GSI Modeling Overview: Requirements for Macroscopic Gas/Surface Interaction Coupling to CFD Codes

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An overview is presented of a generalized finite-rate surface chemistry model that has been developed for gas/surface interaction coupling to the Data-Parallel Line-Relaxation (DPLR) code. Species from the gaseous environment are allowed to interact with species adsorbed onto one or more phase of a surface and with one or more phases of a bulk thermal protection system through an arbitrary number of finite-rate reactions. The reactions may include types such as adsorption, desorption, Eley-Rideal recombination, Langmuir-Hinschelwood recombination, partial or total dissociative adsorption, oxidation, reduction, sublimation, or condensation where forward and reverse rates are constrained by thermodynamics. A simple pyrolysis model is incorporated into the gas species mass balance and energy balance boundary conditions where the pyrolysis production may be specified explicitly from an uncoupled material response analysis or assumed steady-state proportionality to the bulk phase ejection rate. The production rates of all gaseous species are implicitly coupled into the viscous wall boundary condition of the DPLR code to maximize the convergence rate of the solver. Examples are shown for a catalysis system and a TPS system to demonstrate the model. The focus of the work presented is primarily to demonstrate the necessary model, reaction, surface, and material data required.

II. Gas/Surface Interactions (GSI) and Catalysis

Model Parameter	Parameter List / Options / Needs
Allowed GSI phases	One gas phase, multiple surface phases (multiple sets of active sites in each, multiple bulk (TPS) phases)
Types of allowed reactions	(1) Adsorption/desorption, (2) Eley-Rideal/ partial dissociative adsorption, (3) Langmuir-Hinshelwood/dissociative adsorption, (4) Oxidation/reduction, (5) Sublimation/condensation
Surface reaction data	Forward rate coefficient for each surface reaction
Thermodynamic data	Gibbs energy curve fits for each gas and bulk species; specified equilibrium constant or desorption rate for each adsorbed species
Surface phase data	Surface fraction for each surface phase; active site density (in mol/m^2) for each active site set in each surface phase
Bulk phase data	Volume fraction, mass density, and porosity for each bulk phase; species composition of each bulk phase
Pyrolysis data	Specified pyrolysis gas mass flow rates and species composition
Number of surface phases &area fractions	Reflect the composition and microstructure of TPS :manufacturing info and microscopy
Number of active site sets/phase	More than one type of surface site required to model important reactions?
Active site density of each set	Should reflect atomic-scale structure of surface: (x-ray diffraction, Leed/Rheed, Raman, Auger, STM/AFM, etc.) Should reflect expected species-surface interactions: (UHV surface science experiments and ab initio chemistry calculations)
Number of bulk phases &volume fractions	Reflect the composition and microstructure of TPS : (manufacturing info, microscopy)
Species and composition in each phase	Chemical composition of TPS constituents: (manufacturing info, chemical analysis)
Mass density and porosity	Physical measurements: weight, volume, density, porosimetry

Reactions
Adsorption/Desorption Sticking coefficients Energy Barriers Adsorption and desorption
Arrhenius Reactions Pre-exponentials Energy barriers
Kinetic Reactions Sticking Coefficients Sublimation Coefficients Reaction Efficiencies Energy barriers Surface Diffusion Recombination and desorption Condensation and sublimation

Sources
Chemical literature: • Bond strengths • Dissociation energies • Reaction mechanisms Experiments: • Adsorption Isotherms (BET) • Temperature-Programmed Desorption (TPD) • Molecular beam experiments • Flow tube/diffusion reactors Simulations: • Density-functional theory • Kinetic Monte-Carlo • Others