FactSage Practical
MSE302

Practical 2. Reaction Module

Basics
Acknowledgements

The teaching team of MSE302 is grateful to:
Professor Mansoor Barati (UofT)
Professor Elmira Moosavi (ETS)
Professor Arthur Pelton (CRCT)
Professors In-Ho Jung and M. –A. Van Ende (Seoul National University)
Dr. Sina Mostaghel (SNC-Lavalin)
Professor Kinnor Chattopadhyay (UofT)
Drs. Daigen Fukayama, Takahiro Sasaki (RCCM)
Drs. Moritz to Baden and Guixuan Wu (GTT Technologies)
Reaction Module

The **Reaction** Module can do the following:

- **Reaction** calculates the thermodynamic properties of a **species** \((C_P, i, H_i, S_i, V_i, G_i)\) at given temperature and pressure.
- **Reaction** calculates the thermodynamic properties of a **mixture of species** (mechanical mixture or solution) \((C_P, H, S, V, G)\) at given temperature and pressure.
- **Reaction** calculates the thermodynamic properties of a **chemical reaction** \((\Delta_r c_P, \Delta_r h, \Delta_r s, \Delta_r v, \Delta_r g)\) at given temperature and pressure.

**Alert:**

- **Reaction** accesses both compound and solution databases.
- **Reaction** assumes all gases are ideal and ignores expansivities and compressibilities of solids and liquids.
Run the “Reaction” Module

Don’t forget to check the Directory!!!
Reaction Module

A Note on **Pressure**:

- For a gas phase, **Pressure** is its partial pressure.
- For a condensed phase (solid, liquid or aqueous), **Pressure** is the hydrostatic pressure (unimportant except at very high pressures).
- All the species may have the same or different pressure.
A Note on **Pressure**:

For a gas phase, this is its partial pressure. For a condensed phase (solid, liquid or aqueous) this is the hydrostatic pressure (unimportant except at very high pressures). All the species may have the same or different pressures.

Enter a numerical value (e.g., 0.5 or 1.123e-10, 1.0 for the standard state) if the pressure is constant.

Specify "P" if the pressure of a species is to be calculated or entered later in the Tabular Output.

Hover your mouse near “P(atm)”, and right click. Then you will see the explanation about Pressure. This is a very useful feature of FactSage. Try this about Activity and, Temperature, Phase...
Reaction Module

Clear the Reactants:

- Edit
- Add a new Reactant
- Add a new Product
- Insert new reactant before ...
- Delete reactant ...
- Delete all blank reactants
- Mixtures and Streams
- Reorder the reactants
- Export list of reactants
- Clear

**For a gas species, P(atm/bar/ps) is its ideal partial pressure.**

For a liquid or solid, P is the hydrostatic pressure above the phase. Select 'apply volume data' to include molar volume and compressibility data in the 'YdP' term. This does not apply to gases which are treated as ideal.

- non standard states: [ ] apply volume data

FacSage 7.3 | Compound: 1/17 databases
Reaction Module

Let us first perform **standard state** calculations.

<table>
<thead>
<tr>
<th>Quantity(mol)</th>
<th>Species</th>
<th>Phase</th>
<th>T(K)</th>
<th>P(atm)</th>
<th>Energy(J)</th>
<th>Quantity(mol)</th>
<th>Vol(litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**DO NOT** check this. Standard state calculations mean that all the reactants/products are in their standard state (for a gas species, the standard state pressure is 1 atm; for a condensed species, the standard state refers to Raoultian standard state, i.e., pure substance and 1 atm).
Reaction Module

**Reactants** Window: define a reaction using “Edit”

Use “Edit” to define a reaction.
Reactivity Module

**Reactants Window:** define a reaction using “+”

- **New Reaction**
- **Add a Reactant**
- **Add a Product**
Reaction Module

**Reactants Window: set the Units**

- Click on “Units”
- Or click at this region

---

**Universal gas constant:**

\[
R = 8.314510 \text{ J/mol-K} \\
= 8.314510/4.184 = 1.98722... \text{ cal/mol-K} \\
= 22.4141/273.15 = 0.0820576... \text{ l-atm/mol-K}
\]
The first example we will be discussing is to calculate the thermodynamic properties of pure Cu. Therefore, FactPS can be used for this purpose.
**Reactants Window: Help Document**

This is the tutorial document provided by CRCT. In this class, we use this as the supplementary material.
By choosing “most stable”, we are asking FactSage to determine which phase is stable at a given temperature.

Let us consider 1 mol Cu.

Note: Pressure and Activity are locked because this is Standard State Calculation.
Reaction Module: Pure Cu

Table Window: Set Conditions

This shows we are calculating the thermodynamic properties of 1 mol Cu at an unknown temperature $T$.

Click on Back to return to Reactants Window.
Reaction Module: Pure Cu

Table Window: Results

All the thermodynamic properties against $T$ for 1 mol Cu are shown. Note the volume data is zero because we didn’t consider the volumetric data (Reactant Window).

FactSage helps us find the phase transition points.
Reaction Module: Pure Cu

**Table Window: Output Results**

<table>
<thead>
<tr>
<th>T(K)</th>
<th>S(J/K)</th>
<th>Cp(J/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300.00</td>
<td>33.315</td>
<td>24.468</td>
</tr>
<tr>
<td>800.00</td>
<td>58.736</td>
<td>27.431</td>
</tr>
<tr>
<td>1300.00</td>
<td>72.867</td>
<td>32.201</td>
</tr>
<tr>
<td>1350.00</td>
<td>23659.9</td>
<td>-71238.5</td>
</tr>
<tr>
<td>Cu(1)</td>
<td>13138.0</td>
<td></td>
</tr>
<tr>
<td>1350.00</td>
<td>47297.9</td>
<td>-71238.5</td>
</tr>
<tr>
<td>1900.00</td>
<td>57314.9</td>
<td>-110493.4</td>
</tr>
<tr>
<td>2300.00</td>
<td>73736.3</td>
<td>-159201.7</td>
</tr>
<tr>
<td>2800.00</td>
<td>90188.3</td>
<td>-211508.7</td>
</tr>
<tr>
<td>2846.16</td>
<td>91675.0</td>
<td>-216494.2</td>
</tr>
<tr>
<td>Cu(g)</td>
<td>300653.1</td>
<td></td>
</tr>
<tr>
<td>2846.16</td>
<td>352328.1</td>
<td>-216494.2</td>
</tr>
<tr>
<td>3300.00</td>
<td>403914.1</td>
<td>-314439.8</td>
</tr>
<tr>
<td>3500.00</td>
<td>408349.5</td>
<td>-358136.9</td>
</tr>
</tbody>
</table>

Save Tabular Output...
## Reaction Module: Pure Cu

### Table Window: Output Results

<table>
<thead>
<tr>
<th>T(K)</th>
<th>H(J)</th>
<th>G(J)</th>
<th>Vol(litres)</th>
<th>S(J/K)</th>
<th>Cp(J/K)</th>
<th>A(J)</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
<td>-----------</td>
<td>------</td>
<td>-------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>300.00</td>
<td>45.2</td>
<td>-9949.3</td>
<td>0.0000E+00</td>
<td>33.315</td>
<td>24.468</td>
<td>-9949.3</td>
<td></td>
</tr>
<tr>
<td>800.00</td>
<td>13120.4</td>
<td>-33868.0</td>
<td>0.0000E+00</td>
<td>58.736</td>
<td>27.481</td>
<td>-33868.0</td>
<td></td>
</tr>
<tr>
<td>1300.00</td>
<td>27758.9</td>
<td>-66968.7</td>
<td>0.0000E+00</td>
<td>72.867</td>
<td>32.201</td>
<td>-66968.7</td>
<td></td>
</tr>
<tr>
<td>1358.00</td>
<td>29659.9</td>
<td>-71236.5</td>
<td>0.0000E+00</td>
<td>74.298</td>
<td>33.362</td>
<td>-71236.5</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
<td>-----------</td>
<td>------</td>
<td>-------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>Cu(1 mol): DH = 13138.0</td>
<td>DG = 0</td>
<td>------</td>
<td>DS = 9.674</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1358.00</td>
<td>42797.9</td>
<td>-71236.5</td>
<td>0.0000E+00</td>
<td>83.972</td>
<td>32.844</td>
<td>-71236.5</td>
<td></td>
</tr>
<tr>
<td>1800.00</td>
<td>57314.9</td>
<td>-110493.4</td>
<td>0.0000E+00</td>
<td>93.227</td>
<td>32.844</td>
<td>-110493.4</td>
<td></td>
</tr>
<tr>
<td>2300.00</td>
<td>73736.9</td>
<td>-159201.7</td>
<td>0.0000E+00</td>
<td>101.278</td>
<td>32.844</td>
<td>-159201.7</td>
<td></td>
</tr>
<tr>
<td>2800.00</td>
<td>90158.9</td>
<td>-211508.7</td>
<td>0.0000E+00</td>
<td>107.738</td>
<td>32.844</td>
<td>-211508.7</td>
<td></td>
</tr>
<tr>
<td>2845.16</td>
<td>91675.0</td>
<td>-216494.2</td>
<td>0.0000E+00</td>
<td>108.275</td>
<td>32.844</td>
<td>-216494.2</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
<td>-----------</td>
<td>------</td>
<td>-------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>Cu(1 mol): DH = 300653.1</td>
<td>DG = 0</td>
<td>------</td>
<td>DS = 105.635</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2845.16</td>
<td>392328.1</td>
<td>-216494.2</td>
<td>2.3355E+02</td>
<td>213.910</td>
<td>24.400</td>
<td>-240158.6</td>
<td></td>
</tr>
<tr>
<td>3300.00</td>
<td>403914.1</td>
<td>-314439.8</td>
<td>2.7079E+02</td>
<td>217.683</td>
<td>26.675</td>
<td>-341877.7</td>
<td></td>
</tr>
<tr>
<td>3500.00</td>
<td>409349.5</td>
<td>-358136.9</td>
<td>2.8720E+02</td>
<td>219.282</td>
<td>27.674</td>
<td>-387237.7</td>
<td></td>
</tr>
</tbody>
</table>
The second example we will be looking at is the heating of Cu from 300 K. This process can be described by the following reaction:

\[ \text{Cu}(300 \text{ K}) = \text{Cu}(T) \]

Let us determine the amount of heat (strictly speaking, enthalpy) required to melt 1 mole Cu from 300 K.
We only need FactPS because the system exists either as solid pure Cu or liquid pure Cu.
Reactants Window: Set Reactants (Phase and Temperature)

Again, by choosing “most stable”, we are asking FactSage to determine which phase is stable at a given temperature.

The initial temperature is 300 K.

Do not check this option because there is no solution phase for this heating process.
This column shows the amount of heat required to heat Cu. At 1358 K, Cu starts to melt. Right before melting, 29614.6 J are required to heat solid Cu from 300 to the melting temperature. Then 13138.0 J are required to convert solid Cu to liquid Cu. Therefore, the minimum total amount of heat required to melt Cu is $(29614.6 + 13138.0) J = 42752.6 J$. 

\[
\text{Total Heat} = 29614.6 + 13138.0 = 42752.6 \text{ J}
\]
Reaction Module: Heating of Cu

Table Window: Plot Results

Table:

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Delta H*(J)</th>
<th>Delta G*(J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>......</td>
<td>Cu(s)</td>
<td>Cu(s)</td>
</tr>
<tr>
<td>300.00</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>600.00</td>
<td>769.1</td>
<td>-1291.4</td>
</tr>
<tr>
<td>900.00</td>
<td>1585.1</td>
<td>-2995.9</td>
</tr>
<tr>
<td>1200.00</td>
<td>2456.8</td>
<td>-4905.7</td>
</tr>
<tr>
<td>1358.00</td>
<td>2961.4</td>
<td>-6128.7</td>
</tr>
<tr>
<td>......</td>
<td>Cu(l)</td>
<td>Cu(l)</td>
</tr>
<tr>
<td>Cu(l) mol:</td>
<td>DH* = 13138.0</td>
<td>DG* = 0</td>
</tr>
<tr>
<td>1358.00</td>
<td>4275.2</td>
<td>-6128.7</td>
</tr>
<tr>
<td>1500.00</td>
<td>4741.6</td>
<td>-7344.7</td>
</tr>
<tr>
<td>1800.00</td>
<td>5726.3</td>
<td>-10054.4</td>
</tr>
<tr>
<td>2000.00</td>
<td>6306.3</td>
<td>-11354.1</td>
</tr>
</tbody>
</table>

Graph:

Delta H*(J) vs T(K)

Delta A(J) vs T(K)
Reaction Module: Heating of Cu

**Table Window: Plot Results**

This is $\Delta m h^\circ_{\text{Cu,1358 K}} = 13138.0 \text{ J.}$
The third example we will be discussing is to calculate the thermodynamic properties of the oxidation of Cu by pure oxygen. First, let us look at the standard state calculation in which all reactants and products are in their standard state.
Reaction Module: Oxidation of Cu

Reactants Window: Choose the database

Because all the reactants and products are in their standard state, FactPS can be used for this purpose.
Reaction Module: Oxidation of Cu

**Reactants Window: Set Reactants (Phase and Temperature)**

By choosing “most stable”, we are asking FactSage to determine which phase is stable at a given temperature.

Let us consider the following oxidation reaction at an unknown temperature when all the reactants and products are in their standard state: $4\text{Cu} + \text{O}_2 = 2\text{Cu}_2\text{O}$. 

---

**FactSage 7.3 Compound: 1/14 databases**
Reaction Module: Oxidation of Cu

Table Window: Set Conditions

We are calculating the thermodynamic properties for an isothermal standard state reaction:

$$4Cu + O_2 \xrightarrow{T} 2Cu_2O$$

$$\Delta G^* = \Delta H^* - T \Delta S^* = -RT \ln(Keq)$$

In MSE302, we use the following format:

$$\Delta_r g^o = \Delta_r h^o - T \Delta_r s^o = -RT \ln(K)$$
# Reaction Module: Oxidation of Cu

All the thermodynamic properties against $T$ for **1 mol reaction** shown below. Also, check if $\Delta_r g^\circ = \Delta_r h^\circ - T\Delta_r s^\circ = -RT\ln(K)$

Note the state change of Cu and Cu$_2$O (please record these two temperatures).

Then save the results as “.txt”

**Note:** the obtained $\Delta_r g^\circ \sim T$ is the Ellingham Diagram.
Non-standard State Calculation (Part 1)

This time, let us calculate non-standard state reactions. The first scenario is that the oxidation reaction occurs at an unknown temperature when Cu and Cu₂O are pure substance while the partial pressure of O₂ is a variable.

For non-standard state reactions, we have to specify the state of reactants and products because defining activity requires the definition of standard state which either is pure solid or pure liquid. From the preceding calculation of the standard state reaction, we have,

\[
\begin{align*}
2\text{Cu}(s) + 0.5\text{O}_2(g) &= \text{Cu}_2\text{O}(s); T < 1358 \text{ K} \\
2\text{Cu}(l) + 0.5\text{O}_2(g) &= \text{Cu}_2\text{O}(s); 1358 \text{ K} < T < 1516.7 \text{ K} \\
2\text{Cu}(l) + 0.5\text{O}_2(g) &= \text{Cu}_2\text{O}(l); T > 1516.7 \text{ K}
\end{align*}
\]

Therefore, we need to perform 3 calculations for 3 different temperature ranges. Here, we only demonstrate the calculation for the first temperature range.
This time, let us consider the following oxidation reaction at an unknown temperature $2\text{Cu}(s) + 0.5\text{O}_2(g) = \text{Cu}_2\text{O}(s)$ in which solids are pure, and the partial pressure of $\text{O}_2$ is $P_{\text{O}_2}$.

**Note:** we are studying how partial pressure of $\text{O}_2$ affects the thermodynamics of the oxidation of Cu.
**Reaction Module: Oxidation of Cu**

**Reactants Window: Set Reactants (Phase and Temperature)**

<table>
<thead>
<tr>
<th>Quantity(mol)</th>
<th>Species</th>
<th>Phase</th>
<th>T(K)</th>
<th>P(atm)**</th>
<th>Activity</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Cu</td>
<td>solid</td>
<td>T</td>
<td>P(1.0)</td>
<td>Hydrostatic pressure over Cu(solid) = 1.0 (atm)</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>O2</td>
<td>gas</td>
<td>T</td>
<td>P</td>
<td></td>
<td></td>
</tr>
<tr>
<td>= 1</td>
<td>Cu2O</td>
<td>solid</td>
<td>T</td>
<td>P(1.0)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- For a gas species, P(atm/bar/psi) is its ideal partial pressure.
- For a liquid or solid, P is the hydrostatic pressure above the phase. Select ‘apply volume data’ to include molar volume and compressibility data in the VdP term; this does not apply to gases which are treated as ideal.

Don’t forget **right** click to get more info.
We are calculating the thermodynamic properties for an isothermal non-standard state reaction:

\[ 2 \text{Cu}(s) + 0.5 \text{O}_2(g) \xrightarrow{T, P} \text{Cu}_2\text{O}(s) \]

\[ \Delta_r G = \Delta_r G^\circ + R T \ln(Q) \]

In MSE302, we use the following format:

\[ \Delta_r g = \Delta_r g^\circ + R T \ln(Q) \]

The number of variables that need to be specified is determined by the Gibbs phase rule.
Let us study the reaction at 1000 K.

By setting Delta G = 0, we are performing the calculation when the reaction reaches equilibrium.

Variables which are highlighted are the conditions we provided.

This is the equilibrium partial pressure of O₂.
Let us study under a given partial pressure of \( \text{O}_2 \), if pure \( \text{Cu} \) can be oxidized.

Let us study the reaction at 1000 K.

Since \( \Delta_r g > 0 \), the oxidation is not thermodynamically possible.

Let us study under a given partial pressure of \( \text{O}_2 \), if pure \( \text{Cu} \) can be oxidized.
Reaction Module: Oxidation of Cu

Non-standard State Calculation (Part 2)

Now let us consider the removal of impurity Cu from a gold bath by blowing pure oxygen at 1 atm. The operation temperature is 1400 K, and the product is pure $\text{Cu}_2\text{O}$.

The above reaction can be described as:

$$2\text{Cu}(l, \text{solute in liquid Au}) + 0.5\text{O}_2(g, 1 \text{ atm}) = \text{Cu}_2\text{O}(s)$$

To study the equilibrium of this reaction, we use $\Delta_r g$.

$$\Delta_r g = \Delta_r g^\circ + RT \ln\left(\frac{(a^{(s2)}_{\text{Cu}_2\text{O}})^1}{(a^{(l)}_{\text{Cu}})^2 (P_{O_2})^{0.5}}\right) \text{ where } a^{(s2)}_{\text{Cu}_2\text{O}} = 1 \text{ and } P_{O_2} = 1$$

$a^{(l)}_{\text{Cu}}$ depends on the liquid Au-Cu model. Therefore, we need to choose a solution database in which the Au-Cu system has been optimized (using Documentation or View Data).
One of the solution databases can be used is FTLite.
View Data: determine which solution database for the Au-Cu system

Although in FTlite, the liquid model for the Au-Cu system is of good quality, compared with SGnold in which the liquid model is of top quality, we choose FTlite because we don’t have the access to SGnold.
Reaction Module: Oxidation of Cu

**Reactants Window:** Choose the database

- **FactPS** contains the models for gaseous $O_2$ and pure solid $Cu_2O$.
- **FTlite** contains the model for liquid Au-Cu alloy.
Reaction Module: Oxidation of Cu

Reactants Window: Set Reactants (Phase and Temperature)

Choosing the state for all reactants and products.

Operation temperature.

Partial pressure of $O_2$ is set as 1 atm.
Reaction Module: Oxidation of Cu

Table Window: Set Conditions

The number of variables that need to be specified is determined by the Gibbs phase rule.
By setting Delta G = 0, we are performing the calculation when the reaction reaches equilibrium.

This is the activity of Cu in the liquid Au-Cu alloy when the system reaches equilibrium, \( a^{(l)}_{\text{Cu}} \). Unfortunately, we are not able to obtain the concentration of Cu, \( X^{(l)}_{\text{Cu}} \) because of the lack of activity coefficient.
Let us study if pure Cu can be oxidized when the activity of Cu in the liquid Au-Cu alloy is 0.06.

Since $\Delta_r g < 0$, the oxidation is thermodynamically possible.
Non-standard State Calculation (Part 3)

The third part of non-standard state calculation is to include a slag phase. That is, instead of forming pure solid Cu$_2$O, a liquid slag consisting of SiO$_2$ and Cu$_2$O is in contact with the gold bath.

In this case, the activity of Cu$_2$O in the liquid slag should be used, and FToxid contains the model for the liquid SiO$_2$-Cu$_2$O slag.

The set up would be very similar to the previous calculation, except for Cu$_2$O of which the activity must be used.
In-Class Exercise

**Question 1.**
Solve Question 1 and 2 from the first problem set using the Reaction Module.

**Question 2.**
Carry out the following calculations using the View Data and/or Reaction Module (not identical, since you will need to tailor conditions to your particular metal) on one or as many metals as you wish from the following list:

- Nickel, Chromium, Lead, Iron, Manganese, Vanadium, Magnesium, Zinc, Titanium, Sodium, Cobalt.

1. Create a data table for the most stable species of the M over a suitable temperature range.

2. Find the available solution phases the Metal-Fe-S system.

3. Create a data Table for the reaction between Metal, oxygen, and the lowest oxide. The maximum temperature should be at least 2000 K, or as appropriate.
In-Class Exercise

(4a) Create a data Table for the above oxidation reaction for at least five different conditions at equilibrium (always isothermal and always at equilibrium). For example, you could choose to calculate $T$ in three runs with different defined $X$ and $P$. Then you could calculate $X$ at defined $P$ and $T$, and then $P$ at defined $X$ and $T$.

(4b) Next, assume that the reaction needs some super-saturation to nucleate the oxide, so set $\Delta G = \Delta G^o/100$ (which will be a negative number) and find the $P_{O_2}$ needed compared to one of your above equilibrium conditions. Include this result in your data Table and add a written comment.

(5) Create a plot showing the Enthalpy required to heat Metal up to and beyond the boiling point (or as close as you can get).

**Note:** you should annotate all your five sheets by hand as appropriate - to make everything clear to the reader.
FactSage Practical
MSE302

Practical 2. Reaction Module

Advanced Applications
Application 1: Combustion of Methane

The first application is the combustion of gaseous methane in the pressure of excess oxygen. In this case, the combustion products would be CO₂, H₂O and unused O₂ (note: because of the excess of O₂, no CO would form).

Consider the following combustion process.

Let us calculate the adiabatic flame temperature (AFT) in the Reaction Module, and how AFT is affected by the excess ratio of oxygen.

**Note**: we assume the gas phase behaves ideally, and thus standard state calculations could be performed when calculating enthalpy change associated with the combustion process.
Application 1: Combustion of Methane

**Reactants Window: Choose the database**

- All the species considered are gaseous. FactPS should be used.
Application 1: Combustion of Methane

Reactants Window: Set Reactants (Phase and Temperature)

Check the units

The state must be specified if we want to calculate AFT (see what will happen if “most stable” is chosen).

Don’t check
Application 1: Combustion of Methane

**Reactants Window: Set Conditions**

Non-isothermal: “Kequ” has no meaning.

Here, we will choose from $<A>$, $T\,$, and Delta H$^*$
**Application 1: Combustion of Methane**

**Reactants Window: Results**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0000</td>
<td>300.00</td>
<td>-802298.6</td>
<td>-800825.3</td>
<td>0.0000E+00</td>
<td>-4.911</td>
<td>9.937</td>
<td></td>
</tr>
</tbody>
</table>

The minimum value of <A> is 2, which results in complete combustion.

Although the reaction is generally non-isothermal, we can still calculate the standard enthalpy of reaction at 300 K, $\Delta_r h^\circ_{300 \text{ K}}$. 
Application 1: Combustion of Methane

Reactants Window: Results

Note: for each calculation (row), the two highlighted cells are the variables specified. When Delta H* = 0, this corresponds to adiabatic process, and the AFT can be calculated for a given excess ratio of oxygen.

Calculation of excess ratio of oxygen:

\[
\frac{8 \text{ mol} - 2 \text{ mol}}{2 \text{ mol}} \times 100\% = 300\%
\]
Application 1: Combustion of Methane

Reactants Window: Results

This is because the unused $O_2$ is heated up from 300 K to AFT. However, in reality, we always input excess amount of oxygen because this could prevent the soot formation.

Now let us study the effect of excess ratio of oxygen on the AFT.
Application 1: Combustion of Methane

We can also calculate the AFT for a burner that uses air instead of pure oxygen. In this case, equivalent amounts of nitrogen accompanying oxygen should be entered in the reaction.

\[
\begin{align*}
\text{CH}_4 \ (g, \ 300 \ K) & \rightarrow \text{CO}_2 \ (g, \ T) \\
\text{O}_2 \ (g, \ 300 \ K) & \rightarrow \text{H}_2\text{O} \ (g, \ T) \\
\text{N}_2 \ (g, \ 300 \ K) & \rightarrow \text{O}_2 \ (g, \ T) \\
& \rightarrow \text{N}_2 \ (g, \ T)
\end{align*}
\]

Note: since the air composition (mole fraction) can be approximated as “0.79 N\_2 + 0.21 O\_2”, for every mole of O\_2 input, there are 3.76 mol N\_2.
Application 1: Combustion of Methane

**Reactants Window:** Set Reactants (Phase and Temperature)

Check the units

T(K), P(atm), Energy(J), Quantity(mol), Volume(litres)
Application 1: Combustion of Methane

Reactants Window: Results

Can you see the significant difference in the AFT when we switch from pure oxygen to air? That's why the oxygen-enrichment technology is so important for the combustion process.

Again, let us study the effect of excess ratio of oxygen on the AFT when air is used.
Application 2: Pidgeon Process

Magnesium can be produced by reducing MgO with ferrosilicon at low pressures and in the solid state. This is called the Pidgeon Process and was developed by UofT MSE’s Professor Pidgeon in Canada in WWII to produce much-needed magnesium metal then. The essential reaction can be described as:

\[ \text{MgO} (s) + \text{Si} (s) = \text{Mg} (g) + \text{SiO}_2 (s) \]

By controlling the system’s pressure, solid charge composition (which affects the activity of \( \text{SiO}_2 \)), etc., the above reduction can be shifted to improve the productivity of Mg.

The flowsheet of the Pidgeon Process is shown on the next slide.
Application 2: Pidgeon Process

Flowsheet of the Pidgeon Process (Schematic)

Dolomite → Calcination → Pulverization → Mixing → Briquetting

Calcination:

MgO · CaO + Si(Fe) + CaF₂ → Briquetting

~1200 °C

Spent Briquettes (Ca₂SiO₄ + Fe) → Magnesium Crown (Mg)

Ferrosilicon 75% Si

Lloyd M. Pidgeon (1943~1969 UofT MSE Chair)

Kipouros and Sadoway. The Chemistry and Electrochemistry of Magnesium Production.
Application 2: Pidgeon Process

For the purpose of illustration, let us assume that pure solid MgO (not MgO · CaO) and pure solid Si (not ferrosilicon) are charged into the Pidgeon reactor. Then, the simplified Pidgeon process can be described as:

\[ 2\text{MgO}(s) + \text{Si}(s) = 2\text{Mg}(g) + \text{SiO}_2(s) \]

First, let us study the standard-state reaction using the Reaction Module. The temperature is 1423 K.
Application 2: Pidgeon Process

Standard-state Calculation:

Only FactPS is used.

Let FactSage decide which state should be used.
Application 2: Pidgeon Process

Standard-state Calculation:

Delta $H^\ast > 0$, which means the reaction is endothermic.

Delta $G^\ast > 0$, which means the reduction is not possible under the standard-state conditions.

No variables are required to be specified.

Note: the stable structure of SiO$_2$ at 1423 K is s4, which is tridymite (View Data Module)
Application 2: Pidgeon Process

Now, let us go back to the reaction and assume that all reactants/products are not necessarily in their standard state:

\[ 2\text{MgO}(s1) + \text{Si}(s2) = 2\text{Mg}(g) + \text{SiO}_2(s3) \]

To study the direction of this reaction, \( \Delta_r g \) should be used:

\[
\Delta_r g = \Delta_r g^o + RT \ln \frac{(P_{\text{Mg}(g)})^2 \times (a_{\text{SiO}_2})}{(a_{\text{MgO}})^2 \times (a_{\text{Si}})}
\]

Clearly, to drive this reaction to the right, we can consider the following.

1. Increase the reaction temperature (because the reaction is endothermic).
2. Reduce \( a_{\text{SiO}_2} \) by fluxing.
3. Reduce \( P_{\text{Mg}(g)} \) by employing vacuum.

Note: you probably know the Le Chatelier principle, and its mathematical basis is the expression of \( \Delta_r g \).
Application 2: Pidgeon Process

\[ a_{\text{SiO}_2} : \text{from the MgO-SiO}_2 \text{ phase diagram, it is seen that MgO}(s) \text{ and SiO}_2(s) \text{ cannot coexist because they react to form } (\text{MgO})_2 \cdot \text{SiO}_2. \]
Application 2: Pidgeon Process

\( a_{\text{SiO}_2} \): from the MgO-SiO\(_2\) phase diagram, it is seen that MgO(s) and SiO\(_2\)(s) cannot coexist because they react to form (MgO)\(_2\) \cdot \text{SiO}_2 or Mg\(_2\)SiO\(_4\), known as forsterite.

The MgO-SiO\(_2\) phase diagram indicates that given excess MgO(s) in the Pidgeon reactor, the formed SiO\(_2\)(s) will react with MgO(s) to form (MgO)\(_2\) \cdot \text{SiO}_2, and thus, \( a_{\text{SiO}_2}^{(s3)} < 1 \). In other words, SiO\(_2\)(s) is not stable.

The next page shows the calculation of \( a_{\text{SiO}_2} \) for a system consisting of MgO(s) and Mg\(_2\)SiO\(_4\)(s). You can also consider \( a_{\text{SiO}_2} \) as the activity of solid SiO\(_2\) when it exists as solid (MgO)\(_2\) \cdot \text{SiO}_2. To do this, the following reaction which contains SiO\(_2\)(s) is considered.

\[
2\text{MgO}(s) + \text{SiO}_2(s) = \text{Mg}_2\text{SiO}_4(s)
\]
Application 2: Pidgeon Process

Calculation of $a_{\text{SiO}_2}$:

Again, only FactPS is used.

MgO exists as pure solid.

Mg$_2$SiO$_4$ also exists as pure solid.

SiO$_2$ is not stable, and $a_{\text{SiO}_2} < 1$. 
Application 2: Pidgeon Process

Calculation of $a_{\text{SiO}_2}$:

This is $a_{\text{SiO}_2}$. This small number shows the strong fluxing effect of excess MgO which greatly reduce the activity of SiO$_2$. 
Application 2: Pidgeon Process

Also, in our simplified Pidgen Process:

\[ a_{\text{MgO}}^{(s1)} : \text{because MgO exists as a pure solid}, a_{\text{MgO}}^{(s1)} = 1. \]

\[ a_{\text{Si}}^{(s2)} : \text{because Si exists as a pure solid}, a_{\text{Si}}^{(s2)} = 1. \]
Application 2: Pidgeon Process

Non Standard-state Calculation: Calculate the equilibrium, i.e., $\Delta r g = 0$

Again, only FactPS is used.

This is $P_{Mg}$.

This is $a_{SiO_2}$.

The state must be specified so that activity is meaningful.

**For a gas species, $P(\text{atm/bar/ps})$ is its ideal partial pressure. For a liquid or solid, $P$ is the hydrostatic pressure above the phase. Select 'apply volume data' to include molar volume and compressibility data in the Vdp term - this does not apply to gases which are treated as ideal.**

Check 'non standard states'
Application 2: Pidgeon Process

**Non Standard-state Calculation:** Calculate the equilibrium, i.e., $\Delta_r g = 0$

There are an infinite number of $(P_{\text{Mg}}, a_{\text{SiO}_2})$ combinations which could give $\Delta_r g = 0$ and $K_{\text{equ}}$. Here we will select three special cases (next page).
Application 2: Pidgeon Process

Non Standard-state Calculation: Calculate the equilibrium, i.e., $\Delta_r g = 0$

You can save the results as “.dat” (input some comments).

At equilibrium ($\Delta_r g = 0$), when $a_{SiO_2} = 6.6139 \times 10^{-3}$ (calculated in Slide), $P_{Mg} = 1.0876 \times 10^{-3}$ atm.

At equilibrium ($\Delta_r g = 0$), when $a_{SiO_2} = 1$, $P_{Mg} = 8.8451 \times 10^{-5}$ atm.

At equilibrium ($\Delta_r g = 0$), when $P_{Mg} = 1$ atm, $a_{SiO_2} = 7.8235 \times 10^{-9}$.
Application 2: Pidgeon Process

The above calculation verified that the magnesium production at a certain temperature can be enhanced by:

1. Reduce the total pressure ($< 1.0876 \times 10^{-3} \text{ atm}$).
2. Reduce $a_{\text{SiO}_2}$ by fluxing – this is done automatically due to the formation of $\text{Mg}_2\text{SiO}_4(s)$, and the presence of CaO can reduce $a_{\text{SiO}_2}$ further.
Another way of studying this simplified Pidgeon process is to write the reaction as:

\[ 4\text{MgO}(s) + \text{Si}(s) = 2\text{Mg}(g) + \text{Mg}_2\text{SiO}_4(s) \]

In doing so, we don’t need to consider the unstable phase – solid \( \text{SiO}_2 \). Please perform the equilibrium calculations using this reaction.
Application 3: Vapor Pressure of Lead

Recall from Chapter 4.1 that for any condensed phase, there is a vapor pressure above it.

\[
\begin{array}{c|c}
\text{Gas} & P_B^* \\
\hline
\text{Liquid B} \\
\end{array}
\quad
\begin{array}{c|c|c}
\text{Gas} & P_A & P_B \\
\hline
\text{Liquid (A and B)} \\
\end{array}
\]

Say we are interested in the vapor pressure of lead above a lead-based solder bath (Sn-Pb) so that we can determine the safety precautions for the workers. Assume we have already known that the activity of lead in a eutectic solder is around 0.5 relative to the pure liquid \(a_{\text{Pb}}^{(\text{solder})} = 0.5\). The solder temperatures of interest are from 480~530 K (207~257 °C).
Application 3: Vapor Pressure of Lead

**Gaseous Species of Lead.** First, let us use the View Data Module to find what gaseous species of lead are modeled in the FactSage databases.

Choose FactPS which contains the models of most gaseous species.

Input Pb and another element, for example, Pb-O.
Application 3: Vapor Pressure of Lead

Gaseous Species of Lead. First, let us use the View Data Module to find what gaseous species of lead are modeled in the FactSage databases.

Two gaseous species of lead: Pb and Pb₂.
Application 3: Vapor Pressure of Lead

**Lead Monomer Vapor Pressure.**

We are performing non-standard state calculations.

FactPS is used.

Specify the state so that activity is meaningful.

It is assumed that $a_{\text{Pb}} = 0.5$.

This is $P_{\text{Pb}}$.

We are performing non-standard state calculations.

FactSage Team

MSE Department, University of Toronto
Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure.

The lead monomer vapor pressure is very low.

Temperature range and step.

We wish to calculate the equilibrium vapor pressure, which means $\Delta_{r,g} = 0$

2 variables need to be specified.
Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>480.00</td>
<td>1.9804E-16</td>
<td>189422.2</td>
<td>0.0</td>
<td>1.9889E+17</td>
<td>394.630</td>
<td>-10.199</td>
<td></td>
</tr>
<tr>
<td>490.00</td>
<td>5.2156E-16</td>
<td>189320.4</td>
<td>0.0</td>
<td>7.7093E+15</td>
<td>386.368</td>
<td>-10.163</td>
<td></td>
</tr>
<tr>
<td>500.00</td>
<td>1.3207E-15</td>
<td>189218.9</td>
<td>0.0</td>
<td>3.1065E+15</td>
<td>378.438</td>
<td>-10.127</td>
<td></td>
</tr>
<tr>
<td>510.00</td>
<td>3.2233E-15</td>
<td>189117.8</td>
<td>0.0</td>
<td>1.2983E+15</td>
<td>370.819</td>
<td>-10.091</td>
<td></td>
</tr>
<tr>
<td>520.00</td>
<td>7.5578E-15</td>
<td>189017.1</td>
<td>0.0</td>
<td>5.6161E+15</td>
<td>363.494</td>
<td>-10.057</td>
<td></td>
</tr>
<tr>
<td>530.00</td>
<td>1.7331E-14</td>
<td>188916.7</td>
<td>0.0</td>
<td>2.5094E+15</td>
<td>356.447</td>
<td>-10.022</td>
<td></td>
</tr>
</tbody>
</table>
Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.

![Diagram showing a table with temperature (T(K)) and vapor pressure (P(atm)) values, and a plot configuration window. The window includes options for Y-axis and X-axis variables, with settings for maximum, minimum, and tick every values. The table includes temperature values like 480, 490, 500, 510, 520, 530, and corresponding vapor pressure values in atm.]
Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.

You can choose the variable of axes and their format.
Application 3: Vapor Pressure of Lead

Lead Monomer Vapor Pressure: plot the data.

![Graph showing the vapor pressure of lead monomer over temperature.](image)
Application 3: Vapor Pressure of Lead

Lead Dimer Vapor Pressure.

FactPS is used. It is assumed that $a_{\text{Pb}} = 0.5$. This is $P_{\text{Pb}_2}$. 
Application 3: Vapor Pressure of Lead

Lead Dimer Vapor Pressure.

The lead dimer vapor pressure is even lower.

Temperature range and step.
Application 3: Vapor Pressure of Lead

Lead Dimer Vapor Pressure: plot the data
In-Class Exercise

Question 1.
Plot the “liquidus line” for ideal nickel alloys.
Tip: perform the equilibrium calculation for the melting reaction $\text{Ni}(s) = \text{Ni}(l)$ and note $\text{Ni}(s)$ is pure solid whereas $\text{Ni}(l)$ is in the solution state, i.e., $a_{\text{Ni}} < 1$ relative to pure liquid Ni.
(You can find help from the supplementary materials: “02 FACTSage_Raction Module_Supplementary”)

Question 2.
Calculate the AFT for combustion of propane ($\text{C}_3\text{H}_8$) in air (0 to 100% excess air – meaning from stoichiometric air to twice as much).
In-Class Exercise

Question 3.

In each case below, is the metal recovery possible from the slag and what is the effect of temperature?

Note: for reduction by Fe, the FeO activity in the oxide melt will be assumed to be 0.4; and for reduction by Si, the SiO₂ activity will be 0.3. Activities in molten alloys and slags are relative to pure liquid (i.e., Raoultian pure substance standard state). If no data for liquid oxide, then choose solid.

(3a) Treatment of arc furnace dust. Look at the reduction of ZnO, initially with an activity of 0.1, by solid iron scrap. Temperature range is 1200~1600 °C. The zinc must come off as vapor at 1 atm (partial pressure of zinc).

(3b) Recovery of cobalt from scrap superalloys. Look at the reduction of CoO initially with an activity of 0.01 in a molten slag, by iron scrap. The cobalt will form as a liquid in a molten alloy and should have an activity of 0.2. Temperature range is 1500~1700 °C.
In-Class Exercise

Question 3.

(3c) Recovery of cadmium from “NiCad” battery scrap. Look at the reduction of CdO, initially with an activity of 0.002 in a molten slag, by solid iron scrap. Temperature range is 1200~1600 °C. The cadmium must come off as vapor at 1 atm (partial pressure of cadmium).

Question 4.

Look at the vapor species for a metal (Fe, Ni, Zn, etc.) using the View Data Module. Then use the Reaction Module to plot log(P) vs. 1/T (K) for the monomer species above the pure liquid. Choose Y-axis numbers between 10 and 0.0001 initially [log(P) between 1 and −4] and use that to help you find the appropriate temperature range. (Choose one metal)