Sensitivity Tests on the Uncertainties of Thermodynamic Properties

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Sensitivity Test Objectives

Calculate the level of sensitivity of thermodynamic properties on the concentration of combustion pollutants using detailed mechanisms

Method:

Establish "Sensitivity Coefficient" to use in calculating thermodynamic properties

Rank the species to indicate their importance in observed flame property

What is sensitivity?

Sensitivity is the impact of parameters variation on calculated properties. For the system of equations in chemical kinetics simulations (ϕ is the solution vector, α is the parameter vector):

$$F(\phi,\ \alpha) = 0$$

$$\phi = (T_1, Y_{1,1}, \ldots, Y_{K,1}, \ldots, T_J, Y_{1,J}, \ldots, Y_{K,J}, \dot{m})^T$$

$$\alpha = (\text{kinetic, thermodynamic, species transport parameters})$$

Differentiating with respect to α we obtain $\frac{\delta F}{\delta \phi}\frac{\delta \phi}{\delta \alpha} + \frac{\delta F}{\delta \alpha} = 0$, where $S'_\alpha \equiv \frac{\delta \phi_K}{\delta \alpha_i}$ is the sensitivity coefficient - measure of system's response to parameter change

- Thermodynamic Sensitivity: Impact of uncertainties in thermodynamic properties on flame properties, as:
  - species concentration
  - flame speed
  - ignition delay

Approach:

- Introduce a "thermodynamic sensitivity coefficient" through appropriate weight factor, to be able to evaluate the influence of thermodynamic uncertainties to flame simulations

Thermodynamics influences the reaction rates through the equilibrium constant:

$$K_{p,i} = \exp^{\frac{-\Delta G\ i}{RT}} = \frac{k_{f,i}(T)}{k_{b,i}(T)} \qquad \Delta G_i = \Delta H_i - T\Delta S_i$$

We can introduce single "thermodynamic weight" factor to augment all thermodynamic properties:

$$\frac{c_p^{0*}}{R} = w_T \frac{c_p^0}{R} = w_T \left(a_1 T^{\ 2} + a_2 T^{\ 1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4\right)$$

$$s^{0*} = \frac{c_p^{0*}}{T} dT = w_T s^0$$

$$h^{0*} = c^*_p\, dT = w_T\, c_P dT = w_T h^0$$

$$\rightarrow \quad k_{b,i} = k_{f,i} \cdot \exp^{\frac{w_{T,i}\,\Delta G_i}{RT}}$$

We now define "thermodynamic sensitivity coefficient" as:

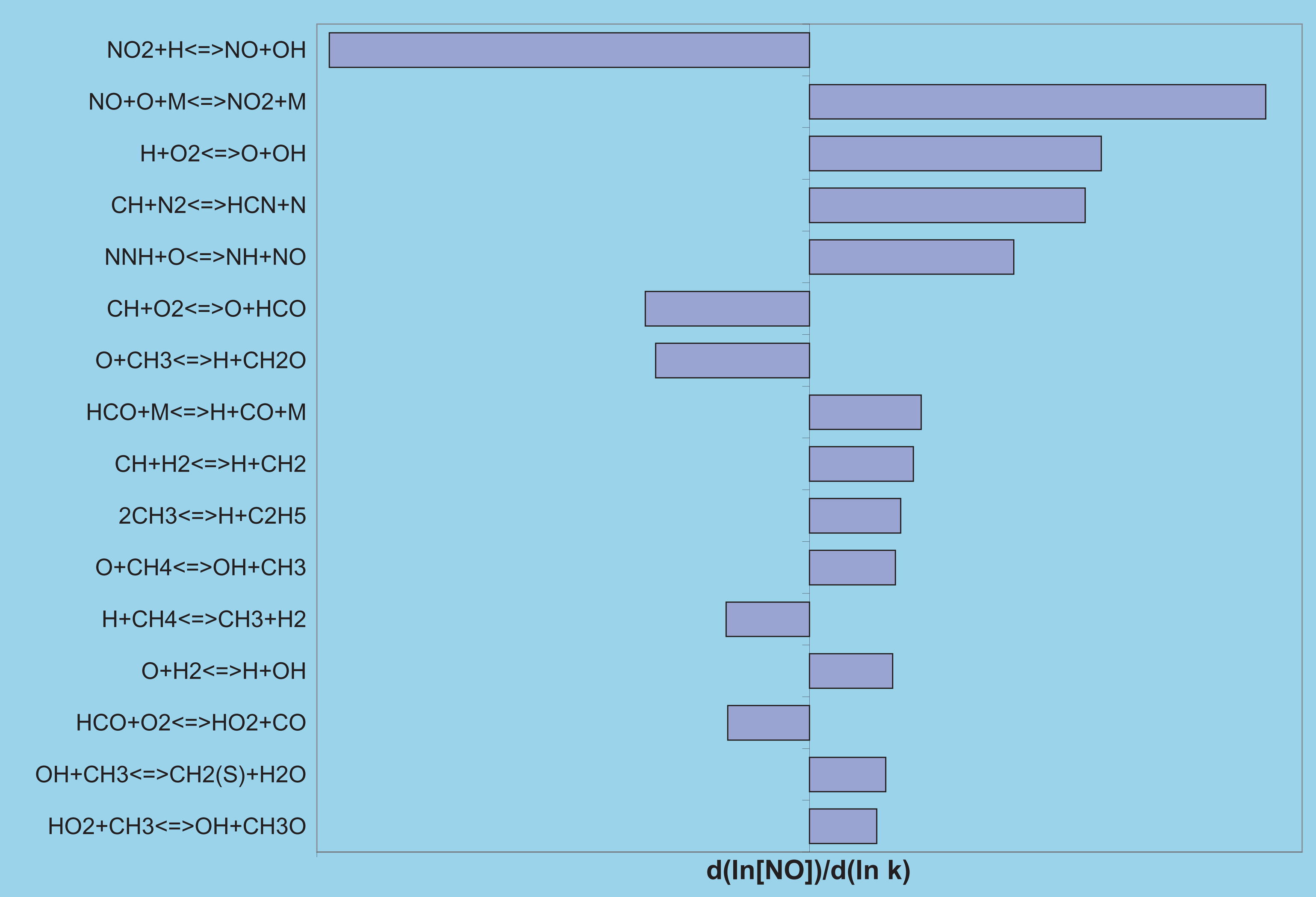
$$S_T = \frac{\partial Y_k}{\partial w_{T,i}}$$

Application:

- Measure the effect of the uncertainties in thermodynamic properties on modeling the pollutants formation from gas-fired furnaces

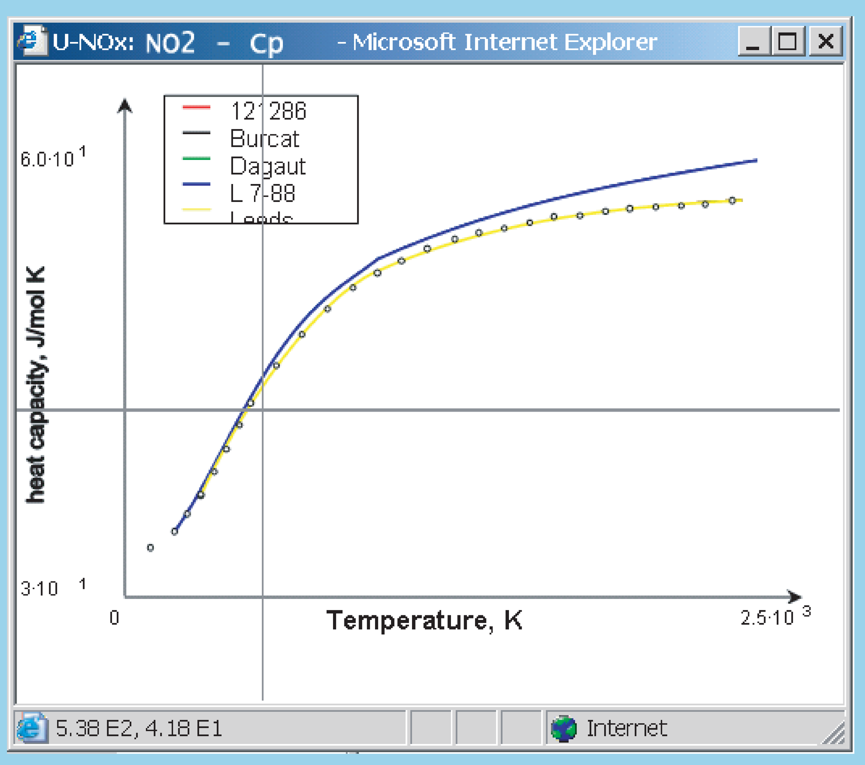
Thermodynamic sensitivity is implemented in CkemKin II simulation software in Senkin, Premix, PSR, OppDiff and Equil modules.

Traditional sensitivity analysis reveals which chemical reactions are the most influential for observed flame property, in this case NO concentration. Sensitivity analysis was performed for lean oxidation of simplified natural gas in plug flow reactor at 1900 K and 1 atm. Sensitivity is shown for the point in the reactor where prompt NO formation peaked.



The sensitivity analysis indicates that NO concentration at this point is most sensitive to NO conversion to NO2. While the uncertainty in that rate coefficient may effect simulation accuracy, the source of uncertainty does not have to be the rate coefficient itself.

The analysis of available thermodynamic data reveals uncertainty for NO2 especially pronounced at high temperatures.



As shown, this uncertainty propagates through Gibbs energy and equilibrium constant, thus impacts the net rate of the reaction most that has the highest effect on NO emissions.

Concluding remarks

Uncertainties in values of thermodynamic properties affect Gibbs energy and consequently the reaction rate coefficients. That in turn impacts all calculated flame properties.

High level theoretical calculations can be used to obtain more accurate thermodynamic values. Although it is a costly and time consuming process, it will be performed only on species identified by thermodynamic sensitivity analysis

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