General Approach to Equilibrium and Numerical Methods

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General Approach to Chemical Equilibrium

The following approach is used in most computer codes.

Start by minimizing the Gibbs function:

$$dG = -SdT + VdP + \sum_j \mu_j dN_j = 0$$

Since T and P constant, we have

$$\sum_j \mu_j dN_j = 0$$

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This minimization is subject to the constraint that atoms are conserved

$$p_k = \sum_j^a n_{kj} N_j$$

where p_k is the number of k type atoms in the mixture. a is the number of types of atoms and n_{kj} is the number of k type atoms in j type molecules.

The equilibrium problem is solved using the method of undetermined multipliers. Set dp_k to zero, multiply by λ_j and add to dG. Then

$$\sum_j (\mu_j - \sum_k^a \lambda_k n_{kj}) dN_j = 0$$

For this to be satisfied, each term must be zero, so that

$$\mu_j - \sum_k^a \lambda_k n_{kj} = 0$$

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For a perfect gas

$$\mu_j(T,P_j) = \bar{g}_j(T,P_j) = \bar{g}_j(T,P) + R_u T \ln(P_j / P)$$

Therefore, noting $x_j = P_j / P$

$$x_j = \exp(-(\bar{g}_j(T,P) - \sum_k^a \lambda_k n_{kj}) / R_u T$$

Plugging this into atom conservation, we get

$$p_k = P \exp(-(\bar{g}_j(T,P) - \sum_k^a \lambda_k n_{kj}) / R_u T$$

If we sum these over all species, we get

$$1 = \sum_j \exp(-(\bar{g}_j(T,P) - \sum_k^a \lambda_k n_{kj}) / R_u T$$

These provide a+1 equations for the λ_k's and N_{tot}.

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In all these programs, thermodynamic data are stored as polynomials

$$\frac{C_{pk}^0}{R} = a_{1k} + a_{2k}T_k + a_{3k}T_k^2 + a_{4k}T_k^3 + a_{5k}T_k^4$$

$$\frac{H_k^0}{RT_k} = a_{1k} + \frac{a_{2k}}{2}T_k + \frac{a_{3k}}{3}T_k^2 + \frac{a_{4k}}{4}T_k^3 + \frac{a_{5k}}{5}T_k^4 + \frac{a_{6k}}{6}T_k^5$$

$$\frac{S_k^0}{RT_k} = a_{1k}\ln T_k + a_{2k}T_k + \frac{a_{3k}}{2}T_k^2 + \frac{a_{4k}}{3}T_k^3 + \frac{a_{5k}}{4}T_k^4 + a_{7k}$$

The polynomials are given over two temperature ranges.

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The Polynomials

```
species(name='C2H6',
      atoms='C:2 H:6',
      thermo=(NASA([300.00, 1800.00],
                [-2.41778723E-01,  2.53475709E-02, -1.39645112E-05,
                  4.03257452E-09, -4.87754387E-13, -1.10391121E+04,
                  2.19572625E+01]),
              NASA([1800.00, 3500.00],
                [ 4.07959141E+00,  1.57445262E-02, -5.96197393E-06,
                  1.06867182E-09, -7.61012341E-14, -1.25948053E+04,
                 -1.43089411E+00])),
      transport=gas_transport(geom='nonlinear',
                              diam=4.35,
                              well_depth=247.5,
                              rot_relax=1.5))
```

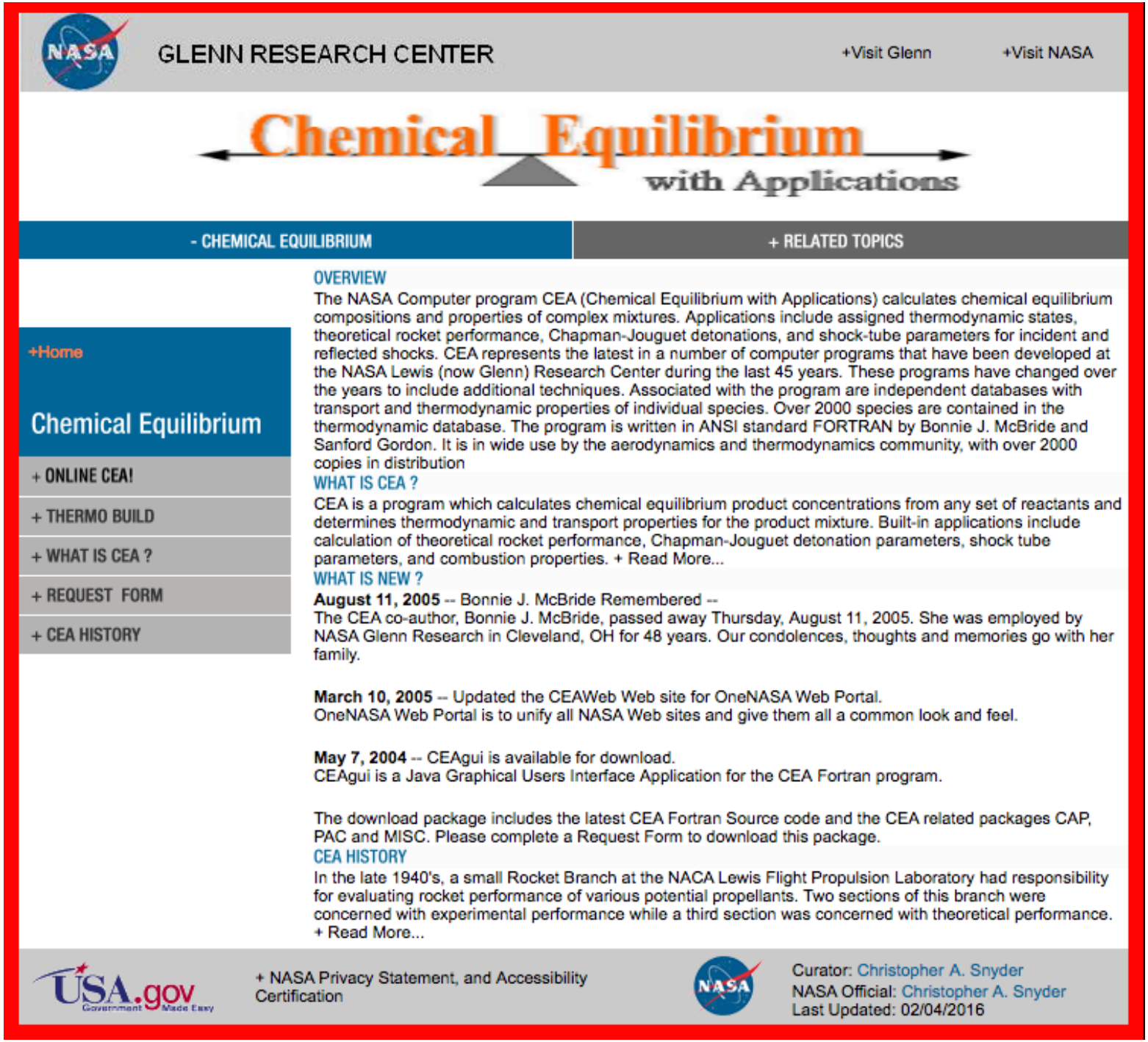
This is the format for Cantera and includes transport coefficient information (more on that later)

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Equilibrium Software

- NASA Lewis Code (Free, Now comes with GUI)
  - http://www.grc.nasa.gov/WWW/CEAWeb/
- Cantera
  - https://cantera.org
- CHEMKIN ($$$)
  - www.ansys.com

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Cantera is an open-source suite of tools for problems involving chemical kinetics, thermodynamics, and transport processes.

Automation

Cantera automates the chemical kinetic, thermodynamic, and transport calculations so that the users can efficiently incorporate detailed chemical thermo-kinetics and transport models into their calculations.

Object-Oriented

Cantera utilizes object-oriented concepts for robust yet flexible phase models, and algorithms are generalized so that users can explore different phase models with minimal changes to their overall code.

Multiple Interfaces

Cantera can be used from Python and Matlab, or in applications written in C/C++ and Fortran 90.

Broad Applications

Cantera is currently used for applications including combustion, detonations, electrochemical energy conversion and storage, fuel cells, batteries, aqueous electrolyte solutions, plasmas, and thin film deposition.

Tutorials

New? Start here!

The tutorials linked below will get you started using Cantera on your own machine.

Python Matlab Convert Input Files

Open Binder

Try Cantera in your Browser!

Cantera can be used online in Jupyter Notebooks via the Binder service! Try it out now!

launch binder

Examples

What can Cantera do?

We have a number of examples demonstrating the use of Cantera in some of our interfaces.

Python Matlab Jupyter Notebook

Installing & Compiling

Instructions to install pre-built Cantera binaries or to build Cantera from the source

Science

A description of the equations that Cantera solves, including equations of state, energy and mass conservation, and chemical kinetics.

Documentation

Documentation for the classes and functions that make up Cantera.

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```
# Demo Cantera Equilibrium

import cantera as ct
import numpy as np

# Set the
gas1 = ct.Solution('gri30.xml')

# Set state
gas1.TP = 2500, 101325

# Set initial composition
gas1.X = 'CH4:1, O2:2, N2:7.52'

# Output equilibrium state
gas1.equilibrate('TP')
gas1()
```


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