



Parameter Study Facility for Surface Chemistry Analysis

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Summary

This application note describes how the CHEMKIN Parameter Study Facility can be used to investigate the impacts of parameter variations on simulations of surface chemistry automatically.

Introduction

The science of surface chemistry has undergone rapid development in recent years, and there is a trend towards use of more detailed “microkinetic” models, especially in the field of catalysis. However, compared with gas-phase combustion problems, surface reaction mechanisms often contain larger uncertainties in reaction-rate coefficients that must often be estimated by semi-empirical methods. For this reason, and because there are variations in the catalyst properties, it is often necessary to adjust kinetic parameters to model a specific catalytic system. Thus it is of interest to see how uncertainties that exist in surface mechanisms affect predicted modeling results. Performing a parameter study, which varies reaction-rate parameters for key reactions in the system, is one way to analyze these effects.

In this application note, we apply a parameter study to investigate the effects of one reaction-rate coefficient for a simulation involving catalytic oxidation of methane on a platinum catalyst. For the gas-phase kinetics, we employ the GRI gas-phase chemistry set, including reactions and thermodynamic data for homogeneous methane combustion. For the catalytic surface-chemistry that describes the oxidation of methane on a platinum catalyst, we use the surface chemistry mechanism reported by Chou, et al.¹ In this example’s reactor model, we focus on the first stage (Honeycomb Catalytic Reactor) of the Two-stage Catalytic Combustor Sample.

Determining Influential Reactions with Sensitivity Analysis

We first intend to identify those surface reactions that will be the most influential to our output parameters of interest for the conditions in this sample. Since this is a catalytic combustion case, where the catalytic stage serves to preheat the gas, the reactor temperature is of interest. We therefore first run a sensitivity analysis in order to determine the sensitivity of Temperature to the Arrhenius pre-exponential factors (A-factors) of the various reaction-rate constants. In order to accomplish this, first open the *honeycomb_monolith_reaction_rate_param_study.ckprj* project from the CHEMKIN samples45 directory then and pre-process the chemistry set. Then look at the nominal case, which is

¹ C.-P. Chou, J.-Y. Chen, G. H. Evans and W. S. Winters, *Combustion Science and Technology*, **150**:27 (2000).

set up in the Reactor and Inlet panels and which can be run from the Run Model node on the project tree.

Follow the steps below to run the sensitivity analysis.

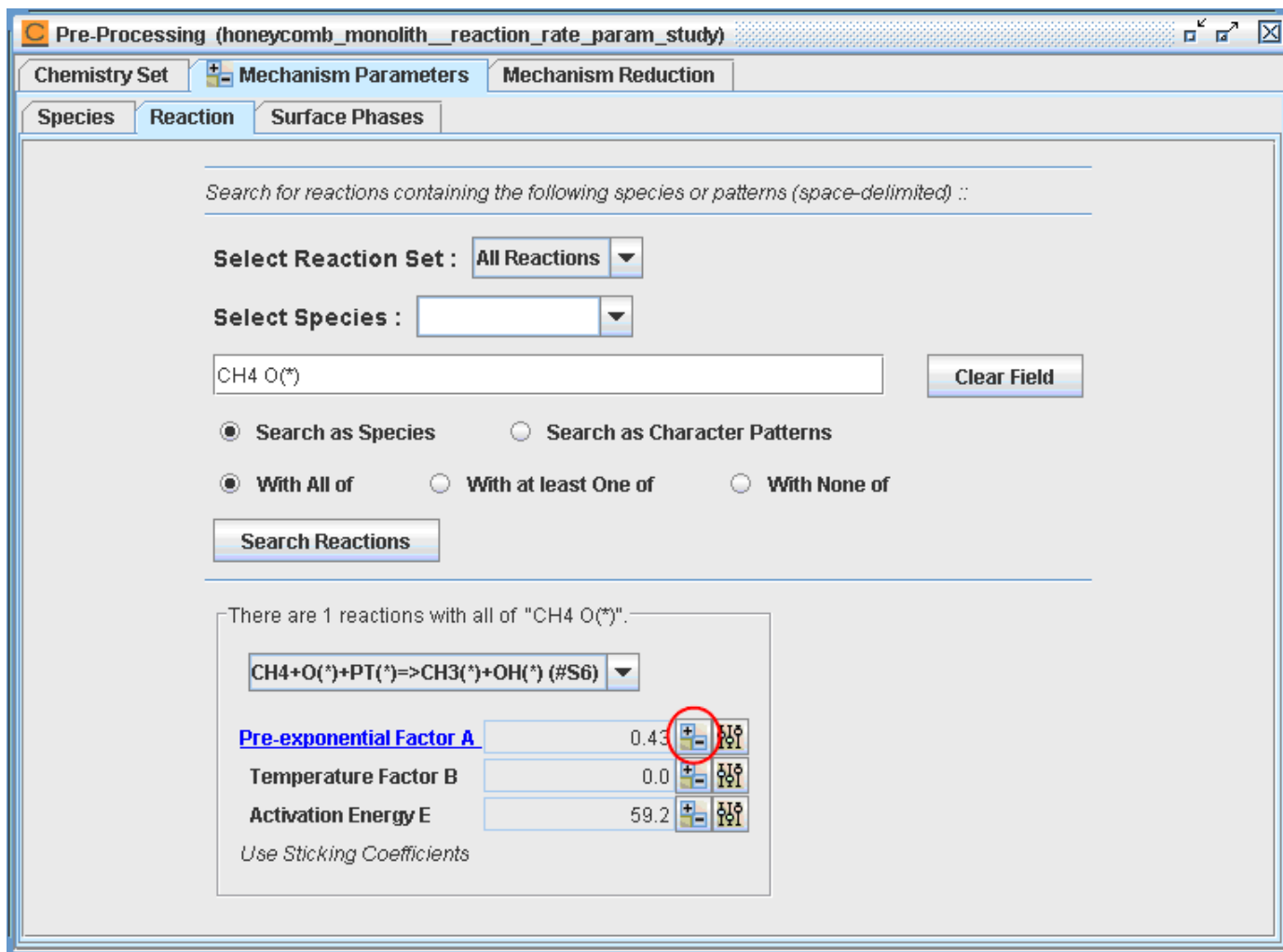
1. Double-click on the Output Control in the Open Projects tree.
2. To select the sensitivity analysis, on the Output Control tab under the Basic tab, select **Temperature A-factor Sensitivity**.
3. Begin the analysis by opening the Run Calculations panel. Then select **Model** and click **Begin**.
3. Once the run has completed successfully, click **Analyze Results** in the Project Tree and click **Next Step** on the Analyze Results panel.
5. On the Select Post-Processing Variables panel, click **Sens**. Check the box next to **Temperature**, and then click **Process Solution Data**.
6. In the Post-Processor control panel, use the Plot Set pull-down menu to select **sensitivity for solution no1**.
7. Select: **Distance** for the **X Variable** and all of the surface reaction sensitivities that are listed as Y variables.
8. Click **Display Plot**.

From the plot results, you should see that Surface reactions #1, $O_2 + 2PT(*) \rightarrow O(*) + O(*)$ and #6, $(CH_4 + O(*) + PT(*) \rightarrow CH_3(*) + OH(*)$), are particularly important in determining the resulting temperature. In the case of both of these reactions, the A-factors are actually sticking coefficients as indicated by the keyword `STICK` in the surface-chemistry file. This means that the A-factors represent the probability that the reaction occurs, relative to the collision frequency between the gas molecule and the surface-site on the left-hand-side of the reaction.

Using the Parameter Study Feature

It is now of interest to vary the sticking coefficients for these rates one by one, and see how such variations will affect predicted temperature profiles in the reactor. A Parameter Study has already been set up to do this in the *honeycomb_monolith_reaction_rate_param_study.ckprj* project. To see how this is done, go to the Mechanism Parameters tab in the Pre-processing panel. On the Reaction sub-tab, select COMBUST (which is the name of our surface material, so we're selecting reactions related to this material only) from the pull-down menu of the Select Reaction Set and click on the Search Reactions button. The first reaction to show up in the pull-down window under the Search Reactions button is highlighted in blue, indicating that a parameter study has been set up for this reaction rate constant. Click on the **Setup Parameter Study** button next to the Pre-exponential Factor "A" value for this reaction to view the Parameter Study Setup.

Figure 1 Setting up a Parameter Study for Sticking Coefficients vs. Predicted Temperature Profiles

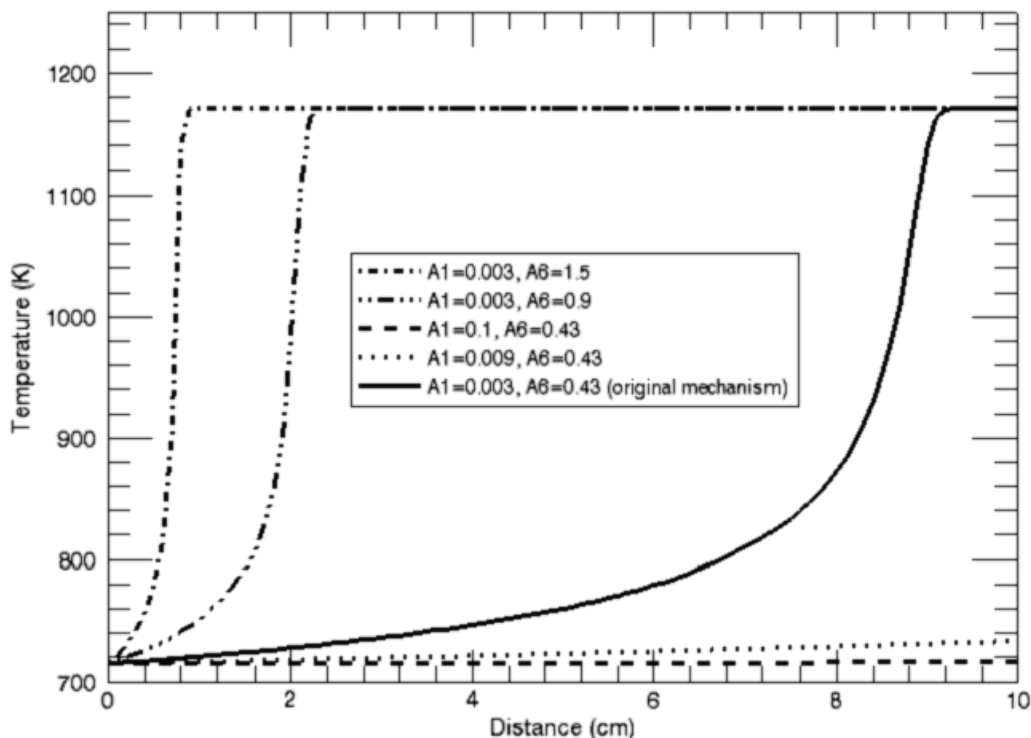


Viewing Results with the Post-Processor

Run the Parameter Study by selecting all of the runs in the Run Parameter Study window and clicking the **Post-Process** button. Once in the Post-Processor control panel, select Line Plot for Plot Type. Under Plot Set, select Solution no 1. Ctrl-click all of the temperature profiles for each of the Parameter Study runs as the Y Variables. Click on Display Plot.

Figure 2 demonstrates the results of the Parameter Study displayed by the CHEMKINpost-processor. The results clearly indicate that if we keep the sticking coefficient of reaction 1 constant, and increase the sticking coefficient for reaction 6, the ignition occurs much sooner and the maximum combustion temperature is reached almost as soon as the reactants enter the catalytic reactor. This makes sense, because reaction 6, $\text{CH}_4 + \text{O}^* + \text{PT}^* \rightarrow \text{CH}_3^* + \text{OH}^*$, is a branching reaction that liberates radicals CH_3 and OH , thus rapidly increasing the radical pool that in turn is responsible for catalytic light-off. On the other hand, increasing the sticking probability of the $\text{O}_2 + 2\text{PT}^* \rightarrow \text{O}^* + \text{O}^*$ reaction delays ignition, probably because it is competing with the adsorption of CH_4 on open sites.

Figure 2 Varying Rate Constants of Reactions 1 and 6



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