

# Kinetic Monte-Carlo models

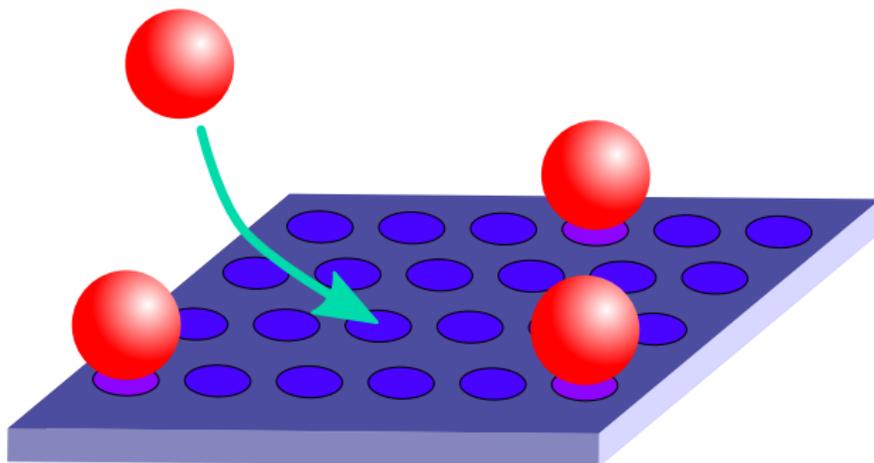
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Friday 18, 2018

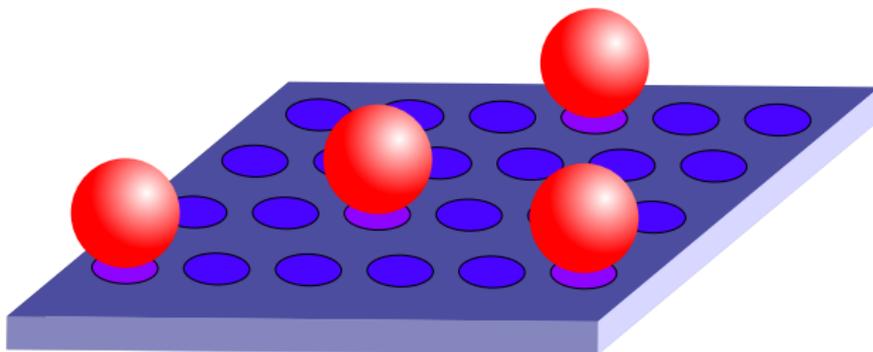
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# Model presentation



**Figure:** Reactant is adsorbed on an unoccupied adsorption site, independently of local coverage.

# Model presentation



**Figure:** Adsorbed reactant at an adsorption site does not feel the influence of other adsorbed species.

# Model presentation

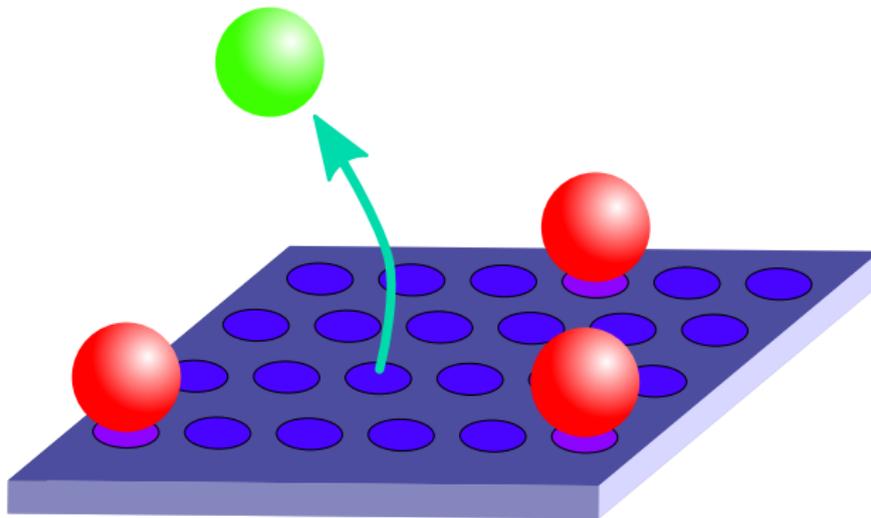
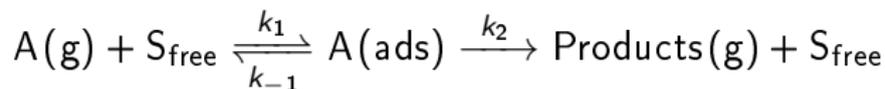


Figure: Reactant is decomposed and rapidly desorbed.

# Unimolecular decomposition

Reaction considered:



Assuming elementary steps, the total reaction rate  $r$  is:

$$r = -\frac{dP_A}{dt} = k_2[A(\text{ads})] = k_2\theta[S] \quad (1)$$

where  $\theta$  is the surface coverage (i.e. fraction of sites occupied), and  $[S]$  is the surface concentration of adsorption sites

Applying a *steady-state approximation to A(ads)*, we get:

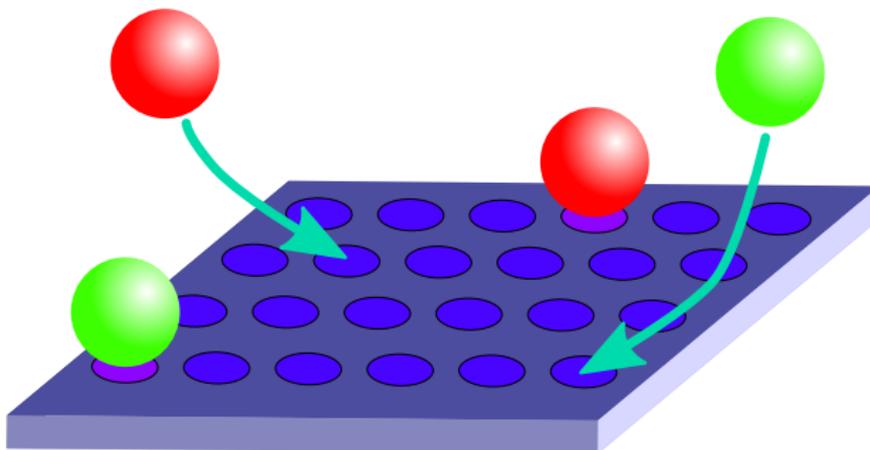
$$r = \frac{k_1 k_2 P_A [S]}{k_1 P_A + k_{-1} + k_2} \quad (2)$$

# Limitations

This approach has multiple limitations/approximations:

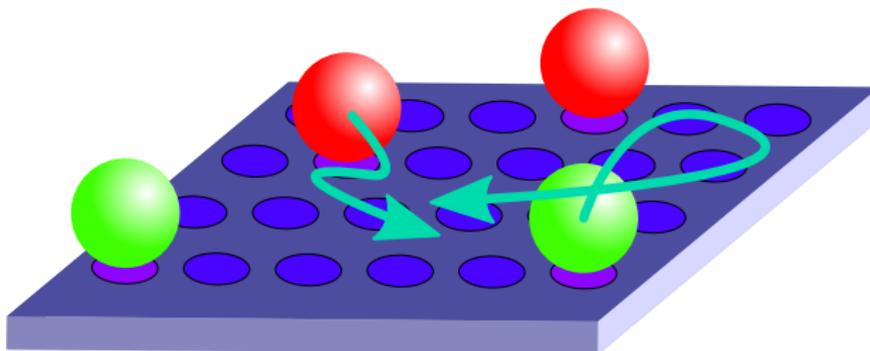
- Only unimolecular decomposition is considered
- Steady-state approximation of adsorbed species
- All catalytic sites are equivalent
- Adsorption sites can only be occupied by the reactant
- Each site can be occupied by at most one adsorbate
- The adsorption and decomposition/desorption steps are considered elementary
- No spatial correlation/lateral interactions
- Kinetic constants are independent of coverage

# Model presentation



**Figure:** Reactants are adsorbed on unoccupied adsorption sites, independently of local coverage.

# Model presentation



**Figure:** Adsorbed reactants at an adsorption site does not feel the influence of other adsorbed species, and diffuse freely over the surface.

# Model presentation

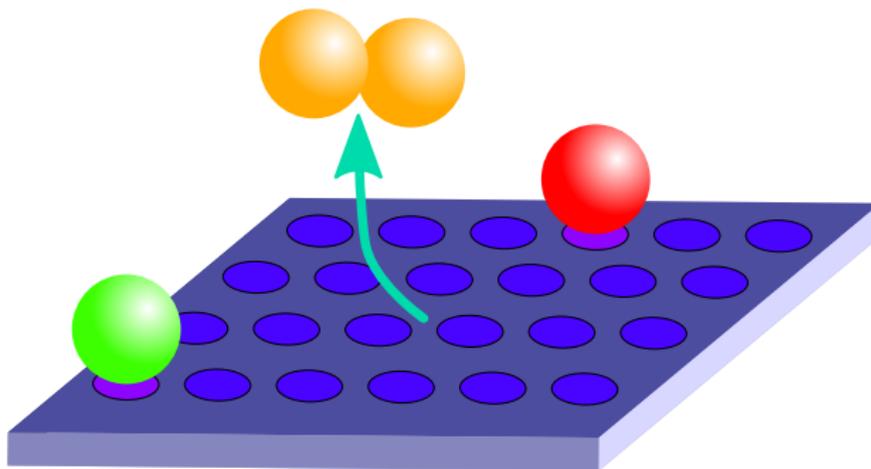
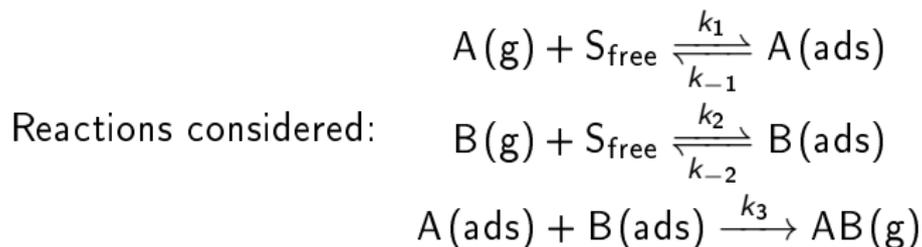


Figure: Bimolecular reaction occurs and product is rapidly desorbed.

# Reaction rate



Assuming elementary steps, the total reaction rate  $r$  is:

$$r = -\frac{dP_A}{dt} = -\frac{dP_B}{dt} = k_3 \theta_A \theta_B [S]^2 \quad (3)$$

Applying a *steady-state approximation* to  $A(\text{ads})$  and  $B(\text{ads})$ , and considering the rate determining step being the reaction/diffusion, we get:

$$r = \frac{K_A K_B P_A P_B [S]^2}{(1 + K_A P_A + K_B P_B)^2} \quad (4)$$



# Limitations

This approach also has multiple limitations/approximations:

- Steady-state approximation of adsorbed species
- Reaction/diffusion between A(ads) and B(ads) is the rate determining step
- All catalytic sites are equivalent
- Adsorption sites can only be occupied by the reactants
- Each site can be occupied by at most one adsorbate
- The adsorption and decomposition/desorption steps are considered elementary
- No spatial correlation/lateral interactions
- Kinetic constants are independent of coverage

# Metropolis-Hastings theory

- Multiple MCMC (Monte-Carlo Markov Chain) methods for generating samples from a probability distribution  $P(\mathcal{S})$ .

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- Based on random walk onto a Markov chain, with initial proposal distribution  $g(\mathcal{S}_i \rightarrow \mathcal{S}_j)$ .

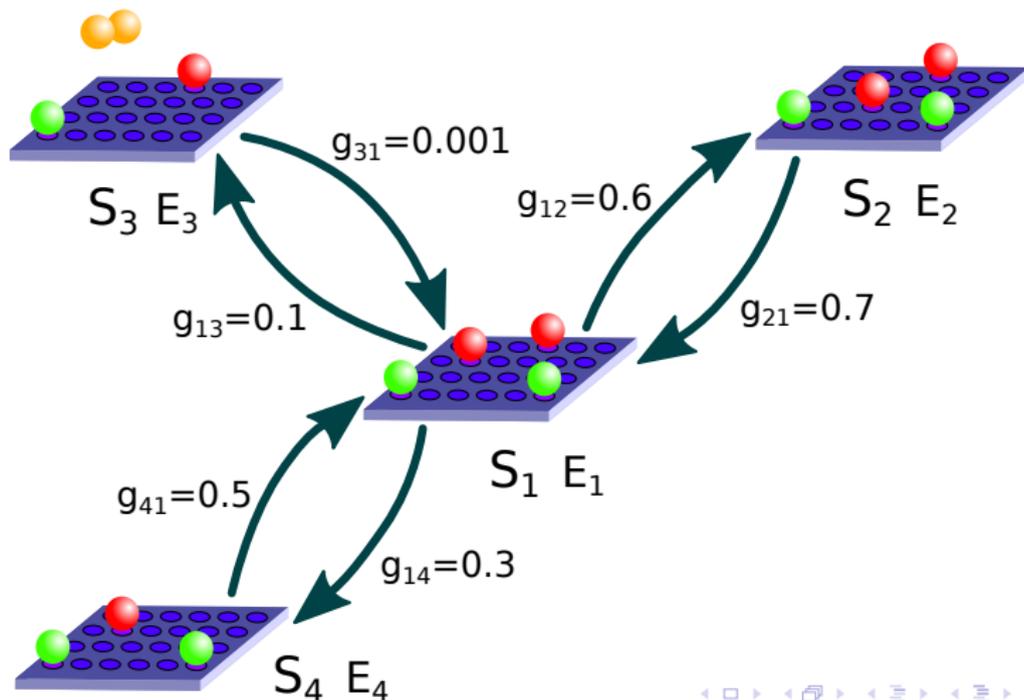
# Metropolis-Hastings theory

- Multiple MCMC (Monte-Carlo Markov Chain) methods for generating samples from a probability distribution  $P(\mathcal{S})$ .
- Based on random walk onto a Markov chain, with initial proposal distribution  $g(\mathcal{S}_i \rightarrow \mathcal{S}_j)$ .
- Reaches asymptotically a stationary distribution  $\pi(\mathcal{S})$ , such that  $\forall \mathcal{S}, \pi(\mathcal{S}) = P(\mathcal{S})$ .

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- Reaches asymptotically a stationary distribution  $\pi(\mathcal{S})$ , such that  $\forall \mathcal{S}, \pi(\mathcal{S}) = P(\mathcal{S})$ .
- Requires only the computation of an estimator  $W(\mathcal{S})$  proportional to  $P(\mathcal{S})$ , over all possible  $\mathcal{S}$ .

# Metropolis-Hastings theory



# Metropolis-Hastings practical algorithm

- A next candidate  $\mathcal{S}_j$  is selected from the current state  $\mathcal{S}_i$  using the proposal distribution  $g$ .

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$$A(\mathcal{S}_i, \mathcal{S}_j) = \min\left(\frac{W(\mathcal{S}_j)g(\mathcal{S}_i \rightarrow \mathcal{S}_j)}{W(\mathcal{S}_i)g(\mathcal{S}_j \rightarrow \mathcal{S}_i)}, 1\right)$$

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- In practice the targeted probability distribution  $P(\mathcal{S})$  is usually a Boltzmann distribution. No need for partition function, as  $W(\mathcal{S}_i) = e^{\frac{-G_i}{kT}} \propto P(\mathcal{S}_i)$  is enough.

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- Pick random number  $x \in [0, 1]$ , candidate  $\mathcal{S}_j$  accepted iff:

$$x \leq \min\left(e^{\frac{-(G_j - G_i)}{kT}} \times \frac{g(\mathcal{S}_i \rightarrow \mathcal{S}_j)}{g(\mathcal{S}_j \rightarrow \mathcal{S}_i)}, 1\right)$$

# Limitations

- With such acceptance criterion, asymptotic behaviour is mathematically proven<sup>1</sup>.
- Sampling at the thermodynamic equilibrium.
- No time defined, no temporal evolution, no kinetics.
- Need to introduce kinetic elements.

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<sup>1</sup>Proof is straightforward, starting from detailed balance condition. ◀ ▶ ☰ ☷ ↺ ↻

# Theoretical background

- Master equation<sup>2</sup>:

$$\frac{dP(\mathcal{S}_i, t)}{dt} = \sum_{j \neq i} (R(\mathcal{S}_j \rightarrow \mathcal{S}_i)P(\mathcal{S}_j, t) - R(\mathcal{S}_i \rightarrow \mathcal{S}_j)P(\mathcal{S}_i, t))$$

- Note: In the Metropolis-Hastings MC, a stronger version of the master equation (with  $\forall i, \frac{dP(\mathcal{S}_i, t)}{dt} = 0$ ) was satisfied: detailed balance.
- Need to define states  $\{\mathcal{S}_1, \mathcal{S}_2, \dots\}$ , transitions  $\mathcal{S}_i \rightarrow \mathcal{S}_j$ , and associated transition rates  $R(\mathcal{S}_i \rightarrow \mathcal{S}_j)$
- Analytical solution cannot be computed for real systems  
 $\Rightarrow$  numerical methods are required

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<sup>2</sup>Can be proven from first principles

# Standard algorithm

- 1 Generate all  $N(\mathcal{S}_i)$  possible transitions (i.e. elementary steps)  $\mathcal{S}_i \rightarrow \mathcal{S}_j$  from current state  $\mathcal{S}_i$ .
- 2 Choose a transition  $\mathcal{S}_i \rightarrow \mathcal{S}_j$  at random.
- 3 Retrieve associated transition rate  $R(\mathcal{S}_i \rightarrow \mathcal{S}_j)$ , and compute  $R_{\max}(\mathcal{S}_i) = \max_{j \neq i}(R(\mathcal{S}_i \rightarrow \mathcal{S}_j))$ .
- 4 Pick a random number  $r_1 \in [0, 1]$ . Apply transition  $\mathcal{S}_i \rightarrow \mathcal{S}_j$  iff  $r_1 \leq \frac{R(\mathcal{S}_i \rightarrow \mathcal{S}_j)}{R_{\max}(\mathcal{S}_i)}$ .
- 5
  - If transition accepted, pick a random number  $r_2 \in (0, 1]$ , and increase time by  $\Delta t = \frac{-\ln(r_2)}{N(\mathcal{S}_i)R_{\max}(\mathcal{S}_i)}$ .
  - Otherwise, transition is rejected. (If most transition rates are negligible compared to  $R_{\max} \Rightarrow$  most attempts rejected).
- 6 Repeat.

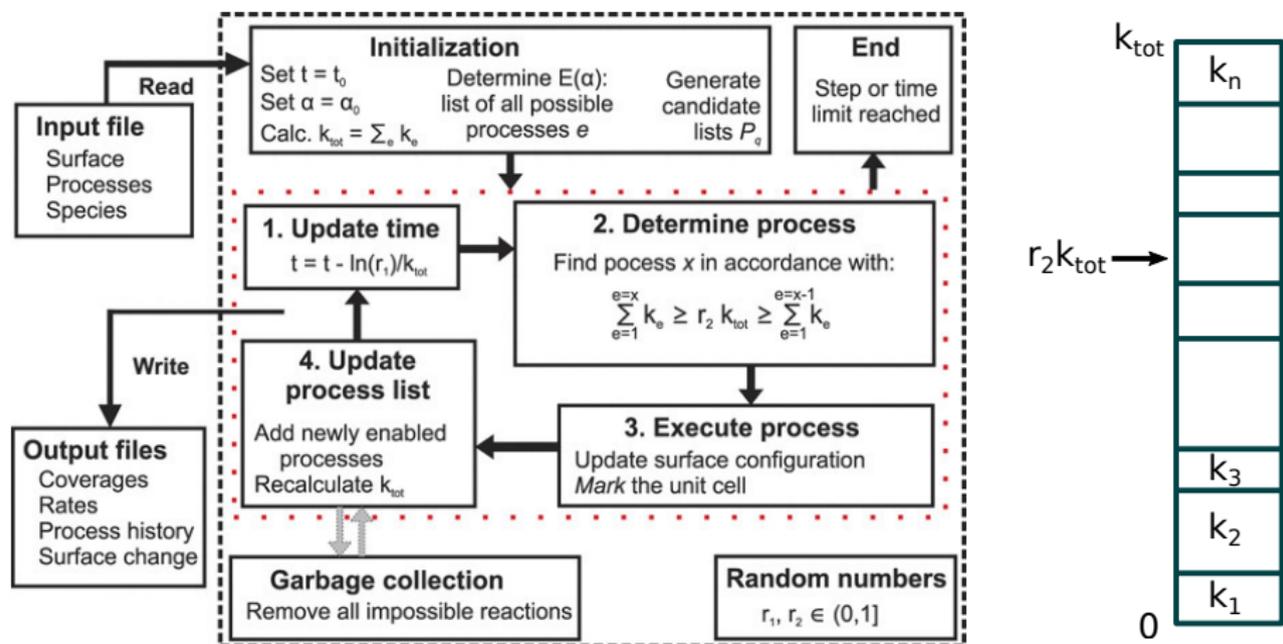
# First Reaction Method

- 1 Generate all possible transitions (i.e. elementary steps)  $\mathcal{S}_i \rightarrow \mathcal{S}_j$  from current state  $\mathcal{S}_i$ , and retrieve associated transition rate  $R(\mathcal{S}_i \rightarrow \mathcal{S}_j)$
- 2 For each possible transition  $\mathcal{S}_i \rightarrow \mathcal{S}_j$ , pick random number  $r_j \in (0, 1]$  and compute associated time  $\tau_j = \frac{-\ln(r_j)}{R(\mathcal{S}_i \rightarrow \mathcal{S}_j)}$ .
- 3 Select transition  $\mathcal{S}_i \rightarrow \mathcal{S}_j$  with lowest  $\tau_j$ .
- 4 Apply selected transition, and increase time by  $\tau_j$ .
- 5 Repeat (previous computations might be stored, and updated).

## Variable Step Size Method / N-fold way / BLK algorithm

- 1 Generate and store in a list all  $N(\mathcal{S}_i)$  possible transitions (i.e. elementary steps)  $\mathcal{S}_i \rightarrow \mathcal{S}_j$  from current state  $\mathcal{S}_i$ , and retrieve associated transition rate  $R(\mathcal{S}_i \rightarrow \mathcal{S}_j)$ .
- 2 Compute the cumulative function  $R_c(\mathcal{S}_i, j) = \sum_{k \neq i}^j R(\mathcal{S}_i \rightarrow \mathcal{S}_k)$ , and define  $R_{\text{tot}}(\mathcal{S}_i) = R_c(\mathcal{S}_i, N(\mathcal{S}_i))$ .
- 3 Pick random number  $r_1 \in (0, 1]$ , and select transition  $\mathcal{S}_i \rightarrow \mathcal{S}_j$  such that  $R_c(\mathcal{S}_i, j - 1) < r_1 R_{\text{tot}}(\mathcal{S}_i) \leq R_c(\mathcal{S}_i, j)$ .
- 4 Apply selected transition, pick a random number  $r_2 \in (0, 1]$ , and increase time by  $\Delta t = \frac{-\ln(r_2)}{R_{\text{tot}}(\mathcal{S}_i)}$ .
- 5 Update list of stored possible positions (add new transitions, update rates, delete transitions no longer possible).
- 6 Repeat.

# BLK algorithm flowchart



# Transition state theory

- How to compute transition rates  $R(\mathcal{S}_i \rightarrow \mathcal{S}_j)$ ?

- Common model, transition state theory:

$$k_{\text{TST}} = \kappa \frac{k_B T}{h} \exp\left(-\frac{\Delta G_{ij}^\ddagger}{k_B T}\right)$$

- In practice, we define:

$$R(\mathcal{S}_i \rightarrow \mathcal{S}_j) = k_{\text{TST}} = \kappa \frac{Q_{ij}^\ddagger}{Q_i} \frac{k_B T}{h} \exp\left(-\frac{\Delta E_{ij}^\ddagger}{k_B T}\right)$$

where  $Q_{ij}^\ddagger$  and  $Q_i$  are the partition functions of the activated complex and current state  $\mathcal{S}_i$ , and  $\Delta E_{ij}^\ddagger$  is the energy barrier for the elementary step  $\mathcal{S}_i \rightarrow \mathcal{S}_j$ .

# Lateral interactions

- How to compute  $\Delta E_{ij}^\ddagger$ ? Depends on the composition and configuration of  $\mathcal{S}_i$  and  $\mathcal{S}_j$
- Cluster expansion techniques:

$$\Delta E_{ij} = E_j - E_i = (E_{j,0} + L_j) - (E_{i,0} + L_i) = \Delta E_{ij,0} + L_{ij}$$

where  $E_{i,0}$  is the total energy of state  $\mathcal{S}_i$  as if the entities were infinitely separated; and  $L_i$  are the lateral interactions present in state  $\mathcal{S}_i$ .

- Activation energies are calculated with linear interpolation:

$$\Delta E_{ij}^\ddagger = \Delta E_{ij,0}^\ddagger + \omega \cdot L_{ij}$$

where  $\omega \in [0, 1]$  is a proximity factor expressing how reactant- or product-like the transition state is.

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# Unimolecular decomposition: derivations

Using steady-state approximation to A(ads):

$$\frac{d[A(\text{ads})]}{dt} = 0 = k_1 P_A [S_{\text{free}}] - (k_{-1} + k_2)[A(\text{ads})] \quad (5)$$

$$\Leftrightarrow 0 = k_1(1 - \theta)P_A[S] - (k_{-1} + k_2)\theta[S] \quad (6)$$

$$\Leftrightarrow \theta = \frac{k_1 P_A}{k_1 P_A + k_{-1} + k_2} \quad (7)$$

Injecting (7) into (1):

$$r = k_2 \theta [S] = \frac{k_1 k_2 [A][S]}{k_1 [A] + k_{-1} + k_2} \quad (8)$$

## Langmuir-Hinshelwood model: derivations (part 1)

Using steady-state approximation to A(ads) and B(ads):

$$\frac{d[A(\text{ads})]}{dt} = 0 = k_1 P_A [S_{\text{free}}] - k_{-1} [A(\text{ads})] - k_3 \theta_A \theta_B [S]^2 \quad (9)$$

$$\Leftrightarrow 0 = k_1 P_A [S_{\text{free}}] - k_{-1} \theta_A [S] - k_3 \theta_A \theta_B [S]^2 \quad (10)$$

$$\Leftrightarrow 0 = k_1 (1 - \theta_A - \theta_B) P_A [S] - (k_{-1} + k_3 \theta_B [S]) \theta_A [S] \quad (11)$$

$$\Leftrightarrow 0 = k_1 (1 - \theta_A - \theta_B) P_A - (k_{-1} + k_3 \theta_B [S]) \theta_A \quad (12)$$

$$\frac{d[B(\text{ads})]}{dt} = 0 = k_2 P_B [S_{\text{free}}] - k_{-2} [B(\text{ads})] - k_3 \theta_A \theta_B [S]^2 \quad (13)$$

$$\Leftrightarrow 0 = k_2 P_B [S_{\text{free}}] - k_{-2} \theta_B [S] - k_3 \theta_A \theta_B [S]^2 \quad (14)$$

$$\Leftrightarrow 0 = k_2 (1 - \theta_A - \theta_B) P_B [S] - (k_{-2} + k_3 \theta_A [S]) \theta_B [S] \quad (15)$$

$$\Leftrightarrow 0 = k_2 (1 - \theta_A - \theta_B) P_B - (k_{-2} + k_3 \theta_A [S]) \theta_B \quad (16)$$

## Langmuir-Hinshelwood model: derivations (part 2)

Assuming that the rate determining step is the reaction between A(ads) and B(ads):

$$k_{-2} \gg k_3 \theta_A [S] \quad (17)$$

$$k_{-1} \gg k_3 \theta_B [S] \quad (18)$$

Therefore, we obtain (defining  $K_A = \frac{k_1}{k_{-1}}$  and  $K_B = \frac{k_2}{k_{-2}}$ ):

$$\frac{d[A(\text{ads})]}{dt} = 0 = k_1(1 - \theta_A - \theta_B)P_A - k_{-1}\theta_A \quad (19)$$

$$\Leftrightarrow 0 = K_A(1 - \theta_A - \theta_B)P_A - \theta_A \quad (20)$$

$$\frac{d[B(\text{ads})]}{dt} = 0 = k_2(1 - \theta_A - \theta_B)P_B - k_{-2}\theta_B \quad (21)$$

$$\Leftrightarrow 0 = K_B(1 - \theta_A - \theta_B)P_B - \theta_B \quad (22)$$

## Langmuir-Hinshelwood model: derivations (part 3)

Ratioing (22) by (20), we get:

$$\frac{\theta_B}{\theta_A} = \frac{K_B P_B}{K_A P_A} \quad (23)$$

Injecting (23) into (20) and (22):

$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \quad (24)$$

$$\theta_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \quad (25)$$

Leading finally to:

$$r = k_3 \theta_A \theta_B [S]^2 = \frac{K_A K_B P_A P_B [S]^2}{(1 + K_A P_A + K_B P_B)^2} \quad (26)$$

## Time step justification

Let us assume state  $\mathcal{S}_i$  is accepted at time  $t = t_i$ , and define  $\tau = t - t_i \geq 0$ . So that  $P(\mathcal{S}_i, 0) = 1$ .

$$P(\mathcal{S}_i, \tau + \Delta\tau) = P(\mathcal{S}_i, \tau) \frac{\text{(no-transition proba)}}{\text{(any-transition proba)}} \left(1 - \frac{R_{\text{tot}}(\mathcal{S}_i)\Delta\tau}{\text{(any-transition proba)}}\right) \quad (27)$$

$$\Leftrightarrow \frac{dP(\mathcal{S}_i, \tau)}{d\tau} = -P(\mathcal{S}_i, \tau)R_{\text{tot}}(\mathcal{S}_i) \quad (28)$$

$$\Rightarrow P(\mathcal{S}_i, \tau) = e^{-R_{\text{tot}}(\mathcal{S}_i)\tau} \quad (29)$$

Probability  $p$  to time  $\tau$  meaningful conversion:

$$\tau = -\frac{\ln(p)}{R_{\text{tot}}(\mathcal{S}_i)} \quad (30)$$

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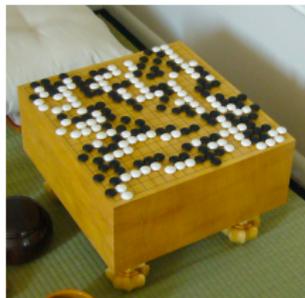


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