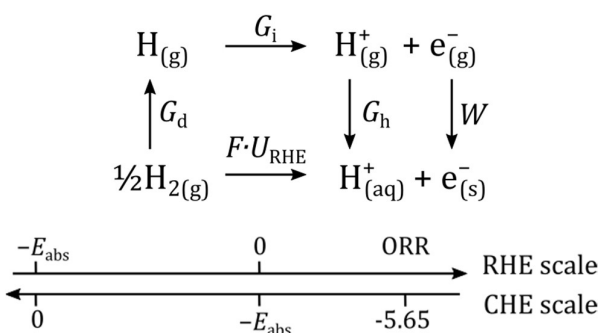


## Basics of electrocatalysis

Renewable energy, such as sunlight and wind, will sustain the hydrogen economy and capture carbon dioxide from the atmosphere in the foreseen future. Electrolyzers and fuel cells transform energy into H<sub>2</sub> and generate electricity, respectively. Captured CO<sub>2</sub> can be electroreduced to valuable chemicals.

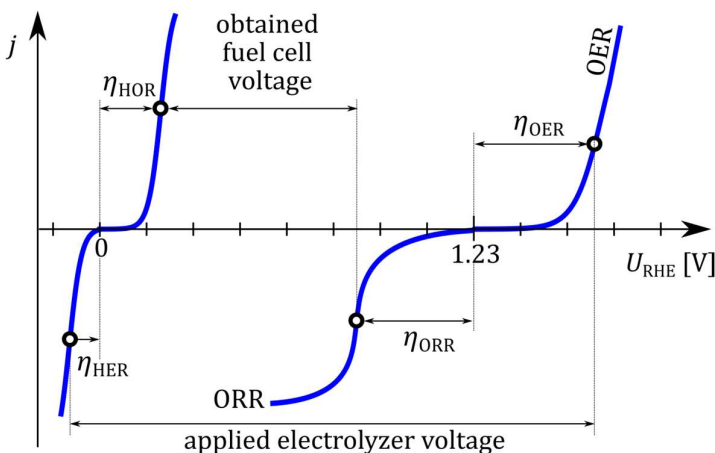
- a)** Write equations for essential electrochemical half-reactions under acidic conditions with the participation of e<sup>-</sup> and H<sup>+</sup>: **i)** hydrogen evolution reaction (HER); **ii)** oxygen reduction reaction (ORR); carbon dioxide reduction reaction (CO<sub>2</sub>RR) to **iii)** methane. (1.5)

H<sub>2</sub> and H<sup>+</sup> play central roles in electrocatalysis, where the hydrogen electrode is the universal reference electrode. In experiments, the standard potential of the reversible hydrogen electrode (RHE) is set to 0 V and it serves as the reference for redox reactions in aqueous solutions. In theoretical chemistry, the absolute potential of the computational hydrogen electrode (CHE) plays a similar role. The following Born–Haber cycle relates standard and absolute potentials. The Born–Haber cycle follows the Hess law stating that the total energy change during the complete course of a chemical reaction is independent of the number of steps taken.



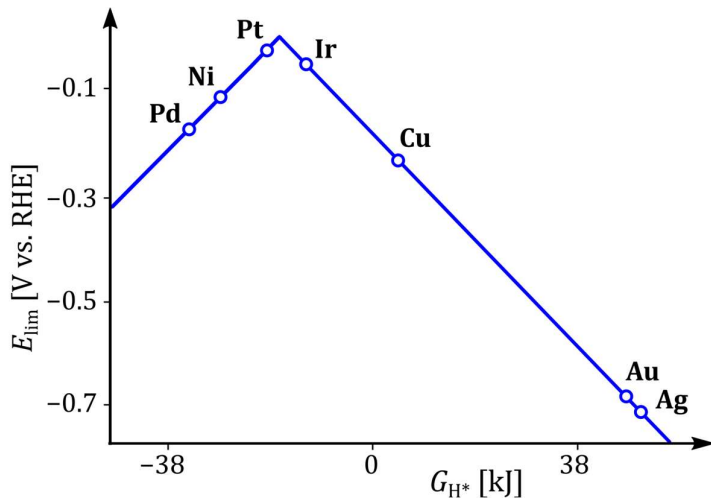
$F \cdot U_{\text{RHE}}$  is the oxidation energy of H<sub>2</sub>,  $F = 96.485 \text{ kJ} \cdot \text{V}^{-1}$  is the Faraday constant,  $G_d = 214 \text{ kJ}$  is the dissociation energy of H<sub>2</sub>,  $G_i = 1312 \text{ kJ}$  is the ionization energy of H,  $G_h = -1100 \text{ kJ}$  is the absolute hydration energy of H<sup>+</sup>, and  $W$  is the electrode specific work function (in kJ). The computational hydrogen electrode defines the absolute potential relative to the energy of an electron in a vacuum.

- b)** Calculate with two significant figures the absolute hydrogen electrode potential ( $E_{\text{abs}} = W$  at  $U_{\text{RHE}} = 0$  and pH = 0). (1)
- c)** Calculate the standard potentials of the CO<sub>2</sub> reduction reactions to **i)** CO and **ii)** C<sub>2</sub>H<sub>5</sub>OH if the absolute potential values for these reactions are -4.31 V and -4.50 V, respectively. *Hint: Your answer should show that CO<sub>2</sub>RR and HER are competing reactions.* (1)



At a given electrode surface, the standard reduction potential differs from the *limiting potential* ( $E_{\text{lim}}$ ) at which the redox reaction happens by an *overpotential* ( $\eta$ ). The smaller the overpotential, the higher the reaction current density ( $j$ ) and the lower the difference in energy consumed by electrolyzers and released in fuel cells. That is why much effort is dedicated to searching catalysts with the smallest overpotentials.

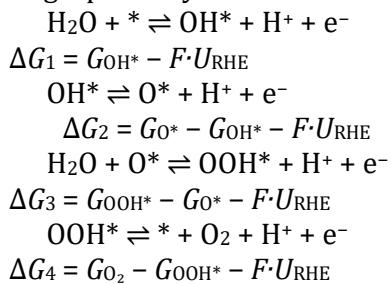
- d)** **i)** Estimate from the graph the sum  $\eta_{\text{OER}} + \eta_{\text{ORR}}$  that corresponds to values obtained with the best-performing electrocatalysts. (0.5)
- ii)** Estimate the efficiency of energy conversion from electrolyzer to fuel cell. (0.5)



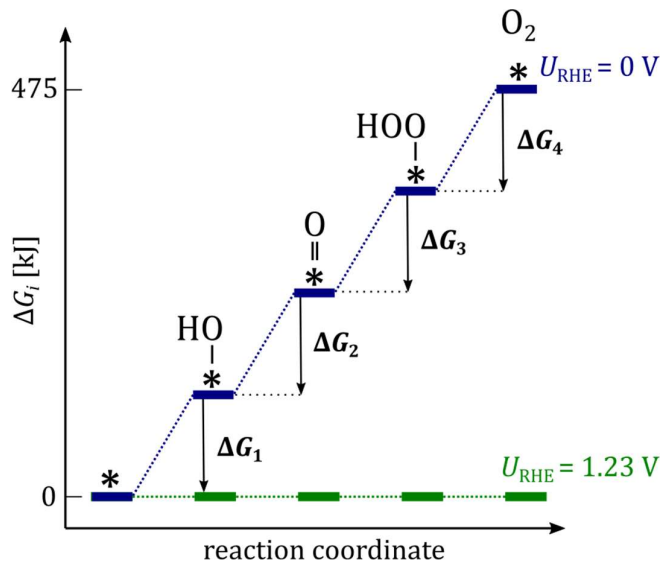
The volcano plot shows a correlation between the limiting potential and the hydrogen adsorption energy. It illustrates a key criterion of searching for better catalysts. It is known as the Sabatier principle and is commonly presented in the form of a volcano plot with the best-performing catalyst on the volcano's top.

- e) Choose the proper formulation of the Sabatier principle: (1)
- i) The binding energy between the catalyst and the reactant should be weak
  - ii) The binding energy between the catalyst and the reactant should be neither too strong nor too weak
  - iii) The binding energy between the catalyst and the reactant should be strong.

Among other metals, platinum is close to an ideal catalyst for HER. Platinum is also one of the best-known catalysts for ORR. However, even for Pt, the overpotential is substantial due to a more complex ORR mechanism. Both ORR and OER can be described as a sequence of four reactions forming a pathway from  $H_2O$  to  $O_2$  and back:

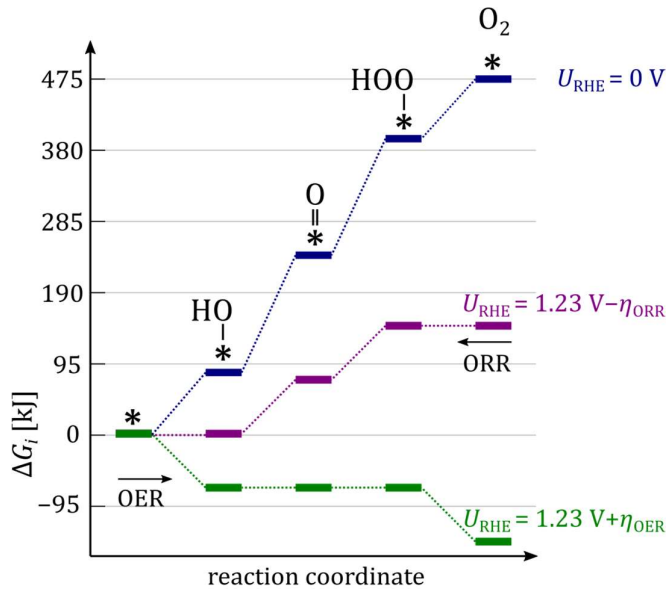


where  $*$  denotes an adsorption site on the surface of the catalyst,  $X^*$  denotes an adsorbed  $X$  species,  $G_{O_2}$ ,  $G_{OH^*}$ ,  $G_{O^*}$ , and  $G_{OOH^*}$  are the adsorption energies relative to  $G_{H_2O}$  at  $pH = 0$ .



For an ideal catalyst, each reaction represents a step of equal height. At  $U_{RHE} = 0$ ,  $\Delta G_1^0 = \Delta G_2^0 = \Delta G_3^0 = \Delta G_4^0 = F \cdot E^0(\frac{1}{2}O_2/H_2O) = \frac{1}{4} \cdot 475$  kJ and the reaction can only proceed in the direction of oxygen evolution. At  $U_{RHE} = 1.23$  V,  $\Delta G_1^{E^0} = \Delta G_2^{E^0} = \Delta G_3^{E^0} = \Delta G_4^{E^0} = 0$  kJ and in the absence of thermodynamic barriers the reaction proceeds in both directions.

- f) Calculate  $G_{OH^*}$ ,  $G_{O^*}$  and  $G_{OOH^*}$  for an ideal catalyst if  $G_{O_2} = 475$  kJ. (1)



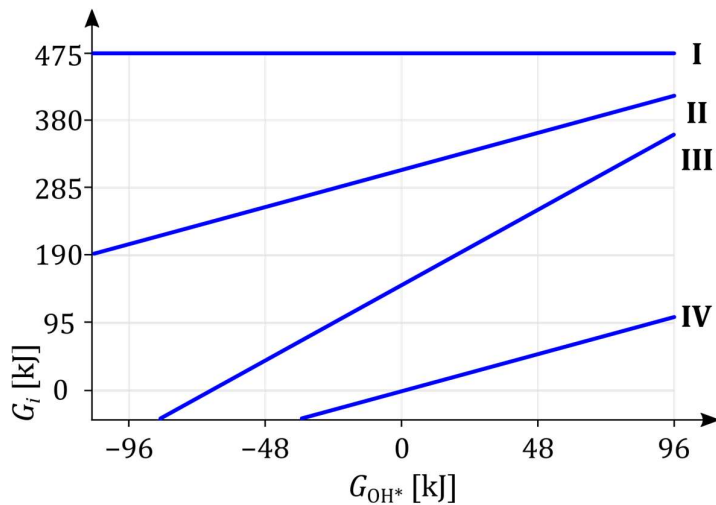
For a non-ideal catalyst, the reaction starts when all thermodynamic barriers are less or equal to zero. The corresponding overpotentials equal

$$\eta_{\text{ORR}} = 1.23 \text{ V} - \min(\Delta G_i^0)/F$$

$$\eta_{\text{OER}} = \max(\Delta G_i^0)/F - 1.23 \text{ V}$$

when  $\min(\Delta G_i^0)$  and  $\max(\Delta G_i^0)$  are respectively the smallest and largest values among  $\Delta G_1^0 - \Delta G_4^0$  (i.e. values of  $G_i$  at  $U_{\text{RHE}} = 0$ ).

**g)** Estimate the values of  $\eta_{\text{OER}}$  and  $\eta_{\text{ORR}}$  from the left graph. (1)

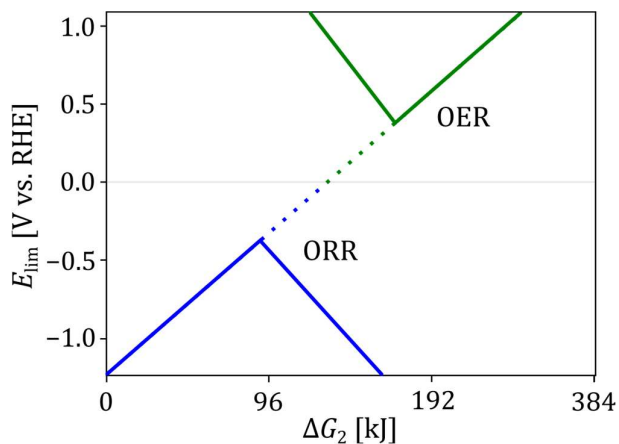


Due to basic chemical principles, the adsorption energies are interrelated by scaling relations:

$$G_i = a_i/a_{\text{OH}^*} G_{\text{OH}^*} + b_{\text{OH}^*-i}$$

where  $a_i$  and  $a_{\text{OH}^*}$  are the valencies of the species  $i$  and OH, and  $b_{\text{OH}^*-i}$  describes the bond strength difference resulting from adsorbate interaction with the electrode and electrolyte.

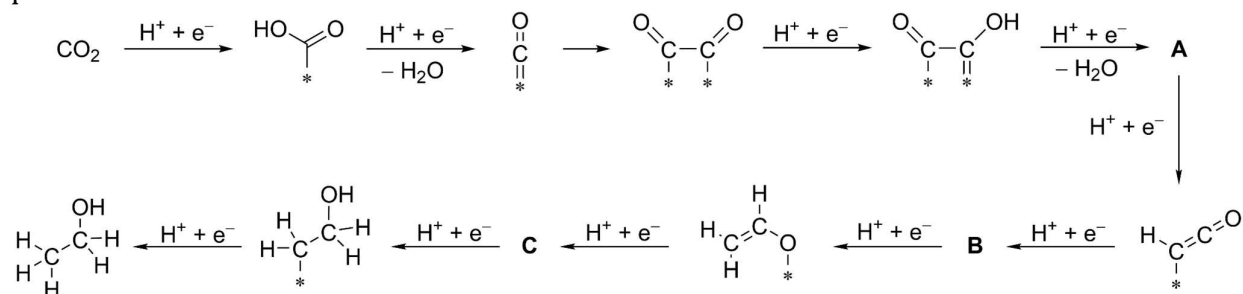
**h)** Determine which lines correspond to OH\*, O\*, OOH\*, and O<sub>2</sub>. (2)



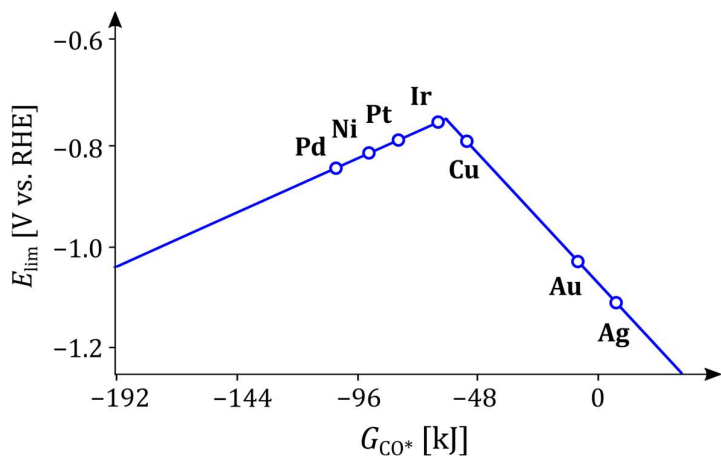
When  $G_i$  vs.  $G_{\text{OH}^*}$  plot is transformed into  $\Delta G_i$  vs.  $\Delta G_2$ , it becomes clear that the smallest and largest values (the top of volcanoes) are reached when  $\Delta G_1 = \Delta G_4$  and  $\Delta G_2 = \Delta G_3$ . It turns out that the overpotentials of the OER and ORR can be expressed with a single parameter  $b_{\text{OH}^*-\text{OOH}^*}$ .

**i)** Estimate  $b_{\text{OH}^*-\text{OOH}^*}$  from the above plots and calculate the theoretical values of  $\eta_{\text{OER}}$  and  $\eta_{\text{ORR}}$ . (2)

In the case of CO<sub>2</sub>RR, unlike for HER and ORR, there are multiple pathways towards valuable products such as C<sub>2</sub>H<sub>5</sub>OH.



**j)** Draw structures of intermediates **A-C** in the given pathway if **B** and **C** are coordinated to two adsorption sites (labeled with \*). (3)



Due to the complexity of the mechanism, it is not easy to express the overpotential of CO<sub>2</sub>RR as elegantly as for HER, OER and ORR. Some volcano plots allow us to predict catalysts for CO<sub>2</sub>RR with some specific products, yet, the main challenge here is the selectivity of CO<sub>2</sub>RR, which is affected by the hydrogen adsorption. Instead of studying numerous pathways or plotting product-specific volcano plots, it is possible to classify various catalysts by adsorption energies of CO and H.

**k)** Plot  $G_{\text{CO}^*}$  vs  $G_{\text{H}^*}$  graph and deduce the unique metal **Y** that catalyzes CO<sub>2</sub> electroreduction to products with two or more carbon atoms (like C<sub>2</sub>H<sub>4</sub>). *Hint: metals with  $G_{\text{H}^*} < -10$  kJ catalyze HER, and metals with  $G_{\text{CO}^*} > -30$  kJ catalyze CO<sub>2</sub>RR to CO and HCOOH formation.* (1)

