

Supporting Information

Reversibility Iteration Method for Understanding Reaction Networks and for Solving Microkinetics in Heterogeneous Catalysis

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Supporting Information 1: Derivation of electric circuit-like reaction rate equations by chemical potential notation

Supporting Information 1-0: Chemical potential notation

The chemical potential notation in heterogeneous catalysis was developed and applied in our other works.¹ In order to give a clear depiction, the main derivation steps are listed in the beginning of this supplementary information. Firstly, the basis of the concept is to express chemical potential of a surface species in the Langmuir adsorption paradigm:

$$\mu_I(T, \theta_I) = \mu_I^o(T) + RT \ln \frac{\theta_I}{\theta_*} = E^{tot} + \Delta\mu_I(T) + RT \ln \frac{\theta_I}{\theta_*} \quad (1)$$

where θ_I and θ_* represent the coverage of adsorbed species I and free sites $*$ on the surface; E^{tot} is the total energy which can be gotten from DFT calculations routinely, μ stands for the chemical potential. For gas phase species, the chemical potential can be expressed as:

$$\mu_X(T, p_X) = \mu_X^o(T) + RT \ln \frac{p_X}{P^o} = E^{tot} + \Delta\mu_X(T) + RT \ln \frac{p_X}{P^o} \quad (2)$$

where p_X / P^o stands for the relative pressure of gas phase species X . Besides:

$$\Delta\mu(T) = [H(T) - H(0K)] - TS(T) \quad (3)$$

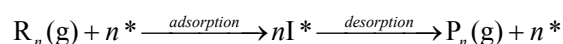
Since the difference of enthalpy in different temperature is small and the entropy of surface species is usually very small, we deem that $\Delta\mu(T)$ is zero for surface species (including transition states) and $-TS(T)$ for gas phase species throughout the paper. In fact, the energy corrections can be readily included in the chemical potential terms.

For simplicity, we will drop the labels of temperature in the following:

$$\mu_I = \mu_I^o + RT \ln \frac{\theta_I}{\theta_*} \quad (4)$$

$$\mu_X = \mu_X^o - TS(T) + RT \ln \frac{p_X}{P^o} \quad (5)$$

The rate equations of the generalized two-step model



can be formulated under the framework of transition state theory as:

$$r_{ads} = \frac{k_B T}{h} e^{\frac{-\Delta G_R^{\ddagger,0}}{RT}} \frac{P_R}{P^o} \theta^n (1 - z_{ads}) \quad (6)$$

$$r_{des} = \frac{k_B T}{h} e^{\frac{-\Delta G_P^{\ddagger,0}}{RT}} \theta_I^n (1 - z_{des}) \quad (7)$$

$$z_{ads} = \frac{\theta_I^n}{K_{eq1} \theta_*^n P_R / P^o} \quad (8)$$

$$z_{des} = \frac{\theta_*^n P_P / P^o}{K_{eq2} \theta_I^n} \quad (9)$$

where ΔG is the standard Gibbs free energy in the transition state minus that in the reactant state, K_{eq} represents equilibrium constant of a reaction. In the subscript, we use R (P) to represent R_n (P_n) for simplicity. The reversibility (z) used in our current work is the reversibility defined Dumesic,^{2,3} The definition and its physical meaning are presented briefly as follows:

The affinity for step i is simply its thermodynamic driving force, which can be expressed in terms of the activities of the species present in the reaction mixture:

$$A_i = -\sum_j \nu_{ij} G_j = -\sum_j \nu_{ij} [G_j^o + RT \ln(a_j)] \quad (10)$$

where ν_{ij} is the stoichiometric coefficient for species j in step i (negative for reactants and positive for products), a_j is the activity of species j (related closely to its concentration), Dumesic defined the reversibility of step i , z_i , as

$$z_i = \exp\left(\frac{-A_i}{RT}\right) = \frac{\prod_j a_j^{\nu_{ij}}}{K_{eqi}} \quad (11)$$

Based on equation (4) and (5), the rate equations above can be rearranged as follows:

$$r_{ads} = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_R^{\ddagger,0}}{RT}} \theta_*^n (1 - z_{ads}) \quad (12)$$

$$r_{des} = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_P^{\ddagger,0}}{RT}} \theta_*^n z_{ads} (1 - z_{des}) \quad (13)$$

$$z_{ads} = e^{\frac{\mu_I - \mu_R}{RT}} \quad (14)$$

$$z_{des} = e^{\frac{\mu_P - \mu_I}{RT}} \quad (15)$$

$$z_{tot} = e^{\frac{\mu_p - \mu_R}{RT}} = z_{des} z_{ads} \quad (16)$$

where $\mu_R^{\ddagger,0}$ ($\mu_P^{\ddagger,0}$) is the standard chemical potentials of the transition states of the adsorption (desorption) processes; μ_R (μ_P) stands for chemical potentials of the reactant (product). It is worth mentioning that μ_I represents total chemical potential of nI^* , under this circumstance, equation (4) should be reformulated as:

$$\mu_I = \mu_I^0 + nRT \ln \frac{\theta_I}{\theta_*} \quad (17)$$

Besides, the chemical potential of free site $*$ is zero.¹

We further introduce an adjusted equilibrium constant in order to simplify our formulation. It is defined as:

$$K'_{eq1} = K_{eq1} * \frac{P_R}{P^0} = e^{\frac{\mu_R^0 - \mu_I^0}{RT}} * \frac{P_R}{P^0} = e^{\frac{\mu_R - \mu_I^0}{RT}} \quad (18)$$

The overall reaction rate should satisfy $r = r_{ads} = r_{des}$ at the steady state.⁴ Thus, from equation (12)-(16) and together with $r_{ads} = r_{des}$, we obtain:

$$\frac{k_B T}{h} e^{\frac{\mu_R - \mu_R^{\ddagger,0}}{RT}} \theta_*^n (1 - e^{\frac{\mu_I - \mu_R}{RT}}) = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_P^{\ddagger,0}}{RT}} \theta_*^n e^{\frac{\mu_I - \mu_R}{RT}} (1 - e^{\frac{\mu_P - \mu_I}{RT}}) \quad (19)$$

After simplification:

$$e^{\frac{\mu_I}{RT}} = \frac{e^{\frac{\mu_R - \mu_R^{\ddagger,0}}{RT}} + e^{\frac{\mu_P - \mu_P^{\ddagger,0}}{RT}}}{e^{\frac{-\mu_R^{\ddagger,0}}{RT}} + e^{\frac{-\mu_P^{\ddagger,0}}{RT}}} \quad (20)$$

Substituting it into z_{ads} :

$$z_{ads} = e^{\frac{\mu_I - \mu_R}{RT}} = e^{\frac{-\mu_R}{RT}} \frac{e^{\frac{\mu_R - \mu_R^{\ddagger,0}}{RT}} + e^{\frac{\mu_P - \mu_P^{\ddagger,0}}{RT}}}{e^{\frac{-\mu_R^{\ddagger,0}}{RT}} + e^{\frac{-\mu_P^{\ddagger,0}}{RT}}} = \frac{e^{\frac{\mu_P^{\ddagger,0}}{RT}} + z_{tot} e^{\frac{\mu_R^{\ddagger,0}}{RT}}}{e^{\frac{\mu_R^{\ddagger,0}}{RT}} + e^{\frac{\mu_P^{\ddagger,0}}{RT}}} \quad (21)$$

Besides, according to equation (17):

$$\left(\frac{\theta_I}{\theta_*}\right)^n = e^{\frac{\mu_I - \mu_I^0}{RT}} = e^{\frac{(\mu_I - \mu_R) - (\mu_I^0 - \mu_R)}{RT}} = z_{ads} e^{\frac{\mu_R - \mu_I^0}{RT}} = z_{ads} K'_{eq1} \quad (22)$$

We subsequently apply $\theta_I + \theta_* = 1$ conservation condition to obtain the free site coverage:

$$\theta_* = \frac{1}{1 + \sqrt[n]{z_{ads} K'_{eq1}}} \quad (23)$$

Then, rearranging rate equations (12) and (13):

$$r_{ads} e^{\frac{\mu_R^{\pi,o}}{RT}} = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} \theta_*^n (1 - z_{ads}) \quad (24)$$

$$r_{des} e^{\frac{\mu_P^{\pi,o}}{RT}} = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} \theta_*^n z_{ads} (1 - z_{des}) \quad (25)$$

$$r_{ads} e^{\frac{\mu_R^{\pi,o}}{RT}} + r_{des} e^{\frac{\mu_P^{\pi,o}}{RT}} = \theta_*^n (1 - z_{ads}) + \theta_*^n z_{ads} (1 - z_{des}) = \theta_*^n (1 - z_{tot}) \quad (26)$$

Since $r = r_{ads} = r_{des}$ under steady state, equation (26) can be further simplified as:

$$r = \frac{k_B T}{h} \frac{e^{\frac{\mu_R}{RT}} (1 - z_{tot})}{\left(e^{\frac{\mu_R^{\pi,o}}{RT}} + e^{\frac{\mu_P^{\pi,o}}{RT}} \right)} \theta_*^n \quad (27)$$

Substituting θ_* into equation (27), we finally get:

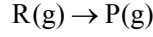
$$r = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} \frac{(1 - z_{tot})}{\left(e^{\frac{\mu_R^{\pi,o}}{RT}} + e^{\frac{\mu_P^{\pi,o}}{RT}} \right) \left(1 + \sqrt[n]{z_{ads} K'_{eq1}} \right)^n} \quad (28)$$

where $z_{ads} = \frac{e^{\frac{\mu_P^{\pi,o}}{RT}} + z_{tot} e^{\frac{\mu_R^{\pi,o}}{RT}}}{e^{\frac{\mu_R^{\pi,o}}{RT}} + e^{\frac{\mu_P^{\pi,o}}{RT}}}$, $K'_{eq1} = e^{\frac{\mu_R - \mu'_R}{RT}}$, $z_{tot} = e^{\frac{\mu_P - \mu_R}{RT}} = z_{des} z_{ads}$, according to equation (21), (18),

and (16).

Supporting Information 1-1: Gas-phase catalytic reaction

In order to depict our derivation clearly, we start from a simple gas-phase reaction:



Using the chemical potential notation, we can formulate its rate equation as follows:

$$r = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_1^{\ddagger,0}}{RT}} (1 - e^{\frac{\mu_P - \mu_R}{RT}}) = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_1^{\ddagger,0}}{RT}} (1 - z_t) \quad (29)$$

where μ stands for chemical potential and z_t is the reversibility of the overall reaction.

Then, we assign some notations which are analogous to that of circuit:

$$\Delta G_R^\ddagger = \mu_1^{\ddagger,0} - \mu_R \quad (30)$$

$$k_R = \frac{k_B T}{h} e^{-\frac{\Delta G_R^\ddagger,0}{RT}} \quad (31)$$

$$R_R = \frac{1}{k_R} \quad (32)$$

$$U = 1 - z_t \quad (33)$$

Substituting them into Eq.(29), we get:

$$r = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_1^{\ddagger,0}}{RT}} (1 - z_t) = \frac{U}{R_R} \quad (34)$$

which is exactly the same form of Ohm's law. The scheme below is the circuit diagram that indicates this reaction.

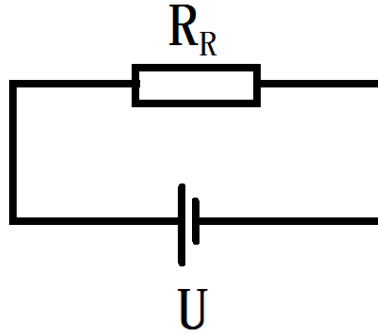
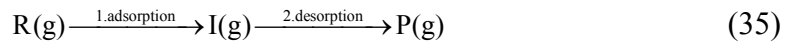


Figure S1: circuit diagram that indicates reaction $R(g) \rightarrow P(g)$.

Next, for a more complicated gas-phase reaction:



We can formulate its rate equation as follows

$$r_1 = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_1^{\ddagger,0}}{RT}} (1 - e^{\frac{\mu_I - \mu_R}{RT}}) = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_1^{\ddagger,0}}{RT}} (1 - z_1) \quad (36)$$

$$r_2 = \frac{k_B T}{h} e^{\frac{\mu_I - \mu_2^{\ddagger,0}}{RT}} (1 - e^{\frac{\mu_P - \mu_I}{RT}}) = \frac{k_B T}{h} e^{\frac{\mu_R - \mu_2^{\ddagger,0}}{RT}} z_{ads} (1 - z_2) \quad (37)$$

$$z_t = e^{\frac{\mu_P - \mu_R}{RT}} = z_1 z_2 \quad (38)$$

At the steady state, the concentration of intermediate I remains constant, therefore $r = r_1 = r_2$.

With this condition and by simplifying the form of z_1 , we can get:

$$z_1 = \frac{e^{\frac{\mu_2^{\ddagger,0}}{RT}} + z_t e^{\frac{\mu_1^{\ddagger,0}}{RT}}}{e^{\frac{\mu_1^{\ddagger,0}}{RT}} + e^{\frac{\mu_2^{\ddagger,0}}{RT}}} \quad (39)$$

Substituting it into equation (36), we can get:

$$r = \frac{k_B T}{h} \frac{e^{\frac{\mu_R}{RT}} (1 - z_t)}{e^{\frac{\mu_1^{\ddagger,0}}{RT}} + e^{\frac{\mu_2^{\ddagger,0}}{RT}}} \quad (40)$$

Similarly, let us define:

$$\Delta G_R^\ddagger = \mu_1^{\ddagger,0} - \mu_R; \Delta G_P^\ddagger = \mu_2^{\ddagger,0} - \mu_R \quad (41)$$

$$k_R = \frac{k_B T}{h} e^{-\frac{\Delta G_R^\ddagger}{RT}}; k_P = \frac{k_B T}{h} e^{-\frac{\Delta G_P^\ddagger}{RT}} \quad (42)$$

$$R_R = \frac{1}{k_R}; R_P = \frac{1}{k_P} \quad (43)$$

$$U = 1 - z_t \quad (44)$$

Thus, the rate equation (40) can be simplified as:

$$r = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} \frac{(1 - z_t)}{(e^{\frac{\mu_1^{\ddagger,0}}{RT}} + e^{\frac{\mu_2^{\ddagger,0}}{RT}})} = \frac{U}{R_R + R_P} \quad (45)$$

which can be schematically seen as follows:

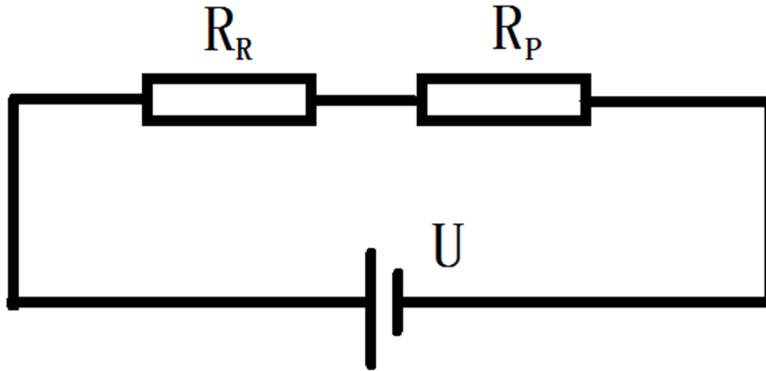


Figure S2: circuit diagram that indicates reaction $R(g) \rightarrow I(g) \rightarrow P(g)$

Supporting Information 1-2: Heterogeneous catalytic reaction (case 1)

Above two examples exhibit electric circuit-like gas-phase reaction rate equations, which is relevantly simple. For heterogeneous catalysis, however, it will be a bit more complicated with the incorporation of surface free site. We apply the generalized two-step model we used previously⁵ to show our derivation:



Applying equation (28), the reaction rate can be expressed as:

$$r = \frac{k_B T}{h} \frac{e^{\frac{\mu_R}{RT}} (1 - z_i)}{\left(e^{\frac{\mu_1^{\ddagger,0}}{RT}} + e^{\frac{\mu_2^{\ddagger,0}}{RT}} \right)} \theta_*^n = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} \frac{(1 - z_i)}{\left(e^{\frac{\mu_1^{\ddagger,0}}{RT}} + e^{\frac{\mu_2^{\ddagger,0}}{RT}} \right) (1 + \sqrt[n]{z_1 K'_{eq1}})^n} \quad (47)$$

Since there is free site term θ_* in the equation, it should also be included in the electric resistance term (R). We define:

$$\Delta G_R^\ddagger = \mu_1^{\ddagger,0} - \mu_R; \Delta G_P^\ddagger = \mu_2^{\ddagger,0} - \mu_R \quad (48)$$

$$k_R = \frac{k_B T}{h} e^{-\frac{\Delta G_R^\ddagger}{RT}}; k_P = \frac{k_B T}{h} e^{-\frac{\Delta G_P^\ddagger}{RT}} \quad (49)$$

$$R_{K,R} = \frac{1}{k_R}; R_{K,P} = \frac{1}{k_P} \quad (50)$$

$$R_T = \frac{1}{\theta_*^n} = (1 + \sqrt[n]{z_1 K'_{eq1}})^n \quad (51)$$

$$R_R = R_{K,R} R_T; R_P = R_{K,P} R_T \quad (52)$$

$$U = 1 - z_i \quad (53)$$

Finally, we get:

$$r = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} \frac{(1 - z_i)}{\left(e^{\frac{\mu_1^{\ddagger,0}}{RT}} + e^{\frac{\mu_2^{\ddagger,0}}{RT}} \right) (1 + \sqrt[n]{z_1 K'_{eq1}})^n} = \frac{U}{R_R + R_P} \quad (54)$$

which is exactly in the same form as that of equation (45), and the same circuit diagram. It should be noted that electric resistance terms (R) here include free site (θ_*) term.

Supporting Information 1-3: Heterogeneous catalytic reaction (case 2)

Some catalytic reactions have several different reaction pathways from reactants to products (Fig. S3):

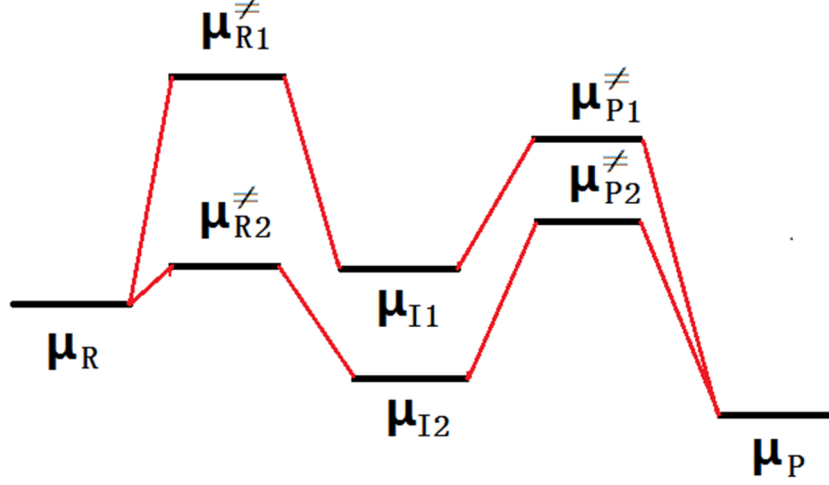


Figure S3: energy profile of heterogeneous catalytic reaction (case 2)

In this case (two pathways: path 1 and path 2), the total rate equation can be derived as follows:

$$z_{11} = e^{-\frac{\mu_{I1} - \mu_R}{RT}}; z_{12} = e^{-\frac{\mu_{I2} - \mu_R}{RT}} \quad (55)$$

$$z_{21} = e^{-\frac{\mu_P - \mu_{I1}}{RT}}; z_{22} = e^{-\frac{\mu_P - \mu_{I2}}{RT}} \quad (56)$$

$$z_t = e^{-\frac{\mu_P - \mu_R}{RT}} = z_{11}z_{21} = z_{12}z_{22} \quad (57)$$

$$K'_{eq11} = e^{-\frac{\mu_R - \mu_{I1}^0}{RT}}; K'_{eq12} = e^{-\frac{\mu_R - \mu_{I2}^0}{RT}} \quad (58)$$

With these pathways specified notations, we get the rate equations of these two pathways:

$$r_1 = \frac{k_B T}{h} \frac{e^{-\frac{\mu_R}{RT}} (1 - z_{tot})}{\left(e^{-\frac{\mu_{I1}^0}{RT}} + e^{-\frac{\mu_{I2}^0}{RT}} \right)} \theta_*^n \quad (59)$$

$$r_2 = \frac{k_B T}{h} \frac{e^{-\frac{\mu_R}{RT}} (1 - z_t)}{\left(e^{-\frac{\mu_{I2}^0}{RT}} + e^{-\frac{\mu_{I1}^0}{RT}} \right)} \theta_*^n \quad (60)$$

where

$$\theta_* = \frac{1}{1 + \sqrt[n]{z_{11} K'_{eq11}} + \sqrt[n]{z_{12} K'_{eq12}}} \quad (61)$$

Then the total reaction rate r can be expressed as $r = r_1 + r_2$:

$$r = r_1 + r_2 = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} (1 - z_t) \theta_*^n \left(\frac{1}{e^{\frac{\mu_{11}^{\neq,o}}{RT}} + e^{\frac{\mu_{21}^{\neq,o}}{RT}}} + \frac{1}{e^{\frac{\mu_{12}^{\neq,o}}{RT}} + e^{\frac{\mu_{22}^{\neq,o}}{RT}}} \right) \quad (62)$$

Similarly, we define the Gibbs free barriers:

$$\Delta G_{R1}^{\neq} = \mu_{11}^{\neq,o} - \mu_R; \Delta G_{P1}^{\neq} = \mu_{21}^{\neq,o} - \mu_R \quad (63)$$

$$\Delta G_{R2}^{\neq} = \mu_{12}^{\neq,o} - \mu_R; \Delta G_{P2}^{\neq} = \mu_{22}^{\neq,o} - \mu_R \quad (64)$$

and the corresponding rate constants:

$$k_{R1} = \frac{k_B T}{h} e^{-\frac{\Delta G_{R1}^{\neq,o}}{RT}}; k_{P1} = \frac{k_B T}{h} e^{-\frac{\Delta G_{P1}^{\neq,o}}{RT}} \quad (65)$$

$$k_{R2} = \frac{k_B T}{h} e^{-\frac{\Delta G_{R2}^{\neq,o}}{RT}}; k_{P2} = \frac{k_B T}{h} e^{-\frac{\Delta G_{P2}^{\neq,o}}{RT}} \quad (66)$$

Similarly, the driving force and the kinetic resistance are:

$$U = 1 - z_t \quad (67)$$

$$R_{K,R1} = \frac{1}{k_{R1}}; R_{K,P1} = \frac{1}{k_{P1}} \quad (68)$$

$$R_{K,R2} = \frac{1}{k_{R2}}; R_{K,P2} = \frac{1}{k_{P2}} \quad (69)$$

Then, the thermodynamic resistance is:

$$R_T = \frac{1}{\theta_*^n} = (1 + \sqrt[n]{z_{11} K'_{eq1}} + \sqrt[n]{z_{12} K'_{eq2}})^n \quad (70)$$

and the total resistance is:

$$R_{R1} = R_{K,R1} R_T; R_{P1} = R_{K,P1} R_T \quad (71)$$

$$R_{R2} = R_{K,R2} R_T; R_{P2} = R_{K,P2} R_T \quad (72)$$

We eventually have:

$$r = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} (1 - z_t) \theta_*^n \left(\frac{1}{e^{\frac{\mu_{11}^{\neq,o}}{RT}} + e^{\frac{\mu_{21}^{\neq,o}}{RT}}} + \frac{1}{e^{\frac{\mu_{12}^{\neq,o}}{RT}} + e^{\frac{\mu_{22}^{\neq,o}}{RT}}} \right) = \frac{U}{R_{R1} + R_{P2}} + \frac{U}{R_{R2} + R_{P2}} \quad (73)$$

Also, the selectivity (S) of the reaction can be formulated as:

$$S = \frac{r_1}{r_2} = \frac{U_1}{R_1} / \frac{U_2}{R_2} = \frac{R_{R2} + R_{P2}}{R_{R1} + R_{P1}} = \frac{R_{K,R2} + R_{K,P2}}{R_{K,R1} + R_{K,P1}} \quad (74)$$

We can see the parallel reaction can be exactly viewed as a parallel circuit of path 1 and path 2 (Fig. S4):

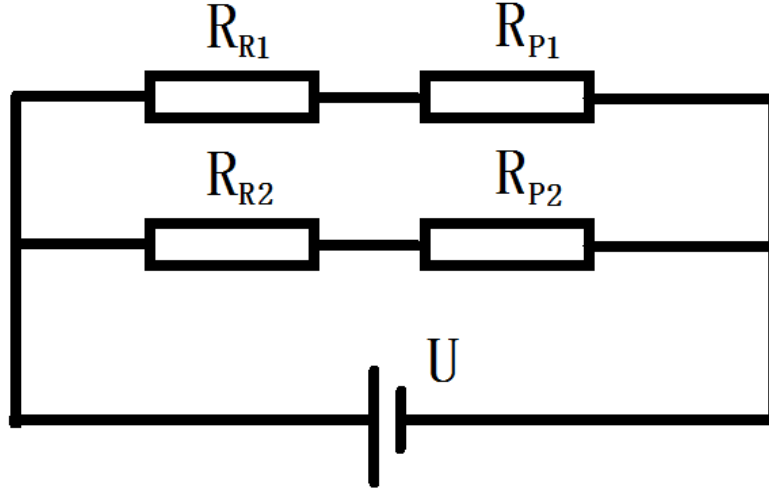


Figure S4: circuit diagram of heterogeneous catalytic reaction (case 2)

It should be noted that, in this case, different from gas reaction, the resistance is not only determined by kinetic resistance (R_K), but also determined by thermodynamic resistance (R_T). More importantly, if all the steps of the reaction need the same sites (θ_*), the thermodynamic resistance is the same, and the difference of total resistance is determined by the kinetic resistance. Therefore, the selectivity of the two parallel paths is totally determined by the Gibbs free barrier of each path.

Comparing to the electric circuit, the reversibility (z_i) is similar to the voltage (U_i):

$$z_{11} = \frac{R_{K,P1} + z_i R_{K,R1}}{R_{K,R1} + R_{K,P1}} = 1 - (1 - z_i) \frac{R_{K,R1}}{R_{K,R1} + R_{K,P1}} \quad (75)$$

$$U_1 = 1 - z_{11} = \frac{R_{K,R1}}{R_{K,R1} + R_{K,P1}} U \quad (76)$$

$$U_2 = z_{11} (1 - z_{21}) = \frac{R_{K,P1}}{R_{K,R1} + R_{K,P1}} U \quad (77)$$

We can see that in the same serial reactions, the voltage across each of the barriers is in the same proportion as their resistances. This corresponds well to that of serial circuit.

Supporting Information 1-4: Heterogeneous catalytic reaction (case 3)

If two paths lead to the different productions P1 and P2 (Fig. S5),

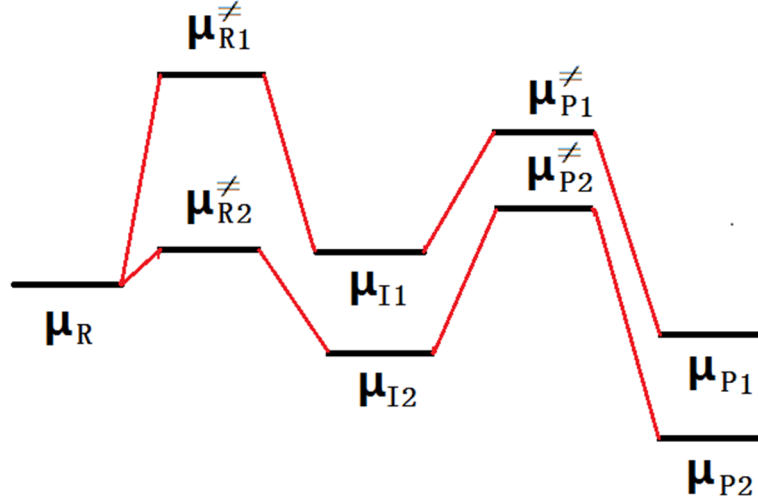


Figure S5: energy profile of heterogeneous catalytic reaction (case 3)

we can derive its rate equation as follows:

$$r = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} \theta_*^n \left(\frac{1 - z_{t1}}{e^{\frac{\mu_{R1}^{\neq,0}}{RT}} + e^{\frac{\mu_{P1}^{\neq,0}}{RT}}} + \frac{1 - z_{t2}}{e^{\frac{\mu_{R2}^{\neq,0}}{RT}} + e^{\frac{\mu_{P2}^{\neq,0}}{RT}}} \right) = \frac{U_{p1}}{R_{R1} + R_{P2}} + \frac{U_{p2}}{R_{R2} + R_{P2}} \quad (78)$$

and the selectivity of the two paths is

$$S = \frac{r_{p1}}{r_{p2}} = \frac{U_{p1}}{R_1} / \frac{U_{p2}}{R_2} = \frac{1 - z_{t1}}{1 - z_{t2}} \frac{R_{R2} + R_{P2}}{R_{R1} + R_{P1}} = \frac{1 - z_{t1}}{1 - z_{t2}} \frac{R_{K,R2} + R_{K,P2}}{R_{K,R1} + R_{K,P1}} \approx \frac{R_{K,R2} + R_{K,P2}}{R_{K,R1} + R_{K,P1}} \quad (79)$$

Its circuit diagram can be depicted as follows:

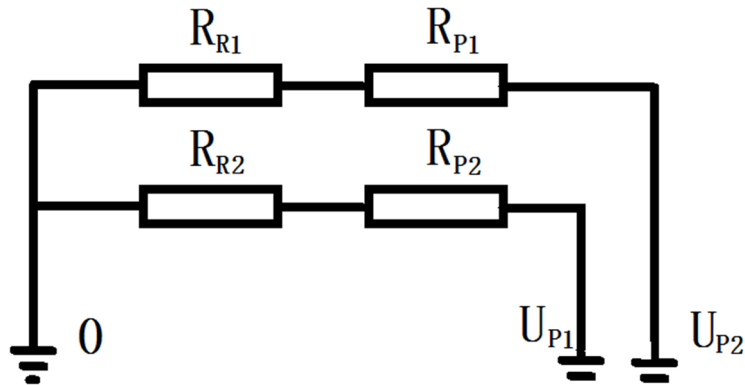


Figure S6: circuit diagram of heterogeneous catalytic reaction (case 3)

Supporting Information 1-5: Heterogeneous catalytic reaction (case 4)

Finally, for a complex reaction (Fig. S7), we can deem it as a mixing of serial and parallel circuit (Fig. S8).

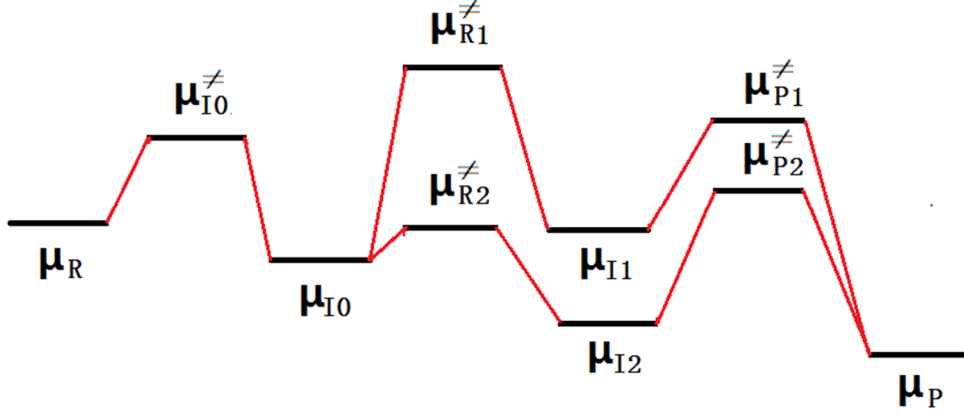


Figure S7: energy profile of complex heterogeneous catalytic reaction (case 4)

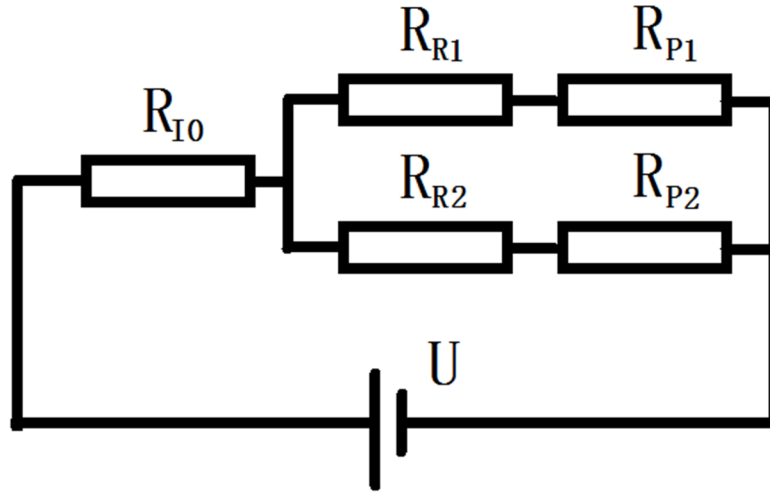


Figure S8: circuit diagram of complex heterogeneous catalytic reaction (case 4)

By defining:

$$\Delta G_{I0}^\ddagger = \mu_{I0}^{\ddagger,o} - \mu_R \quad (80)$$

$$\Delta G_{R1}^\ddagger = \mu_{R1}^{\ddagger,o} - \mu_R; \Delta G_{P1}^\ddagger = \mu_{P1}^{\ddagger,o} - \mu_R \quad (81)$$

$$\Delta G_{R2}^\ddagger = \mu_{R2}^{\ddagger,o} - \mu_R; \Delta G_{P2}^\ddagger = \mu_{P2}^{\ddagger,o} - \mu_R \quad (82)$$

we thus have:

$$k_{I0} = \frac{k_B T}{h} e^{\frac{\Delta G_{I0}^\ddagger}{RT}} \quad (83)$$

$$k_{R1} = \frac{k_B T}{h} e^{\frac{\Delta G_{R1}^\ddagger}{RT}}; k_{P1} = \frac{k_B T}{h} e^{\frac{\Delta G_{P1}^\ddagger}{RT}} \quad (84)$$

$$k_{R2} = \frac{k_B T}{h} e^{\frac{\Delta G_{R2}^{\ddagger,0}}{RT}}; k_{P2} = \frac{k_B T}{h} e^{\frac{\Delta G_{P2}^{\ddagger,0}}{RT}} \quad (85)$$

and the kinetic resistances as:

$$R_{K,I0} = \frac{1}{k_{I0}} \quad (86)$$

$$R_{K,R1} = \frac{1}{k_{R1}}; R_{K,P1} = \frac{1}{k_{P1}} \quad (87)$$

$$R_{K,R2} = \frac{1}{k_{R2}}; R_{K,P2} = \frac{1}{k_{P2}} \quad (88)$$

and the thermodynamic resistance as:

$$R_T = \frac{1}{\theta_*^n} = (1 + \sqrt[n]{z_{I0} K'_{eqI0}} + \sqrt[n]{z_{I0} z_{I1} K'_{eqI0} K'_{eqI1}} + \sqrt[n]{z_{I0} z_{I1} K'_{eqI0} K'_{eqI2}})^n \quad (89)$$

Combining them, it gives:

$$R_{I0} = R_{K,I0} R_T \quad (90)$$

$$R_{R1} = R_{K,R1} R_T; R_{P1} = R_{K,P1} R_T \quad (91)$$

$$R_{R2} = R_{K,R2} R_T; R_{P2} = R_{K,P2} R_T \quad (92)$$

Then, the total resistances of two paths are:

$$\frac{1}{R_I} = \frac{1}{R_{R1} + R_{P2}} + \frac{1}{R_{R2} + R_{P2}} \quad (93)$$

With the driving force $U = 1 - z_{tot}$, we eventually get:

$$r = \frac{U}{R_{I0} + R_I} = \frac{k_B T}{h} e^{\frac{\mu_R}{RT}} (1 - z_t) \theta_*^n \left(\frac{1}{e^{\frac{\mu_{I0}^{\ddagger,0}}{RT}} + \frac{1}{\frac{1}{e^{\frac{\mu_{R1}^{\ddagger,0}}{RT}} + e^{\frac{\mu_{P1}^{\ddagger,0}}{RT}}} + \frac{1}{e^{\frac{\mu_{R2}^{\ddagger,0}}{RT}} + e^{\frac{\mu_{P2}^{\ddagger,0}}{RT}}}}} \right) \quad (94)$$

Supporting Information 1-6: General case for serial catalytic reaction

For a general serial catalytic reaction (Fig. S9):

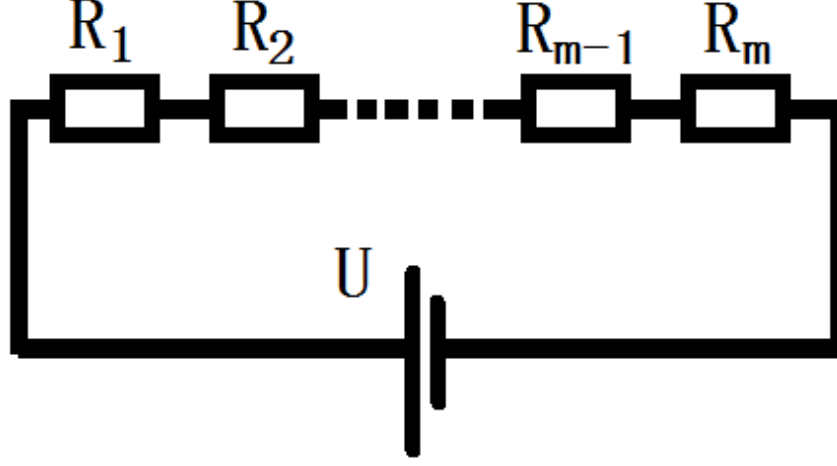
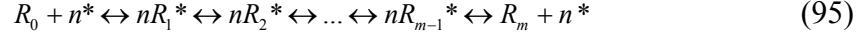


Figure S9: circuit diagram of general serial catalytic reaction

By defining the following:

$$\Delta G_i^\ddagger = \mu_i^{\ddagger,0} - \mu_R \quad (96)$$

$$k_i = \frac{k_B T}{h} e^{-\frac{\Delta G_i^\ddagger}{RT}} \quad (97)$$

$$R_{K,i} = \frac{1}{k_i}; R_T = \frac{1}{\theta_s^n}; R_i = R_{K,i} R_T \quad (98)$$

the total resistance can be written as the sum of individual resistance:

$$R_{K,tot} = \sum_{i=1}^m R_{K,i} \quad (99)$$

Assuming $z_0 = 1$, the overall voltage is:

$$U = z_0 - z_t = z_0 - \prod_{j=1}^{j=m} z_j \quad (100)$$

Specifically, the voltage on each resistance is:

$$U_i = \prod_{j=0}^{j=i-1} z_j - \prod_{j=0}^{j=i} z_j = \frac{R_{K,i}}{R_{K,tot}} U \quad (101)$$

where

$$\prod_{j=1}^{j=i} z_j = \frac{z_t \sum_{j=1}^{j=i} R_{K,j} + \sum_{j=i+1}^{j=m} R_{K,j}}{R_{K,tot}} \quad (102)$$

$$z_i = \frac{z_t \sum_{j=1}^{j=i} R_{K,j} + \sum_{j=i+1}^{j=m} R_{K,j}}{z_t \sum_{j=1}^{j=i-1} R_{K,j} + \sum_{j=i}^{j=m} R_{K,j}} \quad (103)$$

The final reaction rate is:

$$r = \frac{k_B T}{h} \frac{e^{\frac{\mu_R}{RT}} (1 - z_t)}{\sum_{i=1}^m e^{\frac{\mu_i^{\ddagger}}{RT}}} \theta_*^n \quad (104)$$

where:

$$\theta_*^{-1} = 1 + \sum_{i=1}^{i=m-1} \sqrt[n]{e^{\frac{\mu_0 - \mu_i^0}{RT}} \prod_{j=1}^{j=i} z_j} \quad (105)$$

At the steady state, we have:

$$r = r_1 = r_2 = \dots = r_{m-1} = r_m \quad (106)$$

The above rate equations can be finally expressed as a voltage-resistance term:

$$r_i = \frac{U_i}{R_i} = \frac{\prod_{j=0}^{j=i-1} z_j (1 - z_i)}{R_i} \quad (107)$$

where U_i , R_i , and z_i are defined in equations (101), (98), and (100), respectively. It is worth mentioning that equation (107) is regarded as the “standard reaction rate forms” that will be used for iteration in our reversibility iteration method.

In our derivation, the reaction networks appear naturally to be equivalent to the electrical circuits. Similarly, based on our formulism, if we redefine the reaction rate (r) to flex displacements (x), and the driving force of the reaction ($1 - z_t$) to spring force (F), the reactions network can also appear to be equivalent to the spring system.

Supporting Information 2: Examples of our methods in practical catalytic reactions

Prior to discussing the practical catalytic cases, we briefly describe the strategy to obtain the accurate kinetic solution, *i.e.* the so-called “benchmark”, aiming to evaluate the relative error of RIM method. Firstly, it is worth noting that an automatic code based on MATLAB has been developed in our group. The code can read energy inputs, generate the expressions of reaction rates and steady-state equations, and solve these equations by modified Newton iteration method with arbitrary precision. Nevertheless, the Newton iteration method, which only works when the trial guess is within Newton's domain of convergence,⁵ cannot guarantee to converge for every initial guess. To obtain an efficiently accurate solution as a benchmark, we tried various methods to obtain a proper initial guess of coverages for the Newton iteration method with arbitrary precision arithmetic, such as the Gibbs distribution, ODE solution at different initial conditions or time intervals,⁵ and using a nearby-point solution along volcano curve⁶ or even random initial guesses until the correct solution was found. With the extensive tests, for ammonia synthesis and iodine reduction reaction which are two used example reactions, we fortunately obtain the solution at each point along the volcano curves, although they were extremely time-consuming to solve. Additionally, for some simple cases such as iodine reduction reaction, we also directly solved them with an analytic way by MATLAB and used the solution as the benchmarks. Overall, we have used these approaches to calculate the total rate (r_b) as the benchmarks.

Supporting Information 2-1: Hydrogen evolution reaction (HER)

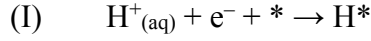
In addition to the reactions in series, our method can also apply to the reaction complex networks involving both series and parallel reactions. As shown in the supporting information (see sections from 1-3 to 1-5), the reversibility iteration equations for parallel reactions (SI-1-3 and 1-4) and complex networks (SI-1-5) have been constructed. Also, as stated in SI-1-6, every reaction step can be expressed in a voltage-resistance form: $R_i = \frac{U_i}{r_i}$, which can

be rearranged as:

$$r_i = \frac{U_i}{R_i} = \frac{\prod_{j=0}^{i-1} z_j (1 - z_i)}{R_i} \quad (108)$$

It is named as the “standard reaction rate equation” that is used in the iteration in our method. To show the applicability of our method to parallel and complex reactions, hydrogen

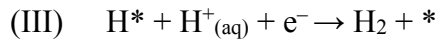
evolution reaction (HER) is chosen as an example. HER seems to be simple; however, the generally accepted mechanism contains steps occurring consecutively and parallelly. The reaction starts with the following step:⁷



in which H^+ adsorbs on the surface of a catalyst by receiving an electron, forming an adsorbed hydrogen atom (H^*). Subsequently, two H^* can combine together to generate H_2 and desorb from the catalyst surface following the Tafel mechanism:



Alternatively, H^* can be directly protonated to produce H_2 following the Heyrovsky mechanism:



We can formulate their rate equations as follows:

$$r_1 = \frac{k_B T}{h} e^{\frac{\mu_{\text{H}^*} + \mu_{\text{e}^-} - \mu_1^{\text{e},0}}{RT}} \theta_* (1 - z_1) = \frac{\theta_* (1 - z_1)}{R_{K,1}} \quad (109)$$

$$r_2 = \frac{k_B T}{h} e^{\frac{2\mu_{\text{H}^*} + 2\mu_{\text{e}^-} - \mu_2^{\text{e},0}}{RT}} \theta_*^2 z_1^2 (1 - z_2) = \frac{\theta_*^2 z_1^2 (1 - z_2)}{R_{K,2}} \quad (110)$$

$$r_3 = \frac{k_B T}{h} e^{\frac{2\mu_{\text{H}^*} + 2\mu_{\text{e}^-} - \mu_3^{\text{e},0}}{RT}} \theta_* z_1 (1 - z_3) = \frac{\theta_* z_1 (1 - z_3)}{R_{K,3}} \quad (111)$$

$$z_t = e^{\frac{\mu_{\text{H}_2} - 2\mu_{\text{H}^*} - 2\mu_{\text{e}^-}}{RT}} = z_1^2 z_2 = z_1 z_3 \quad (112)$$

According to the definition of reversibility, we can obtain:

$$\theta_H = e^{\frac{\mu_{\text{H}^*} - \mu_{\text{H}^*} - \mu_{\text{e}^-}}{RT}} z_1 \theta_* = M_1 z_1 \theta_* \quad (113)$$

Since $\theta_H + \theta_* = 1$, we have:

$$\theta_*^{-1} = 1 + M_1 z_1 \quad (114)$$

In the following, we show how to translate this problem into ‘standard reaction rate equations’. Firstly, under the steady state condition, following the conservation of mass and the thermodynamic consistency, we have:

$$r = r_1 = 2r_2 + r_3 \quad (115)$$

$$z_1 \sqrt{z_2} = \sqrt{z_t}, z_1 z_3 = z_t \quad (116)$$

which can be expressed in the following standard form:

$$r = r_1' = r_2' + r_3'; \text{ where } r_1' = r_1, r_2' = 2r_2, r_3' = r_3 \quad (117)$$

$$Z_1 Z_2 = \sqrt{z_t}, Z_1 Z_3 = z_t; \text{ where } Z_1 = z_1, Z_2 = \sqrt{z_2}, Z_3 = z_3 \quad (118)$$

Then, converting the rate equations above into a standard form similar to equation (108), we can write:

$$r_1' = r_1 = \frac{1}{R_{K,1}} \theta_* (1 - z_1) = \frac{\theta_* (1 - Z_1)}{R_{K,1}'} \quad (119)$$

$$r_2' = 2r_2 = \frac{1}{R_{K,2}} 2\theta_* z_1 (1 + \sqrt{z_2}) \theta_* z_1 (1 - \sqrt{z_2}) = \frac{\theta_* Z_1 (1 - Z_2)}{R_{K,2}'} \quad (120)$$

$$r_3' = r_3 = \frac{1}{R_{K,3}} \theta_* z_1 (1 - z_3) = \frac{\theta_* Z_1 (1 - Z_3)}{R_{K,3}'} \quad (121)$$

where

$$R_{K,1}' = R_{K,1} \quad (122)$$

$$R_{K,2}' = R_{K,2} \frac{1}{2\theta_* z_1 (1 + \sqrt{z_2})} \quad (123)$$

$$R_{K,3}' = R_{K,3} \quad (124)$$

Substituting equations (119)-(121) to equation (115), we can obtain:

$$Z_1 = \frac{1/R_{K,1}' + \sqrt{z_i}/R_{K,2}' + z_i/R_{K,3}'}{1/R_{K,1}' + 1/R_{K,2}' + 1/R_{K,3}'} \quad (125)$$

The corresponding circuit-like diagrams are shown in Figure S10. Thus, the RIM procedure can be performed. We used the analytic solution solved by MATLAB as the “benchmark”, and the results are shown in Figure S11, which verifies the reliability of our method.

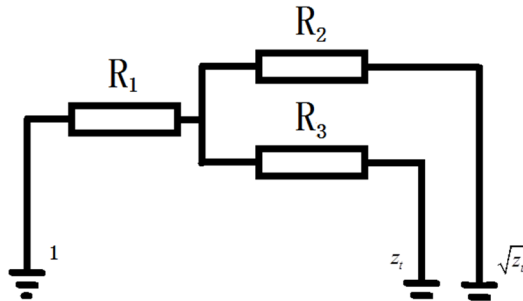


Figure S10. Circuit diagrams of the hydrogen evolution reaction.

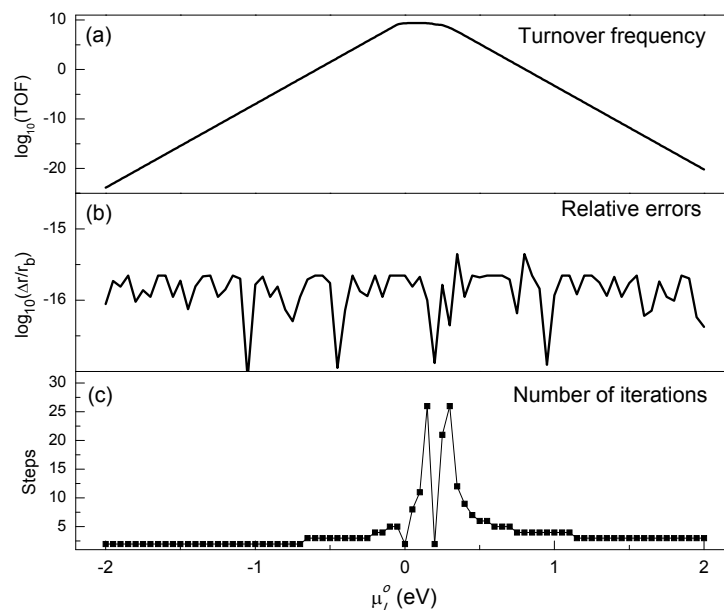
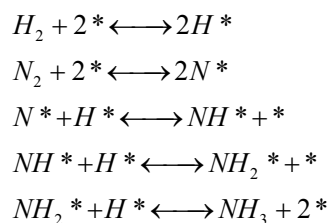


Figure S11. Plots of (a) TOF of HER, (b) relative errors of each TOF, and (c) the number of iterations at different adsorption energies of the key intermediate (H) obtained by the reversibility iteration method. It should be noted that the used energetic data for HER here is taken from Ref. ⁸.

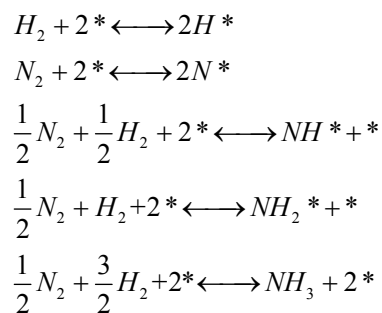
Supporting Information 2-2: Ammonia synthesis

Ammonia synthesis ($N_2 + 3H_2 \longleftrightarrow 2NH_3$) is a very important catalytic reaction in industry.

Generally, its mechanism can be described as follows⁶:



To the benefit of formulating rate equations, we can write above reactions as follows:



The corresponding rate equations are:

$$r_1 = \frac{k_B T}{h} e^{\frac{\mu_{H_2} - \mu_{H^*}^o}{RT}} \theta_*^2 (1 - z_1) = \frac{\theta_*^2 (1 - z_1)}{R_{K,1}} \quad (126)$$

$$r_2 = \frac{k_B T}{h} e^{\frac{\mu_{N_2} - \mu_{N^*}^o}{RT}} \theta_*^2 (1 - z_2) = \frac{\theta_*^2 (1 - z_2)}{R_{K,2}} \quad (127)$$

$$r_3 = \frac{k_B T}{h} e^{\frac{\frac{1}{2}\mu_{N_2} + \frac{1}{2}\mu_{H_2} - \mu_3^o}{RT}} \theta_*^2 \sqrt{z_1 z_2} (1 - z_3) = \frac{\theta_*^2 \sqrt{z_1 z_2} (1 - z_3)}{R_{K,3}} \quad (128)$$

$$r_4 = \frac{k_B T}{h} e^{\frac{\frac{1}{2}\mu_{N_2} + \mu_{H_2} - \mu_4^o}{RT}} \theta_*^2 z_1 \sqrt{z_2 z_3} (1 - z_4) = \frac{\theta_*^2 z_1 \sqrt{z_2 z_3} (1 - z_4)}{R_{K,4}} \quad (129)$$

$$r_5 = \frac{k_B T}{h} e^{\frac{\frac{1}{2}\mu_{N_2} + \frac{3}{2}\mu_{H_2} - \mu_5^o}{RT}} \theta_*^2 \sqrt{z_1^3 z_2 z_3 z_4} (1 - z_5) = \frac{\theta_*^2 \sqrt{z_1^3 z_2 z_3 z_4} (1 - z_5)}{R_{K,5}} \quad (130)$$

where:

$$\theta_H = e^{\frac{\mu_{H_2} - \mu_{2H^*}}{2RT}} \sqrt{z_1} \theta_* = \sqrt{M_1} \sqrt{z_1} \theta_* \quad (131)$$

$$\theta_N = e^{\frac{\mu_{N_2} - \mu_{2N^*}}{2RT}} \sqrt{z_2} \theta_* = \sqrt{M_2} \sqrt{z_2} \theta_* \quad (132)$$

$$\theta_{NH} = e^{\frac{\frac{1}{2}\mu_{N_2} + \frac{1}{2}\mu_{H_2} - \mu_{NH^*}}{RT}} \sqrt{z_1 z_2 z_3} \theta_* = M_3 \sqrt{z_1 z_2 z_3} \theta_* \quad (133)$$

$$\theta_{NH_2} = e^{\frac{\frac{1}{2}\mu_{N_2} + \mu_{H_2} - \mu_{NH_2^*}}{RT}} z_1 \sqrt{z_2 z_3 z_4} \theta_* = M_4 z_1 \sqrt{z_2 z_3 z_4} \theta_* \quad (134)$$

Since $\theta_H + \theta_N + \theta_{NH} + \theta_{NH_2} + \theta_* = 1$, we have:

$$\theta_*^{-1} = 1 + \sqrt{M_1 z_1} + \sqrt{M_2 z_2} + M_3 \sqrt{z_1 z_2 z_3} + M_4 z_1 \sqrt{z_2 z_3 z_4} \quad (135)$$

where R_k refers to the kinetic resistance. In addition, it should meet the following two requirements:

$$z_i = \sqrt{z_1^3 z_2 z_3 z_4 z_5} \quad (136)$$

$$r = \frac{2}{3} r_1 = 2r_2 = r_3 = r_4 = r_5 \quad (137)$$

Then, we convert the rate equations above into a standard form:

$$r_1' = \frac{2}{3} r_1 = \frac{1}{R_{K,1}} \frac{2}{3} \frac{1 + \sqrt{z_1^3}}{(1 + z_1 + z_1^2)} \theta_*^2 (1 - \sqrt{z_1^3}) = \frac{\theta_*^2 (1 - Z_1)}{R_{K,1}'} \quad (138)$$

$$r_2' = 2r_2 = \frac{1}{R_{K,2}} 2 \frac{(1 + \sqrt{z_2})}{\sqrt{z_1^3}} \theta_*^2 \sqrt{z_1^3} (1 - \sqrt{z_2}) = \frac{\theta_*^2 Z_1 (1 - Z_2)}{R_{K,2}} \quad (139)$$

$$r_3' = r_3 = \frac{1}{R_{K,3}} \frac{1}{z_1} \theta_*^2 \sqrt{z_1^3 z_2} (1 - z_3) = \frac{\theta_*^2 Z_1 Z_2 (1 - Z_3)}{R_{K,3}} \quad (140)$$

$$r_4' = r_4 = \frac{1}{R_{K,4}} \frac{1}{\sqrt{z_1}} \theta_*^2 \sqrt{z_1^3 z_2 z_3} (1 - z_4) = \frac{\theta_*^2 Z_1 Z_2 Z_3 (1 - Z_4)}{R_{K,4}} \quad (141)$$

$$r_5' = r_5 = \frac{1}{R_{K,5}} \theta_*^2 \sqrt{z_1^3 z_2 z_3 z_4} (1 - z_5) = \frac{\theta_*^2 Z_1 Z_2 Z_3 Z_4 (1 - Z_5)}{R_{K,5}} \quad (142)$$

where:

$$Z_1 = \sqrt{z_1^3}; Z_2 = \sqrt{z_2}; Z_3 = z_3; Z_4 = z_4; Z_5 = z_5 \quad (143)$$

$$z_i = \sqrt{z_1^3 z_2 z_3 z_4 z_5} = Z_1 Z_2 Z_3 Z_4 Z_5 \quad (144)$$

$$R_{K,1}' = R_{K,1} \frac{3(1 + z_1 + z_1^2)}{2(1 + \sqrt{z_1^3})} \quad (145)$$

$$R_{K,2}' = R_{K,2} \frac{\sqrt{z_1^3}}{2(1 + \sqrt{z_2})} \quad (146)$$

$$R_{K,3}' = R_{K,3} z_1 \quad (147)$$

$$R_{K,4}' = R_{K,4} \sqrt{z_1} \quad (148)$$

$$R_{K,5}' = R_{K,5} \quad (149)$$

where the translation relationships could be seen clearly:

$$\theta_H = e^{\frac{\mu_{H_2} - \mu_{2H^*}}{2RT}} \sqrt{z_1} \theta_* = \sqrt{K_{eq1} P_{H_2}} \sqrt{z_1} \theta_* \quad (150)$$

$$\theta_N = e^{\frac{\mu_{N_2} - \mu_{2N^*}}{2RT}} \sqrt{z_2} \theta_* = \sqrt{K_{eq2} P_{N_2}} \sqrt{z_2} \theta_* \quad (151)$$

$$\theta_{NH} = e^{\frac{\frac{1}{2}\mu_{N_2} + \frac{1}{2}\mu_{H_2} - \mu_{NH^*}}{RT}} \sqrt{z_1 z_2 z_3} \theta_* = \sqrt{K_{eq1} P_{H_2} K_{eq2} P_{N_2} K_{eq3}} \sqrt{z_1 z_2 z_3} \theta_* \quad (152)$$

$$\theta_{NH_2} = e^{\frac{\frac{1}{2}\mu_{N_2} + \mu_{H_2} - \mu_{NH_2^*}}{RT}} z_1 \sqrt{z_2 z_3 z_4} \theta_* = K_{eq1} P_{H_2} \sqrt{K_{eq2} P_{N_2} K_{eq3} K_{eq4}} z_1 \sqrt{z_2 z_3 z_4} \theta_* \quad (153)$$

$$\theta_*^{-1} = 1 + \sqrt{K_{eq1} P_{H_2} z_1} + \sqrt{K_{eq2} P_{N_2} z_2} + \sqrt{K_{eq1} P_{H_2} K_{eq2} P_{N_2} K_{eq3}} \sqrt{z_1 z_2 z_3} + K_{eq1} P_{H_2} \sqrt{K_{eq2} P_{N_2} K_{eq3} K_{eq4}} z_1 \sqrt{z_2 z_3 z_4} \quad (154)$$

$$R_{K,1}^{-1} = \frac{k_B T}{h} e^{\frac{\mu_{H_2} - \mu_1^{\sigma,o}}{RT}} = k_1 P_{H_2} \quad (155)$$

$$R_{K,2}^{-1} = \frac{k_B T}{h} e^{\frac{\mu_{N_2} - \mu_2^{\sigma,o}}{RT}} = k_2 P_{N_2} \quad (156)$$

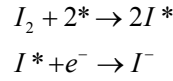
$$R_{K,3}^{-1} = \frac{k_B T}{h} e^{\frac{\frac{1}{2}\mu_{N_2} + \frac{1}{2}\mu_{H_2} - \mu_3^{\sigma,o}}{RT}} = k_3 \sqrt{K_{eq1} P_{H_2} K_{eq2} P_{N_2}} \quad (157)$$

$$R_{K,4}^{-1} = \frac{k_B T}{h} e^{\frac{\frac{1}{2}\mu_{N_2} + \mu_{H_2} - \mu_4^{\sigma,o}}{RT}} = k_4 K_{eq1} P_{H_2} \sqrt{K_{eq2} P_{N_2}} K_{eq3} \quad (158)$$

$$R_{K,5}^{-1} = \frac{k_B T}{h} e^{\frac{\frac{1}{2}\mu_{N_2} + \frac{3}{2}\mu_{H_2} - \mu_5^{\sigma,o}}{RT}} = k_5 \sqrt{K_{eq1}^3 P_{H_2}^3 K_{eq2} P_{N_2}} K_{eq3} K_{eq4} \quad (159)$$

Supporting Information 2-3: Iodine reduction reaction (IRR)

Iodine reduction reaction (IRR) is well studied in our previous works⁹⁻¹². The process is relatively simple and can be displayed as follows:



Its rate equations:

$$r_1 = \frac{k_B T}{h} e^{\frac{\mu_{I_2} - \mu_1^{\sigma,o}}{RT}} \theta_*^2 (1 - z_1) = \frac{\theta_*^2 (1 - z_1)}{R_{K,1}} \quad (160)$$

$$r_2 = \frac{k_B T}{h} e^{\frac{\frac{1}{2}\mu_{I_2} - \mu_2^{\sigma,o}}{RT}} \theta_* \sqrt{z_1} (1 - z_2) = \frac{\theta_* \sqrt{z_1} (1 - z_2)}{R_{K,2}} \quad (161)$$

where R_K refers to the kinetic resistance. Since:

$$\theta_I = e^{\frac{\mu_{I_2} - \mu_{2I^*}}{2RT}} \sqrt{z_1} \theta_* \quad (162)$$

$$\theta_I + \theta_* = 1 \quad (163)$$

the surface free site can be written as:

$$\theta_*^{-1} = 1 + e^{\frac{\mu_{I_2} - \mu_{2I^*}}{2RT}} \sqrt{z_1} \quad (164)$$

Then, we will convert the rate equations above into a standard form:

$$r_1' = 2r_1 = \frac{\theta_*}{R_{K,1}} 2(1 + \sqrt{z_1}) \theta_* (1 - \sqrt{z_1}) = \frac{\theta_* (1 - Z_1)}{R_{K,1}} \quad (165)$$

$$r_2' = r_2 = \frac{1}{R_{K,2}} \theta_* \sqrt{z_1} (1 - z_2) = \frac{\theta_* Z_1 (1 - Z_2)}{R_{K,2}} \quad (166)$$

where:

$$Z_1 = \sqrt{z_1}; Z_2 = z_2 \quad (167)$$

$$z_t = \sqrt{z_1 z_2} = Z_1 Z_2 \quad (168)$$

$$R'_{K,1} = \frac{R_{K,1}}{2\theta_* (1 + z_1)} \quad (169)$$

$$R'_{K,2} = R_{K,2} \quad (170)$$

At the steady state condition, it should have $r = r'_1 = r'_2$.

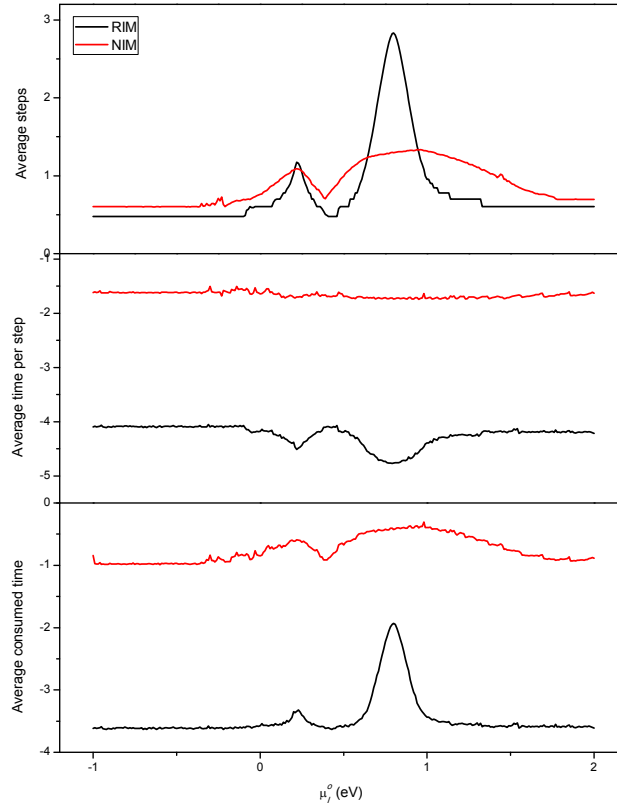


Figure S12. Comparison of (a) average iteration steps; (b) average time per iteration step; (c) average total solving time between RIM and NIM for solving micro-kinetics of IRR. Red lines and black lines refer to all attempts of RIM and NIM (all of them succeeded in this case), respectively. The y axes are log10 scales.

A full comparison between NIM and RIM for IRR with 100 random initial guesses at different adsorption energies along the volcano curve were performed (Figure S12). It can be clearly seen from Figure S12a that at most adsorption energies, RIM needs fewer iteration steps than NIM; usually a dozen steps of RIM are enough to yield a good solution. The average time per step and the total solving time of RIM is two to three orders less than that of NIM, as it is not necessary in our method to calculate Jacobian matrix and its inverse matrix during the iteration, which are time-consuming processes, and nor do we need to employ arbitrary-precision arithmetic.

Only in a small energy range (as shown in Figure S12a) RIM will lead to the convergence oscillation that reduces the convergence speed as shown in Figure 5c. Instead of directly updating by the iteration equation $z_{i+1} = \varphi(z_i)$, we find that a random damp strategy would significantly overcome the problem:

$$z_{i+1} = z_i + \text{rand} \cdot (\varphi(z_i) - z_i) \quad (171)$$

The numeric results of ammonia synthesis and IRR are shown in Figure S13, and the low relative errors verify the reliability of the strategy. All the iteration step numbers are around 15 to 60, which evidently decreases the iteration number for the oscillation range of convergence in IRR.

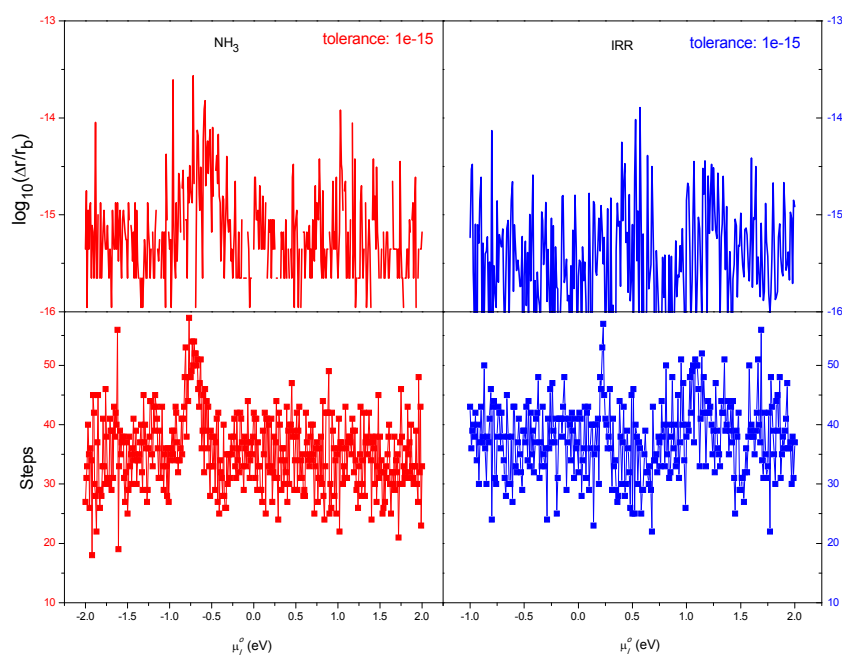
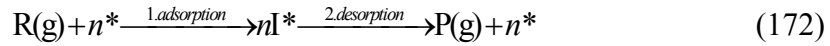


Figure S13 Relative errors of each TOF (a, b) and corresponding number of iterations (c, d) at different adsorption energies of the key intermediate (I) of ammonia synthesis (a, c) and iodine reduction reaction (b, d) calculated by the reversibility iteration method with a random damp strategy.

Supporting Information 2-4: Discussion on the convergence of RIM

Firstly, the Newton iteration method, which only works when the trial guess is within Newton's domain of convergence,⁵ cannot guarantee to converge for every initial guess. For our method, because the expressions of coverage and equivalent kinetic resistance ($R'_{K,i}$) with reversibilities (z_i) are dependent on reaction mechanisms, it is difficult to give a generalized proof of its convergence. However, we can quantitatively discuss this issue. Mathematically, it is known that, for iteration equation $z = \varphi(z)$, the iterative method could guarantee convergence when $|\varphi'(z)| < 1$. Using the heterogeneous catalytic reaction of our generalized two-step model:



the iteration expression of reversibility is $\varphi(z) = \frac{z_t R_{K1} + R_{K2}}{R_{K1} + R_{K2}}$, and it can be solved directly for a standard series reaction, while for a real reaction the kinetic resistance is a function of reversibility:

$$R_{K1} = R_{K1}^o \cdot f_1(z); R_{K2} = R_{K2}^o \cdot f_2(z) \quad (173)$$

Taking the partial derivative, we have:

$$\begin{aligned} \left| \frac{\partial \varphi(z)}{\partial z_1} \right| &= \left| (1 - z_t) \frac{R'_{K1} R_{K2} - R_{K1} R'_{K2}}{(R_{K1} + R_{K2})^2} \right| \\ &= \left| (1 - z_t) \frac{R_{K1} R_{K2} (\partial \ln f_1(z) - \partial \ln f_2(z)) / \partial z_1}{(R_{K1} + R_{K2})^2} \right| \\ &= \frac{(1 - z_t)(z_1 - z_t)}{(1 - z_t)} \left| \frac{\partial \ln f_1(z)}{\partial z_1} - \frac{\partial \ln f_2(z)}{\partial z_1} \right| \end{aligned} \quad (174)$$

Then, we can write:

$$\left| \frac{\partial \ln f_1(z)}{\partial z_1} - \frac{\partial \ln f_2(z)}{\partial z_1} \right| < \frac{(1 - z_t)}{(1 - z_t)(z_1 - z_t)} \quad (175)$$

which corresponds to the convergence condition $|\varphi'(z)| < 1$. In the following, we evaluate whether this condition is tenable along the volcano curve.

On the left side of the volcano curve, the adsorption is strong and the desorption would be the rate-limiting step, i.e. $z_1 \approx 1, z_2 \approx z_t$; similarly, on the right side, the adsorption is weak and can be regarded as the rate-limiting step, thus $z_1 \approx z_t, z_2 \approx 1$. Substituting them in equation (175), the right-hand term tends towards infinity, which would ensure $|\varphi'(z)| < 1$ (i.e. convergence). Only around the volcano-curve peak, the right-hand term in equation (175) would usually correspond to a smaller value and thus relatively slow convergence, which is consistent with our numeric result that it took more steps to converge around the volcano peak. Nevertheless, around the volcano-curve peak, the right-hand term of equation (175) is above 4 at least

according to the easily obtained inequation (176):

$$\frac{(1-z_i)}{(1-z_1)(z_1-z_i)} \geq \frac{4}{(1-z_i)} \approx 4 \quad (176)$$

which indicates that $|\varphi'(z)| < 1$ is not difficult to achieve even in such a case. Specifically, our numeric simulations on ammonia synthesis, iodine reduction reaction and HER reaction at more than one hundred points along the volcano curves for each reaction and each with 100 random initial guesses all converged.

Furthermore, the convergence behaviours with respect to the iterative step for RIM were carried out at the energy points with a maximum number of iteration steps along the volcano curves, as shown in Figure 3c at -0.65 eV for ammonia synthesis and Figure 4d at -0.80 eV for iodine reduction reaction, respectively, which are the worst cases for these two systems. In contrast, the results of NIM in Figure 5c were obtained when they were successfully converged (but often they did not converge). To be clear, we present the residual/relative errors of RIM and NIM in Figure S14. From Figures S14b-c, we can see that the convergence speed of RIM to the “benchmarks” is much faster than NIM and gives rise to a reasonable solution even within a few steps (≤ 10). The results of NIM for ammonia synthesis and IRR (Figure S14) show that once the Newton iteration begins to converge, it rapidly converges to a steady-state solution. But it only works when the trial solutions are within Newton's domain of convergence.⁵

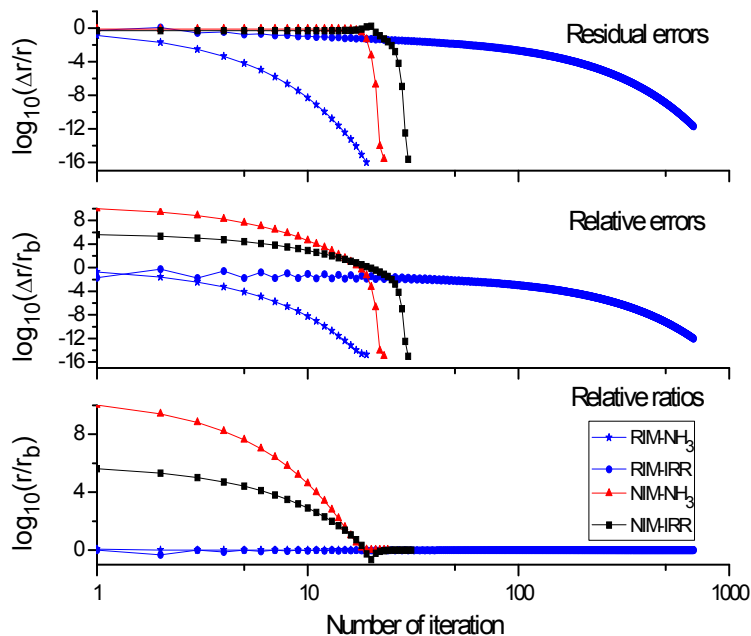


Figure S14 (a) The residual error ($\Delta r/r$) versus the number of iteration of two methods for solving NH_3 synthesis and IRR, and the corresponding (b) relative errors ($\Delta r/r_b$) and (c) relative ratios (r/r_b).

Supporting Information 2-5: Discussion on the application of RIM for obtaining the rate expression without unknown variables

The initially obtained rate expressions (in an analytic form) are usually a set of implicit equations, which include unknown variables (e.g. reversibilities). If combined with the traditional Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach, we can quickly obtain the quasi-steady-state (QSS) rate expression by assuming each step in turn to be rate-limiting ($z_i = z_t$). Here, we take ammonia synthesis as an example. If we assume the H₂ dissociation to be rate-limiting step, i.e. the resistance $R'_{K,1}$ should be dominant, and

$z_i \approx 1; z_1 \approx z_i^{2/3}$, substituting to equation(145) and (135), we can have:

$$R'_{K,1} = R_{K,1} \frac{3(1 + z_2^{2/3} + z_2^{4/3})}{2(1 + z_t)} \quad (177)$$

$$\theta_*^{-1} = 1 + \sqrt{M_2} + z_t^{1/3}(\sqrt{M_1} + M_3 + M_4 z_t^{1/3}) \quad (178)$$

Then, substituting to the total rate equation:

$$\begin{aligned} r &= \frac{1 - z_t}{\sum R'_{K,i}} \theta^2 \approx \frac{1 - z_t}{R'_{K,1}} \frac{1}{(1 + \sqrt{M_2} + z_t^{1/3}(\sqrt{M_1} + M_3 + M_4 z_t^{1/3}))^2} \\ &= \frac{2k_1 P_{H_2} (1 - z_t^{2/3})}{3(1 + \sqrt{K_{eq2} P_{N_2}} + \sqrt{K_{eq1} P_{H_2}} z_t^{1/3} (1 + \sqrt{K_{eq2} P_{N_2}} K_{eq3} + \sqrt{K_{eq1} P_{H_2}} K_{eq2} P_{N_2} K_{eq3} K_{eq4} z_t^{1/3}))^2} \end{aligned} \quad (179)$$

If we assume the N₂ dissociation to be rate-limiting step, i.e. the resistance $R'_{K,2}$ should be dominant and $z_i \approx 1; \sqrt{z_2} \approx z_{tot}$, substituting to equation(146) and (135), we can have:

$$R'_{K,2} = R_{K,2} \frac{1}{2(1 + z_t)} \quad (180)$$

$$\theta_*^{-1} = 1 + \sqrt{M_1} + (\sqrt{M_2} + M_3 + M_4) z_t \quad (181)$$

Substituting to the reaction rate:

$$\begin{aligned} r &= \frac{1 - z_t}{\sum R'_{K,i}} \theta^2 = \frac{1 - z_t}{1/2(1 + z_t) R_{K,2}} \frac{1}{(\sqrt{M_1} + (\sqrt{M_2} + M_3 + M_4) z_t)^2} \\ &= \frac{2k_2 P_{N_2} (1 - z_t^2)}{(1 + \sqrt{K_{eq1} P_{H_2}} + \sqrt{K_{eq2} P_{N_2}} z_t (1 + \sqrt{K_{eq1} P_{H_2}} K_{eq3} + K_{eq1} P_{H_2} K_{eq3} K_{eq4}))^2} \end{aligned} \quad (182)$$

Similarly, If $z_i \approx 1; z_3 \approx z_t$ and keep the dominant resistance $R'_{K,3}$, we can get:

$$r = \frac{1-z_t}{\sum R_{K,i}} \theta^2 = \frac{1-z_t}{R_{K,3}} \frac{1}{(1+\sqrt{M_1}+\sqrt{M_2}+(M_3+M_4)z_t)^2} \quad (183)$$

$$= \frac{k_3 \sqrt{K_{eq1} P_{H_2} K_{eq2} P_{N_2}} (1-z_t)}{(1+\sqrt{K_{eq1} P_{H_2}} + \sqrt{K_{eq2} P_{N_2}} + \sqrt{K_{eq1} P_{H_2}} \sqrt{K_{eq2} P_{N_2}} K_{eq3} z_t (1+\sqrt{K_{eq1} P_{H_2}} K_{eq4}))^2}$$

If $z_i \approx 1; z_4 \approx z_t$ and keep the dominant resistance $R'_{K,4}$, we can get:

$$r = \frac{1-z_t}{\sum R_{K,i}} \theta^2 = \frac{1-z_t}{R_{K,4}} \frac{1}{(1+\sqrt{M_1}+\sqrt{M_2}+M_3+M_3 z_t)^2} \quad (184)$$

$$= \frac{k_3 \sqrt{K_{eq1} P_{H_2} K_{eq2} P_{N_2}} (1-z_t)}{(1+\sqrt{K_{eq1} P_{H_2}} + \sqrt{K_{eq2} P_{N_2}} + \sqrt{K_{eq1} P_{H_2}} K_{eq2} P_{N_2} K_{eq3} + K_{eq1} P_{H_2} \sqrt{K_{eq2} P_{N_2}} K_{eq3} K_{eq4} z_t)^2}$$

If $z_i \approx 1; z_5 \approx z_t$ and keep the dominant resistance $R'_{K,5}$, we can get:

$$r = \frac{1-z_t}{\sum R_{K,i}} \theta^2 = \frac{1-z_t}{R_{K,5}} \frac{1}{(1+\sqrt{M_1}+\sqrt{M_2}+M_3+M_4)^2} \quad (185)$$

$$= \frac{k_5 \sqrt{K_{eq1}^3 P_{H_2}^3 K_{eq2} P_{N_2} K_{eq3} K_{eq4}} (1-z_t)}{(1+\sqrt{K_{eq1} P_{H_2}} + \sqrt{K_{eq2} P_{N_2}} + \sqrt{K_{eq1} P_{H_2}} K_{eq2} P_{N_2} K_{eq3} + K_{eq1} P_{H_2} \sqrt{K_{eq2} P_{N_2}} K_{eq3} K_{eq4})^2}$$

In fact, these expressions under LHHW approach may be still far from the practical application, as they are still too complex, and it may be difficult to decide which one is the correct choice for a given experimental condition. In the following, we show how to use our method to get a simple and correct expression.

Table S1. Reversibilities, resistances and coverage ratios at the N adsorption energies of -0.2 and -1eV, respectively.

		-0.2eV		-1eV		
	z	R'_K	θ_i/θ_*	z	R'_K	θ_i/θ_*
1	1.00E+00	8.51E-06	1	1.00E+00	9.11E-07	1
2	4.72E-03	4.73E+05	4.56E-01	9.76E-01	1.32E-04	3.61E+00
3	1.00E+00	1.71E+01	2.31E-05	1.00E+00	3.78E-06	3.26E+02
4	1.00E+00	1.44E+01	1.40E-04	9.98E-01	2.67E-05	1.97E+03
5	9.99E-01	3.25E+01	3.16E-02	6.96E-02	9.95E-03	7.09E+03

As shown in Table S1, when the adsorption of N is too weak (at -0.2 eV), the N_2 dissociation is the rate-limiting step ($z_2=4.72E-03$), and then the kinetic resistance of this reaction step should be dominant (4.73E+05) and the free site can approach to:

$$\theta_*^{-1} \approx 1 + \sqrt{M_1} \quad (186)$$

Hence, the total rate reaction can be simplified to be:

$$r = \frac{1-z_t}{\sum R'_{K,i}} \theta^2 = \frac{2(1-z_t^2)}{R_{K,2}(1+\sqrt{M_1})^2} = \frac{2k_2 P_{N_2} (1-z_t^2)}{(1+\sqrt{K_{eq1} P_{H_2}})^2} \quad (187)$$

When the adsorption of N to be too strong (at -1 eV), and then the NH₃ desorption to be rate-limiting step ($z_5=6.96E-02$), and then the kinetic resistance of this reaction step should be dominant (9.95E-03) and the free site can approach to:

$$\theta_*^{-1} \approx M_3 + M_4 \quad (188)$$

Hence, the total rate reaction can be simplified to be:

$$r = \frac{1-z_t}{\sum R'_{K,i}} \theta^2 = \frac{1-z_t}{R_{K,5}(M_3 + M_4)^2} = \frac{k_5 \sqrt{K_{eq1} P_{H_2}} K_{eq4} (1-z_t)}{\sqrt{K_{eq2} P_{N_2}} K_{eq3} (1 + \sqrt{K_{eq1} P_{H_2}} K_{eq4})^2} \quad (189)$$

Based on these two expressions, we can plot the corresponding rates as shown in Figure S15, one can see that they can give a reasonable approximation in the respectively ranges, which indicating the reliability of our approach. It is clear that the reaction is mainly limited by N₂ dissociation or NH₃ desorption, and then the kinetic resistances ($R'_{K,2}, R'_{K,5}$) of these reaction steps should be dominant. Hence, the reversibilities can be simplified to be:

$$z_i = 1; \sqrt{z_2} = \frac{z_i R'_{K,2} + R'_{K,5}}{R'_{K,2} + R'_{K,5}}; z_5 = \frac{z_i R'_{K,2} + z_i R'_{K,5}}{z_i R'_{K,2} + R'_{K,5}} \quad (190)$$

$$R'_{K,2} = 2k_2 P_{N_2}; R'_{K,5} = k_5 \sqrt{K_{eq1}^3 P_{H_2}^3 K_{eq2} P_{N_2} K_{eq3} K_{eq4}}$$

Then, the total rate of the reaction can approach to:

$$r = \frac{1-z_t}{\sum R'_{K,i}} \theta^2 \approx \frac{1-z_t}{(R'_{K,2} + R'_{K,5})(1 + M_1 + \sqrt{z_2}(M_3 + M_4))^2} \quad (191)$$

Based on this equation, without solving, we can directly get the volcano curve numerically, and the relative error with respect to the “benchmarks” are shown in figure S15b, indicating that the expression can give rise to considerable results along the volcano curve.

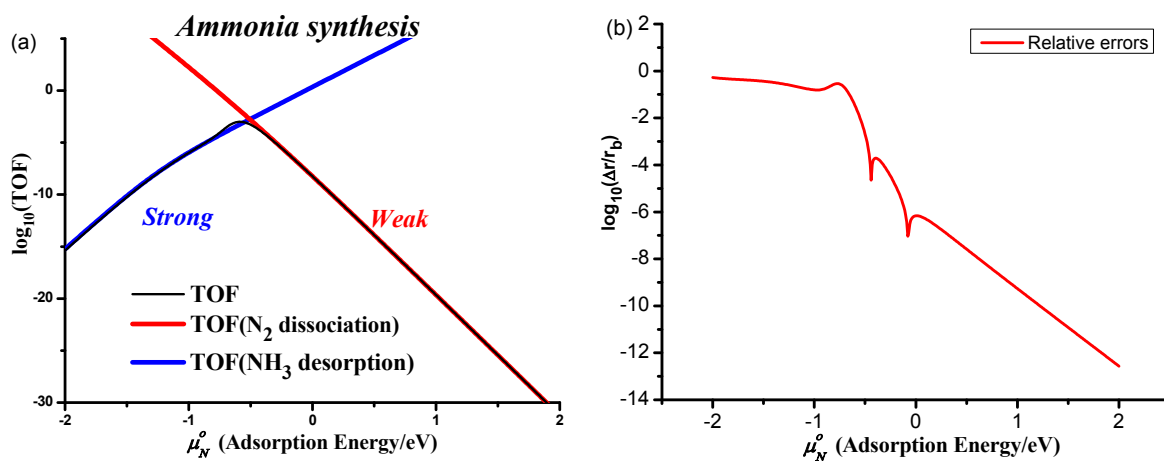


Figure S15 (a) TOF and approximated rates on different adsorption energies, (b) the relative errors using the approximated rate equation (191) on different adsorption energies.

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