Creating Phase and Interface Models

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Every Cantera simulation involves one or more phases of matter

Phases and interfaces involved in a hypothetical solid-oxide fuel cell simulation

**phases:**
- metal catalysts (2)
- electrolyte
- gas phases (2)

**interfaces:**
- electrolyte/metal (2)
- metal/gas (2)
- electrolyte/gas (2)
- triple phase boundaries (2)

5 phases and 8 interfaces!

(of course, many problems may only involve 1 phase, or 1 phase + 1 interface)
Properties of each phase and/or interface are needed

- **Composition**
  - elements and species
  - atomic and molecular weights
  - mole fractions, mass fractions, concentrations

- **Thermodynamic properties**
  - Temperature, pressure, density
  - internal energy, enthalpy, entropy, Gibbs free energy, ...
  - heat capacities, thermal expansion coefficients, compressibilities, ...

- **Transport properties**
  - Viscosity, diffusion coefficients, thermal conductivity, electrical conductivity, ...

- **Kinetics**
  - reaction stoichiometry
  - rates of progress
  - equilibrium constants
  - species production rates
Phase Models

- Specification of chemical composition
  - elements
  - species, and their elemental composition

- Specification of reaction stoichiometry

- Complete set of algebraic equations to compute all required
  - thermo properties
  - transport properties
  - reaction rates

- Numerical values for all parameters in the equations

- Phase models incorporate sub-models
  - Thermo model
  - Transport model
  - Kinetics model
Interface Models

- Specification of the phase(s) adjacent to the interface
- Specification of chemical composition of interfacial species, if any
- Specification of reaction stoichiometry for heterogeneous reactions involving bulk species in any adjacent phase and/or interfacial species
- Complete set of algebraic equations to compute all required
  - thermo properties
  - transport properties (not yet implemented)
  - reaction rates
- Numerical values for all parameters in the equations
Phase and interface models are specified in text files

- Files that can be edited with any text editor, shared, e-mailed, etc.

- Separates phase and interface definition from the simulation itself; allows re-using same phase and interface models for many different applications

- Multiple phases and/or interfaces can be specified in one file

- Species and reaction definitions can be imported from other input files
CTI and CTML files

- The files described here will be called 'CTI' files because they have the default extension '.cti' (CanTera Input)
- These files are designed to be easy for people to write and read
- They are hard for machines to read, however, since they assume chemical knowledge (most) machines don't have (e.g. how to interpret a chemical equation)
CTML

- XML is a widely-used meta-language for data
  - designed to be easy for machines to parse
  - "dumbed down": in good XML code, nothing is assumed, everything is stated explicitly
  - too verbose for direct human writing or reading
  - good as an intermediate format designed for machine use
  - many browsers, validating parsers, editors, etc. developed for XML

- Cantera defines its own XML-based markup language called CTML
  - designed to represent quantities needed by Cantera (rate coefficients, etc.) in XML
  - borrows some features from CML (Chemical Markup Language)
  - as other XML standards develop for kinetics, CTML may evolve for compatibility
The CTI to CTML preprocessor

- CTI files are designed to be written and read by humans

- When a CTI file is specified as an input file in Cantera, it is converted on-the-fly to CTML, and then the CTML is parsed

- The conversion process is done automatically by invoking the Python interpreter

- a single Python script called `ctml_writer.py` is used. The full Cantera Python interface does not need to be installed to process CTI files.

- CTI files are actually executable Python scripts, and may include any valid Python code
Phases and Interfaces

- Most Cantera simulations require properties of at least one phase of matter
  - For combustion simulations, this is often a reacting ideal gas mixture
  - But solid or liquid phases may also be required

- For heterogeneous combustion problems, properties of the interfaces between phases are also needed
Input File Formats

- A widely-used file format for combustion problems is the one used with the Chemkin software package.

- But this format is inconvenient for several reasons:
  - Not extensible - no way to add additional parameters for non-ideal phases
  - Only supports one species thermo parameterization (NASA polynomials)
  - Thermo data format is holdover from punched-card era; fixed-column format prone to errors
The Cantera input file format is designed to be...

- free format
- intuitive to write
- clear and understandable to read
- extensible
Directives and Entries

- CTI files consist of two types of elements:
  - **entries** specify a phase, interface, element, species, or reaction
  - **directives** set options determining how entries will be processed

- Both have a function-like syntax:

  - `<name>( <keyword1> = <value1>, <keyword2> = <value2>, ... )`

- Example: the units directive fields (keyword/value pairs) may appear in any order

```plaintext
units(length = "cm", time = "s", quantity = "mol",
      act_energy = "cal/mol")
```
Setting the Default Units for Input

- Default Cantera unit system is SI (meters, seconds, kmol, Joules/kmol)

- This is often *not* the most convenient system for input

- Any desired unit system may be specified with the `units` directive

- Input values will be converted to SI when they are read in

- Good practice to set the unit system at the top of the file

```plaintext
units(length = "cm", time = "s", quantity = "mol",
      act_energy = "cal/mol")
```
A simple phase: argon gas

The `ideal_gas` entry is used to define a phase that obeys the ideal gas law

The phase definition listed above states that:
- Only element Ar may be present
- Only one species, named ‘AR’, may be present
- The object state should be initially set to $T = 300$ K, $P = 1$ atm.
The Element Database

- Element attributes (the atomic weight) are looked up by symbol in database file ‘elements.xml’

- Database file contains elements of the periodic table with natural abundance atomic weights

- Isotopes D and Tr also included

- Also contains an element ‘E’ representing an electron, to use in specifying the composition of charged species

```
<xml>
  <elements caseSensitive="no">
    <element atomiC=1 name="H" atomicWt="1.00794"/>
    <element atomiC=2 name="D" atomicWt="2.0147"/>
    <element atomiC=3 name="Tr" atomicWt="3.016327"/>
    <element atomiC=4 name="He" atomicWt="4.002602"/>
    <element atomiC=5 name="Li" atomicWt="6.941"/>
    <element atomiC=6 name="Be" atomicWt="9.012182"/>
    <element atomiC=7 name="B" atomicWt="10.811"/>
    <element atomiC=8 name="C" atomicWt="12.011"/>
    <element atomiC=9 name="N" atomicWt="14.00674"/>
    <element atomiC=10 name="O" atomicWt="15.9994"/>
    <element atomiC=11 name="F" atomicWt="18.9984032"/>
    <element atomiC=12 name="Ne" atomicWt="20.1797"/>
  </elements>
```

initial part of elements.xml
Defining Species ‘AR’

- The argon gas phase definition references a species ‘AR’
- This species needs to be defined somewhere in the input file
- Order (before or after the phase entry) doesn’t matter, because the entire file is read before the entries are processed
- A minimal definition of species ‘AR’ is shown here, that specifies only the elemental composition
The complete input file (so far)

This simple input file constitutes a valid definition of an argon ideal gas (although not one that much can be done with yet).

```python
units(length = "cm", time = "s", quantity = "mol", 
      act_energy = "cal/mol")

ideal_gas(name = "argon", 
          elements = "Ar", 
          species = "AR", 
          initial_state = state(temperature = 300.0, 
                                 pressure = OneAtm) )

species(name = "AR", atoms = " Ar:1 ")
```

```python
>>> from Cantera import *
>>> a = importPhase('argon.cti')
>>> a.density()
1.6227653128888044
>>> a.pressure()
101325.0
>>> a.temperature()
300.0
>>> 
```
Adding Thermodynamic Properties

- So far, we have not said anything about the thermodynamic properties of the one species ‘AR’

- For an ideal gas mixture, computing the thermodynamic properties requires that the following (or equivalent) be specified for each species:
  - the function $c_p^0(T) \quad T_{\text{min}} < T < T_{\text{max}}$
  - $h^0(T_{\text{ref}})$
  - $s^0(T_{\text{ref}})$

- Here a superscript 0 denotes properties evaluated under “standard state” conditions
Standard-State Properties

- Ideal gas species

\[ c_p^0 = \lim_{p \to 0} c_p(T) \]

\[ h^0 = \lim_{p \to 0} h(T) \]

\[ s^0 = \lim_{p \to 0} \left[ s(T, p) - R \ln \left( \frac{p_{ref}}{p} \right) \right] \]

- Non-ideal gas models typically use ideal gas species data, then apply corrections for finite density

- Condensed phases

\[ c_p^0 = c_p(T, p_{ref}) \]

\[ h^0 = h(T, p_{ref}) \]

\[ s^0 = s(T, p_{ref}) \]
Specifying species thermo properties

- The *thermo* field of the *species* entry is used to specify parameters to compute the species std. state properties.

- This field should contain an embedded entry of type *const_cp*, *Shomate*, or *NASA*.

- We'll start with *const_cp*, since it is the simplest and can be used for argon.
Argon gas object now produces the correct thermo properties

```python
from Cantera import GasConstant

units(length = "cm", time = "s", quantity = "mol",
       act_energy = "cal/mol")

ideal_gas(name = "argon",
          elements = "Ar",
          species = "AR",
          initial_state = state(temperature = 300.0,
                                  pressure = OneAtm))

species(name = "AR", atoms = " Ar:1 ",
         thermo = const_cp( t0 = 298.15,
                            h0 = 0.0,
                            cp0 = 2.5*GasConstant,
                            s0 = (154.723, 'J/mol/K')) )
```

```plaintext
>>> from Cantera import *
>>> a = importPhase('argon.cti')
>>> a

<table>
<thead>
<tr>
<th>Property</th>
<th>1 kg</th>
<th>1 kmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature</td>
<td>300 K</td>
<td></td>
</tr>
<tr>
<td>pressure</td>
<td>101325 Pa</td>
<td></td>
</tr>
<tr>
<td>density</td>
<td>1.62277 kg/m^3</td>
<td></td>
</tr>
<tr>
<td>mean mol. weight</td>
<td>39,948 amu</td>
<td></td>
</tr>
<tr>
<td>enthalpy</td>
<td>962558 J</td>
<td>3.845e+07 J</td>
</tr>
<tr>
<td>internal energy</td>
<td>900118 J</td>
<td>3.596e+07 J</td>
</tr>
<tr>
<td>entropy</td>
<td>7091.57 J</td>
<td>2.833e+05 J/K</td>
</tr>
<tr>
<td>Gibbs function</td>
<td>-1.16491e+06</td>
<td>-4.654e+07 J/K</td>
</tr>
<tr>
<td>heat capacity c_p</td>
<td>520301 J/K</td>
<td>2.078e+07 J/K</td>
</tr>
<tr>
<td>heat capacity c_v</td>
<td>520093 J/K</td>
<td>2.078e+07 J/K</td>
</tr>
</tbody>
</table>

X

Y

AR 1.000000e+00 1.000000e+00
```
Temperature-dependent $c_p^0$

- For argon, $c_p^0$ is really constant, so the **const** _cp_ model can be used to specify the properties.

- For molecular species, however, $c_p^0$ is temperature-dependent.

- Two other parameterizations implemented:
  - Shomate function
  - NASA polynomials
The Shomate Parameterization


\[
c_p^0 = A + Bt + Ct^2 + Dt^3 + E / t^2
\]

\[
h^0 = At + Bt^2 / 2 + Ct^3 / 3 + Dt^4 / 4 - E / t + F
\]

\[
s^0 = A \ln(t) + Bt + Ct^2 / 2 + Dt^3 / 3 - E / (2t^2) + G
\]

\[
t = T / 1000
\]

Coefficients for methane from the NIST Chem WebBook

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>298. - 1300.</th>
<th>1300. - 6000.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-0.703029</td>
<td>85.81217</td>
</tr>
<tr>
<td>B</td>
<td>108.4773</td>
<td>11.26467</td>
</tr>
<tr>
<td>C</td>
<td>-42.52157</td>
<td>-2.114146</td>
</tr>
<tr>
<td>D</td>
<td>5.862788</td>
<td>0.138190</td>
</tr>
<tr>
<td>E</td>
<td>0.678565</td>
<td>-26.42221</td>
</tr>
<tr>
<td>F</td>
<td>-76.84376</td>
<td>-153.5327</td>
</tr>
<tr>
<td>G</td>
<td>158.7163</td>
<td>224.4143</td>
</tr>
<tr>
<td>H</td>
<td>-74.87310</td>
<td>-74.87310</td>
</tr>
</tbody>
</table>

Reference: Chase, 1998

Comment: Data last reviewed in March, 1961
Shomate Syntax

Single temperature range:

```python
thermo = Shomate(range = (Tmin, Tmax),
                  coeffs = (A, B, C, D, E, F, G))
```

Two temperature ranges:

```python
thermo = ( Shomate(range = (Tmin, Tmid),
                   coeffs = (A1, B1, C1, D1, E1, F1, G1)),
           Shomate(range = (Tmid, Tmax),
                    coeffs = (A2, B2, C2, D2, E2, F2, G2))
)```
The NASA Polynomial Parameterization

- Used in Chemkin and older versions of NASA equilibrium program
- Coefficients for many different molecules available from http://www.ca.sandia.gov/HiTempThermo/index.html

\[ \frac{c_p}{R} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 \]

\[ \frac{h}{RT} = a_0 + \frac{a_1}{2} T + \frac{a_2}{3} T^2 + \frac{a_3}{4} T^3 + \frac{a_4}{5} T^4 + \frac{a_5}{T} \]

\[ \frac{s}{R} = a_0 \ln T + a_1 T + \frac{a_2}{2} T^2 + \frac{a_3}{3} T^3 + \frac{a_4}{4} T^4 + a_6 \]

program ‘ck2cti’ will convert this format to Cantera format
NASA Polynomial Syntax

Single temperature range:

```python
thermo = NASA(range = (Tmin, Tmax),
               coeffs = (a0, a1, a2, a3, a4, a5, a6))
```

Two temperature ranges:

```python
thermo = ( NASA(range = (Tmin, Tmid),
                 coeffs = (a0, a1, a2, a3, a4, a5, a6)),
           NASA(range = (Tmid, Tmax),
                 coeffs = (b0, b1, b2, b3, b4, b5, b6))
)
```
A gas mixture: air

units(length = "cm", time = "s", quantity = "mol", act_energy = "cal/mol")

ideal_gas(name = "air",
    elements = "O N Ar",
    species = "O 02 N NO NO2 N2O N2 AR",
    initial_state = state(temperature = 300.0,
        pressure = OneAtm,
        mole_fractions = 'O2:0.21, N2:0.78, AR:0.01')
)

species(name = "NO",
    atoms = "N:1 O:1",
    thermo = (NASA([ 200.00, 1000.00], [ 4.218476300E+00, -4.638976000E-03,
                                    1.104102200E-05, -9.336135400E-09, 2.803577000E-12,
                                    9.844623000E+03, 2.280846400E+00 ]),
        NASA([ 1000.00, 6000.00], [ 3.260605600E+00, 1.191104300E-03,
                                    -4.291704800E-07, 6.945766900E-11, -4.033609900E-15,
                                    9.920974600E+03, 6.369302700E+00 ])
    ),
    note = "RUS 78"
)
Importing Species Definitions

- Phase definitions can *import* species already defined in another file
- Saves having to re-enter species entries
- A *complete* input file for air that imports species from file gri30.xml:

```plaintext
units(length = "cm", time = "s", quantity = "mol", act_energy = "cal/mol")

ideal_gas(name = "air",
        elements = "O N Ar",
        species = "gri30: O O2 N NO NO2 N2O N2 AR",
        initial_state = state(temperature = 300.0,
                               pressure = OneAtm,
                               mole_fractions = 'O2:0.21, N2:0.78, AR:0.01')
```


This input file builds a complete model for air, just as if the species definitions had been entered in the input file.

```python
>>> from Cantera import *
>>> a = importPhase('air,cti')
>>> a

temperature 300 K
pressure 101325 Pa
density 1.17681 kg/m^3
mean mol. weight 28.9697 amu

<table>
<thead>
<tr>
<th></th>
<th>1 kg</th>
<th>1 kmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>enthalpy</td>
<td>1893.98</td>
<td>5.487e+04 J</td>
</tr>
<tr>
<td>internal energy</td>
<td>-84207.6</td>
<td>-2.439e+06 J</td>
</tr>
<tr>
<td>entropy</td>
<td>6866.03</td>
<td>1.989e+05 J/K</td>
</tr>
<tr>
<td>Gibbs function</td>
<td>-2.05792e+06</td>
<td>-5.952e+07 J/K</td>
</tr>
<tr>
<td>heat capacity  c_p</td>
<td>1003.06</td>
<td>2.906e+04 J/K</td>
</tr>
<tr>
<td>heat capacity  c_v</td>
<td>716.05</td>
<td>2.074e+04 J/K</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000e+00</td>
<td>0.000000e+00</td>
</tr>
<tr>
<td>2.100000e-01</td>
<td>2.319575e-01</td>
</tr>
<tr>
<td>0.000000e+00</td>
<td>0.000000e+00</td>
</tr>
<tr>
<td>0.000000e+00</td>
<td>0.000000e+00</td>
</tr>
<tr>
<td>0.000000e+00</td>
<td>0.000000e+00</td>
</tr>
<tr>
<td>7.800000e-01</td>
<td>7.542530e-01</td>
</tr>
<tr>
<td>1.000000e-02</td>
<td>1.378956e-02</td>
</tr>
</tbody>
</table>

```
Importing from multiple sources

- Species definitions can be kept in separate files, organized by compound type, data source, or in any other way.

- `ideal_gas(name = 'sicvd_gas',
  elements = 'Si H O',
  species = ['silanes: all',
             'si_oxides: SiO SiO2',
             'oh: all',
             'SiH2O'])`

- This specifies the following species:
  - import all species defined in files 'silanes.xml' and 'oh.xml'
  - import SiO and SiO2 from file 'si_oxides.xml'
  - add species SiH2O defined in this file.
Adding Reactions

- At this point, we can construct gas mixtures, but we have not specified any reactions.

- Such definitions are perfectly usable for problems that do not involve kinetics.

- But of course to do kinetics problems, we need to supplement what we have so far with a specification of what reactions we will consider, and their rate parameters.

- Now we'll look at how to add reactions to phases
The reaction entry

short form:

```
reaction( "O + H2 <=> H + OH", [3.87000E+04, 2.7, 6260])
```

sequence of 3 numbers interpreted as A, b, E in Arrhenius expression

\[
k_f = AT^b \exp(-E / RT)
\]

long form:

```
reaction( equation = "O + H2 <=> H + OH",
            kf = Arrhenius(3.87000E+04, 2.7, 6260),
            id = 'oh-1')
```
Reaction rate expression

\[ q_{\text{fwd}} = k_f \prod_j C_j^{v_{(r)}_j} \]

\[ k_f = AT^b \exp(-E/RT) \]

if reversible,

\[ q_{\text{rev}} = k_r \prod_j C_j^{v_{(p)}_j} \]

\[ k_r = \frac{k_f}{K_c} \]
Specified reaction orders for global reactions

- Sometimes global reactions have measured rate laws of the form

$$q_{\text{fwd}} = k_f \prod_j C_j^{R_j}$$

where $R_j$ is an empirical reaction order

- To specify reaction orders, use the `order` field:

```python
reaction(equation = "C3H8 + 5 O2 => 3 CO2 + 4 H2O",
        kf = [1.0e8, 0.0, 0.0],
        order = 'C3H8:0.5 O2:0.2')
```

- Note that the units of $k_f$ are affected by using empirical reaction orders

- Reaction orders can only be specified for irreversible reactions
The Reaction Equation

- Conventions mostly follow those used in the Chemkin-II software package

- All species names must be separated by whitespace
  - "O + H2 <=> OH + H" is OK
  - "O+H2 <=> OH+H" is not OK, and will result in an undeclared species error for species 'O+H2' and 'OH+H'
  - the CK2CTI utility automatically adds spaces when converting Chemkin input files.

- Stoichiometric coefficients must be integers

- equality sign
  - "<=>" or "=": specifies that the reaction is reversible, and the reverse rate is to be computed from detailed balance.
  - "=>" or "->": specifies that the reaction is irreversible, and the reverse rate is to be set to zero.
The Reaction Equation (cont'd)

- "H + O + M = OH + M"
  "CH4 + M = CH3 + H + M"

  If 'M' is specified as a reactant or product (should be on both sides of the equation), then this denotes a third-body collision partner. Use only with entry type `three_body_reaction`

- "CH4 (+M) = CH3 + H (+M)"

  Including '(+M)' denotes a pressure-dependent falloff reaction. Use only with entry type `falloff_reaction`
Three-body reactions

- Third-body collision partner required to conserve energy and momentum
  - collisional dissociation reactions
    \[ \text{H}_2\text{O} + \text{M} \rightarrow \text{OH} + \text{H} + \text{M} \]
  - association (recombination) reactions
    \[ \text{OH} + \text{H} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \]

- Rate expression:
  \[ q_{\text{fwd}} = k_f C_M \prod_j C_j^{\nu_j(r)} \]
  \[ C_M = \sum_j \epsilon_j C_j \]
This set of slides ends here

Please refer to the document 'definingphases.pdf' on the CD for further information on defining phase and interface models.