Criterion for Finding the Optimal Electrocatalyst at Any Overpotential

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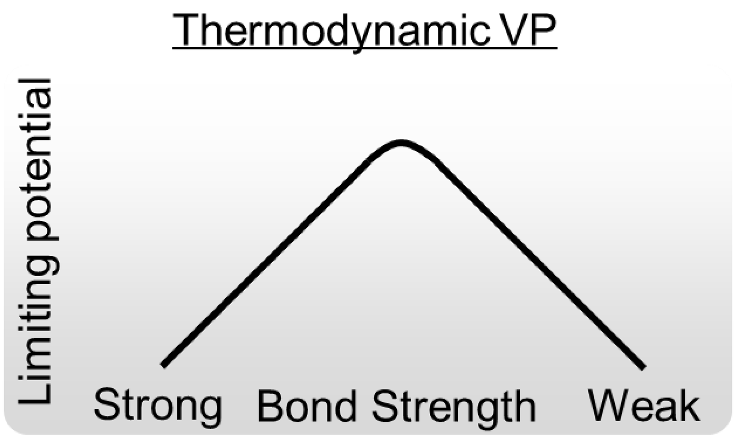
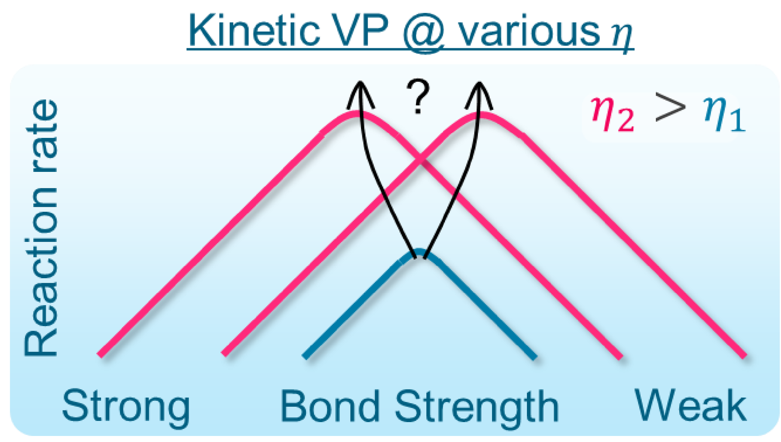
1. Motivation

Question: In which direction will the apex of volcano plot (VP) move with varying potential?



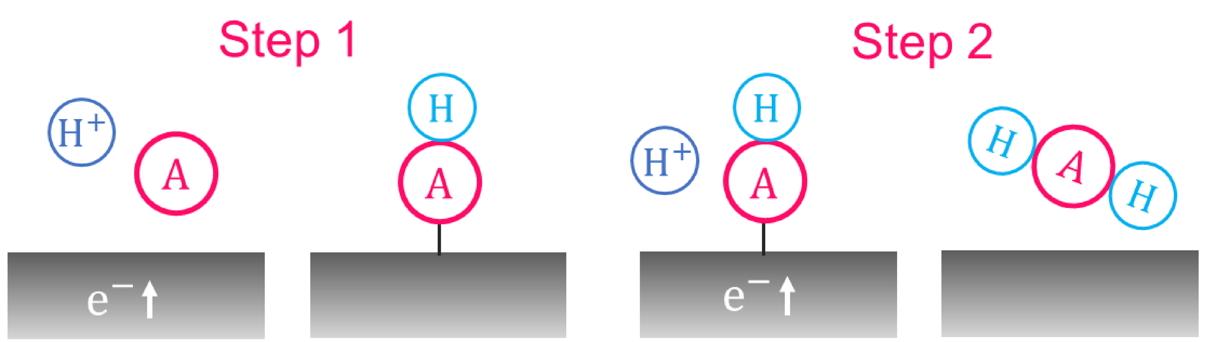


2. Microkinetic model

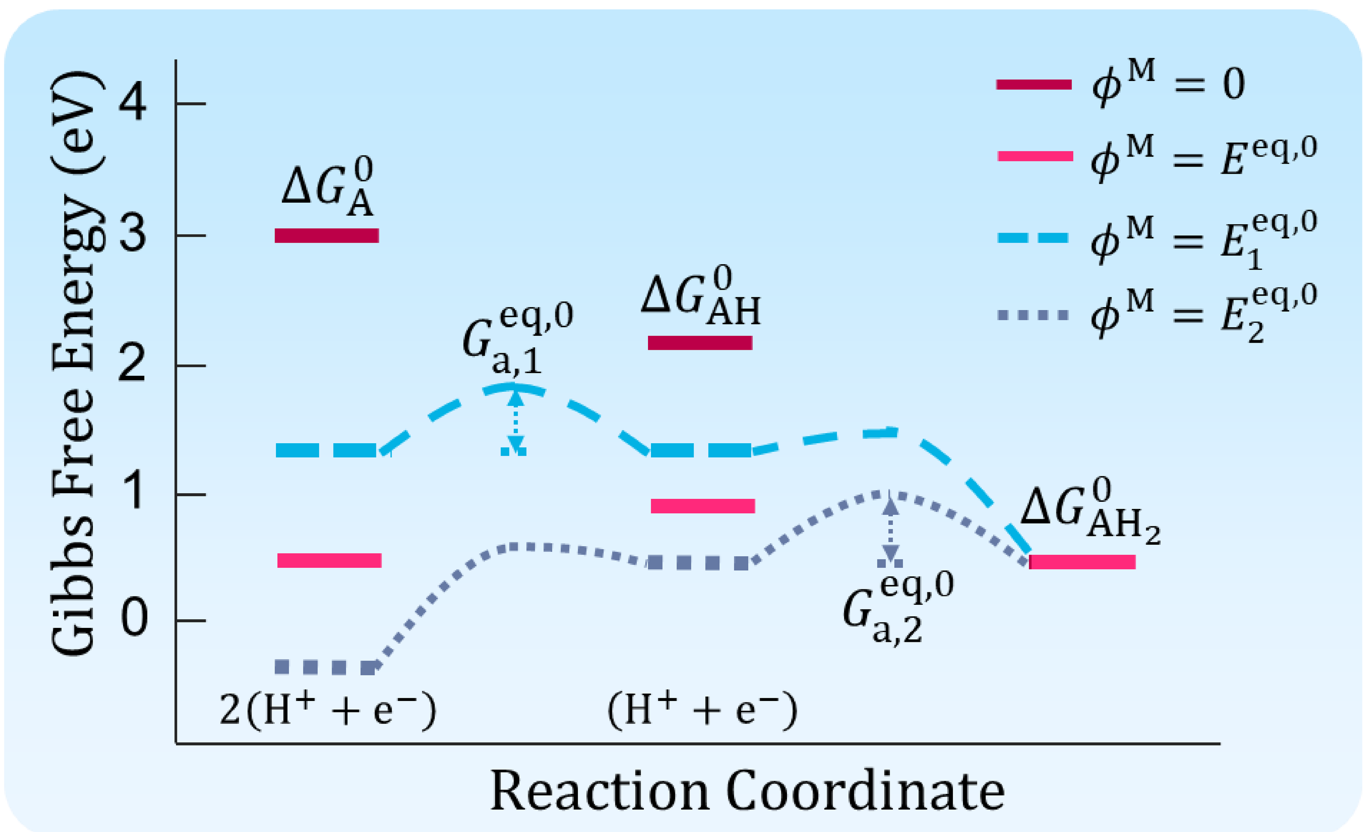
Generic 2-step reaction

Step 1 $\quad * + A + e^- + H^+ = AH^*$

Step 2 $\quad AH^* + e^- + H^+ = AH_2 + *$



Definition of parameters



Rate expressions

Step 1 $\quad v_1 = k_1[H^+][A](1-\theta_{AH}) - k_{-1}\theta_{AH}$

Step 2 $\quad v_2 = k_2[H^+]\theta_{AH} - k_{-2}[AH_2](1-\theta_{AH})$

steady state $v_1 = v_2 = \mathrm{TOF}$

Coverage and turnover frequency (TOF)

$$\theta_{AH} = \frac{k_1[H^+][A] + k_{-2}[AH_2]}{k_1[H^+][A] + k_2[H^+] + k_{-1} + k_{-2}[AH_2]}$$

$$\mathrm{TOF} = \frac{k_1 k_2 [H^+]^2[A] - k_{-1}k_{-2}[AH_2]}{k_1[H^+][A] + k_2[H^+] + k_{-1} + k_{-2}[AH_2]}$$

$$\text{Concentr. } [H^+] = [H^+]_b \exp\left(-\frac{e\phi^{OHP}}{k_B T}\right)$$

with ϕ^{OHP} given by an electrical double layer model

$$\text{Rate constant } k_1 \propto \exp\left(-\frac{G_{a,1}^{eq,0} + \alpha_1 e(\phi^M - \phi^{OHP} - E_1^{eq,0})}{k_B T}\right)$$

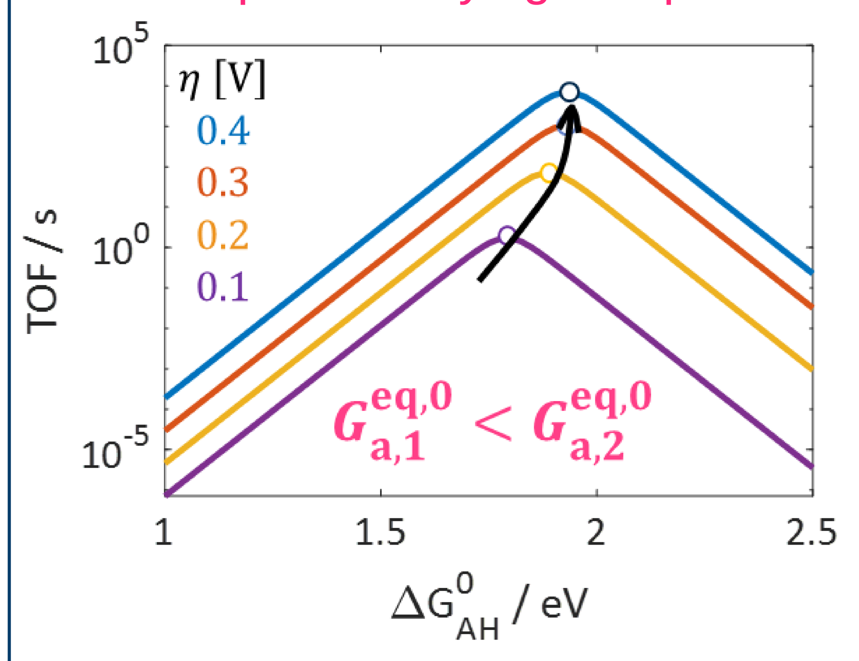
$$\text{Equilibrium potential } E_1^{eq,0} = (\Delta G_A^0 - \Delta G_{AH}^0)/e$$

$$E_2^{eq,0} = (\Delta G_{AH}^0 - \Delta G_{AH_2}^0)/e$$

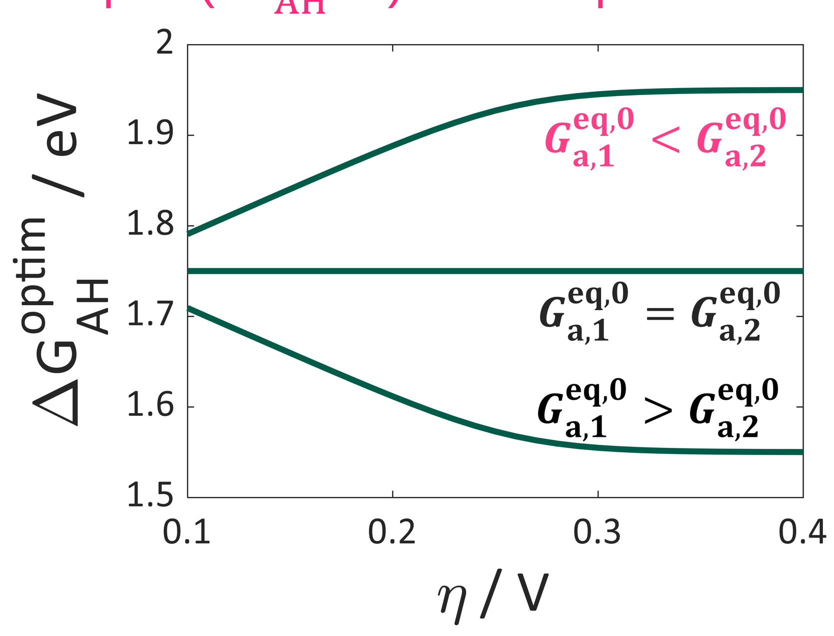
3. Criterion and proof

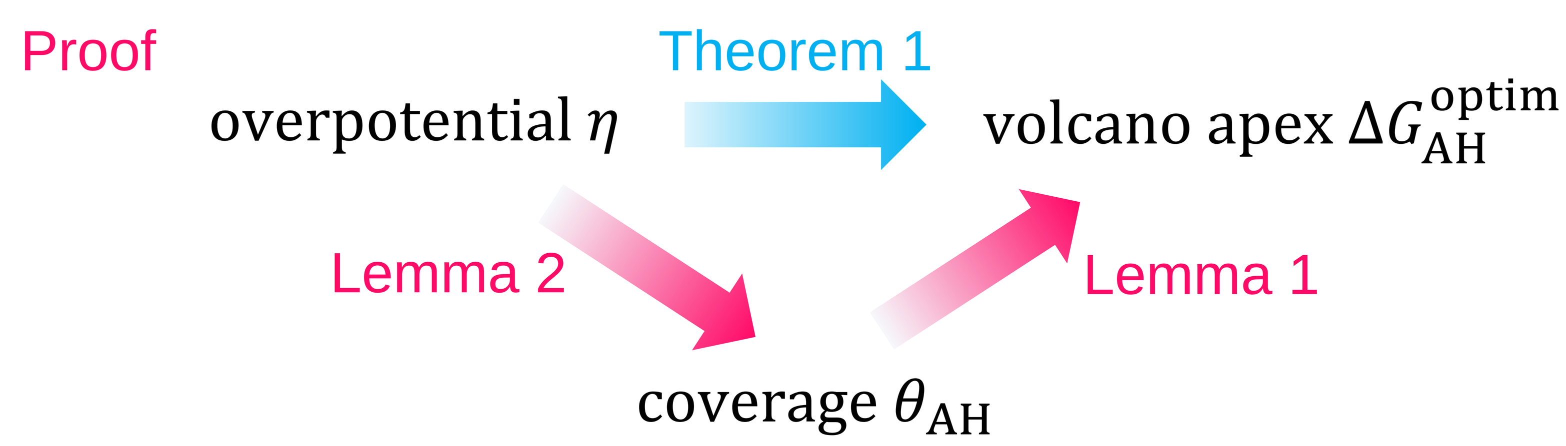
Criterion: Consider a two-step proton-coupled electron transfer reaction in solution with high supporting-electrolyte concentration, transfer coefficient $\alpha = 1/2$ and $[A] = [AH_2]$. If $G_{a,1}^{eq,0} < G_{a,2}^{eq,0}$, then as overpotential (η) increases ΔG_{AH}^{optim} becomes more positive, and levels off at very large η.

Volcano plot at varying overpotential



Apex (ΔG_{AH}^{optim}) vs. overpotential



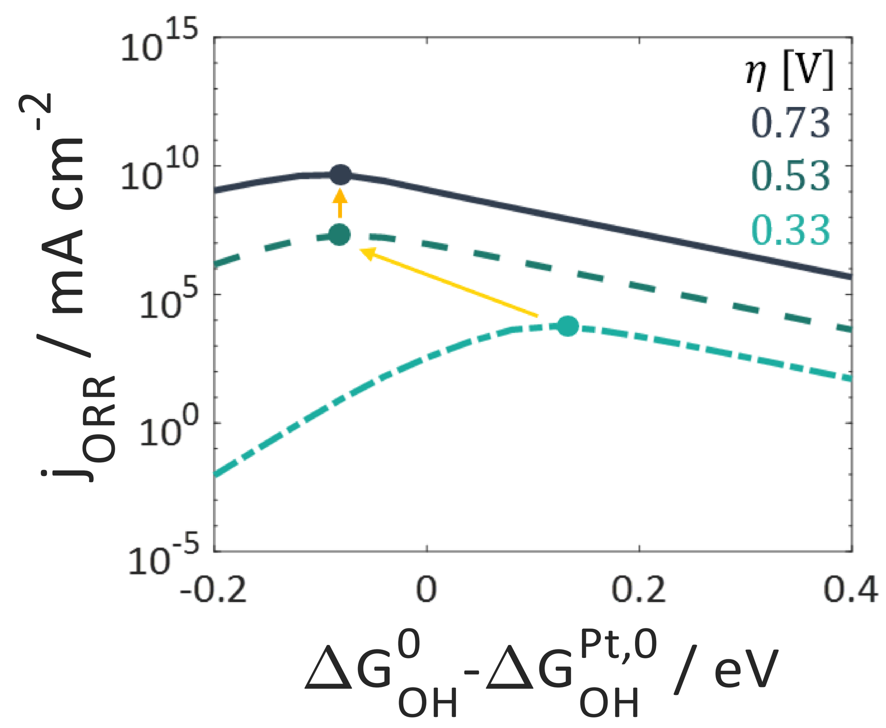


4. Generalization

Assumptions	Generalization
(i) $[A] = [AH_2]$	(i) $[A] \neq [AH_2]$
(ii) Two-step reaction	(ii) Multi-step reaction
(iii) $\alpha = 1/2$	(iii) α randomly sampled in [0.3,0.7]

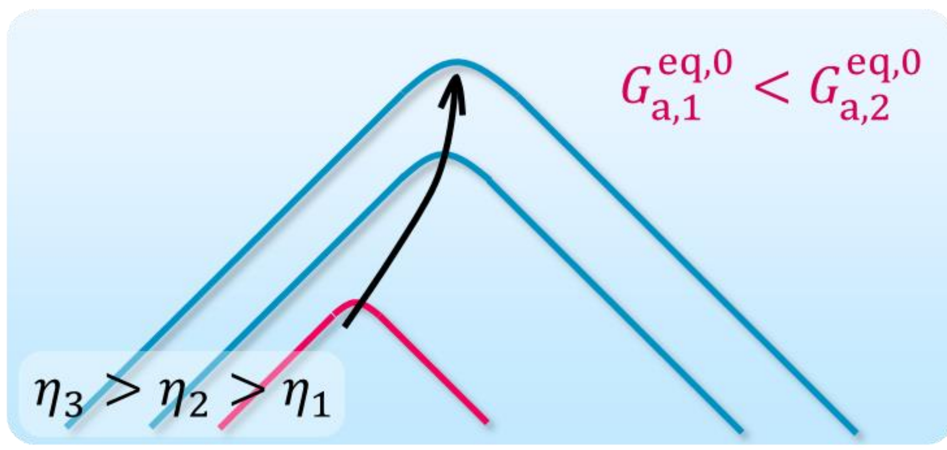
New criterion for multi-step reaction, e.g. ORR

$$G_{a,ad}^{eq,0} - \frac{1}{2}k_B T \ln[O_2] < G_{a,de}^{eq,0} - \frac{1}{2}k_B T \ln[H_2O]$$



5. Conclusion

- A criterion for the shift of the volcano apex is proposed and proved under certain assumptions.
- Generalization of the criterion is done by relaxing the above assumptions and applicability of the criterion is tested.



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