

## Surface Chemical Reaction

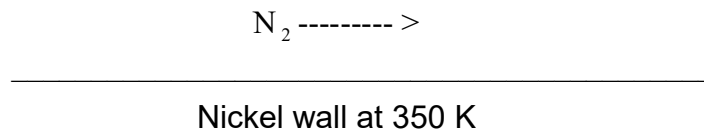
### Theory

Surface chemical reactions occur at a gas-solid, gas-liquid or liquid-solid interface. The detailed mechanism about the reaction procedure is even more complicated than gas phase reaction. Numerically, a phenomenological model is required.

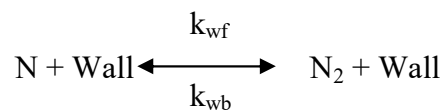
There are two types of surface chemical reactions that are of interest:

- (1) Catalytic reaction;
- (2) Combustion reaction.

The “catalytic reaction” means that the surface (act as catalyst) induces chemical reaction and itself keeps unchanged. For example, consider nitrogen flow passes over a Nickel surface at temperature 350 K.



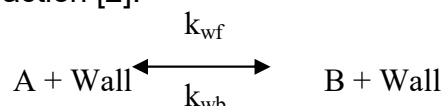
Experiment shows that part of atom N will recombine into molecules  $\text{N}_2$  at the wall [1]:



This reaction is also called an adsorption reaction [6]. Where,  $k_{wf}$  and  $k_{wb}$  are forward and backward reaction rates induced by nickel wall, respectively. Experiments also shows that if a nickel wall is replaced by a copper wall, then  $k_{wf}$  and  $k_{wb}$  will change value for same species. During this reaction procedure, the surface(Nickel wall) will not change anything.

The “Combustion Reaction” is such one that the surface actually participates the chemical reaction. That the oxidizer passes over a solid fuel will induce combustion is an example. In this case, the surface (fuel) will be consumed.

Now, consider a general surface reaction [2]:



The wall may either act only as a catalyst or react with A and B. A and B are chemical species. Phenomenologically, the rate of production of the reactant A per unit area is

$$\dot{\omega}_A = -k_{wf} C_A^{n_A} + k_{wb} C_B^{n_B}$$

Where,  $n_A$  and  $n_B$  are the orders of the forward and backward reaction. At equilibrium state, the above equation gives

$$\frac{k_{wb}}{k_{wf}} = \frac{C_{A,E}^{n_A}}{C_{B,E}^{n_B}}$$

And rate of production becomes

$$\dot{\omega}_A = -k_{wf} \left( C_A^{n_A} - \frac{C_{A,E}^{n_A}}{C_{B,E}^{n_B}} C_B^{n_B} \right)$$

For catalytic reaction,  $k_{wf}$  is usually modeled by introducing catalytic efficiency  $\gamma_w$  [3,4]:

$$k_{wf} = \gamma_w \sqrt{RT / (2\pi m_A)}$$

Where, R is universal gas constant, T, temperature,  $m_A$ , molecule weight of species A.  $\gamma_w$  is given by models. Here are some surface models [1]:

$$k_{wf} = 22 \text{ m/sec for Cr, Ni, Pt, } \quad \gamma_w = 0.10$$

$$k_{wf} = 12 \text{ m/sec for Au, } \quad \gamma_w = 0.056$$

$$k_{wf} = 0.25 \text{ m/sec for SiO}_2, \quad \gamma_w = 0.001$$

For some cases,  $\gamma_w$  is not a constant, but a function of temperature on the wall [4]:

$$\gamma_w = \gamma_0 \exp\left(-\frac{E_w}{RT}\right)$$

Where,  $\gamma_0$  is a constant,  $E_w$  is the activation energy and R universal gas constant. Therefore, the general forward reaction rate is

$$k_{wf} = \gamma_0 \exp\left(-\frac{E_w}{RT}\right) \sqrt{RT / (2\pi m_A)}$$

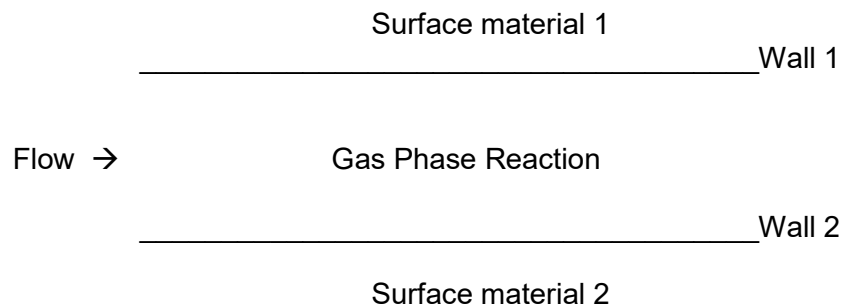
For combustion type reaction,  $k_{wf}$  is still modeled by Arrhenius law[2]:

$$k_{wf} = AT^n \exp\left(-\frac{E_w}{RT}\right) \quad (7)$$

Where,  $E_w$  and A and N are model parameters,  $E_w$  is the activation energy, R, universal gas constant, T, temperature. For the combustion at carbon surface[5], the model constants are:

- |     |               |   |
|-----|---------------|---|
| (1) | Fast Reaction | $A = 3.29 * 10^9 \text{ kg/ [m}^2 \text{ sec]}$<br>$E_w = 44 \text{ kcal/mole}$<br>$n = 0$    |
| (2) | Slow Reaction | $A = 2.18 * 10^5 \text{ kg / [m}^2 \text{ sec]}$<br>$E_w = 42.3 \text{ kcal/mole}$<br>$n = 0$ |

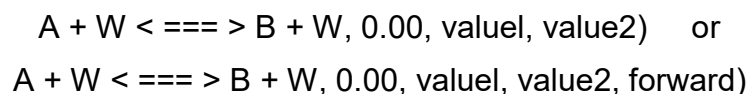
To completely solving the most general chemically reacting flows, which include gas phase reactions and surface reactions, STORM/CFD2000 solves the problem as following:



In this case, different surfaces will induce different surface reactions and also gas phase reaction occurs in incoming flow. This case may require 3 different reaction models.

### Surface Reaction Library

STORM has a surface reaction library, which contains the models of different surface reactions (customization/addition is allowed as well). The reaction step for a catalytic reaction is in the following format:



Where, A, B are species names, W is wall, value1 is the catalytic efficiency constant  $Y_0$ , value2 is the activation energy. Value2 may be zero for a specific model. The “forward” means reaction only proceeds in one direction. If “forward” does not appear, like first reaction, STORM will assume the reaction to be in both directions, forward and backward. This format of reaction step is similar to that in gas phase reactions. However, the meaning of each parameter is different. Here, in the position of A, there is always zero for catalytic type reaction. The following are examples of surface reaction. The keyword “Catalytic” or “Combustion” must be in the last position of the model name.

## References

1. L.A. Anderson, "Effect of Surface Catalytic Activity on Stagnation Heat – Transfer Rate", AIAA J., V. 11, No. 5, p.649, 1973.
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4. H.K. Moffat and K.F. Jensen, "Three – Dimensional Flow Effects in Silicon CVD in Horizontal Reactors", J. of Electrochem. Soc., V.135, No.2,p. 459, 1986.
5. S.M. Scala, IAS paper No. 62-154, 1962.
6. Alexandre Ern, Vincent Giovangigli and Mitchell Smooke", Numerical Study of a Three-Dimensional Chemical Vapor Deposition Reactor with Detailed Chemistry," J. of Computational Physics, V. 126,pp 21-39,1996.