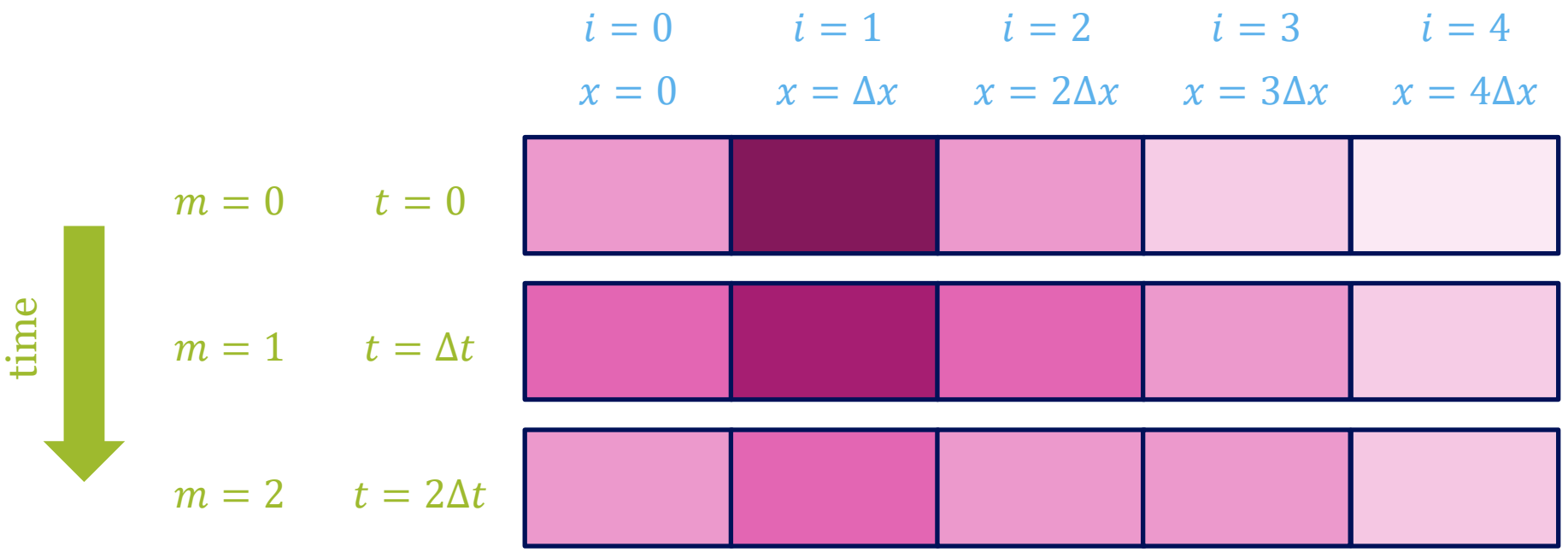
- How to solve?
  - Numerical

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

Next time step

Adjacent fields

$$\frac{c_i^{m+1} - c_i^m}{\Delta t} = D\frac{c_{i-1}^m - 2c_i^m + c_{i+1}^m}{(\Delta x)^2}$$



Simulated diffusion

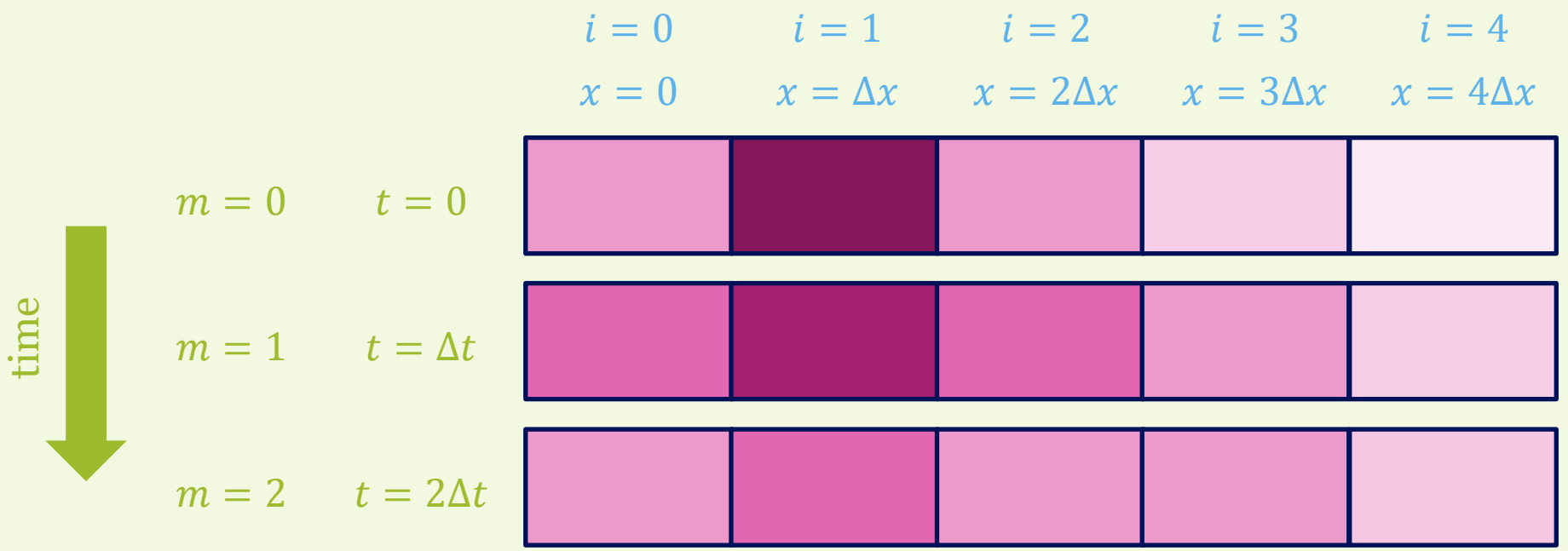
- Lab instructions in folder: Ex4_Diffusion

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

Next time step

Adjacent fields

$$\frac{c_i^{m+1} - c_i^m}{\Delta t} = D\frac{c_{i-1}^m - 2c_i^m + c_{i+1}^m}{(\Delta x)^2}$$



Mass transport

- Diffusion is not all → Nernst-Planck

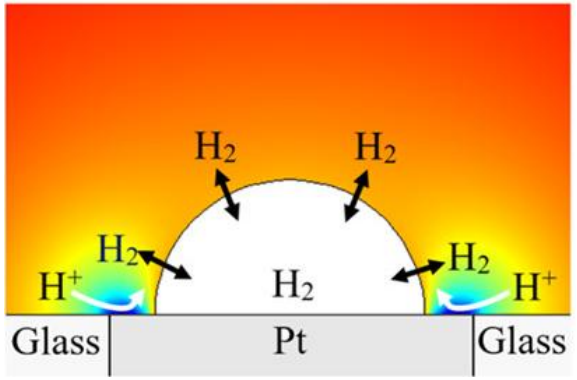
Velocity

Electric field

$$J = -D\frac{dc}{dx} + c \cdot v + Dc\frac{ze}{k_B T} \cdot E$$

Diffusion

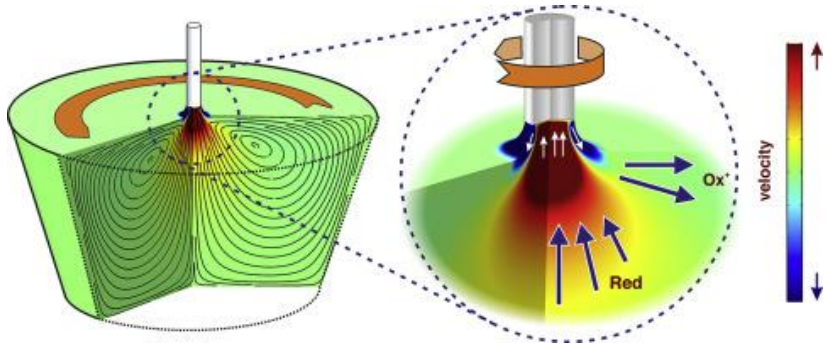
Mass transport at a three-phase boundary during HER.



Y. Liu, M.A. Edwards, S.R. German, Q. Chen, H.S. White Langmuir 2017 33 (8), 1845-1853

Advection/Convection

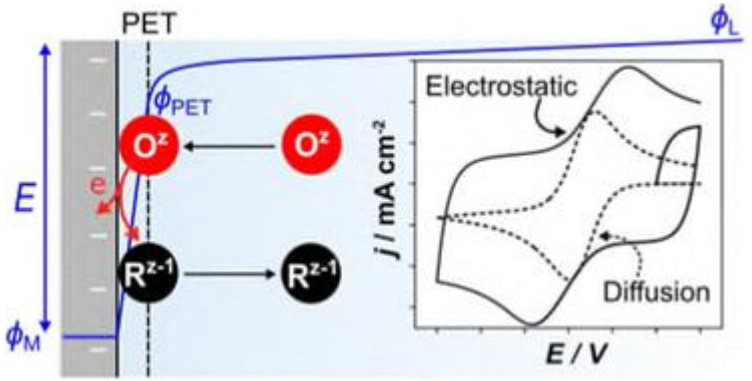
Forced convection using a rotating disk electrode



F. M. Zanotto, M. López Teijelo, S. A. Dassie, Electrochimica Acta 327 (2019) 135032

Electromigration

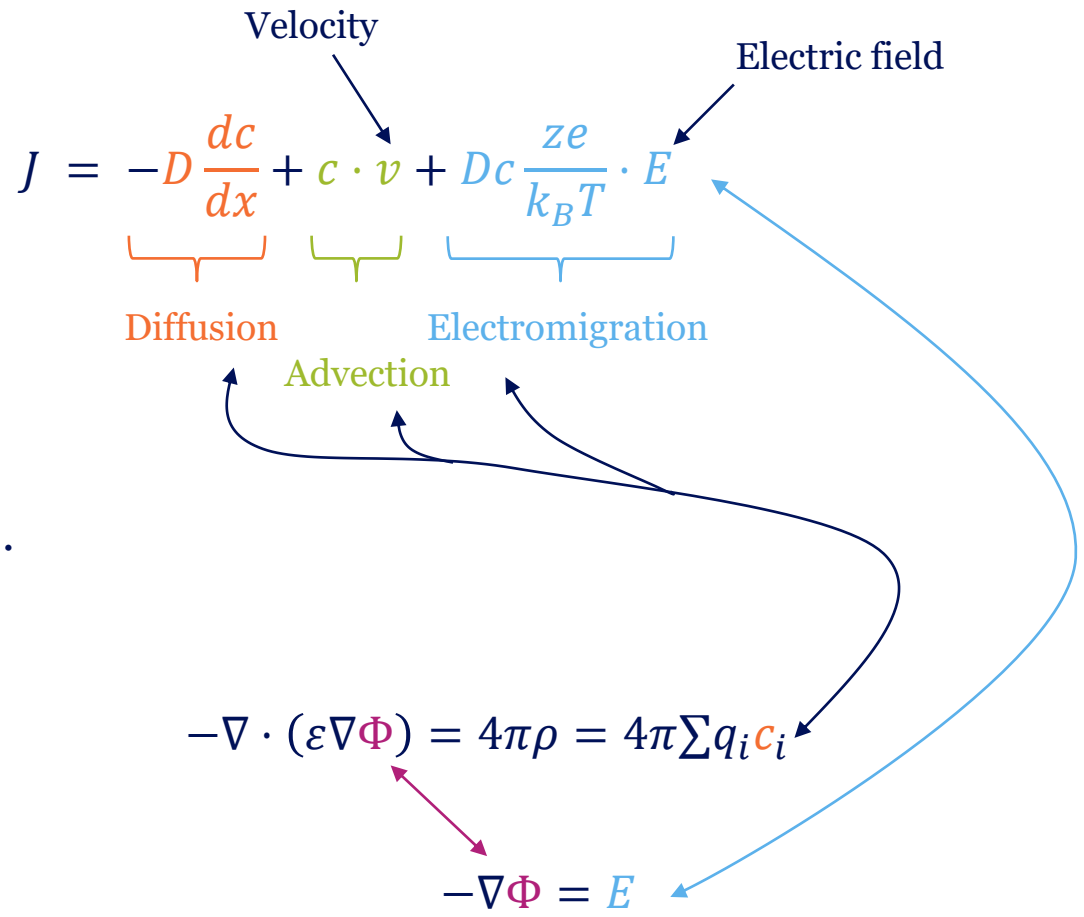
The influence of the EDL



K.J. Levey, M.A. Edwards, H.S. White, J.V. Macpherson, Phys. Chem. Chem. Phys., 2023, 25, 7832

Mass transport

- Diffusion is not all → Nernst-Planck

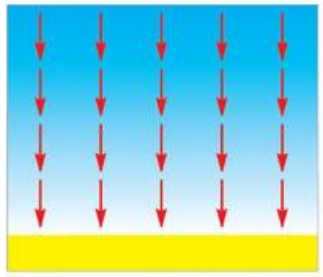


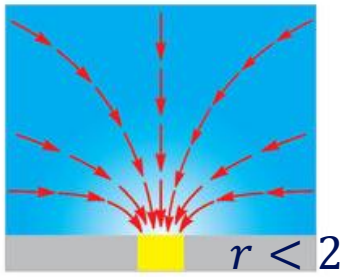
- …But electric field generated by charges, that diffuse…

  → Poisson-Nernst-Planck equations

Example: Ultramicroelectrode Array

Dr Katherine Levey

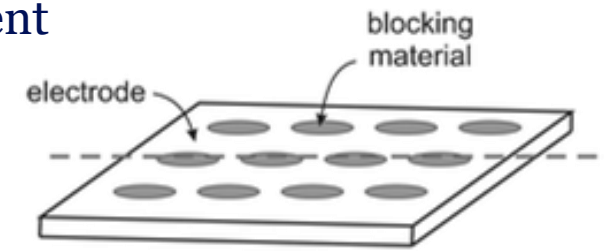




Macroelectrode Ultramicroelectrode

G. Mao, M. Kilani, M. Ahmed, Journal of The Electrochemical Society, 2022 169 022505

- electrochemical sensing @ low analyte concentration (rapid radial diffusion!)
- Individual electrode: low current
  → Use arrays

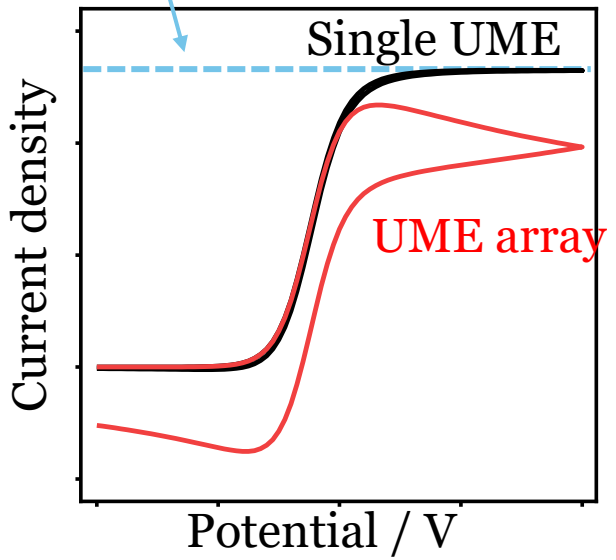


UME array

A.O. Simm, R.G. Compton et.al. , Analyst, 2005,130, 1303-1311

- **Open question:** Why do arrays manufactured according to standard analytical rules give non-steady state response?!

Theoretical limiting current



L.C.R. Alfred, K.B. Oldham J. Electroanal. Chem., 396 (1995), p. 257

Example: Ultramicroelectrode Array

Dr Katherine Levey

Create a Geometry

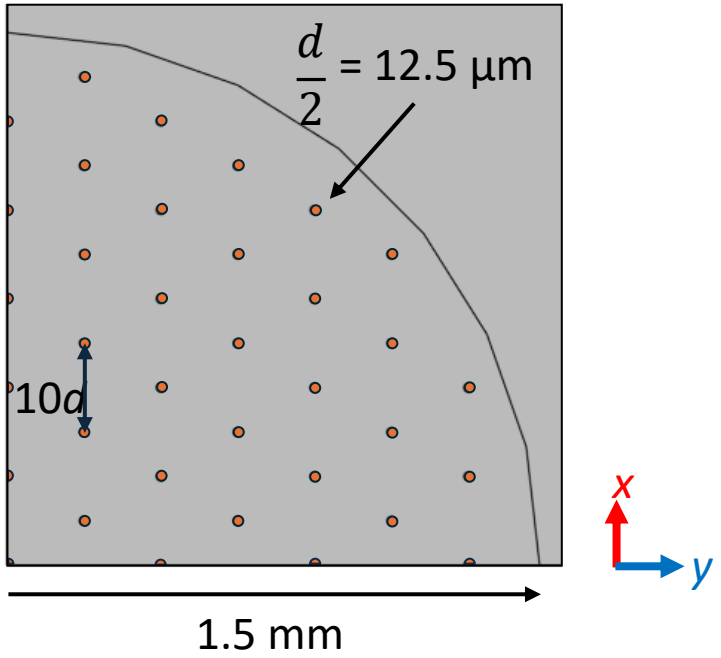
Utilise symmetry to reduces the model size e.g. only ¼ the full system

Define the Physics

Introduce boundary conditions to represent the system e.g.

Create a Mesh

Split geometry into small discrete elements to solve the partial differential eq.



Mass transport is only by diffusion

$$\boldsymbol{J}_i = -D_i \nabla C_i$$

No flux on the insulating material

$$\boldsymbol{n} \cdot J_i = 0$$

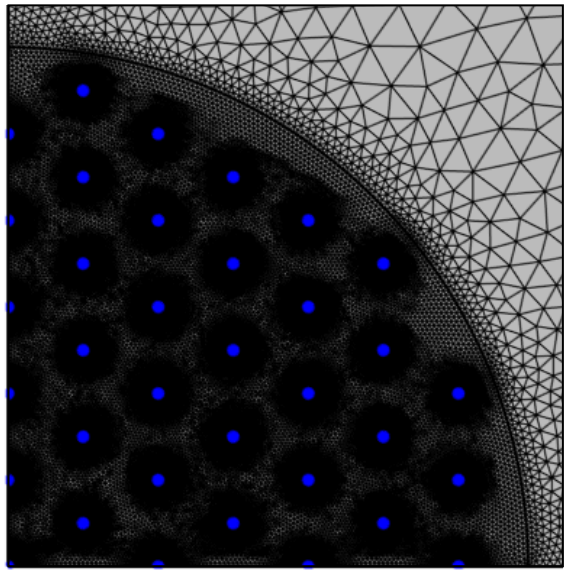


Figure reference: Katherine Levey

Example: Ultramicroelectrode Array

Dr Katherine Levey

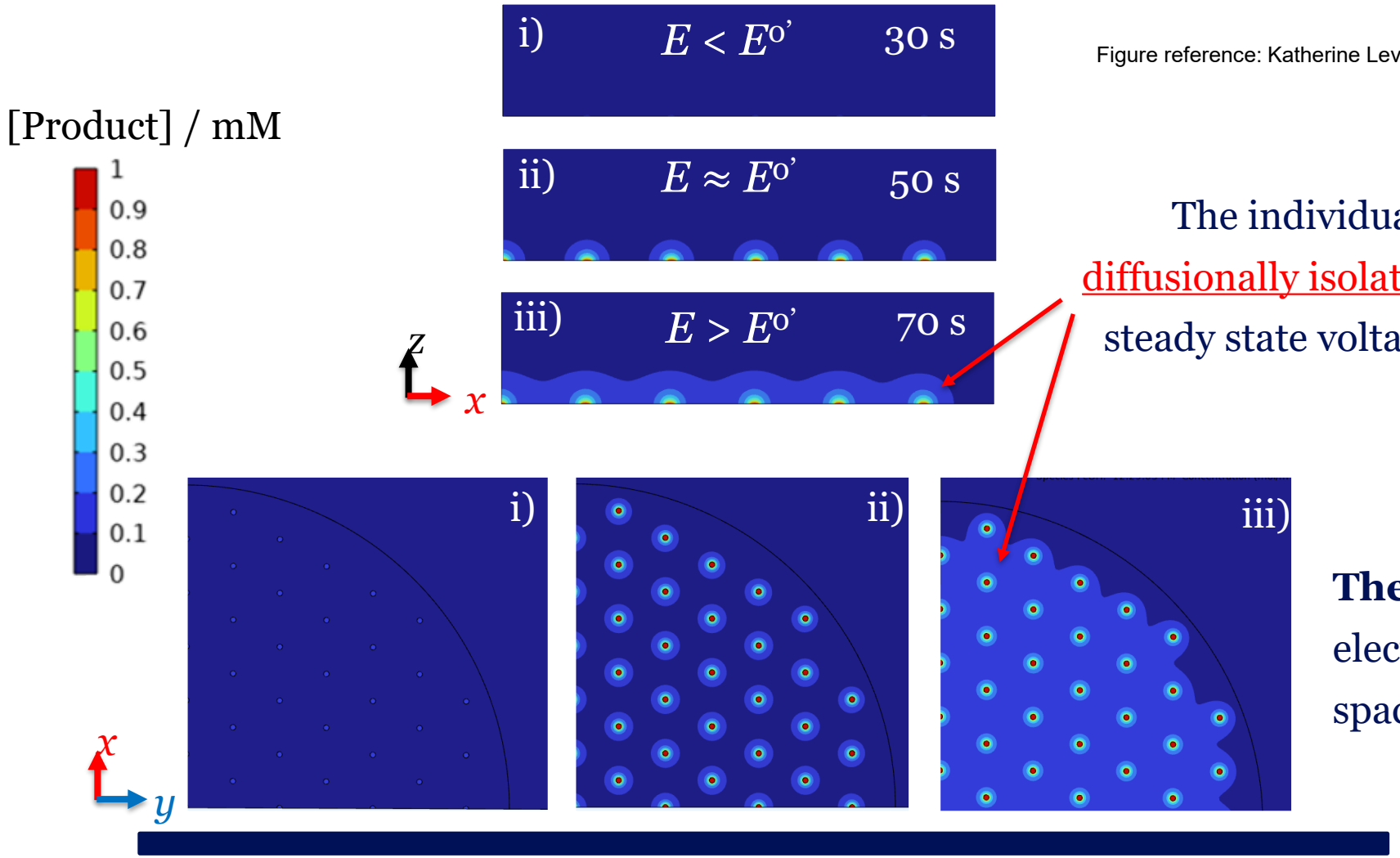


Figure reference: Katherine Levey

The individual UME are not diffusionally isolated leading to a non-steady state voltammetric response.

Therefore, the electrodes should be spaced further apart.