



NanoSim

NanoSim - A Multi-scale Simulation-Based Design Platform for Cost-Effective CO₂ Capture Processes using Nano-Structured Materials



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3	D3.2	First version of REMARC including tutorial	1	Stefan Andersson Ingeborg-Helene Svenum	SINTEF	Other	PU	30/06/2015	07/08/2015

1 Description

REaction Mechanism And Rate Calculator (REMARC) consists of scripts to calculate rate constants and thermodynamics data and classify corresponding reaction mechanisms from DFT output. It fits rate constants to a convenient functional form and also creates input for running simple kinetics models (coupled rate equations) for further use of the detailed rate constants. The output data can also be used for Kinetic Monte Carlo (KMC) simulations for use and processing the detailed rate constants. An upcoming update will allow for the fit of KMC output rate data to kinetics parameters for overall reactions, *i.e.*, not including intermediate species but only initial reactants and final products.

2 REMARC

2.1 Introduction

REMARC can currently process output from DFT calculations obtained through the Vienna Ab initio Simulation Package (VASP) in addition to vibrational frequencies from VASP or Phonopy. In order to run REMARC the Python (2.6 or higher) and Numpy packages are required.

REMARC contains two scripts, one for extracting VASP output (RMC_vasp) and one for calculating rate constants and thermodynamics data (RMC_rate). In order to run RMC_vasp, the output from the VASP calculations must be organized according to the description below. RMC_rate takes the extracted VASP data and calculates rate constants and thermodynamic data.

2.2 Input/data from DFT calculations

2.2.1 Data retrieved from DFT calculations

REMARC is currently set up to get data from VASP calculations, but can easily be adapted to read data from other DFT software.

The information extracted from the VASP calculations is:

- ◆ system_name – same as the root_directory (see below)
- ◆ total_composition – list the atom species and number of atoms
- ◆ species_name – gives the name of the gas phase or surface species, the composition of the surface/solid system is not included
- ◆ state – gas phase, surface/solid, adsorbed/bulk species name of adsorbed, transition state: initial+final state (this is returned based on the file system layout)
- ◆ site_name – name of adsorption/bulk site/configuration (this is returned based on the file system layout).
- ◆ total_energy – Total energy from the VASP calculation
- ◆ frequency – list of frequencies, can be empty if no frequencies are calculated
- ◆ cell – size of the supercell

- ◆ position – array of atom species and atoms positions
- ◆ info – path to the corresponding OUTCAR/CONTCAR file

In REMARC all information needed from a set of VASP calculations can be extracted automatically. This requires that the directories are set up in a specific pattern as described below. The VASP files needed are the OUTCAR and CONTCAR files. The files must be named OUTCAR and CONTCAR. All VASP calculations must be converged. Currently, the RMC_vasp checks if a calculation has finished. The user must check that the calculations have converged. Calculations that should not be included can either be removed from the directory layout or deleted from the generated text-file.

REMARC can be executed to extract this information to a text file by

> RMC_dft path_to_root_directory [options]

Options: -g: path to directory containing gas phase species, default: root_directory/gasphase
 -o: name of output file: default: output_data_system (where system is surface or solid).

2.2.2 Directory layout for retrieving data from DFT calculations

All the DFT calculations are placed in a root directory. The name of the root directory is freely selectable, for example it can be named according to the materials system of interest, e.g., Fe₂O₃.

Under the root directory there is a subfolder indicating a surface or a solid system. The subfolders must be named 'surface' or 'solid', and both can be present. Under these the surface/solid directories are subfolders describing the "clean" system, in absence of any adsorbates or additional bulk species. The adsorbed/bulk species are placed in directories directly under the surface/solid-directories. In addition transition states are placed under "ts".

The corresponding gas phase species are placed under a directory named "gasphase" and its location is optional. Default is that it is located under the root directory.

Subdirectory setup:

- Isolated/free (gas phase) atoms or molecules
 Isolated/free atoms or molecules are located in a separate subdirectory. The name and location of the directory is selectable. By default it is named 'gasphase' and located under the root directory:

~root_directory/gasphase

The VASP calculation is placed in subdirectories under the 'gasphase'-directory. The name of the subfolders should be given according to the gas phase species calculated. The VASP calculation for an isolated H₂ molecule should be placed in a subdirectory under "gasphase" named "H2".

The following setup is for a surface system, and is placed under the `~root_directory/surface`. The setup will be equivalent for a solid system, which should be placed under `~root_directory/solid`.

- Clean surface

The clean surface, i.e., surface in absence of adsorbates, is located in a separate folder called `surface`, where the VASP calculations are placed directly under the "surface"-directory:

`~root_directory/surface/clean`

- Adsorbed species

For calculation of adsorbed species the calculations are placed in subdirectories referring to the adsorbates of interest. The next subdirectory contains information about the number of adsorbate species on the surface (`nads`), with following subdirectories specifying different adsorption sites (`site`). The name of the site-directory is selectable.

For an adsorbate species present on the surface the VASP calculation files are placed in subdirectories:

`~root_directory/surface/adsorbate/nads/site`

If several adsorbate species are present on the surfaces they can be included by adding a '+' sign between each of the adsorbates and subsequent number of adsorbates:

`~root_directory/surface/adsorbate1+adsorbate2/nads1+nads2/site1+site2`

`Adsorbate1` and `adsorbate2` are the two adsorbate species, `nads1` and `nads2` is the number of `adsorbate1` and `adsorbate2`, respectively. `Site1` and `site2` are the name of the two surface sites or a name of the surface geometry/configuration with `nads1+nads2`. The name of the latter directory is selectable.

- Transition states

Calculations of transition states are placed under the surface directory. The next subdirectory describes the reactants in its initial and final state ("`is-fs`"), and the following subdirectory describes the site/configuration of the initial state and final state.

`~root_directory/surface/ts/is-fs/site1+site2-site3/`

Note that the initial and final state must be present as adsorbed states with the corresponding sites as referred to under the "ts"-directory.

REMARC evaluates transition states calculated by the (CI)-NEB or dimer methods. When using the NEB method, the images are placed in subdirectories starting from 00 to `n-1`, where `n` is the number of images. Only data of the transition state is extracted. Note that REMARC will go through the 00 and `n-1` folders and extract the data from the image having the lowest energy. The user should verify that this is the true transition state.

When the dimer method is used, the VASP calculations are placed under a subdirectory named "dim". If both the dimer and NEB methods are used, the dimer method takes precedence.

NEB: ~root_directory/surface/ts/is-fs/site1+site2-site3/00
 ~root_directory/surface/ts/is-fs/site1+site2-site3/n-1

Dimer: ~/root_directory/surface/ts/is-fs/site1+site2-site3/dim

- Vibrational frequency calculations
 Vibrational frequency calculations are optional. Vibrational frequency calculations calculated using VASP or Phonopy are extracted. The vibrational frequency calculations must be placed in subdirectory of the different directories described above, and it must be named "vib", i.e.

~root_directory/surface/adsorbate/nads/site/vib

2.2.3 Planned future additions to functionality of RMC_vasp

We are considering whether updates of RMC_vasp will be necessary or beneficial. At present no updates are planned.

2.3 Rate constants and thermodynamics

In this section we describe the theory behind and the practical use of the script RMC_rate, which uses the data extracted as outlined above, to calculate the rate constants and thermodynamics of the processes that have been studied. So far only processes at solid surfaces can be treated (see Section 2.3.1). A number of output files are created including rate and thermodynamics data. In particular, the rate constants are fitted to Arrhenius-type expressions giving an analytic expression for their temperature dependence. These are written to CHEMKIN-II and SURFACE CHEMKIN input files, which can be directly used with various kinetics modeling codes, such as for instance SURFACE CHEMKIN, Cantera or DETCHEM. Note that so far only the kinetics parameters are fitted to a functional form. Thermodynamic parameters are not fitted to the calculated thermodynamics and written in CHEMKIN format. This might be a future addition to RMC_rate.

The calculations of thermodynamics and rate constants are nearly completely automatic with only limited interaction needed with the user.

2.3.1 Types of reactions

So far, there are two main types of processes that are treated by RMC_rate:

- Non-dissociative(associative) adsorption (desorption) without a barrier
- Surface reactions between adsorbed species on a solid surface

Note that adsorption should proceed without encountering any energy barrier, as typically found for physisorbed species. Chemisorbed states can also be treated if there is no energy barrier to adsorption.

In future updates of RMC_rate we plan to also include the following types of processes (adding these types of reactions will only require minor additions to the existing script):

- Dissociative(associative) adsorption (desorption)
- Adsorption/desorption with a barrier
- Eley-Rideal reactions between gas-phase and adsorbed species
- Reactions in bulk solids
- Reactions between adsorbed species and a solid surface changing the surface composition
- Reactions between gas-phase species and a solid surface changing the surface composition
- Bimolecular gas-phase reactions
- Diffusion at surface
- Diffusion in bulk

2.3.2 Assumptions

The thermodynamics and kinetics of the involved processes are calculated using standard formulae using the following assumptions and approximations:

- A. ideal gas
- B. volume of solid is independent of gas pressure
- C. volume of solid is independent of temperature
- D. volume of solid is independent of chemical reactions causing a minor change in chemical composition
- E. harmonic approximation for calculating vibrational frequencies (harmonic oscillators and corresponding normal modes)
- F. gas-phase molecules are rigid rotors
- G. rotational temperatures of molecules are small compared to the temperature
- H. barriers for transitions are high enough that transitions are "rare events", meaning that transition state theory (TST) is a good approximation to calculate rate constants
- I. effects of quantum tunneling are negligible
- J. effects of electronically degenerate ground states are neglected
- K. effects of electronically excited states are neglected
- L. a first-order saddle point on the potential energy surface and harmonic expansions of the potential around it is a good approximation to the dividing surface constituting the best possible transition state for rate constant calculations using TST
- M. changes in configurational entropy are negligible

These assumptions can become questionable if:

- ◆ gas pressure is high (A, B)
- ◆ temperature is high (A, C, E, F, H, K, L)
- ◆ temperature is low (G, I)

- ◆ bond-stretching is strongly anharmonic (often important in molecules with several H atoms) (E, L)
- ◆ molecules are "floppy" (E, F, L)
- ◆ weakly bound physisorbed states are important (E, L)
- ◆ gas-phase van der Waals complexes are important (E, F)
- ◆ gas-phase radicals are important (J, K)
- ◆ reactions causing significant change of solid structure are very rapid (D, L, M)
- ◆ surface changes composition or structure in a reaction (M)

2.3.3 Calculation of zero-point energy

To fully describe the energetics of the system at $T = 0$ K, one not only needs to include the electronic energy, E_{el} , as calculated by an electronic structure code, but also the energy arising from the quantum mechanical zero-point motion of the atoms, *i.e.*, in their vibrational ground state. This zero-point energy (ZPE) is calculated as:

$$E_{ZPE} = \sum_{i=1}^{\alpha} \frac{h\nu_i}{2}$$

where α is the number of vibrational frequencies of a system of N atoms, *e.g.*, $\alpha = 3N-5$ for a linear molecule, $\alpha = 3N-6$ for a non-linear molecular and $\alpha = 3N$ for a solid.

2.3.4 Thermodynamics

For each process, changes in internal energy (U), enthalpy (H), entropy (S), and Gibbs free energy (G) are calculated. In addition the zero-point energy (ZPE) is calculated. More details behind the derivation of the different formulae can be found in for instance the book by McQuarrie and Simon¹.

For a temperature $T = 0$ K the following expression fully describes the energetics and thermodynamics of the system (neglecting configurational entropy):

$$U = H = G = E_{el} + E_{ZPE}$$

with E_{el} and E_{ZPE} defined in the previous section. For all temperatures $T > 0$ K expressions for the different quantities are given below.

The internal energy is calculated from electronic and vibrational contributions (and also rotational and translational contributions for gas phase species):

$$U_{solid} = U_{el} + U_{vib}$$

¹ D. A. McQuarrie and J. D. Simon, *Molecular Thermodynamics*, University Science Books, 1999.

$$U_{gas} = U_{el} + U_{vib} + U_{rot} + U_{trans}$$

Enthalpy is calculated according to:

$$H = U + pV$$

where p is gas pressure and V is volume. According to the inherent assumptions discussed in Section 2.3.2 the volume of a solid does not change with higher gas pressure and/or temperature or elementary reactions and the following approximation therefore applies to surfaces and solids undergoing change:

$$pV \approx p'V'$$

Since any corresponding change in enthalpy therefore becomes:

$$H' - H = (U' + p'V') - (U + pV) \approx U' - U$$

we simply set

$$H_{solid} \approx U_{solid}$$

since the solid enthalpy and internal energy only will differ by a constant factor.

For gas phase species, the ideal gas relationships are employed to approximate pV according to the following:

$$pV = nRT$$

where R is the gas constant and T is temperature. By calculating molar quantities, *i.e.*, $n = 1$, one arrives at:

$$pV_m = RT$$

where V_m is molar volume, and gas phase enthalpy is therefore calculated as:

$$H_{gas} = U_{gas} + RT$$

Entropy is calculated by summing up contributions from vibrational contributions (as well as rotational and translational contributions for gas phase species). Electronic contributions are assumed to be zero due to neglect of electronic degeneracies and electronically excited states as discussed in Section 2.3.1. The formulae therefore take the following forms:

$$S_{solid} = S_{vib}$$

and

$$S_{gas} = S_{vib} + S_{rot} + S_{trans}$$

The Gibbs free energy is calculated as:

$$G = H - TS$$

Reaction thermodynamics and equilibrium constants

Generally, the absolute thermodynamic quantities of each system are of limited interest and the interesting information that is obtained is in the form of relative thermodynamic quantities for the reactant (initial) and product (final) state of a reaction and the equilibrium constant of the two states. In addition relative properties of the transition state (TS) and reactants and products are also of interest, in particular the free energy barrier. For the two types of processes we consider, different changes in U , H , S , and G are calculated as given below.

Surface reaction

Reaction energy/enthalpy/entropy/free energy (*reac* and *prod* refer to the reactant and product states, respectively):

$$\Delta U_r = U_{prod} - U_{reac}$$

$$\Delta H_r = H_{prod} - H_{reac}$$

$$\Delta S_r = S_{prod} - S_{reac}$$

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

Equilibrium constant:

$$K_r = e^{-\Delta G_r/RT}$$

Free energy barrier (forward reaction; *TS* refers to the transition state):

$$\Delta U^\ddagger = U_{TS} - U_{reac}$$

$$\Delta H^\ddagger = H_{TS} - H_{reac}$$

$$\Delta S^\ddagger = S_{TS} - S_{reac}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Free energy barrier (reverse reaction):

$$\Delta U^\ddagger = U_{TS} - U_{prod}$$

$$\Delta H^\ddagger = H_{TS} - H_{prod}$$

$$\Delta S^\ddagger = S_{TS} - S_{prod}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Desorption and adsorption

Desorption energy/enthalpy/entropy/free energy (*gas* refers to the gas phase species, *surf* to the clean surface, and *ads* to the species adsorbed at the surface):

$$\Delta U_{des} = U_{gas} + U_{surf} - U_{ads}$$

$$\Delta H_{des} = H_{gas} + H_{surf} - H_{ads}$$

$$\Delta S_{des} = S_{gas} + S_{surf} - S_{ads}$$

$$\Delta G_{des} = \Delta H_{des} - T\Delta S_{des}$$

Equilibrium constant:

$$K_{des} = e^{-\Delta G_{des}/RT}$$

Adsorption energy/enthalpy/entropy/free energy:

$$\Delta U_{ads} = -\Delta U_{des}$$

$$\Delta H_{ads} = -\Delta H_{des}$$

$$\Delta S_{ads} = -\Delta S_{des}$$

$$\Delta G_{ads} = -\Delta G_{des}$$

Equilibrium constant:

$$K_{ads} = K_{des}^{-1}$$

Individual contributions

Electronic degrees of freedom

The internal energy contribution from electronic degrees of freedom is simply the ground state (GS) electronic energy as calculated using any electronic structure code for the stationary point (minimum or saddle point on the potential energy surface) in question. Because of the neglect of excited states no temperature-dependent terms enter into the expression:

$$U_{el} = E_{el,GS}$$

As discussed above any electronic contributions to the entropy are neglected:

$$S_{el} \approx 0$$

Vibrational degrees of freedom

Vibrational contributions to the internal energy are calculated as

$$U_{vib} = R \sum_{j=1}^{\alpha} \left(\frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j} e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}} \right) = R \sum_{j=1}^{\alpha} \left(\frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j}}{e^{\Theta_{vib,j}/T} - 1} \right)$$

where α is the number of vibrational frequencies and $\Theta_{vib,j}$ is the vibrational temperature of vibrational mode j calculated as:

$$\Theta_{vib,j} = \frac{h\nu_j}{k_B}$$

where h is the Planck constant, ν_j is the vibrational frequency of vibrational mode j and k_B is the Boltzmann constant. The number of vibrational frequencies for a system of N atoms is $\alpha = 3N-5$ for a linear molecule, $3N-6$ for a non-linear molecule and $3N$ for a solid. The corresponding contribution to the entropy is:

$$S_{vib} = R \sum_{j=1}^{\alpha} \left[\frac{(\Theta_{vib,j}/T)e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}} - \ln(1 - e^{-\Theta_{vib,j}/T}) \right] = R \sum_{j=1}^{\alpha} \left[\frac{(\Theta_{vib,j}/T)}{e^{\Theta_{vib,j}/T} - 1} - \ln(1 - e^{-\Theta_{vib,j}/T}) \right]$$

Rotational degrees of freedom

For gas-phase molecular species rotational motion gives a contribution to the internal energy as

$$U_{rot} = RT$$

for linear molecules (e.g., CO, CO₂, C₂H₂) and

$$U_{rot} = \frac{3}{2}RT$$

for non-linear molecules (e.g., H₂O, NH₃, CH₄).

The corresponding contribution for a linear molecule to the rotational entropy is:

$$S_{rot} = R(\ln q_{rot} + 1)$$

with the rotational partition function being

$$q_{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2} = \frac{2 I k_B T}{\sigma \hbar^2} = \frac{T}{\sigma \Theta_{rot}}$$

The rotational temperature is defined as

$$\Theta_{rot} = \frac{\hbar^2}{2 I k_B}$$

where I is the moment of inertia of the molecule, \hbar is the Planck constant divided by 2π and the symmetry number σ (number of indistinguishable orientations of the molecule) is 1 or 2 for a linear molecule (e.g., $\sigma = 1$: CO, HCN; $\sigma = 2$: H₂, CO₂, C₂H₂).

For a non-linear molecule the rotational entropy is

$$S_{rot} = R \left(\ln q_{rot} + \frac{3}{2} \right)$$

with the rotational partition function

$$q_{rot} = \frac{(8\pi)^{1/2} (I_A I_B I_C)^{1/2} (k_B T)^{3/2}}{\sigma \hbar^3} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{rot,A} \Theta_{rot,B} \Theta_{rot,C}} \right)^{1/2}$$

where I_A , I_B , and I_C are the three moments of inertia of the molecule and $\Theta_{rot,A}$, $\Theta_{rot,B}$, and $\Theta_{rot,C}$ are the corresponding rotational temperatures, calculated as above.

Translational degrees of freedom

The translational contributions to internal energy and entropy have the same forms for all gas-phase species:

$$U_{trans} = \frac{3}{2} RT$$

and

$$S_{trans} = R \left(\ln q_{trans} + \frac{5}{2} \right)$$

where the translational partition function is

$$q_{trans} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V$$

Here M is the total mass of the gas-phase species and V is the volume of the system. Since V generally is not known or well defined, one can use the ideal gas law to rewrite the expression as

$$q_{trans} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{k_B T}{p}$$

where p is the pressure.

2.3.5 Rate constant calculations

The general expression used for calculating rate constants is taken from standard transition-state theory (TST):

$$k = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^r} e^{-\Delta E/k_B T}$$

where Q^\ddagger and Q^r are the partition functions of the transition state and reactant state, respectively, and ΔE is the electronic energy difference between a transition state and a reactant state.

Surface reactions

For surface reactions the transition state is characterized by a saddle point on the potential energy surface and the reactant state is found at a local minimum. Since electronic contributions to the partition functions are neglected, only vibrational contributions contribute to Q in this case. For more background information see for instance the book by Nørskov et al.²

For the surface reactions we consider three levels of approximation to the TST expression:

1. Total neglect of partition functions, since these are generally more time consuming to calculate than the energy difference between two configurations, the former requiring vibrational frequencies and the latter only optimized geometries and the corresponding electronic energies. The rate constant expression then becomes:

$$k = \nu e^{-\Delta E/k_B T}$$

where the prefactor ν is either set to a default value (10^{13} s^{-1}) or specified by the user.

2. Classical vibrational partition functions calculated from a set of 1-dimensional harmonical oscillators (one for each vibrational mode). The expression is then:

$$k = \frac{\prod_{i=1}^{\alpha} \nu_i^r}{\prod_{i=1}^{\alpha-1} \nu_i^{\ddagger}} e^{-\Delta E/k_B T}$$

where the ν_i are the vibrational frequencies of the reactant state (r) and the transition state (\ddagger). There is one less vibrational frequency for the transition state, since the normal mode frequency corresponding to the unstable mode at the saddle point is imaginary (because of negative curvature of the potential).

3. Quantum vibrational partition functions calculated from a set of 1-dimensional harmonical oscillators (one for each vibrational mode). The expression can be written:

$$k = \frac{k_B T}{h} \frac{\prod_{i=1}^{\alpha} \sinh(h\nu_i^r/2k_B T)}{\prod_{i=1}^{\alpha-1} \sinh(h\nu_i^{\ddagger}/2k_B T)} e^{-\Delta E/k_B T}$$

Note that the vibrational partition functions may be calculated in other equivalent ways as well.

Desorption and adsorption

In the case of desorption, the rate constant expressions become somewhat different. For more details consult for instance the book by Jansen³. The transition state is no longer characterized by a saddle point on the potential energy surface, but it is rather characterized by the desorbing species at a "dividing surface" parallel to and some arbitrary distance away from the solid surface (as far as

² J. K. Nørskov, F. Studt, F. Abild-Pedersen, T. Bligaard, *Fundamental Concepts in Heterogeneous Catalysis*, Wiley, Hoboken NJ, 2014.

³ A. P. J. Jansen, *An Introduction to Kinetic Monte Carlo Simulations of Surface Reactions*, Lecture Notes in Physics 856, Springer, 2012.

there is no longer any interaction between the desorbing species and the surface). The expression for the desorption rate constant becomes:

$$k_{des} = \frac{k_B T}{h} \frac{Q^\ddagger}{Q^r} e^{-\Delta E/k_B T} = \frac{k_B T}{h} \frac{q_{vib,surf} q_{vib,gas} q_{rot} q_{trans}^{2D}}{q_{vib,ads}} e^{-\Delta E/k_B T}$$

$$\Delta E = E_{gas} + E_{surf} - E_{ads}$$

where *surf* refers to the clean surface, *gas* to the desorbing species in gas phase, and *ads* to the adsorbed species and the surface. The rotational partition function is the normal one of the gas species, but since the transition state is a two-dimensional plane in space the translational partition function is that of a particle in two dimensions. This takes the form

$$q_{trans}^{2D} = \frac{2\pi M k_B T A_{site}}{h^2}$$

where *M* is the mass of the desorbing species and *A_{site}* is the average area of all possible adsorption sites of this species at the surface (the number of possible sites has to be provided by the user). The vibrational partition functions are calculated in an analogous way to the ones for the surface reactions described above. If the desorbing species is an atom the vibrational and rotational partition functions of the desorbing species are both set equal to 1.

To calculate the *adsorption* rate constant we employ the adsorption equilibrium constant as described in Section 2.3.4 and the relationship between this and the adsorption and desorption rate constants:

$$K_{ads} = \frac{k_{ads}}{k_{des}}$$

This gives the expression for the adsorption rate constant:

$$k_{ads} = K_{ads} k_{des}$$

An alternative, more approximate, way of calculating the desorption rate constant is to use a fixed prefactor analogous to case 1 for the surface reactions above:

$$k_{des} = \nu e^{-\Delta E/k_B T}$$

This can be useful, not only if vibrational frequency calculations are not available, but for instance also if the solid surface is quite rugged, disordered and/or porous and not easily approximated by a flat surface.

2.3.6 Check for importance of quantum tunneling

Under certain circumstances, mostly in the case of transfer of light atoms at low temperatures, quantum tunneling through an energy barrier might increase the reaction rate considerably

compared to the standard estimates of the rate based on thermal energies above the barrier as described above. For most practical cases it is safe to assume that the effects of tunneling are negligible or at least small, but this is not always true.

If, as in the case of the surface reactions described above, there is a transition state characterized by a saddle point on the potential energy surface, a simple check for the potential importance of quantum tunneling is to calculate the *crossover temperature*, T_c , below which quantum tunneling will dominate in determining the rate constant. The calculation requires that vibrational frequencies have been calculated for the saddle point. Using the imaginary frequency, which corresponds to the unstable mode at the saddle point, the crossover temperature is calculated as:

$$T_c = \frac{\hbar\Omega}{2\pi k_B}$$

where Ω is the magnitude of the imaginary frequency. At T_c the actual rate constant is typically a factor 2 (or slightly more) larger than the one calculated by standard TST. For more background information and alternatives for including estimates of quantum tunneling rates, see the paper by Andersson et al.⁴ (and references therein).

The crossover temperature is calculated automatically by RMC_rate if there are frequencies available for a transition state.

2.3.7 Fit of rate constants to Arrhenius-type expression

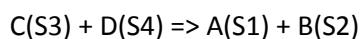
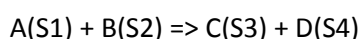
When rate constants have been calculated for a range of temperatures these are fitted to an Arrhenius-type expression, as commonly used for kinetic modelling:

$$k(T) = AT^\beta e^{-E_a/k_B T}$$

where E_a is the *activation energy*.

2.3.8 Information to output files, including CHEMKIN-II and SURFACE CHEMKIN files

Based on the information on chemical species and sites in the input data, reaction mechanisms are calculated automatically from the information on reactants and products and printed as (for surface reactions):



where the text in parentheses are created from first and last characters in the site names, for instance "site1", "site2", "site3", "site4" become "S1", "S2", "S3", "S4". This is the format used in for instance SURFACE CHEMKIN. No check is made that the created site acronyms are unique. Note that forward and reverse reactions are always printed (when available) and are never given in their

⁴S. Andersson, G. Nyman, A. Arnaldsson, U. Manthe, H. Jónsson, 'Comparison of Quantum Dynamics and Quantum Transition State Theory Estimates of the H + CH₄ Reaction Rate', J. Phys. Chem. A, 113 (2009) 4468-4478.

equilibrium form ($A+B \rightleftharpoons C+D$). Gas phase species are given by their chemical name only without any site or state information in parenthesis.

Site densities, as required by for instance SURFACE CHEMKIN, are calculated and printed in units of moles/cm². This requires the user to provide information on the number of sites of a given type per simulation cell.

2.3.9 Planned future additions to functionality of RMC_rate

Additional types of reactions to be added to RMC_rate were mentioned in Section 2.3.1. More detailed planned updates of functionality are detailed below.

Necessary:

- Routines to print out other formats of reaction mechanisms and rate constants, for instance for use in Kinetic Monte Carlo codes
- Fitting of output from Kinetic Monte Carlo codes to overall reaction mechanisms, containing no intermediate surface species but only stable gas phase and solid reactants and products (as required for CHEMKIN-II files)

Optional:

- Fitting of output from other freely available kinetic modelling codes, such as Cantera or Kinetiscope, to overall reaction mechanisms, containing no intermediate surface species but only stable gas phase and solid reactants and products (as required for CHEMKIN-II files)
- Fit of thermodynamics data of intermediate species to standard functional forms for inclusion in CHEMKIN-II and SURFACE CHEMKIN input
- Alternative forms of representing and fitting the temperature-dependence of the rate constants
- Calculation of diffusion coefficients
- Explicit pressure dependence of adsorption rate constants
- Possibility to choose explicit isotopic composition of gas-phase species
- Possibility to include the effects of electronic degeneracies and electronically excited states implicitly (information provided by user)

2.3.10 Input for rate constant and thermodynamics calculations

Thermodynamic data and rate constants are calculated directly using the DFT calculated data placed in the text file generated using RMC_vasp. The user will be prompted with the following when running RMC_rate:

- Start temperature (K)
- End temperature (K)
- Temperature step size (K)
- Typical uncertainty in barrier height (eV)
- Typical uncertainty in adsorption energy (eV)
- Pressure (in atm)
- Use frequencies for rate calculations
- Quantum or classical partition functions for rate calculations

- Use frequencies for clean surfaces

The data can also be placed in a file named remark.in. Example of remark.in file:

```

300.    #T_min (K)
2000.   #T_max (K)
100.    #Delta_T (K)
0.2     #estimated uncertainty in barrier height (electron volts)
0.1     #estimated uncertainty in adsorption energy (electron volts)
1.0     #Gas pressure (atm)
Y       #Should frequencies be used to calculate rate constants? (Y or N)
Y       #Should frequencies be used for clean surface? (Y or N)
Q       #Quantum (Q) or classical (C) vibrational partition functions for rate constant calculations?
1.0E13  #Prefactor for rate constant calculations (s-1) if frequencies are not used
1.0E13  #Prefactor for desorption rate constant calculations (s-1) if frequencies are not used
  
```

In addition the user will be prompted with information about the number of sites of a specific type and the total number of adsorption sites for a given element.

Upon running RMC_rate a set of files will be created:

Chemkin.in	Chemkin file containing information of the overall reaction
SurfaceChemkin.in	Surface chemkin file containing information of the different reaction steps
rate_des.out	Arrhenius parameters and rate constants for adsorption/desorption processes
rate_surf.out	Arrhenius parameters and rate constants for surface reactions
thermo_barrier.out	Thermodynamic data for transition states
thermo_des.out	Thermodynamic data for desorption processes
thermo_reac.out	Thermodynamic data for surface reactions
remark.out	Output information from REMARC

2.4 Example – Running REMARC

This example illustrates the directory layout containing VASP calculation CH₄ interaction on Fe₂O₃-surface. The root directory is Fe2O3. By running RMC_vasp.py -o CH4_Fe2O3, a txt-file named CH4_Fe2O3_surface.txt is created.

Root directory: **Fe2O3**

- Gas phase species
All calculations of relevant gas phase species (such as CH₄, CH₃, H) are placed under the gasphase directory, ie.
Fe2O3/gasphase/CH3/
Fe2O3/gasphase/CH4/
Fe2O3/gasphase/H/

- Clean surface
The calculations for the clean surface are placed under directory:
`Fe2O3/surface/clean`
- Adsorbed species
Calculations of all relevant adsorption states are placed directly under the main directory:
`Fe2O3/surface/CH4/1/site1`
`Fe2O3/surface/CH3+H/1+1/site1+site2`
- Transition states
Transition state of H₂ dissociation on Fe₂O₃ using the dimer method
`Fe2O3/surface/ts/CH4-CH3+H/site1-site1+site2/dim`

Transition state for diffusion of H on Fe₂O₃ using the dimer method
`~/Fe2O3/ts/H-H/1-1/site1-site2/dim`

```

> RMC_vasp.py Fe2O3 -g gaspase -o CH4_Fe2O3

Extracting VASP data from: ../Fe2O3

***** GAS PHASE SPECIES *****

Warning --- No directory with gasphase species found.

***** SYSTEM - surface *****

Checking --- ../Fe2O3/surface/clean
'vib' directory found
WARNING --- 3 imaginary frequencies found
['Fe2O3', 'Fe48O72', 'Fe48O72', 'surface', 'None', -806.91622291]

***** ADSORBATE STRUCTURES *****

Directories containing adsorbed/bulk structures found:
['CH3+H', 'CH4']

Checking --- ../Fe2O3/surface/CH3+H/1+1/site1+site2
'vib' directory found
WARNING --- 3 imaginary frequencies found
['Fe2O3', 'C1H4Fe48O72', 'CH4', 'CH3+H', 'site1+site2', -830.98730485]

Checking --- ../Fe2O3/surface/CH4/1/site1
'vib' directory found
WARNING --- 3 imaginary frequencies found
['Fe2O3', 'C1H4Fe48O72', 'CH4', 'CH4', 'site1', -831.19146894]

***** TRANSITION STATES *****

Directories containing transition states found:
['CH4-CH3+H']

Checking dependencies for transition: CH4-CH3+H
found sites directory for state CH4: ../Fe2O3/surface/CH4/1/site1
found sites directory for state CH3+H: ../Fe2O3/surface/CH3+H/1+1/site1+site2
--- OK

Checking --- ../Fe2O3/surface/ts/CH4-CH3+H/site1-site1+site2/dim
Dimer method - used
'vib' directory found
WARNING --- 4 imaginary frequencies found - is this a true transition state?
['Fe2O3', 'C1H4Fe48O72', 'CH4', 'CH4-CH3+H', 'site1-site1+site2', -830.0677737]

```

The created txt-file (CH4_Fe2O3_surface.txt) is used as input when running RMC_rate.py. Below an example is shown of running RMC_rate.py in the interactive mode, i.e., in absence of the input file remar.in.

```

> RMC_rate.py CH4_Fe2O3_surface.txt
No input file remark.in found!
Interactive mode!
Start temperature (K)?
REMARK>300
End temperature (K)?
REMARK>1000
Temperature step size (K)?
REMARK>100
Typical uncertainty in barrier height (eV)?
REMARK>0.1
Typical uncertainty in adsorption energy (eV)?
REMARK>0.1
Pressure (in atm)?
REMARK>1
Use frequencies for rate calculations? (Y or N)
REMARK>Y
Quantum or classical partition functions for rate calculations?(Q or C)
REMARK>Q
Use frequencies for clean surfaces? (Y or N)
REMARK>Y

=====
SEARCHING FOR ADSORBED SPECIES AND SURFACE REACTIONS
=====

Adsorbed species: CH4 at site site1 at Fe2O3

How many sites of type site1 are there in the simulation cell?
REMARK>4
Area of simulation cell = 90.6564 Angstrom2
Site density = 7.327e-10 moles/cm2

How many adsorption sites for CH4 are there in total
in the simulation cell for surface Fe2O3 (all sites)?
REMARK>4
Average area per adsorption site = 22.6641 Angstrom2
Quantum vibrational partition functions used for desorption and adsorption rate calculation!
Moments of inertia:
  3.2277 amu*Angstrom2
  3.2280 amu*Angstrom2
  3.2287 amu*Angstrom2
Rotational temperatures:
  7.51 K
  7.51 K
  7.51 K
This is a non-linear molecule
What is its symmetry number? Ex. H2O = 2, NH3 = 3, CH4 = 12
REMARK>12

Gas-phase molecular species: get energy and frequency/ies
ZPE = 1.1878 eV

Adsorbed species: get energy and frequencies
All 125 atoms in slab are included in frequency calculation.
Removing 3 lowest frequencies:
5.42790194129j
3.75179511341j
2.56798677785j
ZPE = 8.8092 eV

```

```
Clean surface: get energy and frequencies
All 120 atoms in slab are included in frequency calculation.
Removing 3 lowest frequencies:
4.48272138092j
2.84927320213j
2.3196805537j
ZPE = 7.5964 eV

DeltaE desorption = 0.2331 eV ( 22.49 kJ/mol)
DeltaE desorption incl. ZPE = 0.2081 eV ( 20.08 kJ/mol)
=====

Transition state: CH4-CH3+H at site site1-site1+site2 at Fe2O3
Reactant: CH4 at site site1 at Fe2O3
Product: CH3+H at site site1+site2 at Fe2O3

How many sites of type site2 are there in the simulation cell?
REMARC>4
Area of simulation cell = 90.6564 Angstrom2
Site density = 7.327e-10 moles/cm2

Quantum vibrational partition functions used for rate calculation!

Reactant: get energy and frequencies
All 125 atoms in slab are included in frequency calculation.
Removing 3 lowest frequencies:
5.42790194129j
3.75179511341j
2.56798677785j
ZPE = 8.8092 eV

Product: get energy and frequencies
All 125 atoms in slab are included in frequency calculation.
Removing 3 lowest frequencies:
5.09570902268j
4.39542754503j
2.91763156438j
ZPE = 8.8845 eV

Transition state: get energy and frequencies
All 125 atoms in slab are included in frequency calculation.
Removing 3 lowest frequencies:
27.8989145597j
14.7084304837j
11.8700907205j
Imaginary frequency = 1289.59i cm-1
Crossover temperature for tunneling (Tc) = 295.30 K
ZPE = 8.8351 eV

Barrier height forward = 1.1237 eV ( 108.42 kJ/mol)
Barrier height forward incl. ZPE = 1.1496 eV ( 110.92 kJ/mol)

Barrier height reverse = 0.9195 eV ( 88.72 kJ/mol)
Barrier height reverse incl. ZPE = 0.8702 eV ( 83.96 kJ/mol)

Reaction energy forward = 0.2042 eV ( 19.70 kJ/mol)
Reaction energy forward incl. ZPE = 0.2794 eV ( 26.96 kJ/mol)
=====

=====
DESORPTION AND SURFACE REACTIONS FINISHED
=====
```