Zacros Tutorial 4: Mechanism Input for CO Oxidation on Pt(100)

Michail Stamatakis

University College London

"Workshop on Multiscale Computational Catalysis and Materials Science"

National Institute of Technology, Akashi College, Akashi, Japan

March 3 – 5, 2020

Equations for Calculating Rate Constants

- The general equation for the rate constant from transition state theory (TST) is:

$$k_{TST} = \kappa \cdot \frac{k_B \cdot T}{h} \cdot \frac{q^{\ddagger}}{q_{reac}} \cdot \exp\left(-\frac{E^{\ddagger}}{k_B \cdot T}\right)$$

- The activation energy $E^{\ddagger}$ can be easily obtained as the difference between transition and initial state energies.
- The quasi partition functions involve translational, rotational and vibrational components, as necessary.
- The transmission coefficient κ has to be calculated from expensive MD simulations and is usually assumed = 1.

Rate Constants for Particular Elementary Events

- Non-activated exothermic adsorption: $X_{gas} + * \Leftrightarrow X^*$

Forward (adsorption):

$$k_{TST}^{ads} = \frac{p_X \cdot A_{site}}{\sqrt{2 \cdot \pi \cdot m_{X_{gas}} \cdot k_B \cdot T}}$$

Reverse (desorption):

$$k_{TST}^{des} = \frac{k_B \cdot T}{h} \cdot \frac{q_{vib,X_{gas}} \cdot q_{rot,X_{gas}} \cdot q_{trans2D,X_{gas}}}{q_{vib,X}} \cdot \exp\left(\frac{\Delta E_{ads}}{k_B \cdot T}\right)$$

- Surface reaction: $X^* + Y^* \Leftrightarrow Z^*$

$$k_{TST}^{des} = \frac{k_B \cdot T}{h} \cdot \frac{q_{vib}^{\ddagger}}{q_{vib,X^*} \cdot q_{vib,Y^*}} \cdot \exp\left(-\frac{E^{\ddagger}}{k_B \cdot T}\right)$$

See also: https://pubs.acs.org/doi/suppl/10.1021/cs3005709/suppl_file/cs3005709_si_001.pdf

Rate Constants for Particular Elementary Events

- **Important**: for events that contain gas species, the pre-exponential that *Zacros* expects does not involve the partial pressure of the gas species, e.g. for adsorption:

Forward (adsorption): $k_{TST}^{ads} = p_X \cdot \frac{A_{site}}{\sqrt{2 \cdot \pi \cdot m_{X_{gas}} \cdot k_B \cdot T}}$

Pre-exponential factor to be given to *Zacros*. Units of $bar^{-1} \cdot s^{-1}$

Note: for A_{site}, if more than one site is involved in the event we typically sum the areas of the sites involved.

- At **runtime**, *Zacros* multiplies this pre-exponential with the appropriate partial pressure(s), calculated from information given in **`simulation_input.dat`**.

Equations for Quasi-Partition Functions

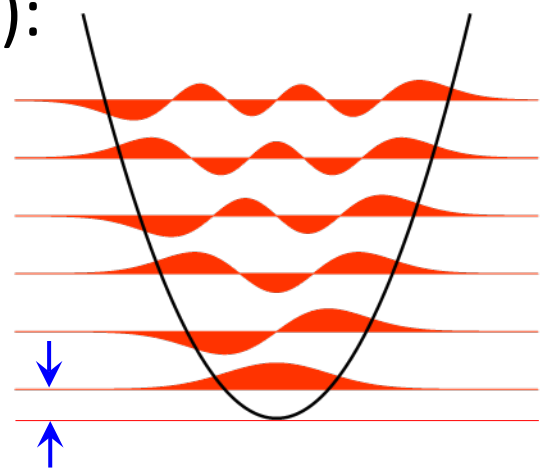
- 2D-translational partition function: $$q_{trans\,2D,X_{gas}} = \frac{2 \cdot \pi \cdot m_{X_{gas}} \cdot k_B \cdot T}{h^2} \cdot A_{site}$$

- Rotational partition function for a linear molecule:

$$q_{rot,X_{gas}} = \frac{T}{\sigma \cdot \theta_{rot,X_{gas}}} \quad \text{where} \quad \theta_{rot,X_{gas}} = \frac{\hbar^2}{2 \cdot I_{X,gas} \cdot k_B}$$

- Vibrational partition function (incl. ZPE):

$$q_{vib,X_{gas}} = \prod_{j=1}^{N_{modes}} \frac{\exp\left(-\frac{h \cdot \nu_j}{2 \cdot k_B \cdot T}\right)}{1 - \exp\left(-\frac{h \cdot \nu_j}{k_B \cdot T}\right)}$$



Raw Data from CO Oxidation Calculations

Gas Species	Vibrational frequencies (cm^{-1})	σ	I ($eV \cdot s^2$)	Mass (amu)
O_2 (g)	2061	2	$1.215 \cdot 10^{-27}$	32
CO (g)	2127	1	$9.093 \cdot 10^{-28}$	28
CO_2 (g)	2347, 1310, 630, 630	2	$4.463 \cdot 10^{-27}$	44

Adsorbed Species	Vibrational frequencies (cm^{-1})
CO Adsorbed on Bridge	1848, 399, 387,374, 197, 51
CO Adsorbed on 4fold	1682, 269, 230, 227, 41, 30
O Adsorbed on Bridge	506, 482, 139
O Adsorbed on 4fold	357, *157i*, *157i*
CO_2 loosely adsorbed	2335, 1309, 617, 600, 56, 41, 32, 19, 12
Transition state (CO-O)	1748, 570, 421, 354, 318, 301, 178, 162, *337i*

- We can use this information to calculate pre-exponentials
- *In view of the imaginary frequencies of* O_{4fold}*, think whether it should be included as a species in the KMC simulation…*

Activity

- Calculate the forward & reverse pre-exponentials of the following 3 reversible elementary events: CO adsorption on a bridge site, O_2 dissociative adsorption on two bridge sites, CO oxidation. Given: T = 900 K, $P_{CO} = P_{O_2} = 0.5$ bar, $P_{CO_2} = 0$ bar, $A_{brg} = 2.57$ Å^2.
- Using the information calculated, create the input file **`mechanism_input.dat`**. For guidance, you can use: the slides of the first tutorial of this workshop, the manual, and the online tutorial: http://zacros.org/tutorials/4-tutorial-1-ziff-gulari-barshad-model-in-zacros
- Complete a *Zacros* simulation for the conditions given. Visualise the results for the CO_2 molecules produced over time, and estimate the turnover frequency.

Physical Constants and Conversion Factors

- **For convenience the following are given:**

- Physical constants: $h = 4.1357 \cdot 10^{-15}\ \mathrm{eV \cdot s}$ $\qquad \hbar = \dfrac{h}{2 \cdot \pi}$

  $k_B = 8.6173 \cdot 10^{-5}\ \mathrm{eV \cdot K^{-1}}$

  $c = 2.9979 \cdot 10^{10}\ \mathrm{cm \cdot s^{-1}}$

- Conversion factors: $1\ \mathrm{amu} = 1.0364 \cdot 10^{-28}\ \mathrm{eV \cdot s^2 \cdot Å^{-2}}$

  $1\ \mathrm{bar} = 6.2415 \cdot 10^{-7}\ \mathrm{eV \cdot Å^{-3}}$

"Converting" wavenumbers (cm^{-1}) to frequencies (s^{-1}) requires multiplying by the speed of light, c.