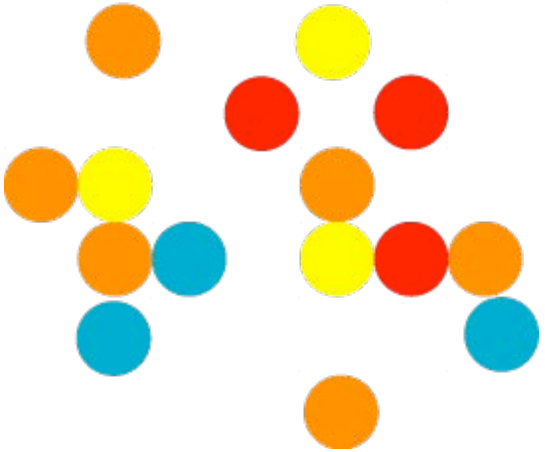
Creating Phase and Interface Models



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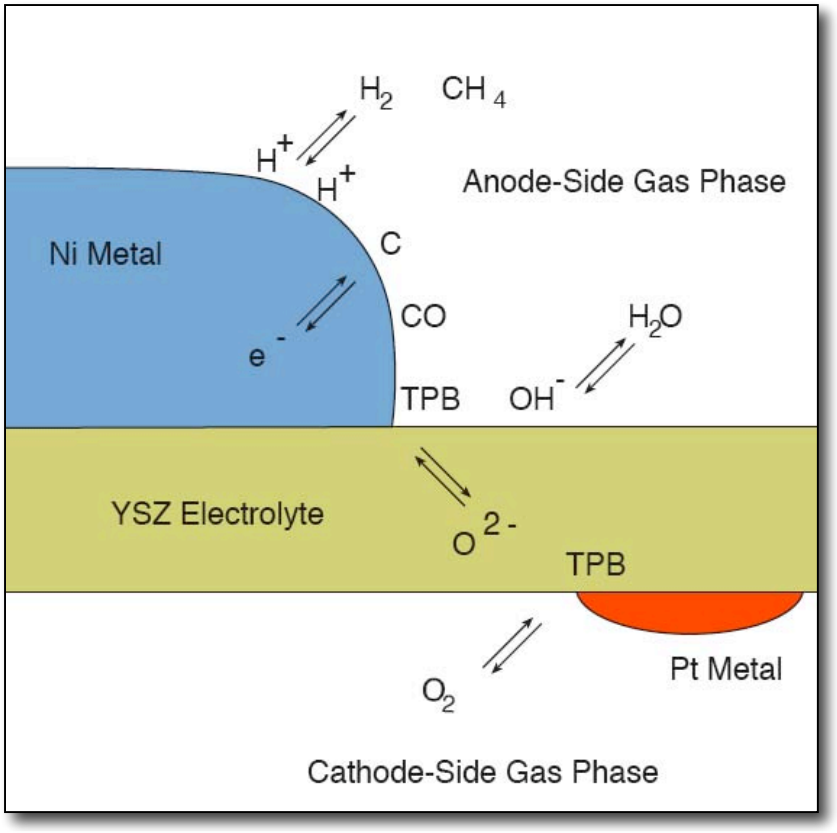
Every Cantera simulation involves one or more phases of matter



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' (**C**an**T**era **I**nput)
- 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 specifed 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

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

Setting the Default Units for Input

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

- 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

A simple phase: argon gas

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

- 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

```
<ctml>
  <elementData caseSensitive="no">
        <element name="H" atomicWt = "1.00794"/>
        <element name="D" atomicWt = "2.0147"/>
        <element name="Tr" atomicWt = "3.016327"/>
        <element name="He" atomicWt = "4.002602"/>
        <element name="Li" atomicWt = "6.941"/>
        <element name="Be" atomicWt = "9.012182"/>
        <element name="B" atomicWt = "10.811"/>
        <element name="C" atomicWt = "12.011"/>
        <element name="N" atomicWt = "14.00674"/>
        <element name="O" atomicWt = "15.9994"/>
        <element name="F" atomicWt = "18.9984032"/>
        <element name="Ne" atomicWt = "20.1797"/>
```

initial part of elements.xml

Defining Species ‘AR’

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

- 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).

```
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 ")
```

```
>>> 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 $c_p^0(T)$ $T_{min} < T < T_{max}$
  - $h^0(T_{ref})$
  - $s^0(T_{ref})$

- Here a superscript 0 denotes properties evaluated under "standard state" conditions

Standard-State Properties

- Ideal gas species

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

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

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

- 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

```
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') )
        )
```

- 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

```
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') )
        )
```

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

      temperature           300  K
         pressure        101325  Pa
          density       1.62277  kg/m^3
 mean mol. weight        39.948  amu

                         1 kg         1 kmol
                    -----------  ------------
         enthalpy        962558   3.845e+07     J
  internal energy        900118   3.596e+07     J
          entropy       7091.57   2.833e+05     J/K
   Gibbs function  -1.16491e+06  -4.654e+07     J
heat capacity c_p        520301   2.078e+07     J/K
heat capacity c_v        520093   2.078e+07     J/K

                             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

- Used in the NIST Chem WebBook http://webbook.nist.gov

$$c_p^0 = A + Bt + Ct^2 + Dt^3 + E/t^2$$

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

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

$$t = T/1000$$

Coefficients for methane from the NIST Chem WebBook

Temperature (K)	298. - 1300.	1300. - 6000.
A	-0.703029	85.81217
B	108.4773	11.26467
C	-42.52157	-2.114146
D	5.862788	0.138190
E	0.678565	-26.42221
F	-76.84376	-153.5327
G	158.7163	224.4143
H	-74.87310	-74.87310
Reference	Chase, 1998	Chase, 1998
Comment	Data last reviewed in March, 1961	Data last reviewed in March, 1961

Shomate Syntax

Single temperature range:

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

Two temperature ranges:

```
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

```
CH4               110203H   4C   1    0    0G   300.000  4000.000 1000.00    0 1
 0.47238333E+00 0.12680758E-01-0.55093741E-05 0.11295575E-08-0.89103779E-13    2
-0.96424500E+04 0.16199090E+02 0.38717898E+01-0.42480466E-02 0.24540181E-04    3
-0.21780766E-07 0.63010622E-11-0.10144425E+05 0.66008135E+00                   4
```

program 'ck2cti' will convert this format to Cantera format

$$\frac{c_p^0}{R} = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4$$

$$\frac{h^0}{RT} = a_0 + \frac{a_1}{2} T + \frac{a_2}{3} T^2 + \frac{a_3}{4} T^3 + \frac{a_4}{5} T^4 + \frac{a_5}{T}$$

$$\frac{s^0}{R} = a_0 \ln T + a_1 T + \frac{a_2}{2} T^2 + \frac{a_3}{3} T^3 + \frac{a_4}{4} T^4 + a_6$$

NASA Polynomial Syntax

Single temperature range:

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

Two temperature ranges:

```
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  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')
          )


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"
        )
```

only one species entry shown

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:

```
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

```
>>> 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

                          1 kg             1 kmol
                       -----------      ------------
          enthalpy         1893.98          5.487e+04     J
   internal energy        -84207.6         -2.439e+06     J
           entropy         6866.03          1.989e+05     J/K
    Gibbs function    -2.05792e+06         -5.962e+07     J
 heat capacity c_p         1003.06          2.906e+04     J/K
 heat capacity c_v          716.05          2.074e+04     J/K

                             X                Y
                       ------------     ------------
                 O     0.000000e+00     0.000000e+00
                O2     2.100000e-01     2.319575e-01
                 N     0.000000e+00     0.000000e+00
                NO     0.000000e+00     0.000000e+00
               NO2     0.000000e+00     0.000000e+00
               N2O     0.000000e+00     0.000000e+00
                N2     7.800000e-01     7.542530e-01
                AR     1.000000e-02     1.378956e-02
>>>
```

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 speification 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

$$q_{fwd} = k_f \prod_j C_j^{\nu^{(r)}_j}$$

$$k_f = A T^b \exp(-E / RT)$$

if reversible,

$$q_{rev} = k_r \prod_j C_j^{\nu_j^{(p)}}$$

$$k_r = \frac{k_f}{K_c}$$

Specified reaction orders for global reactions

- Sometimes global reactions have measured rate laws of the form

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

  where R_j is an empirical reaction order

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

```
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
    H2O + M -> OH + H + M
  - association (recombination) reactions
  - OH + H + M -> H2O + M

- Rate expression:

collision efficiencies

$$q_{fwd} = k_f C_M \prod_j C_j^{\nu^{(r)}}$$

$$C_M = \sum_j \varepsilon_j C_j$$

- 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.