

Supporting information

Brønsted-Evans-Polanyi Relation of Multi-step Reactions and Volcano Curve in Heterogeneous Catalysis

Jun Cheng, P. Hu*, Peter Ellis, Sam French, Gordon Kelly, C. Martin Lok

To formulate the derivation of rate expressions, the Dumesic's method¹ in terms of De Donder relations^{2[19]} is utilized. Dumesic defined the reversibility of the elementary step i , z_i , as:

$$z_i = \frac{\prod_j a_j^{v_{ij}}}{K_{ieq}} \quad (1)$$

where v_{ij} is the stoichiometric coefficient for the j reactant (or product) of step i , a_j is the activity of the j reactant (or product) of the step i and K_{ieq} is the standard equilibrium constant.

It should be noted that the value of z_i is between 0 to 1 if step i proceeds in the forward direction. When the value of z_i approaches zero, step i is irreversible; as it approaches one, step i reaches quasi-equilibrium. The net reaction rate of step i , r_i , can be expressed in terms of the reversibility, z_i :

$$r_i = r_{+i} - r_{-i} = r_{+i}(1 - z_i) \quad (2)$$

where r_{+i} and r_{-i} are the forward and backward reaction rate of step i , respectively.

On the basis of the two-step (adsorption and desorption) model in the main text (Scheme 1 and Figure 1), we derive the reaction rate as follows:

At steady state, the reaction rate (r) is equal to the adsorption (r_{ads}) and desorption (r_{des}) rate:

$$r = r_{ads} = r_{des} \quad (3)$$

According to Eq. (2), the adsorption rate can be expressed as:

$$r_{ads} = k_{ads} P_R \theta_* (1 - z_{ads}) \quad (4)$$

where P_R is the partial pressure of reactant R , θ_* is the coverage of free surface sites, k_{ads} is the rate constant of adsorption and z_{ads} is the reversibility of adsorption. From Eq. (1), z_{ads} is equal to

$$z_{ads} = \frac{\theta_I}{P_R \theta_* K_{ads}} \quad (5)$$

where θ_I is the coverage of surface intermediate I and K_{ads} is the standard equilibrium constant of adsorption.

Similarly, the desorption rate can be written as:

$$r_{des} = k_{des} \theta_I (1 - z_{des}) \quad (6)$$

where k_{des} is the rate constant of desorption and z_{des} is the reversibility of desorption.

The total surface coverage is equal to one, thus,

$$\theta_* + \theta_I = 1 \quad (7)$$

In the sequential reaction system, the overall reversibility (z_{tot}) is equal to the product of the reversibility of each step, thus,

$$z_{tot} = z_{ads} z_{des} = \frac{P_P}{P_R K_{eq}} \quad (8)$$

where P_P is the partial pressure of reactant P and K_{eq} is the overall standard equilibrium constant.

The rate constants and equilibrium constants that appear in the above equations can be expressed:

$$k_{ads} = \frac{k_B T}{h} e^{\frac{S_R}{R}} e^{-\frac{E_R^{dis}}{RT}} \quad (9)$$

$$k_{des} = \frac{k_B T}{h} e^{-\frac{E_P^{ass}}{RT}} \quad (10)$$

$$K_{ads} = e^{-\frac{S_R}{R}} e^{-\frac{\Delta H_R}{RT}} \quad (11)$$

$$K_{eq} = e^{\frac{\Delta G}{RT}} = e^{\frac{\Delta H - T(S_P - S_R)}{RT}} \quad (12)$$

where S_R and S_P are the entropy of reactant and product, respectively, ΔG and ΔH are the Gibbs free energy change and enthalpy change of the overall reaction, respectively, and the other terms are defined in the main text. It should be mentioned that the entropy of surface intermediate I is usually very small and neglected in this treatment.

Combining Eq. (3)-(12), the reaction rate can be derived:

$$r = \frac{k_B T}{h} \frac{(1 - \frac{P_P}{P_R} e^{\frac{\Delta G}{RT}})}{\frac{1}{P_R} e^{\frac{S_R}{R}} e^{-\frac{E_R^{dis}}{RT}} (1 + e^{-\frac{E_R^{ass} - E_P^{ass}}{RT}}) + e^{\frac{E_P^{ass}}{RT}} (1 + \frac{P_P}{P_R} e^{\frac{\Delta G}{RT}} e^{-\frac{E_R^{ass} - E_P^{ass}}{RT}})} \quad (13)$$

If assuming adsorption is the rate-determining step, desorption achieves quasi-equilibrium, z_{des} is close to one and z_{ads} is approximate to z_{tot} . Thus, the reaction rate is expressed as:

$$r = \frac{k_B T}{h} \frac{(1 - \frac{P_P}{P_R} e^{\frac{\Delta G}{RT}})}{\frac{1}{P_R} e^{\frac{S_R}{R}} e^{-\frac{E_R^{dis}}{RT}} + \frac{P_P}{P_R} e^{\frac{\Delta G}{RT}} e^{-\frac{E_R^{ass}}{RT}}} \quad (14)$$

Similarly, the reaction rate is in the following form if assuming desorption is the rate-determining step:

$$r = \frac{k_B T}{h} \frac{(1 - \frac{P_P}{P_R} e^{\frac{\Delta G}{RT}})}{\frac{1}{P_R} e^{\frac{S_R}{R}} e^{\frac{\Delta H_R + E_P^{ass}}{RT}} + e^{\frac{E_P^{ass}}{RT}}} \quad (15)$$

Since both adsorption and desorption follow the BEP relation, the activation energies (E_R^{dis} , E_R^{ass} , E_P^{dis} , and E_P^{ass}) in Eq. (13)-(15) are controlled by ΔH_R and ΔH_P . Moreover, ΔH_R and ΔH_P are related, and their difference is the overall enthalpy change ΔH . So, the overall reaction rate is entirely determined by ΔH_R . The plots of TOF against ΔH_R in Figure 4 in the main text are obtained from Eq. (13)-(15) together with the BEP relations on the stepped surface. The temperature is chosen as 500 K, the entropy of reactant (S_R) and product (S_P) are reasonably assumed to be 200 J/mol/K and the overall enthalpy change (ΔH) is set as -0.5 eV.

References

- 1 (a) Dumesic, J. A. *J. Catal.* **1999**, *185*, 496; (b) Cortright, R. D.; Dumesic, J. A. *Adv. Catal.* **2001**, *46*, 161; (c) Campbell, C. T. *J. Catal.* **2001**, *204*, 520; (d) Dumesic, J. A. *J. Catal.* **2001**, *204*, 525.
- 2 (a) De Donder, Th. in “L’Affinité.” Gauthier-Villiers, Paris, **1927**; (b) Boudart, M. in “Kinetics of Chemical Processes.” Prentice-Hall, Englewood Cliffs, NJ, **1968**; (c) Boudart, M. *J. Phys. Chem.* **1983**, *87*, 2786; (d) Holstein, W. L.; Boudart, M. *J. Phys. Chem. B* **1997**, *101*, 9991.