

Lagrange Multiplier Based Optimization Algorithm

Finds optimal molar fractions by self-consistently solving for stable solutions to the optimum of a function under the constraint that the molar fraction sum to unity.

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Define the CO₂RR/CORR selectivity (x) and CORR activity (y) as

$$x = \frac{1}{2} \sum_i P_i^H(\mathbf{f}) [\Delta E_H^i \geq \Delta E_H^{\text{Cu}}] \quad (1)$$

$$y = \frac{1}{2} \sum_i P_i^H(\mathbf{f}) [\Delta E_H^i \geq \Delta E_H^{\text{Cu}}] \times \sum_i P_i^{\text{CO}}(\mathbf{f}) [\Delta E_{\text{CO}}^i \leq \Delta E_{\text{CO}}^{\text{Cu}}] \quad (2)$$

where the sums are over all possible (within our model of the surface microstructures) hollow surface sites for H and on-top sites for CO. P_i^{ads} is the probability of the surface site i for the surface microstructure defined by the adsorbate ads—i.e. the surface microstructures illustrated in Figure 1 in the manuscript—given by

$$P_i^{\text{ads}}(\mathbf{f}) = \prod_{k=1}^M f_k^{n_{ik}^{\text{ads}}} \quad (3)$$

where \mathbf{f} is the vector of molar fractions, M the number of elements in the alloy, f_k the molar fraction of element k , n_{ik}^{ads} the number of atoms of element k in the surface microstructure i , ΔE_{ads}^i is the adsorption energy of the adsorbate, ads, in the surface microstructure i , and $\Delta E_{\text{ads}}^{\text{Cu}}$ is the adsorption energy of the adsorbate, ads, on Cu(111)—in fact the highest value of the adsorption energy for H where both fcc- and hcp-hollow sites are present.

We note that it is necessary to define $0^0 = 1$ in equation 3; when the element, say m , is not present in the alloy, i.e. $f_m = 0$, and not present in the surface microstructure, i.e. $n_{im}^{\text{ads}} = 0$, then the probability of the surface microstructure i is not—and should not be—affected by f_m , requiring that $f_m^{n_{im}^{\text{ads}}} = 0^0 = 1$

To shorten the notation we define

$$P^H \equiv \sum_i P_i^H(\mathbf{f}) [\Delta E_H^i \geq \Delta E_H^{\text{Cu}}] \quad (4)$$

$$P^{\text{CO}} \equiv \sum_i P_i^{\text{CO}}(\mathbf{f}) [\Delta E_{\text{CO}}^i \leq \Delta E_{\text{CO}}^{\text{Cu}}] \quad (5)$$

so that

$$x = \frac{1}{2} P^H \quad (6)$$

$$y = \frac{1}{2} P^H P^{\text{CO}} \quad (7)$$

The function to optimize for a given set of weights, w_x and w_y for x and y , is

$$g = w_x x + w_y y \quad (8)$$

Using the method of Lagrange multipliers we have to solve the following set of equations to obtain the optimum molar fractions

$$\frac{\partial g}{\partial f_m} = \lambda \frac{\partial h}{\partial f_m}, \quad m \in \{1, 2, \dots, M\} \quad (9)$$

and

$$h(\mathbf{f}) = \sum_{j=1}^M f_j = 1 \quad (10)$$

where h is the constraint that the molar fractions must sum to unity and λ is a Lagrange multiplier.

Taking the partial derivatives of g and h with respect to an arbitrary molar fraction f_m yields

$$\frac{\partial g}{\partial f_m} = w_x \frac{\partial x}{\partial f_m} + w_y \frac{\partial y}{\partial f_m} \quad (11)$$

and

$$\frac{\partial h}{\partial f_m} = 1 \quad (12)$$

The partial derivative with respect to x is

$$\frac{\partial x}{\partial f_m} = \frac{1}{2} \frac{\partial P^H}{\partial f_m} \quad (13)$$

$$= \frac{1}{2} \sum_i \frac{\partial P_i^H(\mathbf{f}) [\Delta E_H^i \geq \Delta E_H^{\text{Cu}}]}{\partial f_m} \quad (14)$$

$$= \frac{1}{2} \sum_i \frac{\partial}{\partial f_m} \prod_{k=1}^M f_k^{n_{ik}^H} \quad (15)$$

$$= \frac{1}{2} \sum_i \left(f_1^{n_{i1}^H} \times f_2^{n_{i2}^H} \times \dots \times n_{im}^H f_m^{n_{im}^H - 1} \times \dots \times f_M^{n_{iM}^H} \right) \quad (16)$$

$$= \frac{1}{2} \sum_i \frac{n_{im}^H}{f_m} \prod_{k=1}^M f_k^{n_{ik}^H} \quad (17)$$

$$= \frac{1}{2 f_m} \sum_i n_{im}^H P_i^H(\mathbf{f}) [\Delta E_H^i \geq \Delta E_H^{\text{Cu}}] \quad (18)$$

$$= \frac{1}{2 f_m} D_m^H \quad (19)$$

where we have shortened the notation by defining

$$D_m^H \equiv \sum_i n_{im}^H P_i^H(\mathbf{f}) [\Delta E_H^i \geq \Delta E_H^{\text{Cu}}] \quad (20)$$

We note that

$$f_m^{n_{ik}^{\text{ads}}} = \begin{cases} 1, & \text{if } f_m = 0 \text{ and } n_{im}^{\text{ads}} = 0 \\ 0, & \text{if } f_m = 0 \text{ and } n_{im}^{\text{ads}} > 0 \end{cases} \quad (21)$$

The partial derivative with respect to y is

$$\frac{\partial y}{\partial f_m} = \frac{1}{2} \left(\frac{\partial P^H}{\partial f_m} P^{\text{CO}} + P^H \frac{\partial P^{\text{CO}}}{\partial f_m} \right) \quad (22)$$

$$= \frac{1}{2f_m} (D_m^H P^{\text{CO}} + P^H D_m^{\text{CO}}) \quad (23)$$

where $\partial P^H / \partial f_m$ was derived above, and where we equivalently have introduced

$$D_m^{\text{CO}} \equiv \sum_i n_{im}^{\text{CO}} P_i^{\text{CO}}(\mathbf{f}) [\Delta E_{\text{CO}}^i \leq \Delta E_H^{\text{Cu}}] \quad (24)$$

By combining the above results we can write equation 9 as

$$\frac{1}{2f_m} (w_x D_m^H + w_y (D_m^H P^{\text{CO}} + P^H D_m^{\text{CO}})) = \lambda \quad (25)$$

solving for f_m yields

$$f_m = \frac{1}{2\lambda} (w_x D_m^H + w_y (D_m^H P^{\text{CO}} + P^H D_m^{\text{CO}})) \quad (26)$$

and inserting f_m into equation 10 yields

$$1 = \frac{1}{2\lambda} \sum_{j=1}^M (w_x D_j^H + w_y (D_j^H P^{\text{CO}} + P^H D_j^{\text{CO}})) \quad (27)$$

so that λ is given by

$$\lambda = \frac{1}{2} \sum_{j=1}^M (w_x D_j^H + w_y (D_j^H P^{\text{CO}} + P^H D_j^{\text{CO}})) \quad (28)$$

Inserting λ into equation 26 then yields an equation that can be solved self-consistently to obtain the optimal molar fractions

$$f_m = \frac{w_x D_m^H + w_y (D_m^H P^{\text{CO}} + P^H D_m^{\text{CO}})}{\sum_{j=1}^M (w_x D_j^H + w_y (D_j^H P^{\text{CO}} + P^H D_j^{\text{CO}}))} \quad (29)$$

where all P 's and D 's are functions of \mathbf{f} as seen in the definitions 4, 5, 20, and 24.

adsorption site	no. of atoms, N_A	no. of atoms in each zone, N_z			no. of surface microstructures, $N_{SM} = M^{N_A}$	no. of input features, $N_{IF} = \prod_{z=1}^3 \frac{(N_z+M-1)!}{N_z!(M-1)!}$
on-top	10	1	6	3	$5^{10} = 9,765,625$	$5 \times 210 \times 35 = 36,750$
fcc-hollow	9	3	3	3	$5^9 = 1,953,125$	$35 \times 35 \times 35 = 42,875$
hcp-hollow	7	3	3	1	$5^7 = 78,125$	$35 \times 35 \times 5 = 6,125$

Table 1: **Number of surface microstructures and input features for different adsorption sites.** $M = 5$ is the number of elements in the alloy. See Figure 1 in the manuscript for a visual interpretation of the 3 zones.

In practice the algorithm is implemented with a grouping of all the possible surface microstructures (within our model) so that the sum over surface microstructures i are written as a sum over possible input features of which there are way fewer terms, e.g.

$$\sum_{\substack{i \in \text{surface} \\ \text{microstructures}}}^{N_{SM}} P_j^{\text{ads}}(\mathbf{f}) = \sum_{\substack{j \in \text{input} \\ \text{features}}}^{N_{IF}} P_i^{\text{ads}}(\mathbf{f}) \times m_j \quad (30)$$

where N_{SM} is the number of surface microstructures, N_{IF} is the number of input features, and m_j is the multiplicity—i.e. the number of configurations with the same input features—of the set of input features j given by

$$m_j = \prod_{z=1}^3 \frac{N_z!}{\prod_{k=1}^M n_{jzk}} \quad (31)$$

where N_z is the number of atoms in zone j of the surface microstructure—of which there are 3 within our model—and n_{jzk} is the number of element k in zone z in the set of input features j . Numbers for the different adsorption sites are given in Table 1.