

# **FactSage Practical**

## **MSE302**

### **Practical 4. Equilib Module**

# Acknowledgements

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The teaching team of MSE302 is grateful to:

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# Outline

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# Some Important Thermodynamic Terms

Term	Physical Meaning
Heat Capacity $C_P$	The amount of heat required to raise the temperature of <b>the system</b> by 1 K during an isobaric process.
Enthalpy $H$	Total energy of the system. The change in Enthalpy refers to the amount of heat that is exchanged with the surroundings during an isobaric process.
Entropy $S$	A thermodynamic function that is used to determine the process spontaneity. The entropy for an isolated system always increases for spontaneous processes.
Gibbs Energy $G$	A thermodynamic function that is used to determine the process spontaneity. The Gibbs energy of a closed system always decreases for spontaneous processes with constant temperature and pressure.
Fugacity (Gas Species)	A thermodynamic function that describes the deviation from the ideal gas behavior. It is sometimes named as <b>effective</b> partial pressure of gas species. For ideal gases, fugacity is numerically equal to partial pressure.
Activity (Solution Species)	A thermodynamic function that describes the deviation from the ideal solution behavior. It represents effective concentration of components in a solution. For ideal solutions, activity is numerically equal to mole fraction.

# Equilib Module: Some Important Terms

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Term	Physical Meaning
Fugacity_Total (Gas Phase) Activity_Total (Solution Phase) Activity (Compound)	Theses terms are considered as “phase activity”. When their value is 1, the phase is stable; otherwise, the phase is not stable. When their value is close to 1, this indicates that if the temperature and pressure change slightly, the phase might become stable.

# Equilib Module: Basics

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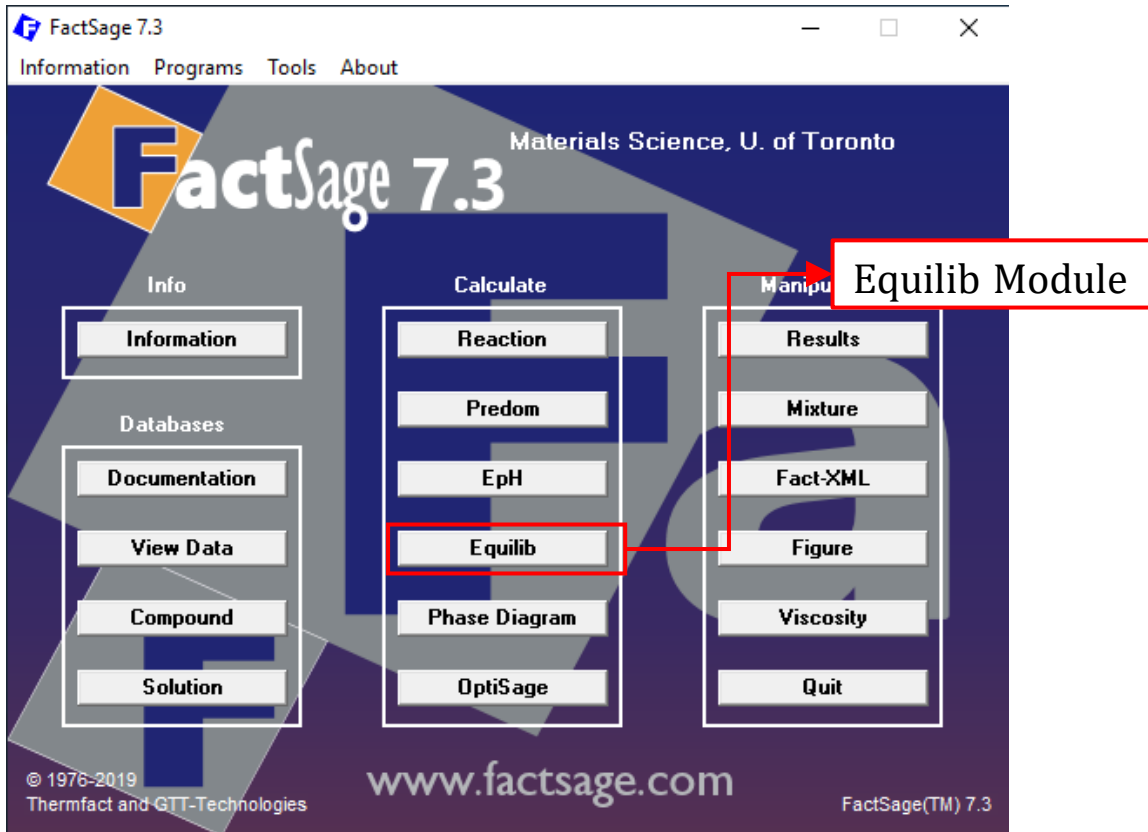
The Equilib Module is the **most powerful module** of FactSage.

- ✓ The module calculates the equilibrium for multiphase, multicomponent equilibria, with a wide variety of tabular and graphical output modes, under a large range of constraints (for example, given temperature, pressure, composition, etc.).
- ✓ The module uses the “Gibbs energy minimization” principle to find the phases that exist at equilibrium and their respective compositions & amounts.
- ✓ The module accesses both Compound and Solution databases.

Different from the Reaction Module, the Equilib Module does not require a well-defined reaction equation. The user only needs to tell the Equilib Module the input elements and the equilibrium conditions, and then the Equilib Module will calculate the products at equilibrium from the list of the **possible** phases the user has selected.

# Equilib Module: Basics

**Equilib Module** in the home page.



# Equilib Module: Basics

After you run the Equilib Module, you will see the following screen:

The screenshot shows the Equilib software interface for a "Simple gas reaction". The main window displays the reaction:  $2 \text{H}_2 + \text{O}_2$  at 25°C. The interface includes a menu bar (File, Units, Parameters, Help), a toolbar, and several panels: Reactants (2), Products (Compound species, Solution phases), Target (Estimate T(K): 1000, Quantity(mol): 0), and Final Conditions (T(C): 1000, P(atm): 1). A "Calculate >>" button is visible at the bottom right. Red callout boxes with arrows point to specific elements: "Menu Window" points to the menu bar; "Reactants Window" points to the Reactants section; "List Window" points to the Solution phases table; and "Results Window" points to the Final Conditions section.

Equilib - Menu: Simple gas reaction

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Reactants (2)

2 H<sub>2</sub> + O<sub>2</sub>  
(25C.g.#1) (25C.g.#1)

Products

Compound species

gas  ideal  real 9  
aqueous 0  
pure liquids 0  
pure solids 0

species: 9

Target

- none -  
Estimate T(K): 1000  
Quantity(mol): 0

Final Conditions

<A>	<B>	T(C)	P(atm)	Delt
		1000	1	

10 steps  Table 1 calculation

Calculate >>

Menu Window

Reactants Window

List Window

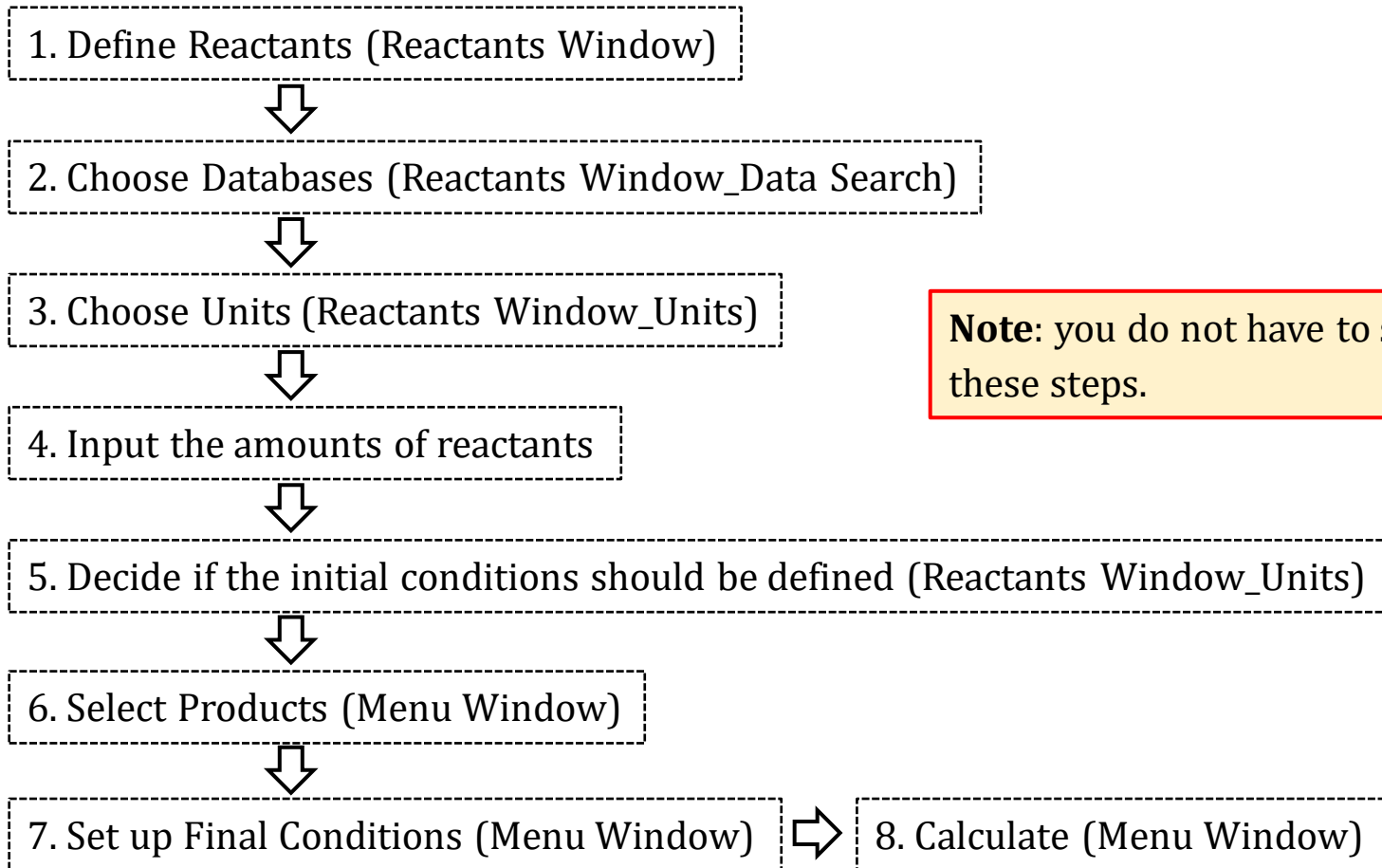
Results Window



# Equilib Module: Basics

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## General Steps in the Equilib Module



**Note:** you do not have to strictly follow these steps.

# Equilib Module: Basics

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## A Note on “Initial Conditions”

The equilibrium that is calculated under given conditions is independent of the input species and only depends on the amounts of the various **elements** added (element matrix). For example, consider the following two scenarios:

- (a) we add 1.0 mole of chalcopyrite ( $\text{CuFeS}_2$ ) and 1.0 mole of oxygen ( $\text{O}_2$ ) into the smelter; or,
- (b) we add 0.5 mole of  $\text{Cu}_2\text{O}$ , 1.0 mole of hematite ( $\text{Fe}_2\text{O}_3$ ), 1.0 mole of sulfur gas ( $\text{S}_2$ ), and 0.25 mole of oxygen ( $\text{O}_2$ ) into the smelter.

Note in both scenarios, the number of moles of elements added:

Cu: 1.0, Fe: 2.0, S: 2.0, and O: 2.0.

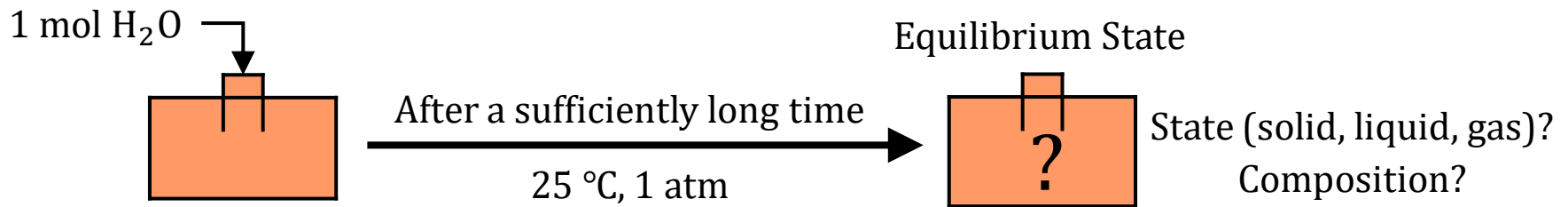
If the temperature and pressure in the smelter are maintained at the same level, the final products when the system reaches equilibrium must be same for the above two scenarios, although the heat of reaction will be different.

# Equilib Module: H<sub>2</sub>O Equilibrium

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We will start with a simple example: H<sub>2</sub>O.

Say we have 1 mole of H<sub>2</sub>O. We would like to know when the system reaches equilibrium at 25 °C and 1 atm, what phase(s) are present and what are their compositions.



# Equilib Module: H<sub>2</sub>O Equilibrium

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Before we use the Equilib Module, let us perform some manual calculations so we can better understand how FactSage works based on **the Gibbs energy minimization** principle.

**[Problem]** Find the equilibrium state for 1 mole of H<sub>2</sub>O at 25 °C and 1 atm.

**[Step 1]** First, the system at equilibrium must meet the requirement of **mass conservation**, that is, **2 mole of hydrogen** and **1 mole of oxygen**. Clearly, there are an **infinite** number of ways (or, system configuration) so that this requirement can be met. **A few of them** are listed below:

- (1) 1 mole of H<sub>2</sub>O (*s*), i.e., ice
- (2) 1 mole of H<sub>2</sub>O (*l*), i.e., liquid water
- (3) 1 mole of H<sub>2</sub>O (*g*), i.e., water vapor
- (4) 1 mole of H<sub>2</sub> (*g*) + 0.5 mole of O<sub>2</sub> (*g*) etc.

# Equilib Module: H<sub>2</sub>O Equilibrium

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**[Step 2]** We can use the FactPS database to calculate the Gibbs energy for the above system configurations at 25 °C and 1 atm (**next page**).

(1) –306.09 kJ      (2) –306.69 kJ      (3) –298.10 kJ      (4) –71.86 kJ

**[Step 3]** The system at equilibrium should possess the minimum Gibbs energy. Therefore, the equilibrium state should be configuration (2).

**A Note:** the Gibbs energy minimizer in FactSage employs an efficient algorithm (Lagrange's Multipliers, FactSage-Teach) that can find the system configuration with the minimum Gibbs energy under the constraints of mass balance.

# Equilib Module: H<sub>2</sub>O Equilibrium

## Compound Module: FactPS

Energy: Joules Pressure: atm H<sub>2</sub>O

File Edit Units View Tools ViewData Help

Formula O<sub>2</sub>

FactPSBASE

- H<sub>2</sub>
  - G1
    - Cp 1200
    - Cp 4100
    - Cp 6000
  - Aq1
- O<sub>2</sub>
  - G1
    - Cp 1000
    - Cp 4000
    - Cp 6000
  - Aq1
- H<sub>2</sub>O
  - S1**
    - Cp 273
  - L1
    - Cp 500
  - G1
    - Cp 1100

S1 properties

Heat of form. + Entropy Heat + Temperature of transf.

Form. of S1

ΔH 298 (Joules)	S298 (J/(mol K))
-292816.2	44.529

Phase Name Reference no. Density g/cc

Ice	1	0.917
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$$g^{\circ}_{i,298 \text{ K}} = h^{\circ}_{i,298 \text{ K}} - (298 \text{ K}) \times s^{\circ}_{i,298 \text{ K}}$$
$$= \Delta_f h^{\circ}_{i,298 \text{ K}} - (298 \text{ K}) \times s^{\circ}_{i,298 \text{ K}}$$

FactSage 7.3 C:\FactSage\FACTDATA\F553base.cdb (v7.30) 4920 compounds read-only

# Equilib Module: H<sub>2</sub>O Equilibrium

## Reactants Window: Define Reactants

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Don't forget the Directory.

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	H2O				1	

H<sub>2</sub>O molecule is introduced.

Do not check "Initial Conditions" because we are **NOT** interested in the change in the thermodynamic properties.

Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

# Equilib Module: H<sub>2</sub>O Equilibrium

## Reactants Window: Database(s)

The screenshot shows the 'Data Search' dialog box in the Equilib - Reactants window. The 'FactPS' checkbox is checked and highlighted with a red box. A red arrow points from this box to a text box containing the explanation: 'H<sub>2</sub>O consists of H and O. These two elements can only form gaseous species and pure solids (e.g., ice) and pure liquid (e.g., water). Therefore, only FactPS is required.'

The dialog box includes the following sections:

- Databases - 1/14 compound databases, 0/15 solution databases**
- Fact** (checked), **FactSage**, **SGTE**
- Private Databases**: **EXAM** (unchecked)
- Other**: **ELEM** (checked), **SGnobl**, **SpMCBN**, **TDmeph**, **TDnucl**
- Options - search for product species**:
  - Include compounds:
    - gaseous ions (plasmas)
    - aqueous species
    - limited data compounds (25C)
  - Limits:
    - Organic species CxHy..., X(max) = 2
    - Minimum solution components:  1  2 cpts



# Equilib Module: H<sub>2</sub>O Equilibrium

## Reactants Window: Choose Units and Input the Quantity of Species

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Choose the units.

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	H2O				1	

We will consider 1 mole of H<sub>2</sub>O.

Specifying the quantity requires we choose the units first.

Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

# Equilib Module: H<sub>2</sub>O Equilibrium

## Menu Window: Selection of Products (Compounds and Solution Phases)

The screenshot shows the 'Equilib Menu' window. The 'Reactants' section contains 'H2O'. The 'Products' section has a 'Compound species' list with the following items:

Species	Count
gas (ideal)	9
gas (real)	0
aqueous	0
pure liquids	2
pure solids	1
<b>Total species</b>	<b>12</b>

The 'Solution phases' table is empty. The 'Volume data' section has the following options:

- assume molar volumes of solids and liquids = 0
- include molar volume data and physical properties data
- paraequilibrium & Gmin

The 'Final Conditions' section shows 'Estimate T(K): 1000' and 'Quantity(mol): 0'. The 'Target' is set to 'none'.

Choose all the Compound species. Normally, when only one compound database (FactPS) is selected, there is no need to screen the phases from the list. For the gas phase, we choose the **ideal gas model** because the gas species in the real gas model are quite limited and the assumption of ideal gas model is valid at low pressures.

# Equilib Module: H<sub>2</sub>O Equilibrium

## Menu Window: Set up the Final Conditions

The screenshot shows the Equilib Module software interface. The menu bar includes 'Equilib', 'File', 'Units', 'Parameters', and 'Help'. The 'Parameters' menu is open, showing options for 'Menu:', 'Parameters', and 'Help'. A red box highlights the 'Menu:' option with the text: "We will use the default settings for Parameter."

The main window displays the 'Final Conditions' section. A red box highlights the 'T(C)' field with the value '25' and the 'P(atm)' field with the value '1'. A red box highlights the 'Product H(J)' dropdown menu with the value '1 calculation'. A red box highlights the 'Equilibrium' section with the 'normal' radio button selected. A red box highlights the 'Volume data' section with the 'assume molar volumes of solids and liquids = 0' radio button selected. A red box highlights the 'Total Spec' field with the value '0'. A red box highlights the 'Total Sol' field with the value '0'. A red box highlights the 'Total Phas' field with the value '0'. A red box highlights the 'Equilibrium' section with the 'normal' radio button selected. A red box highlights the 'Equilibrium' section with the 'normal' radio button selected.

Annotations:

- "These are the equilibrium conditions under which we want to calculate: 25 °C and 1 atm." (points to T and P fields)
- "For most calculations, we are not interested in the volume data." (points to Volume data section)
- "Leave this cell blank because this will be calculated." (points to Total Spec field)
- "Only 1 calculation will be performed under the given conditions." (points to Product H(J) dropdown)



# Equilib Module: H<sub>2</sub>O Equilibrium

## Results: ChemSage Format

Equilib Results 25 C

Output Edit Show Pages Final Conditions

T = 25 C  
P = 1 atm  
V = 0 dm<sup>3</sup>

These are the conditions under which the system reaches equilibrium. In most cases, the volume data for **condensed** phases are not considered, and only the volume of gas phase will be shown.

STREAM CONSTITUENTS	AMOUNT/mol
H2O	1.0000E+00

This is the input material and its amount.

PHASE: gas ideal	EQUIL AMOUNT mol	MOLE FRACTION	FUGACITY atm
H2O	0.0000E+00	1.0000E+00	3.1352E-02
H2	0.0000E+00	7.9733E-27	2.4998E-28
O2	0.0000E+00	3.9867E-27	1.2499E-28
OH	0.0000E+00	5.5710E-33	1.7466E-34
HOOH	0.0000E+00	3.0017E-36	9.4110E-38
HOO	0.0000E+00	1.8813E-43	5.8982E-45
H	228E-48	3.8337E-50	3.8337E-50
O	368E-54	2.8019E-55	2.8019E-55
O3	577E-69	3.6296E-71	3.6296E-71
TOTAL:	0.0000E+00	1.0000E+00	3.1352E-02

Gas Phase.

Components of gas phase.

Since the ideal gas model was used, fugacity is partial pressure.

Total fugacity is less than 1 atm. Therefore, no gas is present.

	mol	ACTIVITY
H2O liquid(liq)	1.0000E+00	1.0000E+00
H2O Ice(s)	T 0.0000E+00	7.8723E-01
HOOH_liquid(liq)	0.0000E+00	3.3420E-35

When activity of a phase is 1, this means that the phase is stable.

Final Conditions

Cp	<A>	<B>	T(C)	P(atm)	Product H(J)
J K					1 calculation

"T" mark means the thermodynamic data are no longer within the effective temperature range.

# Equilib Module: H<sub>2</sub>O Equilibrium

## Results: ChemSage Format

Equilib - Results 25 C

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Species	T	P	Energy(J)	Quantity(mol)	Vol(litre)
O3			0.0000E+00	1.1577E-69	3.6296E-71
TOTAL:			0.0000E+00	1.0000E+00	3.1352E-02
mol ACTIVITY					
H2O_liquid(liq)			1.0000E+00		1.0000E+00
H2O_Ice(s)	T		0.0000E+00		7.8723E-01
HOOH_liquid(liq)			0.0000E+00		3.3420E-35

Cp	H	S	G	V
J.K-1	J	J.K-1	J	dm3
7.53754E+01	-2.85830E+05	6.99500E+01	-3.06686E+05	0.00000E+00

Cp	H	S	G
J.K-1	J	J.K-1	J
7.53754E+01	-2.85830E+05	6.99500E+01	-3.06686E+05

Cut-off limit for gaseous fractions/phase activities = 1.00E-75

Data on 1 product species identified with "T" have been extrapolated outside their valid t

Databases: FactPS 7.3

Data Search options: exclude gas ions, organic CxHy.. X(max) = 2, 12

Final conditions: T(C) = 25, P(atm) = 1

Final Conditions

<A>	<B>	T(C)	P(atm)	Product H(J)
		25	1	

1 calculation X

Calculate >>

Thermodynamic quantities of the entire system.

Thermodynamic quantities of stable phases. In this example, only liquid water.

# Equilib Module: H<sub>2</sub>O Equilibrium

## Menu Window: Set up the Final Conditions

Equilib - Menu: last system

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Reactants (1)

Products

Compound species

- gas  ideal  real 9
- aqueous 0
- pure liquids 2
- pure solids 1

species: 12

Target

Estimate T(K): 1000

Quantity(mol): 0

Solution phases

*	+	Base-Phase	Full Name
---	---	------------	-----------

Legend

Show  all  selected

species: 0

solutions: 0

Select

Custom Solutions

0 fixed activities

0 ideal solutions

Pseudonyms

apply  Edit ...

Volume data

assume molar volumes of solids and liquids = 0

include molar volume data and physical properties data

paraequilibrium & Gmin edit

Virtual species: 0

Total Species (max 5000) 12

Total Solutions (max 200) 0

Total Phases (max 1500) 4

Equilibrium

normal  normal + transitions

transitions only

open

Calculate >>

Final Conditions

<A>	<B>	T(C)	P(atm)	Product H(J)
10		25	0.031352	

10 steps  Table

FactSage 7.3

# Equilib Module: H<sub>2</sub>O Equilibrium

## Results: ChemSage Format

Equilib - Results 25 C

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

T = 25 C  
P = 3.1352E-02 atm  
V = 780.35 dm<sup>3</sup>

STREAM CONSTITUENTS

STREAM CONSTITUENTS	AMOUNT/mol
H2O	1.0000E+00

PHASE: gas\_ideal

	EQUIL AMOUNT mol	MOLE FRACTION	FUGACITY atm
H2O	1.0000E+00	1.0000E+00	3.1352E-02
H2	7.9733E-27	7.9733E-27	2.4998E-28
O2	3.9867E-27	3.9867E-27	1.2499E-28
OH	5.5710E-33	5.5710E-33	1.7466E-34
HOOH	3.0017E-36	3.0017E-36	9.4110E-38
HOO	1.8813E-43	1.8813E-43	5.8982E-45
H	1.2228E-48	1.2228E-48	3.8336E-50
O	8.9368E-54	8.9368E-54	2.8019E-55
O3	1.1577E-69	1.1577E-69	3.6296E-71
TOTAL:	1.0000E+00	1.0000E+00	1.0000E+00

System component

System component	Amount/mol	Amount/gram	Mole fraction	Mass fraction
O	1.0000	15.999	0.33333	0.88810
H	2.0000	2.0159	0.66667	0.11190

ACTIVITY

	mol	ACTIVITY
H2O liquid(liq)	0.0000E+00	9.9999E-01
H2O_Ice(s)	0.0000E+00	7.8722E-01
HOOH_liquid(liq)	0.0000E+00	3.3420E-35

\*\*\*\*\*

Cp	H	S	G	V
J.K-1	J	J.K-1	J	dm <sup>3</sup>
3.35886E+01	-2.41834E+05	2.17513E+02	-3.06686E+05	7.80351E+02

This time, we changed the pressure. Because the volume is not zero, this time the system certainly contains gas.

Gas Phase.

Total fugacity is 1 atm. This means the gas phase is stable.

This activity of liquid H<sub>2</sub>O is not 1, but very close to 1. This means that liquid H<sub>2</sub>O is very close to be a stable phase.

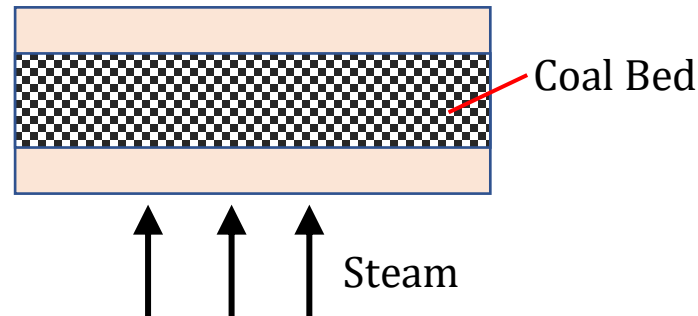
This is expected because when we reduce the pressure, gas tends to be stable.



# Equilib Module: Gasification of Coal

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The second example we will be looking at is the gasification of coal by steam. Say we inject the hot steam into a coal bed. The temperature of the coal bed is maintained at 1000 K, and the pressure at 10 atm. We would like to know what species are obtained at equilibrium as well as their respective amounts.



# Equilib Module: Gasification of Coal

## Reactants Window: Define Reactants

Equilib Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

Quantity(g)	Species	Phase	T(C)	P(total)**	Stream#
1	C				1
+ 1	H2O				2

Don't forget the Directory.

Two input reactants

Do not check "Initial Conditions" because we are **NOT** interested in the change in the thermodynamic properties.

Initial Conditions

Stream

This is the reactant stream number. This appears when the box "Initial Conditions" has been checked. Specifying initial conditions is only useful if you want to calculate or constrain changes in the extensive properties (Delta V, Delta H, etc.).

All reactants in a given stream are grouped together - they have the same temperature and total pressure. If you change the temperature (or pressure) of any one member of a stream, then the temperature (pressure) of all the other members of the stream will be changed to this same common value.

For condensed phases, the total pressure is the hydrostatic pressure above the phase. For gases, the total pressure is the sum of all the gaseous partial pressures in that stream.

For example, for an ideal gas if reactants  $4 \text{ mol N}_2(\text{g}) + 1 \text{ mol O}_2(\text{g})$  are in the same stream at  $P(\text{total}) = 1 \text{ atm}$ , then  $P(\text{N}_2) = 0.8 \text{ atm}$  and  $P(\text{O}_2) = 0.2 \text{ atm}$ .

OK

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 1/15 databases

# Equilib Module: Gasification of Coal

## Reactants Window: Database(s)

Equilib - Reactants

File Edit Table Units **Data Search** Data Evaluation Help

Data Search

Databases - 1/14 compound databases, 0/15 solution databases

**Fact** **FactSage™** **SGTE**  compounds only  solutions only  no database **Private Databases**

**FactPS**  FScopp  BINS  EXAM

FToxid  FSlead  SGPS

FTsalt  FSstel  SGTE

FTmisc  FSupsi  SGsold

FThall

FT0xCN

FTfritz

FThelp  ELEM  SGnobl

FTpulp  FTdemo  SpMCBN

FTlite  FTnucl  TDmeph

TDnucl

Clear All

Add/Remove Data

RefreshDatabases

Information -

Options - search for product species

Default

Include compounds

gaseous ions (plasmas)

aqueous species

limited data compounds (25C)

Limits

Organic species CxHy..., X(max) = 2

Minimum solution components:  1  2 cpts

Cancel Summary ... OK

There is no condensed solutions. Only pure solids (carbon) and gas mixture are considered. Therefore, only FactPS is required.

# Equilib Module: Gasification of Coal

## Reactants Window: Choose Units and Input the Quantity of Species

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(K) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 2

Choose the units.

Quantity(mol)	Species	Phase	T(K)	P(total)**	Stream#	Data
2	C				1	
+ 1	H2O				1	

We will consider a very simple case: 2 mole of C reacts with 1 mole of steam

Specifying the quantity requires we choose the units first.

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

# Equilib Module: Gasification of Coal

## Menu Window: Selection of Products (Compounds and Solution Phases)

The screenshot shows the Equilib software interface with the following components:

- Menu Window:** Equilib - Menu last system
- File Units Parameters Help**
- Units:** T(K) P(atm) Energy(J) Quantity(mol) Vol(litre)
- Reactants (2):** 2 C + H2O
- Products:**
  - Compound species:** gas (ideal/real), aqueous, pure liquids, pure solids. Total species: 53.
  - Solution phases:** Table with columns: \*, +, Base-Phase, Full Name.
- Target:** Estimate T(K): 1000, Quantity(mol): 0
- Legend:** Show all selected, species: 0, solutions: 0, Select
- Final Conditions:** T(K): 1000, P(atm): 1, Product H(J): 10 steps, 1 calculation
- Equilibrium:** normal, normal + transitions, transitions only, open, Calculate >>

Annotations in the image:

- A red box around the units menu with an arrow pointing to the text "Choose the units."
- A red box around the compound species list with an arrow pointing to the text "Choose all the Compound species."
- A red box around the "Calculate >>" button.

# Equilib Module: Gasification of Coal

## Menu Window: Set up the Final Conditions

Equilib - Menu last system

File Units Parameters Help

T(K) P(atm) Energy(J) Quantity(mol) Vol(litre)

Reactants (2)

2 C + H2O

Products

Compound species

gas ideal real 41

aqueous 0

pure liquids 9

pure solids 3

species: 53

Target

Estimate T(K): 1000

Quantity(mol): 0

Final Conditions

<A>	<B>	T(K)	P(atm)	Product H(J)
10	steps	1000	10	1 calculation

Equilibrium

normal normal + transitions

transitions d

open

and physical properties data

paraequilibrium & Gmin edit

Virtual species: 10

Total Species (max 5000) 53

Total Solutions (max 200) 0

Total Phases (max 1500) 13

Leave this cell blank.

Only 1 calculation will be performed under the given conditions.

These are the equilibrium conditions under which we want to calculate.

# Equilib Module: Gasification of Coal

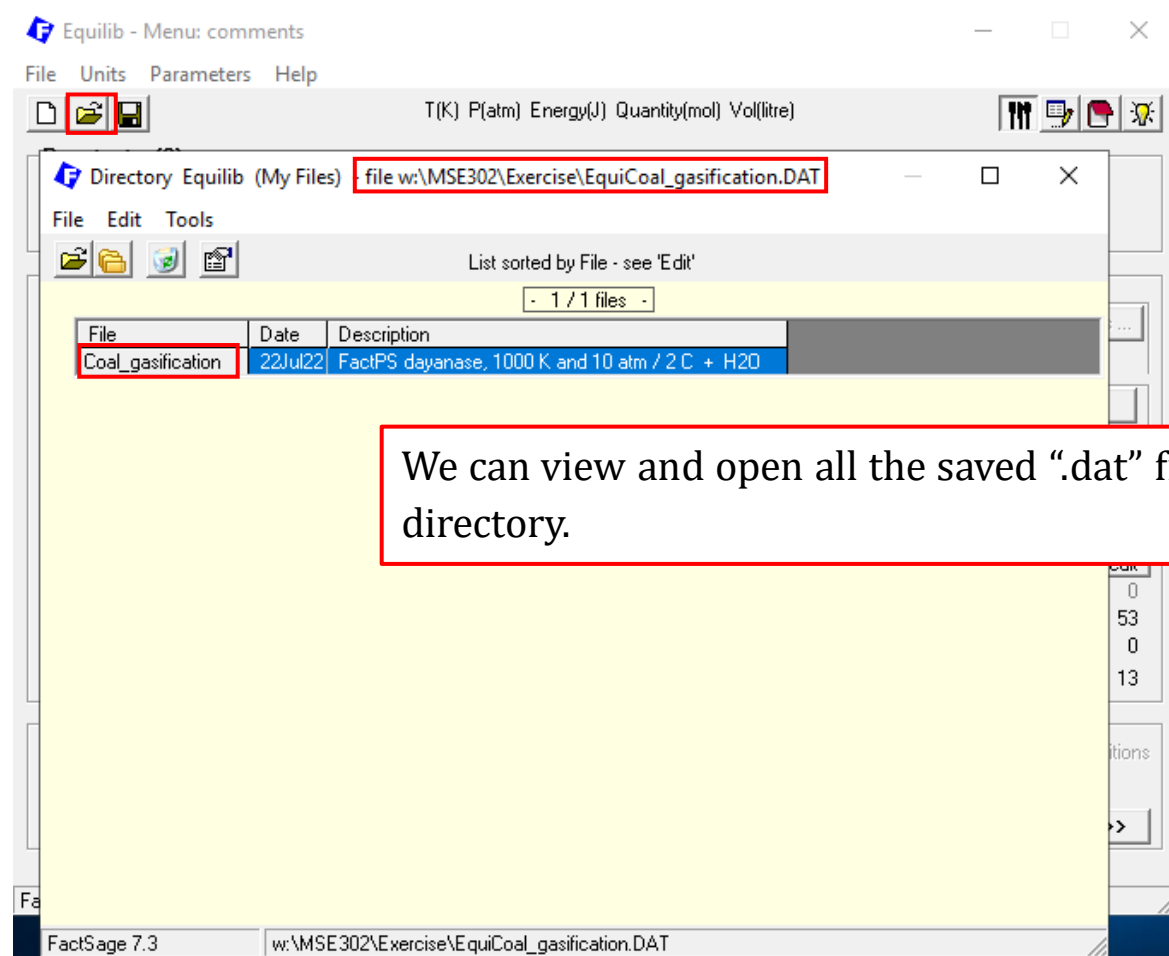
## Save the Equilib settings: “.dat” file

In the Equilib Module, we can save the settings for a calculation as a “.dat” file.

The screenshot illustrates the process of saving Equilib settings as a .dat file. On the left, the 'Equilib - Menu: last system' window is shown with the 'File' menu open. The 'Save As ...' option is highlighted in blue, and a red box is drawn around it. A red arrow points from this option to the first dialog box on the right. This dialog box, titled 'Save File in w:\MSE302\Exercise\Equi\*.dat', prompts the user to 'Enter the file number (1 - 9999)' or 'enter the file name, for example'. The text 'My very favorite calculation' is entered, and a note below the input field says '- avoid the special characters ?/!~.``&.;\'. The text 'Coal gasification' is entered in the input field. Below this, a second dialog box is shown, titled 'Save File w:\MSE302\Exercise\EquiCoal\_gasification.DAT'. It prompts the user to 'Saving file Coal\_gasification' and 'Enter one line of comments'. A note below the input field says '- to add additional notes, terminate the line of comments with the character +'. The text 'FactPS dayanase, 1000 K and 10 atm' is entered in the input field.

# Equilib Module: Gasification of Coal

## Open the “.dat” file



The screenshot shows the Equilib software interface. A file directory window is open, displaying a list of files. The file 'Coal\_gasification' is highlighted in the table below.

File	Date	Description
Coal_gasification	22Jul22	FactPS dayanase, 1000 K and 10 atm / 2 C + H2O

The status bar at the bottom of the window shows 'FactSage 7.3' and the file path 'w:\MSE302\Exercise\EquiCoal\_gasification.DAT'.

We can view and open all the saved “.dat” files from the directory.



# Equilib Module: Gasification of Coal

## Results: ChemSage Format

Equilib Results 1000 K

Output Edit Show Pages Final Conditions

T(K) P(atm) Energy(J) Quantity(mol) Vol(litre)

Phase and phase constituents.

Because the gas phase is ideal, mole fractions are numerically equal to fugacity.

The fugacity of the gas phase: “= 1” means the gas phase is stable; “< 1” means the gas phase is unstable.

Pure solids/liquids. Their activity: “= 1” means the gas phase is stable; “< 1” means the gas phase is unstable.

Thermodynamic properties of the system and stable phases.

```

T = 1000 K
P = 10 atm
V = 10.916 dm3

STREAM CONSTITUENTS      AMOUNT/mol
C                          2.0000E+00
H2O                        1.0000E+00

EQUIL AMOUNT             MOLE FRACTION           FUGACITY
mol                      atm
H2                        4.2984E-01             3.2311E+00
H2O                       3.0005E-01             2.2555E+00
CO2                       2.3458E-01             1.7634E+00
CO                         2.3078E-01             1.7348E+00
CH4                       1.3504E-01             1.0151E+00
TOTAL:                    1.3303E+00             1.0000E+00

System component         Amount/mol             Amount/gram           Mole fraction         Mass fraction
O                         1.0000                15.999                0.27775                0.63422
C                         0.60042               7.2115                0.16676                0.28587
H                         2.0000                2.0159                0.55549                7.9910E-02

mol                      ACTIVITY
C_Graphite(s)            1.3996E+00            1.0000E+00
C_diamond(s2)            0.0000E+00            4.9589E-01
H2O_liquid(liq)         T 0.0000E+00          4.2144E-03

*****
Cp      H          S          G          V
J.K-1   J          J.K-1   J          dm3
*****
3.72530E+02  -1.49300E+05  3.17718E+02  -4.67019E+05  1.09162E+01

Cp      H          S          G
J.K-1   J          J.K-1   J
gas_ideal  3.42302E+02  -1.65809E+05  2.83493E+02  -4.49301E+05
C_Graphite(s)  3.02283E+01  1.65075E+04  3.42256E+01  -1.77181E+04

Final Conditions
Cut-off limit for gaseous fractions/
Data on 1 product species identified
    
```

# Equilib Module: Gasification of Coal

## Save the Results: Spreadsheet Format

You can choose different file type. Here, we use the Text file because the results are very simple.

**Output**

Page Range:  All pages  Current page 1 (1000 K)

**Type of Output**

- Printer (Printer setup ...)
- Text file (\*.txt)
- Equilib Results File (Equi\*.res)
- Xml file (\*.xml)
- Excel Spreadsheet (Spreadsheet setup ...)
- Open Text Spreadsheet
- Save Text Spreadsheet
- Swap rows & columns

**Final Conditions**

<A>	<B>	T(K)	P(atm)	Product H(J)
		1000	10	

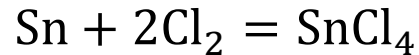
1 calculation **Calculate >>**

CO  
CH4  
TOTAL:  
System component  
O  
C  
H  
mol  
ACTIVITY  
C\_Graphite(s) 1.3996E+00 1.0000E+00  
C\_diamond(s2) 0.0000E+00 4.9589E-01  
H2O\_liquid(liq) T 0.0000E+00 4.2144E-03  
\*\*\*\*\*  
Cp H S G V  
J.K-1  
\*\*\*\*\*  
3.72530E+02 -1.

# Equilib Module: Recovery of Tin from Tin Cans

---

The third example is to recover tin from tin cans by chlorination, represented by the following reaction:



**Tin cans are made of tin-coated steel.** Progressive chlorination of tin results in the exposure of iron. To avoid the chlorination of iron which would lower the grade of  $\text{SnCl}_4$ , oxygen is introduced to form  $\text{Fe}_2\text{O}_3$ . This means that we need to study the thermodynamics of the Fe-Sn-Cl-O system for this chlorination process if the steel is considered to consist of pure iron. Under the controlled conditions, the desired solid products should be  $\text{SnCl}_4$  and  $\text{Fe}_2\text{O}_3$ .

To help you better understand the underlying thermodynamic principle on which the above process is based, the predominance diagram of the Fe-Sn-Cl-O system was calculated.

# Equilib Module: Recovery of Tin from Tin Cans

## Predominance Diagram of the Fe-Sn-Cl-O System at 700 °C.

The screenshot displays the Predom software interface. The main window is titled "Predom" and has a menu bar with "File", "Units", "Data Search", and "Help". The "Data Search" menu item is highlighted with a red box. Below the menu bar, there are icons for file operations and a status bar showing "T(C) P(atm) Mass(mol)".

The "Elements" section has three radio buttons: "1-Metal", "2-Metal" (selected), and "3-Metal". Below these are three "Example .." buttons. A red box highlights the "2-Metal" option. Below the radio buttons are two input fields for "Metals": "Fe" and "Sn", and two input fields for "Non-metals": "Cl" and "O". A "Clear" button and an "optional" label are also present. A red box highlights the "Metals" input fields. A "Next >>" button is located below the "Non-metals" input fields, with a red box around it and a red arrow pointing to it from the "System components" text box.

The "Parameters" section includes a "Pressure" section with an "Isobar" checkbox (checked) and a "P(atm)" input field set to "1.0". Below this is a "Constants" section with a "Temperature" input field set to "700". There are also input fields for "Z" and "log10(Z)".

The "Y-axis" section has a dropdown menu set to "log10(Y)" and a "Y:" dropdown menu set to "P(Cl2)". Below these are input fields for "max:" (0), "min:" (-12), and "step:" (1). The "X-axis" section has a dropdown menu set to "log10(X)" and an "X:" dropdown menu set to "P(O2)". Below these are input fields for "max:" (0), "min:" (-20), and "step:" (1).

The "Labels and Display" section has three radio buttons: "chemical" (selected), "number", and "none". There are also input fields for "size" (12) and "color" (blue). There are checkboxes for "full screen" and "titles" (checked).

The "Calculate" section has three radio buttons: "diagram" (selected), "invariant point", and "detailed point". A "Calculate >>" button is located at the bottom right of this section.

The "Metal Mole Fraction" section has a "2-Metal Diagram" section with a formula  $R = \text{Sn}/(\text{Fe} + \text{Sn})$  and an input field for the range "0.0000 < R < 1.0000". Below this is a "3-Metal Diagram" section with two empty input fields.

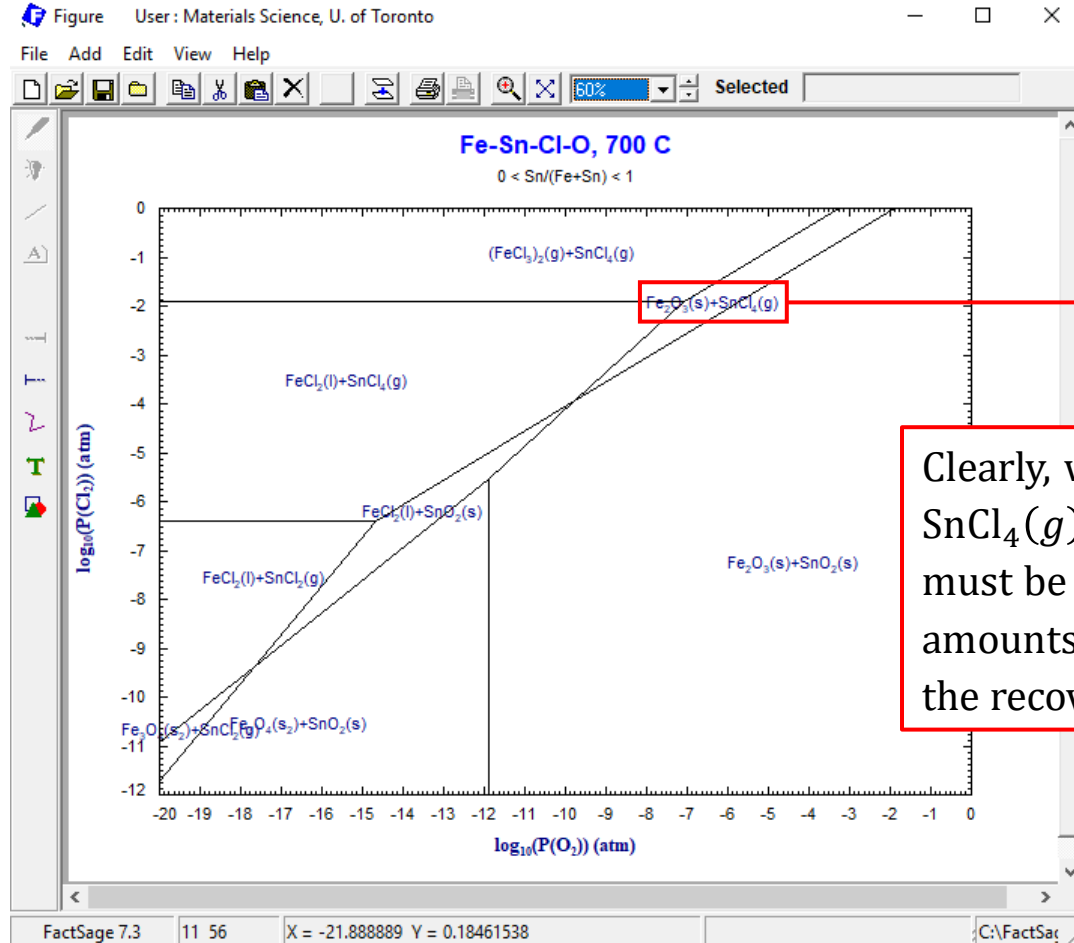
The "Species" section has four checkboxes: "gas" (checked), "liquids" (unchecked), "aqueous" (unchecked), and "solids" (checked). There are also input fields for "29", "0", "0", and "1.0". A "List" button is located at the bottom right of this section.

The "Data Search" dialog box is open on the right side of the screen. It has a title bar "Data Search" and a menu bar with "Fact", "FactSage", and "SGTE". Below the menu bar, there is a section "Databases - 1/14 compound databases, 0/15 solution database". There are three columns of checkboxes for databases: "Fact" (FactPS, FToxid, FTsalt, FTmisc, FTHall, FTfritz, FTHelg, FTpulp, FTlite), "FactSage" (FS Copp, FSlead, FSstel, FSupsi), and "SGTE" (BINS, SGPS, SGTE, SGsold). There are also checkboxes for "ELEM", "FTdemo", "FTnucl", "SGnobl", "SpMCBN", "TDmeph", and "TDnucl". There are buttons for "Add/Remove Data" and "RefreshDatabases". There are also three radio buttons for "compounds only" (checked), "solutions only", and "no database". There is a "Clear All" button.

A red box highlights the "Data Search" dialog box. A red arrow points from the "Data Search" menu item in the main window to the "Data Search" dialog box. A red box highlights the "System components" text box, which is positioned over the "Metals" and "Non-metals" input fields.

# Equilib Module: Recovery of Tin from Tin Cans

## Predominance Diagram of the Fe-Sn-Cl-O System at 700 °C.



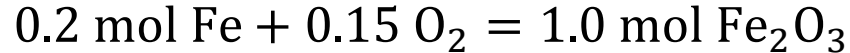
Clearly, when the system exists as “ $\text{Fe}_2\text{O}_3(\text{s}) + \text{SnCl}_4(\text{g})$ ”, the partial pressure of  $\text{O}_2$  and  $\text{Cl}_2$  must be carefully controlled. That is, the input amounts of  $\text{O}_2$  and  $\text{Cl}_2$  are the key factors in the recovery of high-grade  $\text{SnCl}_4$ .

# Equilib Module: Recovery of Tin from Tin Cans

---

## Part I.

Let us start with a simple calculation. Say we are recovering 1.0 mol of Sn, and the exposed iron is **assumed** to be 0.2 mol. Clearly, the minimum number of moles of Cl<sub>2</sub> is 2.0 mol when all Sn is recovered as SnCl<sub>4</sub>; and the minimum number of moles of O<sub>2</sub> when all the exposed iron is oxidized to Fe<sub>2</sub>O<sub>3</sub> is 0.15 mol.



Of course, if O<sub>2</sub> is supplied from air (21 vol. % O<sub>2</sub> + 79 vol. % N<sub>2</sub>), then the number of moles of N<sub>2</sub> is  $3.76 \times 0.15 \text{ mol} = 0.564 \text{ mol}$ .

Also, we assume all the reactants are introduced into the reactor at room temperature.

# Equilib Module: Recovery of Tin from Tin Cans

## Reactants Window: Define Reactants (Species)

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 5

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	Sn				1	
+ 1	Fe				1	
+ 1	Cl2				1	
+ 1	O2				1	
+ 1	N2				1	

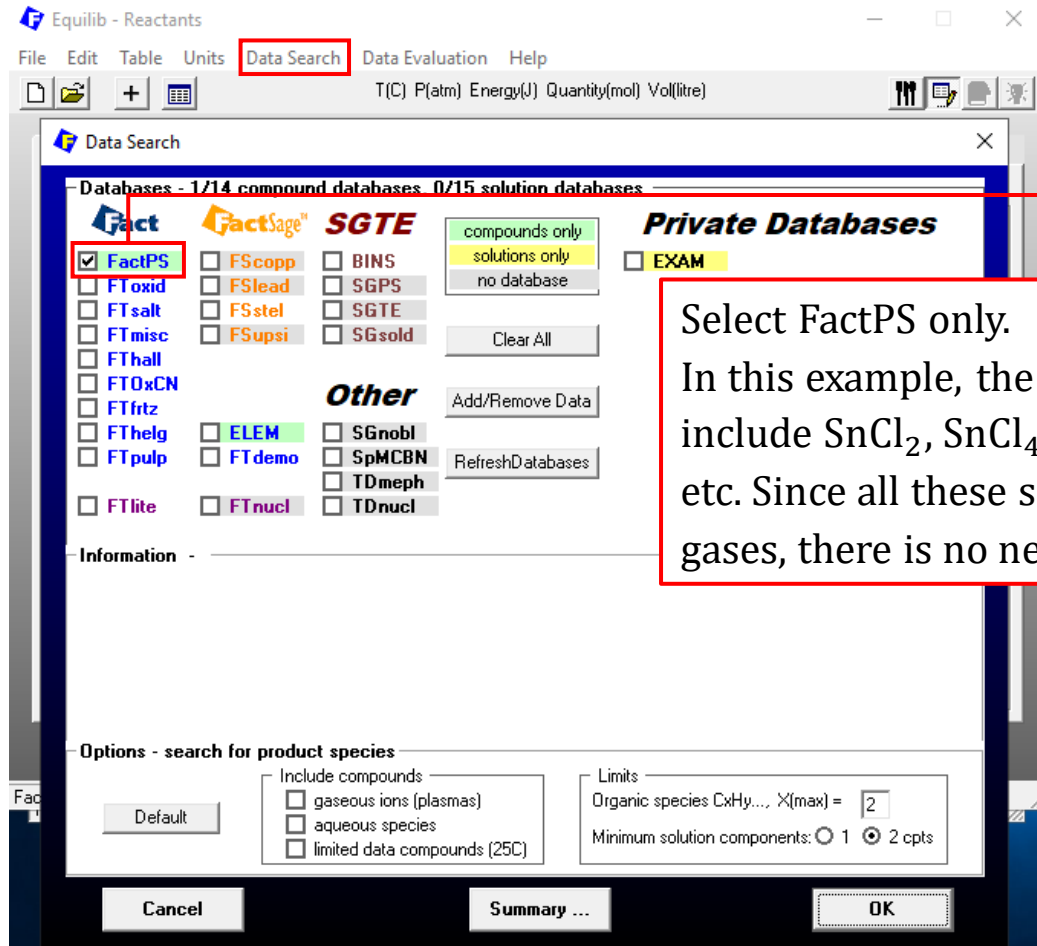
Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

# Equilib Module: Recovery of Tin from Tin Cans

## Reactants Window: Select Database(s)



Select FactPS only.

In this example, the **major** species we are interested in include  $\text{SnCl}_2$ ,  $\text{SnCl}_4$ ,  $\text{SnO}_2$ ,  $\text{FeCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cl}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , etc. Since all these species are either pure solids/liquid or gases, there is no need to choose any solution database.



# Equilib Module: Recovery of Tin from Tin Cans

## Reactants Window: Choose Units and Input the Quantity of Species

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 5

Choose the units.

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	Sn				1	
+ 0.2	Fe				1	
+ 2	Cl2				1	
+ 0.15	O2				1	
+ 0.564	N2				1	

After choosing the units, input the quantity of species.

Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

# Equilib Module: Recovery of Tin from Tin Cans

## Reactants Window: Choose “Initial Conditions”

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	Sn	solid-1 Solid(wh)	25	1.0	1	
+ 0.2	Fe	solid-1 bcc	25	1.0	1	
+ 2	Cl <sub>2</sub>	gas	25	1.0	2	
+ 0.15	O <sub>2</sub>	gas	25	1.0	3	
+ 0.564	N <sub>2</sub>	gas	25	1.0	3	

\*\*\* P(total) is the hydrostatic pressure.  
For a gaseous stream this is the partial pressures of the species in that stream.

Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

Once “Initial Conditions” is checked, we need to specify the phase (i.e., structure) of species (see next pages for more information).

Also, we want to assign **Stream#** to the reactants (Sn and Fe are in 1<sup>st</sup> Stream, Cl<sub>2</sub> in 2<sup>nd</sup> Stream, and air in 3<sup>rd</sup> Stream). You can right click “Stream#” to see more details.

# Equilib Module: Recovery of Tin from Tin Cans

## View Data Module: Structure of Sn and Fe at 25 °C, 1 atm

View Data

View compounds - enter a list of elements or a compound or ALL

Examples:

- Al Ca O - compounds of Al, Ca and/or O
- SiO2 - compound
- Fe2(SO4)3 - compound
- Cu(++) - cation
- OH(-) - anion
- ALL - all compounds
- ALL Fe - all compounds of Fe
- ALL SO4 - all compounds with SO4
- ALL Fe S O - all compounds with Fe, S and O

Pressure: atm (selected), bar

Energy: J (selected), cal

Data: compound (selected), solution

minimum solution components: 1 (selected), 2 cpts

Compound Databases (14): FactPS - FACT pure substances database (2019)

Elements or Compound or ALL: SnFe

View Data Sn Units: T(K) P(atm) Energy(J) Quantity(mol)

8 compounds, 14 phases

Compounds ordered by alphabet (see "Sort Compounds")

Compound	FactPS	S1	S2	L	G
Fe	FactPS	S1	S2	L	G
Fe(+)	FactPS	G			
Fe(-)	FactPS	G			
Fe(2+)	FactPS	Aq			
Fe(3+)	FactPS	Aq			
Sn	FactPS	S1	S2	L	G
Sn2	FactPS	G			
Sn(2+)	FactPS	Aq			

View Data Fe Units: T(K) P(atm) Energy(J) Quantity(mol)

4 Phases

Name: Iron

Standard State: S1

At 25 °C, S1 which is bcc is stable.

Transition	T(K)	T(C)	Delta H J/mol	Delta S J/mol-K	Delta Cp J/mol-K
S1 -> S2	1184.81	911.66	1012.9	0.855	-7.681
S2 -> S1	1667.47	1394.32	825.8	0.495	2.183
S1 -> L1	1810.95	1537.80	13806.9	7.624	4.653
L1 -> G1 (1 atm)	3131.93	2858.78	349631.2	111.635	-18.938

View Data Sn Units: T(K) P(atm) Energy(J) Quantity(mol)

4 Phases

Name: Tin

Standard State: S1

At 25 °C, S1 which is solid(wh) is stable.

Transition	T(K)	T(C)	Delta H J/mol	Delta S J/mol-K	Delta Cp J/mol-K
L1 -> S2	55.06	-218.09	9955.4	180.808	-421.031
S2 -> S1	296.56	23.41	2090.1	7.048	1.187
S1 -> L1	505.06	231.91	7029.1	13.917	-1.039
L1 -> G1 (1 atm)	2872.94	2599.79	295769.0	102.950	-2.033

# Equilib Module: Recovery of Tin from Tin Cans

## Menu Window: Select the Products

Equilib - Menu: last system

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

**Reactants (5)**

Sn + 0.2 Fe + 2 Cl<sub>2</sub> + 0.15 O<sub>2</sub> + 0.564 N<sub>2</sub>  
(25C,s1,#1) (25C,s1,#1) (25C,g,#2) (25C,g,#3) (25C,g,#3)

**Products**

Compound species

- gas  ideal  real 41
- aqueous 0
- pure liquids 10
- pure solids 22

species: 73

Target

Estimate T(K): 1000

Quantity(mol): 0

Legend

Show  all  selected

species: 0

solutions: 0

Custom Solutions

0 fixed activities

0 ideal solutions

Pseudonyms

apply

Virtual species: 10

Total Species (max 5000) 73

Total Solutions (max 200) 0

Total Phases (max 1500) 33

**Final Conditions**

<A>	<B>	T(C)	P(atm)	Delta H(J)
		1000	1	

10 steps  Table

**Equilibrium**

normal  normal + transitions

transitions only

open

FactSage 7.3

# Equilib Module: Recovery of Tin from Tin Cans

## Menu Window: Set the Final Conditions

Equilib - Menu: last system

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

**Reactants (5)**

Sn + 0.2 Fe + 2 Cl<sub>2</sub> + 0.15 O<sub>2</sub> + 0.564 N<sub>2</sub>  
(25C,s1,#1) (25C,s1,#1) (25C,g,#2) (25C,g,#3) (25C,g,#3)

**Products**

Compound species

- gas  ideal  real 41
- aqueous 0
- pure liquids 10
- pure solids 22

species: 73

Target

- none -

Estimate T(K): 1000

Quantity(mol): 0

**Final Conditions**

<A>	<B>	T(C)	P(atm)	Delta H(J)
		500 800 100	1	

4 calculations

**Equilibrium**

- normal
- normal + transitions
- transitions only
- open

Calculate >>

FactSage 7.3

Set the temperature range from 500 to 800 °C at 100 °C intervals, and the total pressure is 1 atm. This allows us to perform 4 calculations at different temperatures.

# Equilib Module: Recovery of Tin from Tin Cans

## Results: (Here, we again use the ChemSage format)

The screenshot shows the ChemSage Equilib module results for a system at 500 C. The initial conditions are T = 500 C, P = 1 atm, and V = 99.138 dm<sup>3</sup>. The initial stream constituents include Sn<sub>2</sub>Sn, Fe<sub>2</sub>Cl<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. The equilibrium results show that the gas phase is stable, with SnCl<sub>4</sub> and N<sub>2</sub> as the major species. The pure solids Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and FeCl<sub>2</sub> are also stable, while other compound species have activities less than 1.

**Equilibrium Conditions.**

T = 500 C  
P = 1 atm  
V = 99.138 dm<sup>3</sup>

STREAM CONSTITUENTS	AMOUNT/mol	TEMPERATURE/C	PRESSURE/atm	STREAM
Sn <sub>2</sub> Sn(wh)	1.0000E+00	25.00	1.0000E+00	1
Fe <sub>2</sub> bcc	2.0000E-01	25.00	1.0000E+00	1
Cl <sub>2</sub> /gas_ideal/	2.0000E+00	25.00	1.0000E+00	2
O <sub>2</sub> /gas_ideal/	1.5000E-01	25.00	1.0000E+00	3
N <sub>2</sub> /gas_ideal/	5.6400E-01	25.00	1.0000E+00	3

PHASE: gas_ideal	EQUIL AMOUNT mol	MOLE FRACTION	FUGACITY atm
SnCl <sub>4</sub>	9.8690E-01	6.3156E-01	6.3156E-01
N <sub>2</sub>	5.6400E-01	3.6093E-01	3.6093E-01
FeCl <sub>3</sub>	5.8786E-03	3.7620E-03	3.7620E-03
(FeCl <sub>3</sub> ) <sub>2</sub>	5.7030E-03	3.6496E-03	3.6496E-03
TOTAL:	1.5626E+00	1.0000E+00	1.0000E+00

System component	Amount/mol	Amount/gram	Mole fraction	Mass fraction
Sn	0.98690	117.15	0.16094	0.42489
Fe	1.7345E-02	0.96864	2.8286E-03	3.5131E-03
Cl	3.9997	141.80	0.65228	0.51429
O	1.4589E-11	2.3341E-10	2.3791E-12	8.4654E-13
N	1.1280	15.800	0.18395	5.7302E-02

Final Conditions	T[C]	P[atm]	Delta H[J]
<A>	500	800	100
<B>			

Thermodynamic properties of the system at the initial state.

Gas phase: the total fugacity is 1 which means the gas phase is stable. The major gaseous species are SnCl<sub>4</sub> and N<sub>2</sub>. This means Sn is chlorinated and removed very efficiently.

Pure solids: Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and FeCl<sub>2</sub> are stable. Other compound species have an activity less than 1, which are not stable. Also, Fe<sub>2</sub>O<sub>3</sub> is the major species.

# Equilib Module: Recovery of Tin from Tin Cans

## Results: let us plot the data (this time we use Output\Plot)

The screenshot shows the 'Equilib - Results 500 C (page 1/4)' window. The 'Output' menu is open, with 'Plot' and 'Fact-XML' highlighted. The 'Plot' submenu is also open, showing 'Plot Results ...' and 'Repeat Plot - ...'. A text box with a red border and arrow points to the 'Fact-XML' option, containing the text: "Feel free to use Fact-XML. However, some functions in the 'Plot' can not be replaced by 'Fact-XML'". At the bottom, the 'Final Conditions' dialog box is visible, showing a table with columns for components, temperature (T(C)), pressure (P(atm)), and enthalpy change (Delta H(J)).

<A>	<B>	T(C)	P(atm)	Delta H(J)
		500	1	

4 calculations

Calculate >>

# Equilib Module: Recovery of Tin from Tin Cans

## Results: let us plot the data (this time we use Output\Plot)

Equilib - Results 500 C (page 1/4)

Output Edit Show Pages Final Conditions

Save or Print > T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Plot > Plot Results ...

Equilib Results file > Repeat Plot - ...

Stream File > + 0.15 O2 +

Format > (25, 1, g, #2) (25, 1, g, #3)

Fact-XML >

Fact-Optimal > real

Fact-Function-Builder > 1, 99.138 litre, 2.7812E-03 gram.cm-3)

Refresh ... a=1.0000)

Swap loops ... SnCl4

FeCl3

(FeCl3)2

+ 9.1264E-02 mol Fe2O3 hematite

+ 1.2611E-04 mol FeCl2\_solid

(1.5984E-02 gram, 1.2611E-04 mol)

Final Conditions

<A>	<B>	T(C)	P(atm)	Delta H(J)
		500 800 100	1	

4 calculations

Calculate >>

Results Processor: w:\MSE302\Exercise\Equi0.res

File Help

Sn + 0.2Fe + 2Cl2 + 0.15 O2 +

Axes	Variables	Minimum	Maximum
	activity	0	1
	mole	0	4
	mole fract. soln. species	0	0.652276
	gram	0	275.73
	weight % soln. species	0	93.248
	Alpha	0	0
	T(C)	500	800
	P(atm)	1	1
	Delta Cp(J/K)	25.765	115.19
	Delta G(J)	-9.6921E+05	-7.7538E+05
	Vol(litre)	99.138	141.34
	Delta H(J)	-4.8986E+05	-4.3610E+05
	Delta V(litre)	32.738	74.936
	Delta S(J/K)	-26.607	31.403
	- page -	1	4

0 selected

0 selected

Graph

Labels

size: 9 no: 4

Display

color  full screen

reactants  Viewer

file name  Figure

Plot >>

FactSage 7.3 w:\MSE302\Exercise\Equi0.res 26Jul22 4 sets

Feel free to use Fact-XML. However, some functions in the "Plot" can not be replaced by "Fact-XML".



# Equilib Module: Recovery of Tin from Tin Cans

Results: let us plot the data (this time we use Output\Plot)

The screenshot shows the FactSage software interface. On the left is the 'Results Processor' window showing a table of variables and their minimum and maximum values. On the right is the 'Plot Species Selection - Equilib Results: vs' window, which contains a table of species and their properties. The table is divided into 'SOLUTIONS' and 'ELEMENTS' sections. The 'ELEMENTS' section is highlighted in yellow, and the 'Sn\_GAS' row is selected. Below the table is a 'Display' section with options for 'source', 'phase', 'name', and '[page]'. The 'Mass' section has 'mole' selected, and the 'Order' section has 'integer #' selected. The 'Select Top' dropdown is set to 15, and '1 species selected' is shown. The 'OK' button is visible.

#	Species	Mole (min)	Mole (max)	Fraction (min)	Fraction (max)	Activity (min)	Activity (max)
64	Fe3O4	0	0	0	0	1.7240E-12	2.0182E-08
65	Fe3O4	0	0	0	0	1.6186E-12	2.1141E-08
66	FeCl2	0	1.2611E-04	0	0	7.6806E-02	1
67	FeCl3	0	0	0	0	2.8018E-04	2.7126E-03
68	FeOCl	0	0	0	0	1.9588E-03	3.4093E-03
69	Sn	0	0	0	0	1.7487E-17	1.3291E-12
70	Sn	0	0	0	0	9.0733E-18	5.6158E-13
71	SnO	0	0	0	0	5.4089E-09	1.6000E-06
72	SnO2	1.3103E-02	0.116047	0	0	1	1
73	SnCl2	0	0	0	0	1.7381E-06	1.5033E-05
<b>SOLUTIONS</b>							
74	GAS	1.5626	1.605	0	0	1	1
<b>ELEMENTS</b>							
75	Sn_GAS	0.0009953	0.000997	0.143343	0.160942	0	0
76	Fe_GAS	1.7345E-02	0.154734	2.8286E-03	2.5092E-02	0	0
77	Cl_GAS	3.9997	4	0.648646	0.652276	0	0
78	O_GAS	1.4589E-11	7.7342E-06	2.3791E-12	1.2542E-06	0	0
79	N_GAS	1.128	1.128	0.182918	0.183953	0	0

Choose "Sn\_Gas" under the option of "ELEMENTS" (NOT the option of "Gas"). This is all the Sn contained in the gas phase. From the option of "Gas", you would see Sn exists as Sn, Sn<sub>2</sub>, SnO, SnO<sub>2</sub>, O<sub>2</sub>Sn<sub>2</sub>, O<sub>3</sub>Sn<sub>3</sub>, O<sub>4</sub>Sn<sub>4</sub>, SnCl, SnCl<sub>2</sub>, and SnCl<sub>4</sub> (major species of Sn carrier).

Choose "mole" as Mass unit.

# Equilib Module: Recovery of Tin from Tin Cans

Results: let us plot the data (this time we use Output\Plot)

Results Processor: w:\MSE302\Exercise\Equi0.res

File Help

Sn + 0.2 Fe + 2 D12 + 0.15 D2 +

Axes	Variables	Minimum
	activity	0
	mole	0
	mole fract. soln. species	0
	gram	0
	weight % soln. species	0
	Alpha	
	T(C)	500
	P(atm)	1
	Delta Cp(J/K)	25.765
	Delta G(J)	-9.6321E+
	Vol(litre)	99.138
	Delta H(J)	-4.8986E+
	Delta V(litre)	32.738
	Delta S(J/K)	-26.607
	- page -	1

Y-axis: mole

X-axis: T(C)

maximum: 4, minimum: 0, tick every: 0.25

maximum: 800, minimum: 500, tick every: 25

Cancel Refresh OK

activity

- mole
- mole fract. soln. species
- gram
- weight % soln. species
- Alpha
- T(C)
- P(atm)
- Delta Cp(J/K)
- Delta G(J)
- Vol(litre)
- Delta H(J)
- Delta V(litre)
- Delta S(J/K)
- page -

Y

- Y
- log10(Y)
- ln(Y)
- exp(Y)
- 1/Y
- phase distribution

activity

- mole
- mole fract. soln. species
- gram
- weight % soln. species
- Alpha
- T(C)
- P(atm)
- Delta Cp(J/K)
- Delta G(J)
- Vol(litre)
- Delta H(J)
- Delta V(litre)
- Delta S(J/K)
- page -

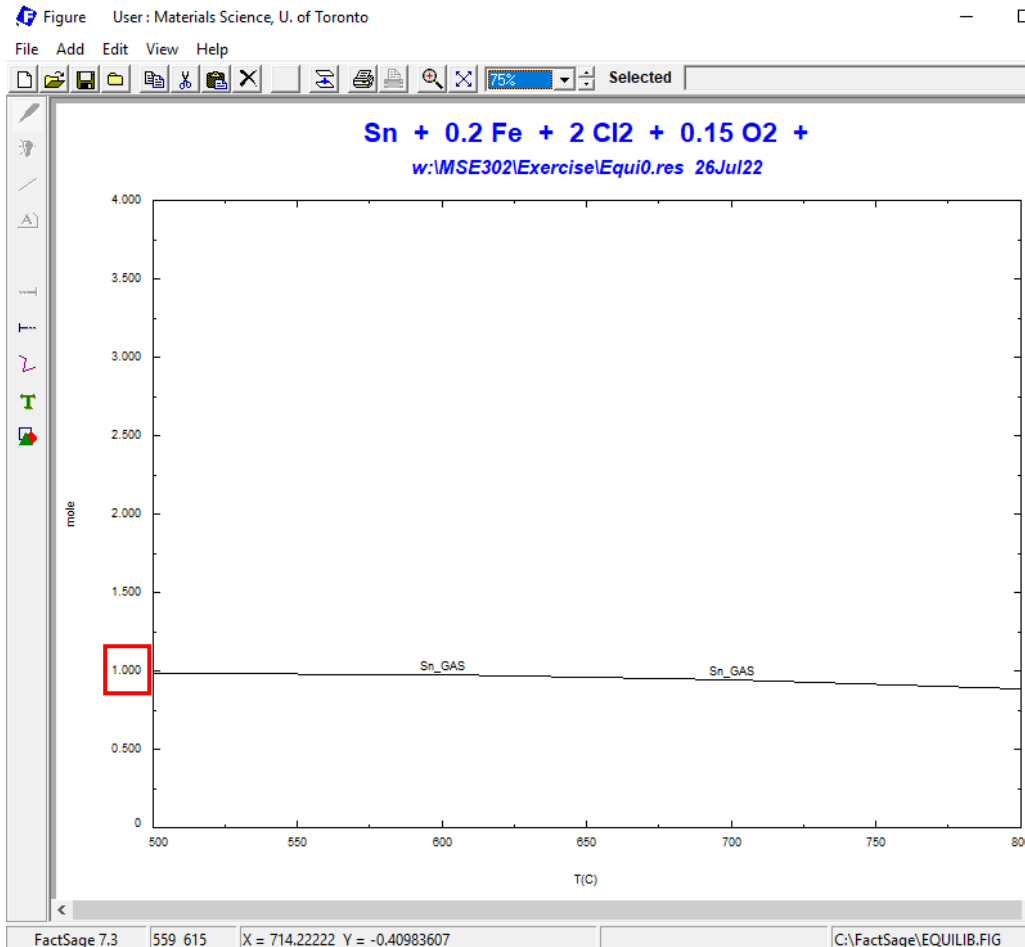
X

- X
- log10(X)
- ln(X)
- exp(X)
- 1/X
- ratio

We wish to plot a  $n_{\text{Sn}}^{(\text{gas})} \sim T$  graph.

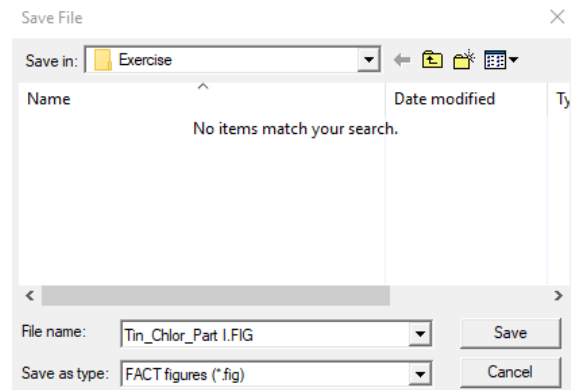
# Equilib Module: Recovery of Tin from Tin Cans

## Results: let us plot the data (this time we use Output\Plot)



As seen from the graph, the total amount of Sn in the gas phase is close to 1.0 mol at the four temperatures we investigated. This means that essentially all the Sn is recovered (Recall the total Sn input is 1.0 mol).

Save the graph.



# Equilib Module: Recovery of Tin from Tin Cans

---

## Part II.

For Part II, we will be looking at what happens if the amount of oxygen supplied is not sufficient to oxidize the exposed iron.

Assume the amount of the exposed iron is a variable: for 1 mol of Sn, the amount of the exposed iron varies from 0.2 to 0.6 mol. The temperature is fixed at 600 °C.

# Equilib Module: Recovery of Tin from Tin Cans

## Back to the Reactants Window:

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 5

Quantity(mol)	Species	Phase
1	Sn	solid-1 Solid(wh)
<A>	Fe	solid-1 bcc
2	Cl2	gas
0.15	O2	gas
0.554	N2	gas

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

**Quantity**

Enter the amount of the reactant. Examples: 10 14.307 1.234e-4  
For example, the formation of water:  
1 H2  
+ 0.5 O2

A composition variable "A" (alpha) may be specified in the form <aA+b> or <a+bA> where a and b are constants. A is calculated or specified later.  
Examples: <A> <-1+2A> <3.7A+6>.  
For example, a binary mixture between copper and nickel:  
<A> Cu  
+ <1-A> Ni

A composition variable "B" (beta) may be specified in the form <aA +bB+cAB+d> where a, b, c and d are constants. A and B are specified later in the Menu Window. Whereas you can specify or calculate a range [First Last Step] of <A>, for example [0.0 1.0 0.1], only one constant value of <B> can be specified. For example the oxidation of various quantities of hydrogen by oxygen diluted in nitrogen. Say you want to have 1 mole total of input gases you might enter:  
<A> H2  
+ <1-A-B> O2  
+ <B> N2  
If the fixed quantity of N2 is 0.1 mole, then in the [Menu Window] you would specify <B> = 0.1 and give a range for alpha, say <A> = [0.0 0.9 0.1].

OK

# Equilib Module: Recovery of Tin from Tin Cans

## Menu Window

The screenshot shows the Equilib software interface. The 'Final Conditions' dialog box is open, providing instructions on how to specify temperature (T) and pressure (P) values. The main window shows the 'Final Conditions' section with a table for specifying parameters. A red box highlights the 'Temperature' column in the table, and a red arrow points to it from a text box labeled 'Temperature'.

**Final Conditions**

In most cases you specify values of T and P (and <A> and <B> if necessary). For example T = 1000 and P = 1.

A range is indicated by [FIRST LAST (STEP, optional)]. For example '[500 1000]' in the T column means T = 500 and 1000; '[500 1050 100]' means T = 500, 600, 700 ... 1000 and finally 1050.

Leave the column blank if it is not specified.

When the reactant initial conditions have been specified ("Initial Conditions" box in [Reactants Window] is 'checked') a column for extensive variables (Delta H, Delta V, etc...) is activated. Now you have the option specifying only one of T or P together with one of the extensive variables.

If you only specify one variable, say P=1, then you can perform a Target Phase calculation i.e. that temperature is calculated when the Target Phase becomes stable. You must specify which compound or solution is the target phase. In the case of solutions, the target may be a Formation Target Phase (unit activity) or Precipitate Target Phase (unit activity, 100% moles). Click on the Target Phase frame with the mouse-right-button for details.

**Final Conditions**

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.2	0.6	0.1	1	

10 steps  Table 5 calculations

**Equilibrium**

normal  normal + transitions  
 transitions only  
 open

**Calculate >>**

Temperature

# Equilib Module: Recovery of Tin from Tin Cans

Results: plot the  $n_{\text{Sn}}^{(\text{gas})} \sim \langle \text{Alpha} \rangle$  graph

Results Processor: w:\MSE302\Exercise\Equi0.res

File Help

Sn + <A> Fe + 2 Cl2 + 0.15 O2 +

Axes	Variables	Minimum	Maximum
	Y-axis: mole		
	X-axis: Alpha		

Y-axis: mole  
X-axis: Alpha

Y-axis: maximum 4, minimum 0, tick every 0.25  
X-axis: maximum 0.6, minimum 0.2, tick every 0.025

Cancel Refresh OK

Species: 1 selected  
Select Repeat

Graph: Labels size: 9 no: 4  
Display:  color,  full screen,  reactants,  file name,  Viewer,  Figure  
Plot >>

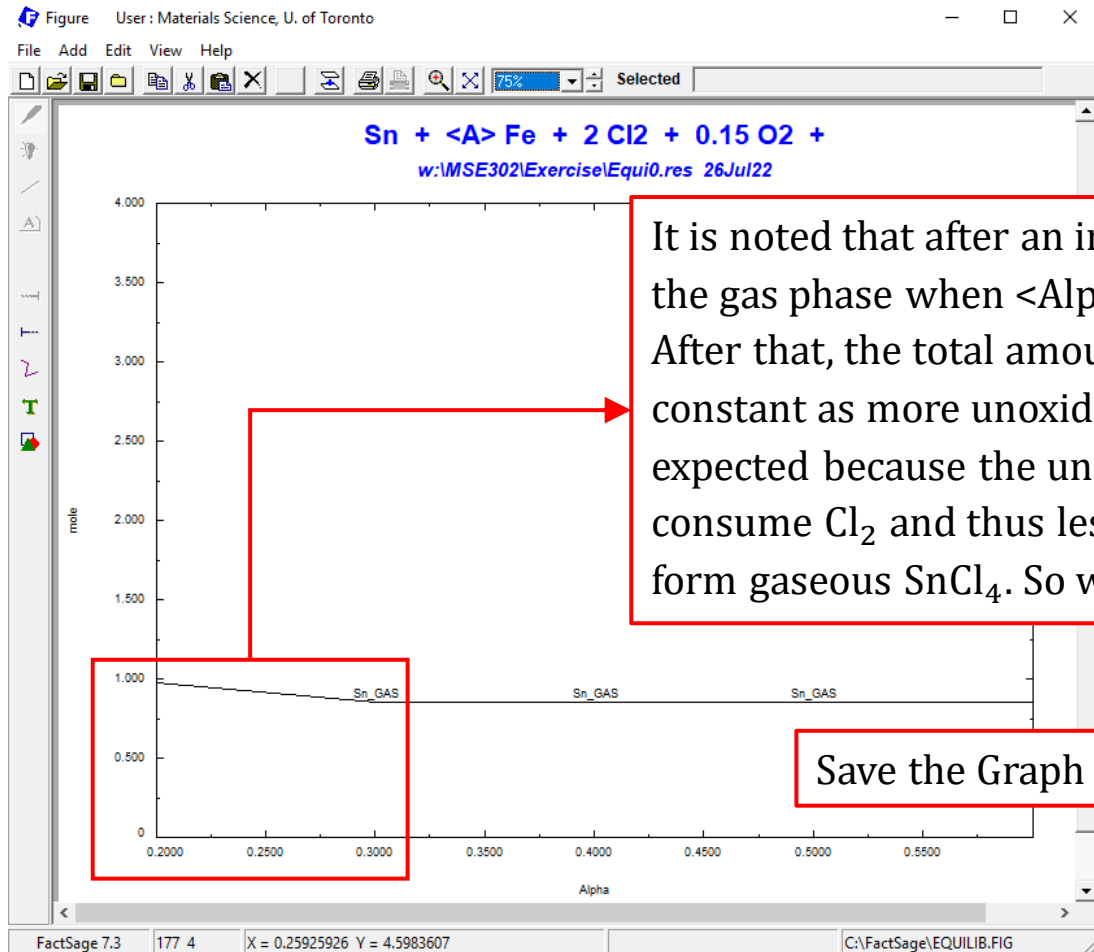
FactSage 7.3 | w:\MSE302\Exercise\Equi0.res | 26Jul22 | 5 sets

Plot Species Selection - Equilib Results: mole vs Alpha

#	Species	Mole (min)	Mole (max)	Fraction (min)	Fraction (max)
65	Fe3O4	0	0	0	0
66	FeCl2	0	0.597804	0	0
67	FeCl3	0	0	0	0
68	FeOCl	0	0	0	0
69	Sn	0	0	0	0
70	Sn	0	0	0	0
71	SnO	0	0	0	0
72	SnO2	2.6813E-02	0.15	0	0
73	SnCl2	0	0	0	0
SOLUTIONS					
74	GAS	1.416	1.5667	0	0
ELEMENTS					
75	Sn_GAS	0.85	0.973187	0.157411	0.157411
76	Fe_GAS	2.1963E-03	3.5750E-02	4.5903E-04	5.903E-04
77	Cl_GAS	2.8044	4	0.58613	0.58613
78	O_GAS	2.2929E-13	1.4044E-09	4.4215E-14	2.2929E-13
79	N_GAS	1.128	1.128	0.183805	0.183805

# Equilib Module: Recovery of Tin from Tin Cans

Results: plot the  $n_{\text{Sn}}^{(\text{gas})} \sim \langle \text{Alpha} \rangle$  graph



It is noted that after an initial drop in the total amount of Sn in the gas phase when  $\langle \text{Alpha} \rangle$  increases from 0.2 to 0.3 mol. After that, the total amount of Sn in the gas phase remains constant as more unoxidized iron is available. This is not expected because the unoxidized iron would presumably consume  $\text{Cl}_2$  and thus less  $\text{Cl}_2$  is available to chloridize Sn to form gaseous  $\text{SnCl}_4$ . So what is going on?

Save the Graph with the name "Tin\_Chlor\_Part II"



# Equilib Module: Recovery of Tin from Tin Cans

## Results: plot the amounts of major species

Plot Species Selection - Equilib Results: mole vs Alpha

File Show Select

		Mole (max)	Fraction (min)	Fraction (max)	Activity (min)	Activity (max)
+ ✓	gas phase					
	aqueous species	6.7206E-26	4.2895E-26	4.5121E-26	4.2895E-26	4.5121E-26
✓	pure liquids	0.564	0.359984	0.398307	0.359984	0.398307
✓	pure solids	4.2531E-29	2.5807E-29	3.0036E-29	2.5807E-29	3.0036E-29
✓	SOLUTIONS	5.5443E-17	2.8856E-21	3.5387E-17	2.8856E-21	3.5387E-17
	ELEMENTS	5.4456E-10	2.3112E-18	3.4758E-10	2.3112E-18	3.4758E-10
	-----					
	All	3.1263E-10	1.7116E-14	1.9954E-10	1.7116E-14	1.9954E-10
	Clear	1.6598E-14	9.5586E-19	1.0594E-14	9.5586E-19	1.0594E-14
		1.8696E-15	8.3464E-24	1.1933E-15	8.3464E-24	1.1933E-15
		3.9870E-27	1.4514E-39	2.5448E-27	1.4514E-39	2.5448E-27
11					E-42	2.7852E-30
12					E-52	3.8960E-36
13					E-64	5.3442E-44
14					E-09	7.2154E-07
15	Cl2	2.4340E-08	4.1771E-04	1.7189E-08	2.6661E-04	1.7189E-08
16	ClO	1.1542E-18	1.9504E-12	8.1510E-19	1.2449E-12	8.1510E-19
17	ClO2	1.7585E-31	3.6443E-21	1.2419E-31	2.3260E-21	1.2419E-31

It is suggested that ELEMENTS not be shown. We want to plot the species not elements.

Clear

Click on the '+' column to add or remove species.

Display

- source
- phase
- name
- [page]

Mass

- mole
- gram

5 pages

Order

- integer #
- mass (max)
- fraction (max)
- activity (max)

Select Top 15

1 species selected

ignore species and phases with zero mass

Select ...

OK

# Equilib Module: Recovery of Tin from Tin Cans

## Results: plot the amounts of major species

Plot Species Selection - Equilib Results: mole vs Alpha

File Show Select

Double left click to sort the species.

#	Species	Mole (min)	Mole (max)	Fraction (min)	Fraction (max)	Activity (min)	Activity (max)
77	Cl_GAS	2.8044	4	0.58613	0.651791	0	0
74	GAS	1.416	1.5667	0	0	1	1
79	N_GAS	1.128	1.128	0.183805	0.235757	0	0
75	Sn_GAS	0.85	0.973187	0.157411	0.177654	0	0
41	SnCl4	0.549816	0.973153	0.38829	0.621135	0.38829	0.621135
66	FeCl2	0	0.597804	0	0	0.434254	1
2	N2	0.564	0.564	0.359984	0.398307	0.359984	0.398307
40	SnCl2	3.4256E-05	0.300184	2.1864E-05	0.211996	2.1864E-05	0.211996
72	SnO2	2.6813E-02	0.15	0	0	1	1
59	Fe2O3	0	8.2125E-02	0	0	6.9173E-04	1
76	Fe_GAS	2.1963E-03	3.5750E-02	4.5903E-04	5.8254E-03	0	0
29	FeCl3	3.6469E-04	2.1823E-02	2.5755E-04	1.3929E-02	2.5755E-04	1.3929E-02
31	(FeCl3)2	2.0331E-06	6.5795E-03	1.4358E-06	4.1995E-03	1.4358E-06	4.1995E-03
28	FeCl						
15	Cl2						
30	(FeCl2)2						
14	Cl						
39	SnCl						

These four species have the most significant amounts (we are not considering "N<sub>2</sub>"). Choose these four species.

Clear

Click on the '+' column to add or remove species.

Display

- source
- phase
- name
- [page]

Mass

- mole
- gram

5 pages

Order

- integer #
- mass (max)
- fraction (max)
- activity (max)

Select Top 15

4 species selected

ignore species and phases with zero mass

Select ...

OK

# Equilib Module: Recovery of Tin from Tin Cans

## Results: plot the amounts of major species

Plot: mole vs Alpha

File Help

Sn + <A> Fe + 2 Cl2 + 0.15 O2 +

Y-axis	X-axis	Minimum	Maximum
			1
			4
			0.651791
			275.14
			92.68
			0.6
			600
			1
			57.462
			-8.3809E+05
			112.25
			5

Y-axis: mole vs Alpha

Y-axis: mole

X-axis: Alpha

maximum: 1

minimum: 0

tick every: 0.25

maximum: 0.6

minimum: 0.2

tick every: 0.025

Adjust the maximum value to 1.

Cancel Refresh OK

Species: 4 selected

Graph: Labels size: 9 no: 4

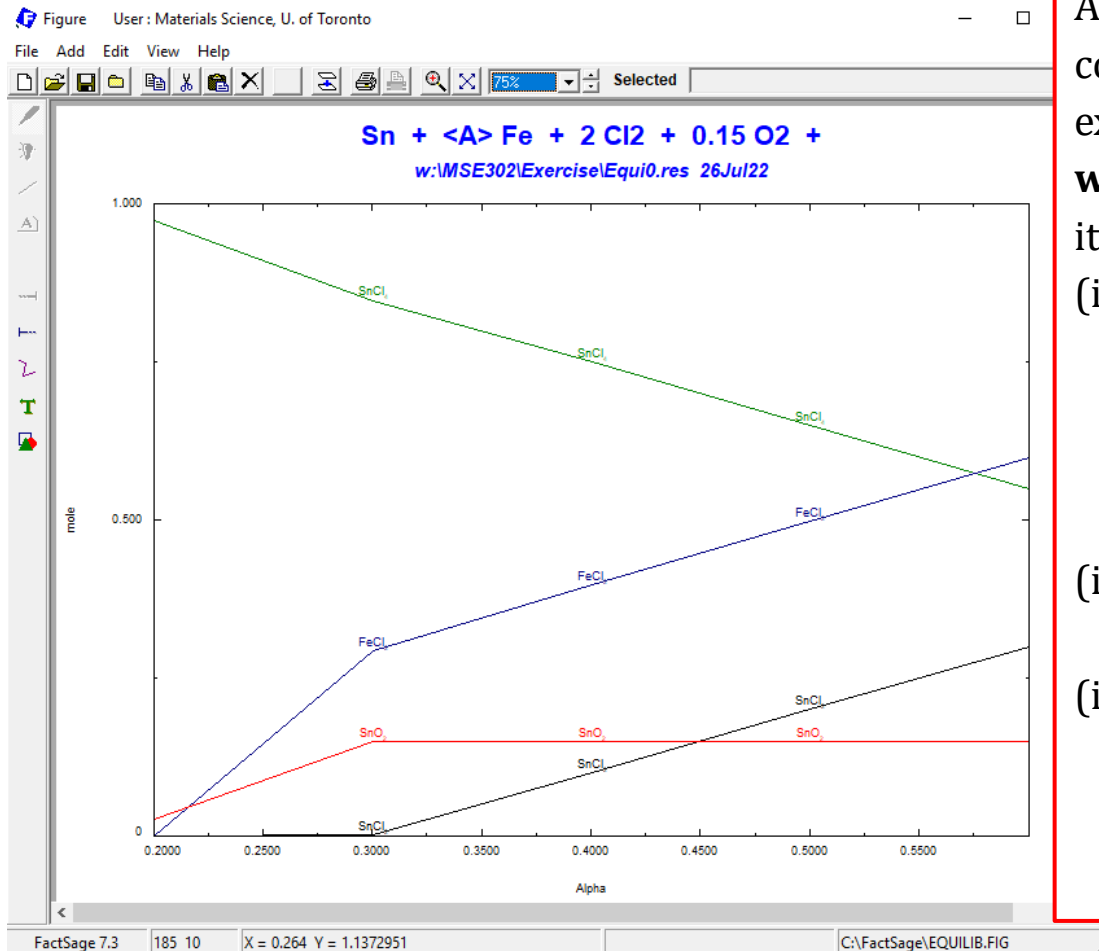
Display: color reactants file name

Plot >>

FactSage 7.3 w:\MSE302\Exercise\Equi0.res 26Jul22 5 sets

# Equilib Module: Recovery of Tin from Tin Cans

## Results: plot the amounts of major species



As seen from the graph, there is a complex chemistry occurring as more exposed iron is available for reaction **without adequate oxygen** to convert it to  $\text{Fe}_2\text{O}_3$ .

- (i) Some Sn forms solid  $\text{SnO}_2$  and this would represent a Sn loss since  $\text{SnO}_2$  is not volatile and will remain with the solid waste stream.
- (ii) Some  $\text{Cl}_2$  is wasted by reaction with iron to form solid  $\text{FeCl}_2$ .
- (iii) The Sn volatilization does remain “respectable” because of the formation of stannous chloride  $\text{SnCl}_2$  in the gas phase.

# Equilib Module: Recovery of Tin from Tin Cans

---

## Part III (Process Control)

The above calculations can be used to guide the production. If significant quantities of  $\text{FeCl}_2$  are detected in the outlet product stream, then this is a sign that we need to add more  $\text{O}_2$  (i.e., air) to oxidize the metallic iron to  $\text{Fe}_2\text{O}_3$ . The **secret** in operating this tin recovery process efficiently is to maintain the oxygen flow to keep the iron as  $\text{Fe}_2\text{O}_3$ , but not to over-oxidize the metals, either.

Bearing this in mind, let us simulate the process in FactSage.

**Note:** in the actual tin recovery process, the amount of the exposed iron is unknown, and the assumption of 0.2 mol of the exposed iron for 1 mol of Sn in Part I calculation is not universally valid.

# Equilib Module: Recovery of Tin from Tin Cans

## Back to the Reactants Window

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 5

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	Sn	solid-1 Solid(wh)	25	1	1	
+ <A>	Fe	solid-1 bcc	25	1	1	
+ 2	Cl2	gas	25	1	2	
+ <0.75A>	O2	gas	25	1	3	
+ <2.82A>	N2	gas	25	1	3	

Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

For every mol of Fe, 0.75 mol of O<sub>2</sub> is required to form 0.5 mol of Fe<sub>2</sub>O<sub>3</sub>.

For every mol of O<sub>2</sub>, 3.76 mol of N<sub>2</sub> is introduced.

# Equilib Module: Recovery of Tin from Tin Cans

## Menu Window

The screenshot shows the Equilib software interface. At the top, the title bar reads "Equilib - Menu: comments". Below it is a menu bar with "File", "Units", "Parameters", and "Help". The main window is divided into several sections:

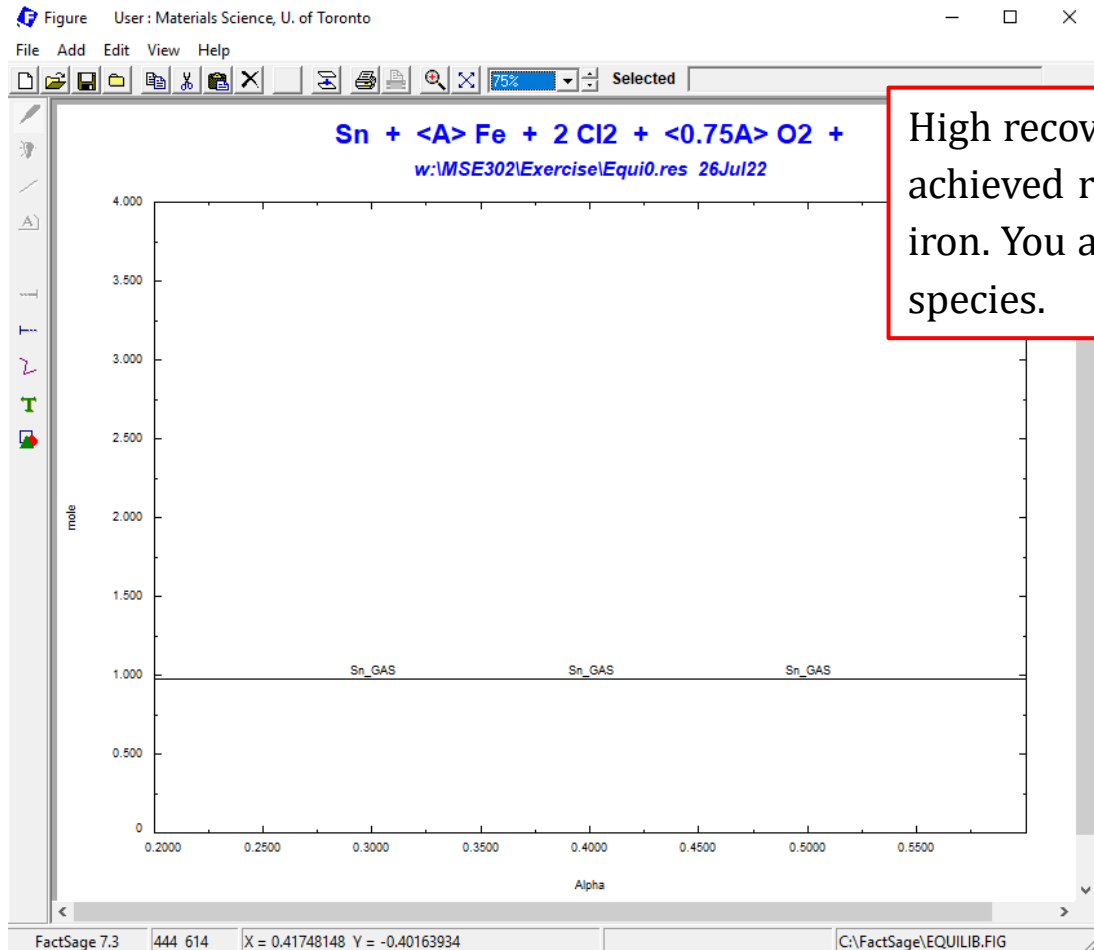
- Reactants (5):** A list of reactants: Sn (25C,s1,#1), <A> Fe (25C,s1,#1), 2 Cl2 (25C,g,#2), <0.75A> O2 (25C,g,#3), and <2.82A> N2 (25C,g,#3).
- Products:** A section for defining product species and solution phases. It includes a table for "Solution phases" with columns for "Base-Phase" and "Full Name".
- Final Conditions:** A table for defining final conditions. The table has columns for "<A>", "<B>", "T(C)", "P(atm)", and "Delta H(J)". The first row contains values 0.2, 0.6, 0.1, and 600. Below the table, there are fields for "steps" (set to 10) and "Table" (unchecked), and a "5 calculations" button.
- Equilibrium:** Radio buttons for "normal", "normal + transitions", "transitions only", and "open". A "Calculate >>" button is at the bottom right.

A red box highlights the "Custom Solutions" section, which contains the text "Same settings as Slide.".

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.2	0.6	0.1	600	1

# Equilib Module: Recovery of Tin from Tin Cans

Results: plot the  $n_{\text{Sn}}^{(\text{gas})} \sim \langle \text{Alpha} \rangle$  graph



High recoveries of Sn to the gas phase are achieved regardless of the amount of exposed iron. You are recommended to check the major species.

Plot Species Selection - Equilib Results: mole vs Alpha

File Show Select

+	#	Species	Mole (min)	Mole (max)	Fraction
	77	Cl_GAS	4	4	0.4765E
	79	N_GAS	1.128	3.384	0.1838E
	74	GAS	1.5667	2.6965	0
	2	N <sub>2</sub>	0.564	1.692	0.3599E
	41	SnCl <sub>4</sub>	0.972948	0.973195	0.3608E
	75	Sn_GAS	0.972994	0.973233	0.1159E
	59	Fe <sub>2</sub> O <sub>3</sub>	8.2125E-02	0.281996	0
	76	Fe_GAS	3.5690E-02	3.6009E-02	4.2903E
	72	SnO <sub>2</sub>	2.6767E-02	2.7006E-02	0
	29	FeCl <sub>3</sub>	2.1823E-02	2.4992E-02	9.2683E
	31	(FeCl <sub>3</sub> ) <sub>2</sub>	5.0137E-03	6.5795E-03	1.8593E
	28	FeCl <sub>2</sub>	6.8357E-04	9.0366E-04	3.3513E
	15	Cl <sub>2</sub>	4.1771E-04	5.3951E-04	2.0008E
	40	SnCl <sub>2</sub>	3.4256E-05	4.5637E-05	1.6925E

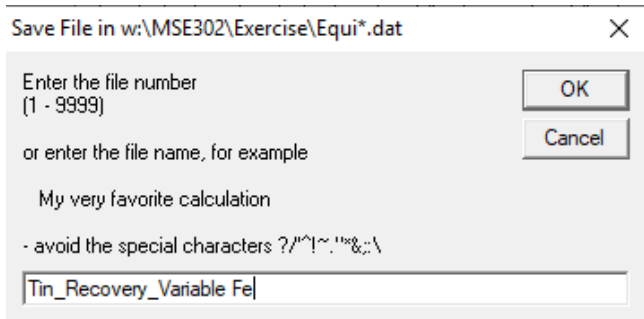


# Equilib Module: Recovery of Tin from Tin Cans

---

## Save the Graph and Equilib settings: “.dat” file

Save the Graph with the name “Tin\_Chlor\_Part III”. Also, go back to the Menu Window, save the Equilib settings as a “.dat” file.



# Equilib Module: Recovery of Tin from Tin Cans

---

## A Note on the Real-world Production

In the actual production, with the majority of Sn being recovered as  $\text{SnCl}_4$  to the gas phase,  $\text{Fe}_2\text{O}_3$  that forms on the exposed iron will become a “protective” layer. Consequently, the amount of  $\text{O}_2$  required will be difficult to predict ahead of time, and we will need to monitor the process for free  $\text{Cl}_2$  and  $\text{FeCl}_2$  to ensure that we:

- (a) add enough chlorine – we will need to keep the free  $\text{Cl}_2$  at around 2% in the gas phase; and,
- (b) add enough air to prevent iron chlorination.

For the commercial-scale production, an effective operating strategy that has been proven successful is to monitor the **oxygen** level in the off-gas and to control the feed rates of **chlorine** and **oxygen** (in air) to match the amounts of iron and tin that are actually reacting.

The following exercise focuses on the tin chlorination process with variable **oxygen** and **chlorine**.

# Equilib Module: Recovery of Tin from Tin Cans

---

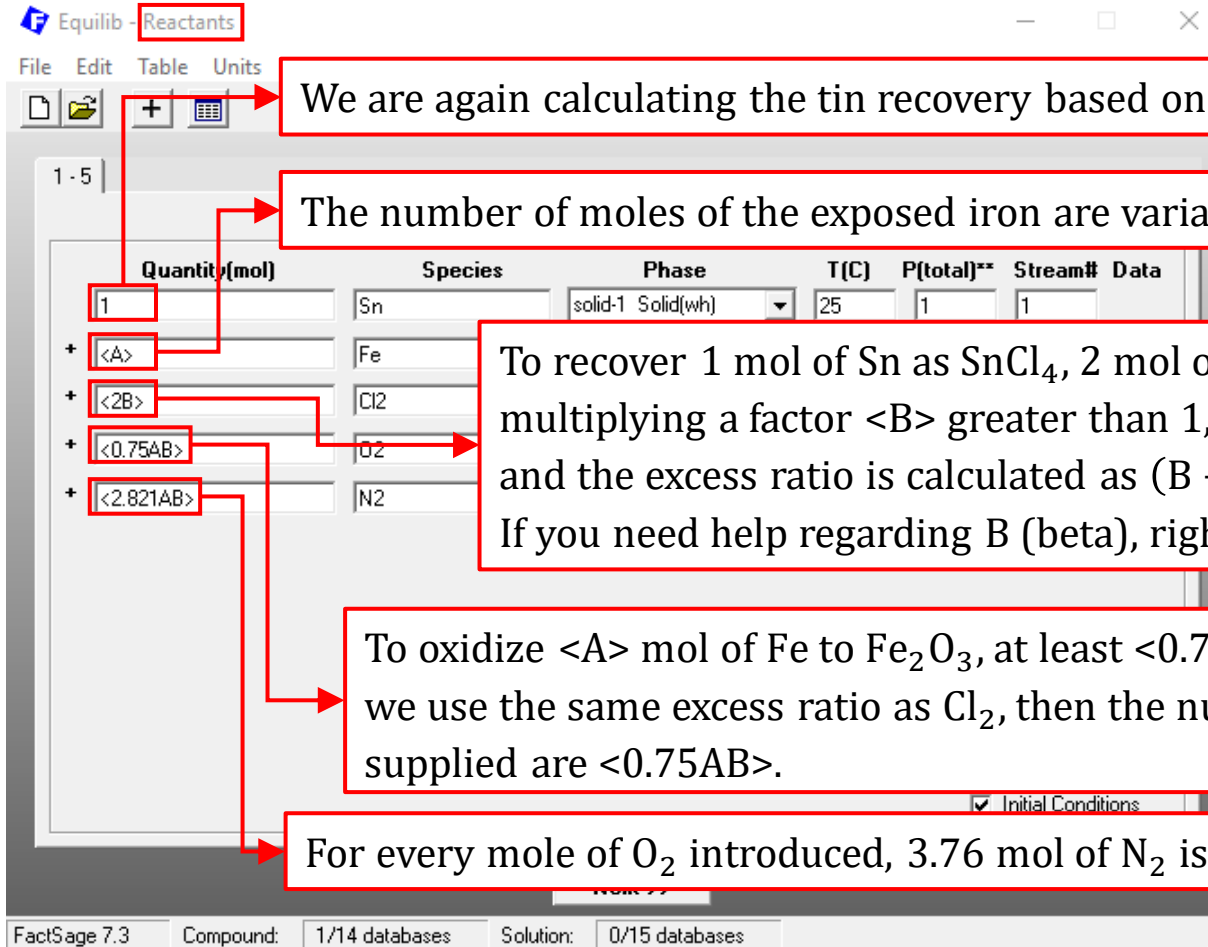
## Exercise 1. A Small Excess of Both Chlorine and Oxygen

In the first exercise, we will supply **excess chlorine** and **oxygen** to the reactor. In doing so, we will have some oxygen that can be measured in the product stream and some excess chlorine (that we can absorb and reuse). By having a (small) excess of both the reacting gases, we ensure that there will always be a driving force for the reactions we want.

For simplicity, we shall assume chlorine and oxygen that are supplied have the same excess ratio.

# Equilib Module: Recovery of Tin from Tin Cans

## Exercise 1. A Small Excess of Both Chlorine and Oxygen



The screenshot shows the 'Reactants' window in the Equilib software. The table below is a representation of the data shown in the interface:

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	Sn	solid-1 Solid(wh)	25	1	1	
<A>	Fe					
<2B>	Cl2					
<0.75AB>	O2					
<2.821AB>	N2					

Annotations in the image explain the variables and their relationships:

- We are again calculating the tin recovery based on 1 mol of Sn.
- The number of moles of the exposed iron are variable.
- To recover 1 mol of Sn as  $\text{SnCl}_4$ , 2 mol of  $\text{Cl}_2$  are required. By multiplying a factor  $\langle B \rangle$  greater than 1, we are providing excess  $\text{Cl}_2$ , and the excess ratio is calculated as  $(B - 1) \times 100\%$ . If you need help regarding B (beta), right click to open "Help".
- To oxidize  $\langle A \rangle$  mol of Fe to  $\text{Fe}_2\text{O}_3$ , at least  $\langle 0.75A \rangle$  mol of  $\text{O}_2$  are required. If we use the same excess ratio as  $\text{Cl}_2$ , then the number of moles of  $\text{O}_2$  that are supplied are  $\langle 0.75AB \rangle$ .
- For every mole of  $\text{O}_2$  introduced, 3.76 mol of  $\text{N}_2$  is introduced.

# Equilib Module: Recovery of Tin from Tin Cans

## Exercise 1. A Small Excess of Both Chlorine and Oxygen

The screenshot shows the FactSage Equilib module interface. The reactants are Sn, Fe, Cl<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. The products are listed as gas, aqueous, pure liquids, and pure solids. The final conditions are set to 0.21 for <A>, 0.2 for <B>, and 500 for T(C). The equilibrium options are set to normal.

Equilib - Menu: comments

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

**Reactants (5)**

Sn + <A> Fe + <2B> Cl<sub>2</sub> + <0.75AB> O<sub>2</sub> + <2.821AB> N<sub>2</sub>  
(25C,s1,#1) (25C,s1,#1) (25C,g,#2) (25C,g,#3) (25C,g,#3)

**Products**

Compound species

- gas  ideal  real 41
- aqueous 0
- pure liquids 10
- pure solids 22

Solution phases

*	+	Base-Phase	Full Name
---	---	------------	-----------

Custom Solutions

- fixed activities
- ideal solutions

Pseudonyms

apply  Edit ...

Volume data

- assume molar volumes of solids and liquids

Target

Estimate T(K): 1000

Quantity(mol): 0

solutions: 0

Total Phases (max 1500) 33

**Final Conditions**

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.21	0.2	500	1	

10 steps  Table 5 calculations

**Equilibrium**

- normal
- normal + transitions
- transitions only
- open

Calculate >>

FactSage 7.3 w:\MSE302\Exercise\EquiTin\_R

We are considering the effect of the amount of the iron that is reacting.

A small excess ratio (~10%) is used for both the input chlorine and oxygen.

We are considering the process at 500 °C.

# Equilib Module: Recovery of Tin from Tin Cans

---

## **Exercise 1. A Small Excess of Both Chlorine and Oxygen**

After the calculation, plot the total amount of Sn in the gas phase. For varying amounts of iron reacting, is the recovery of Sn efficient? What are the levels of oxygen and chlorine in the off-gas?

# Equilib Module: Recovery of Tin from Tin Cans

---

## **Exercise 2. Adding Too Much Air**

In the second exercise, we will consider the situation if the process is out of control and too much air is introduced to the reactor.

We will consider the fixed amount of the exposed iron: for 1 mol of Sn, 0.2 mol of the exposed iron. For the input chlorine, the excess ratio is set as 10%.

Let us vary the amount of oxygen supplied.

# Equilib Module: Recovery of Tin from Tin Cans

## Exercise 2. Adding Too Much Air

Equilib - Reactants

We are again calculating the tin recovery based on 1 mol of Sn.

The number of moles of the exposed iron are 0.2.

Quantity(mol)	Species	Phase	T (C)	P(total)**	Stream#	Data
1	Sn	solid-1 Solid(wh)	25	1	1	
0.2	Fe	solid-1 bcc	25	1	1	
<2B>	Cl2	gas	25	1	2	
<0.15A>	O2	gas	25	1	3	
<0.564A>	N2	gas	25	1	4	

Excess  $\text{Cl}_2$  is supplied, <B> will be set as 1.1 (Menu Window) to give 10% excess ratio.

To oxidize 0.2 mol of Fe to  $\text{Fe}_2\text{O}_3$ , at least 0.15 mol of  $\text{O}_2$  are required. If excess  $\text{O}_2$  are supplied, a factor, <A>, greater than 1, is multiplied. The excess ratio of  $\text{O}_2$  is then  $(A - 1) \times 100\%$ .

For every mole of  $\text{O}_2$  introduced, 3.76 mol of  $\text{N}_2$  is introduced.

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases



# Equilib Module: Recovery of Tin from Tin Cans

## Exercise 2. Adding Too Much Air

The screenshot shows the Equilib software interface. The reactants list includes Sn, 0.2 Fe, <2B> Cl<sub>2</sub>, <0.15A> O<sub>2</sub>, and <0.564A> N<sub>2</sub>. The final conditions section shows a table with columns <A>, <B>, T(C), P(atm), and Delta H(J). The values are 1 2 0.1, 1.1, 500, 1, and an empty field respectively. Three red boxes highlight the <A> and <B> columns, the T(C) field, and the T(C) value. Three red callout boxes provide additional context: one points to the O<sub>2</sub> coefficient, another to the T(K) field, and a third to the T(C) value.

Equilib - Menu: comments

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

**Reactants (5)**

Sn + 0.2 Fe + <2B> Cl<sub>2</sub> + <0.15A> O<sub>2</sub> + <0.564A> N<sub>2</sub>  
(25C,s1,#1) (25C,s1,#1) (25C,g,#2) (25C,g,#3) (25C,g,#3)

**Products**

Compound species: gas (ideal/real), aqueous, pure liquids, pure solids

Solution phases: Base-Phase, Full Name

Custom Solutions: 0 fixed activities, 0 ideal solutions

Pseudonyms: apply, Edit ...

Target: none

Estimate T(K): 1000

Quantity(mol): 0

solutions: 0

Total Phases (max 1500): 33

**Final Conditions**

<A>	<B>	T(C)	P(atm)	Delta H(J)
1 2 0.1	1.1	500	1	

Equilibrium: normal, normal + transitions, transitions only, open

Calculate >>

FactSage 7.3

w:\MSE302\Exercise\EquiTin\_R

The excess ratio of O<sub>2</sub> is between 0 to 100%, which means <A> varies from 1 to 2.

A small excess ratio (~10%) is used for the input chlorine.

We are considering the process at 500 °C.

# Equilib Module: Recovery of Tin from Tin Cans

---

## Exercise 2. Adding Too Much Air

After the calculation, plot the number of moles of  $\text{SnCl}_4(g)$ ,  $\text{Cl}_2(g)$ ,  $\text{Fe}_2\text{O}_3(s)$  and  $\text{SnO}_2(s)$  against  $\langle A \rangle$ . With increasing the excess oxygen supplied, is Sn efficiently recovered to the gas stream? Why?

Also, plot the **mole fraction** of oxygen in the off-gas against  $\langle A \rangle$ . If the oxygen level in the off-gas is measured and it reaches  $\sim 150$  ppm, you would know to cut back on the air feed to the reactor. This means that it would be possible, at least in principle, to use an oxygen analyzer to drive an air flow control valve.

Note that the partial pressure of oxygen does not rise very steeply with excess air, because it is “buffered” by the formation of  $\text{SnO}_2$ . The formation of  $\text{SnO}_2$  means that less chlorine is used for chlorination of Sn so that chlorine will rise in tandem with oxygen, and the chlorine is present at much higher concentrations (please plot the mole fraction of chlorine in the off-gas against  $\langle A \rangle$ ).

# Equilib Module: Recovery of Tin from Tin Cans

---

## Exercise 2. Adding Too Much Air

In an actual process, the excess  $\text{Cl}_2$  supplied to the reactor would result in the presence of free  $\text{Cl}_2$  in the off-gas. It would be necessary to keep the free  $\text{Cl}_2$  in the off-gas in a range of 11~20 vol.%, or even higher, to provide the driving force for the chlorination process. This requires a careful control of the addition rate of chlorine. The free  $\text{Cl}_2$  in the off-gas can be recovered and recycled.

# Equilib Module: Recovery of Tin from Tin Cans

---

## **Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor**

In the third exercise, we will be looking at the effects of **the varying amounts of both  $\text{Cl}_2$  and the exposed iron that reacts** on the chlorination process. This can be done by setting the amounts of  $\text{Cl}_2$  and iron as variables (next page).

**Note:** when <B> is used, the calculations are repeated for each value.

# Equilib Module: Recovery of Tin from Tin Cans

## Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor

Equilib - Reactants

We are again calculating the tin recovery based on 1 mol of Sn.

The number of moles of the exposed iron are variable  $\langle B \rangle$ .

Quantity (mol)	Species	Phase	T (C)	P (total)**	Stream#	Data
1	Sn	solid-1 Solid(wh)	25	1	1	
$\langle B \rangle$	Fe	solid-1 bcc	25	1	1	
$\langle 2A \rangle$	Cl <sub>2</sub>					
$\langle 0.825B \rangle$	O <sub>2</sub>					
$\langle 3.102B \rangle$	N <sub>2</sub>					

Different levels of input Cl<sub>2</sub> are tested by changing  $\langle A \rangle$ :  $A = 1$  means stoichiometric addition of Cl<sub>2</sub>.

To oxidize  $\langle B \rangle$  mol of Fe to Fe<sub>2</sub>O<sub>3</sub>, at least  $\langle 0.75B \rangle$  mol of O<sub>2</sub> are required. If we assume the excess rate of O<sub>2</sub> is 10%, then  $\langle 0.825B \rangle$  mol of O<sub>2</sub> are added.

For every mole of O<sub>2</sub> introduced, 3.76 mol of N<sub>2</sub> is introduced.

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

# Equilib Module: Recovery of Tin from Tin Cans

## Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor

The screenshot shows the Equilib software interface. The reactants list includes Sn, Fe, Cl<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>. The products list includes gas, aqueous, pure liquids, and pure solids. The final conditions section shows the following values:

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.8	0.2	500	1	

Annotations in red boxes provide additional context:

- We cover the range from under-supply of Cl<sub>2</sub> (i.e.,  $A < 1$ ) to over-supply of Cl<sub>2</sub> (i.e.,  $A > 1$ ).
- For every mole of Sn recovered, 0.2 mol of Fe reacts.
- We are considering the process at 500 °C.

# Equilib Module: Recovery of Tin from Tin Cans

## Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor

The screenshot shows the FactSage Equilib module interface. The reactants are Sn (25C,s1,#1), Fe (25C,s1,#1), Cl<sub>2</sub> (25C,g,#2), O<sub>2</sub> (25C,g,#3), and N<sub>2</sub> (25C,g,#3). The products are listed in a table with columns for Base-Phase and Full Name. The final conditions are set to T(C) = 500, P(atm) = 1, and Delta H(J) = 0. The equilibrium options are set to normal.

Equilib - Menu: comments

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

**Reactants (5)**

Sn + <B> Fe + <2A> Cl<sub>2</sub> + <0.825B> O<sub>2</sub> + <3.102B> N<sub>2</sub>  
(25C,s1,#1) (25C,s1,#1) (25C,g,#2) (25C,g,#3) (25C,g,#3)

**Products**

Compound species

gas  ideal  real 41  
aqueous 0  
pure liquids 10  
pure solids

Solution phases

*	+	Base-Phase	Full Name
---	---	------------	-----------

Custom Solutions

0 fixed activities Details ...  
0 ideal solutions

Pseudonyms

apply Edit ...

Target

Estimate T(K): 1000  
Quantity(mol): 0

solutions: 0 select

Total Phases (max 1500) 33

**Final Conditions**

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.8 2 0.2	0.6	500	1	

10 steps Table

**Equilibrium**

normal  normal + transitions  
 transitions only  
 open Calculate >>

FactSage 7.3 w:\MSE302\Exercise\EquiTin\_R

We cover the range from under-supply of Cl<sub>2</sub> (i.e.,  $A < 1$ ) to over-supply of Cl<sub>2</sub> (i.e.,  $A > 1$ ).

For every mole of Sn recovered, 0.6 mol of Fe reacts.

We are considering the process at 500 °C.

# Equilib Module: Recovery of Tin from Tin Cans

---

## **Exercise 3. Changing the Amounts of Both Chlorine and Iron to the Reactor**

After each calculation with different  $\langle B \rangle$ , plot the levels of oxygen and chlorine in the off-gas (e.g., mol fraction) against  $\langle A \rangle$ .

Save the three graphs and use the Figure Module to superimpose them. Make sure you use different line types so that the conditions can be differentiated.

- (a) From the superimposed graph, can you see the correlation between the oxygen level in the off-gas and the chlorine supplied to the reactor?
- (b) Can you suggest proper operating conditions (i.e.,  $\langle A \rangle$  and  $\langle B \rangle$  values) based on the total Sn recovered to the gas phase?
- (c) Given  $B = 2$ , if we wish to increase the recovery of Sn to the gas phase, should we increase or decrease the excess rate of  $O_2$ ?



# Equilib Module: Recovery of Tin from Tin Cans

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## **Final Thought**

You need to be aware that all the above calculations that have been performed using FactSage are equilibrium calculations. The real process may behave differently, because of kinetics.

# Equilib Module: Oxidation of Iron

---

The oxidation of metals is one of the very important chemical reactions. Take the oxidation of iron for example. The species that may exist at equilibrium include metallic iron (bcc, fcc) and various types of iron oxides. The thermodynamic data for metallic iron are stored in FactPS, and the data for oxides can be found in both FactPS and FToxid. (You should use the View Data Module to check the Compounds and Solutions for the Fe-O system)

**Reminder:** when multiple thermodynamic databases are selected, special care must be taken so that the same compound is selected only once.

For iron oxides, iron can take the oxidation state of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . To aid your understanding, we can view  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  as two separate species. The relative amounts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  depend on the oxygen potential (i.e., oxygen partial pressure). Therefore, when calculating the equilibrium involving the metal oxides with different oxidation states, the oxygen partial pressure,  $P_{\text{O}_2}$ , must be specified. The input amount of the gas component will be automatically adjusted so that the desired  $P_{\text{O}_2}$  is met.

# Equilib Module: Oxidation of Iron

---

Let us study the oxidation of iron by looking at the dependence of the oxidation state of iron on the oxygen partial pressure. We will adjust  $P_{O_2}$  and see what iron oxide is stable. We will fix the temperature at 1400 °C, the pressure at 1 atm.

# Equilib Module: Oxidation of Iron

## Reactants Window

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Don't forget the Directory.

Select the units.

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	Fe				1	
+	0	O2			2	

We will oxidize 1 mole of iron. For the quantity of  $O_2$ , we set the value to 0 since it will be automatically adjusted when we define  $P_{O_2}$  (we only need to tell FactSage that the system contains oxygen).

We don't need to check "Initial Conditions" because we are not calculating the changes in the thermodynamic properties.

Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 0/15 databases

# Equilib Module: Oxidation of Iron

## Reactants Window: Database(s)

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Data Search

Databases - 3/14 compound data

- FactPS
- FToxid
- FTsalt
- FTmisc
- FTHall
- FT0xCN
- FTirtz
- FTHelg
- FTpulp
- FTlite
- FScopp
- FSlead
- FSsteel
- FSopsi
- ELEM
- FTdemo
- FTnucl

Information -

Compound: C:\FactSage\FACTDATA\FTlite60base.cdb  
- FTlite - FACT Al-alloy and Mg-alloy compounds (2019)

Solution: C:\FactSage\FACTDATA\FTlite60soln.sdc  
- FTlite - FACT Al-alloy and Mg-alloy solutions (2019)

Options - search for product species

Default

Include compounds

- gaseous ions (plasmas)
- aqueous species
- limited data compounds (25C)

Limits

Organic species CxHy..., X(max) = 2

Minimum solution components:  1  2 cpts

Cancel Summary ... OK

FactPS is selected because we need to consider  $O_2(g)$ .

FToxid contains models for some solid solutions of iron oxide, for example, spinel and wustite.

FTmisc contains the model for liquid Fe with limited solubility of oxygen.

(Same database selection when calculating the Fe- $O_2$  phase diagram.)

# Equilib Module: Oxidation of Iron

## Menu Window: Set $P_{O_2}$

The screenshot shows the Equilib software interface. The main window displays a list of species with columns for Code, Species, and Phase. The species listed are O(g), O2(g), O3(g), Fe(g), and FeO(g). The O2(g) row is highlighted in blue. A context menu is open over the O2(g) row, with 'Activity' selected. A sub-menu is open over 'Activity', with 'log10(activity)' selected. A 'Fixed Partial Pressure' dialog box is open, with the input field containing '-12-0.1 0.1'. A text box at the top right of the O2(g) row contains the text: 'We set  $P_{O_2}$  from  $10^{-12}$  to  $10^{-0.1}$  atm at  $10^{0.1}$  atm intervals.' A red box highlights the 'Menu' button in the top left corner. A red box highlights the 'gas' radio button in the 'Compound species' section. A red box highlights the 'log10(activity)' option in the sub-menu. A red box highlights the 'Fixed Partial Pressure' dialog box. A red box highlights the 'Calculate >>' button at the bottom right. A red box highlights the text 'All gaseous species are selected, and the ideal gas model is used.' at the bottom left. A blue box highlights the text 'Right Click' in the middle left. A blue box highlights the text 'Right Click' in the middle left. A blue box highlights the text 'We set  $P_{O_2}$  from  $10^{-12}$  to  $10^{-0.1}$  atm at  $10^{0.1}$  atm intervals.' at the top right. A blue box highlights the 'log10(activity)' option in the sub-menu. A blue box highlights the input field in the 'Fixed Partial Pressure' dialog box.

Equilib Menu last system

File Units Parameters Help

Reactants (2)

Products

Compound species

gas  ideal  real 5

aqueous 0

pure liquids 0

pure solids 0

Target

Estimate T(K): 1000

Quantity(mol): 0

Final Conditions

10 steps  Table

1 calculation  open

Calculate >>

Selected: 5/5 GAS [X denotes species excluded by default]

We set  $P_{O_2}$  from  $10^{-12}$  to  $10^{-0.1}$  atm at  $10^{0.1}$  atm intervals.

Fixed Partial Pressure

Enter the value of log10(p) (or for a range of values enter 'first last step') for 2 O2(g).

Press [Cancel] if the partial pressure is no longer fixed.

-12-0.1 0.1

Right Click

Right Click

All gaseous species are selected, and the ideal gas model is used.

# Equilib Module: Oxidation of Iron

## Menu Window: Select Pure Solids

Equilib Menu last system

File Units Parameters Help

Reactants (2)

Products

Compound species

gas  ideal  real 5

aqueous 0

pure liquids 0

\* + pure solids 5

\* - custom selection

Target

- none -

Estimate T(K): 1000

Quantity(mol): 0

Final Conditions

<A> <B> T

2500 1

120 calculations

transitions only

open

Calculate >>

Selection - Equilib - no results -

File Edit Show Sort

Selected: 5/13 SOLID Duplicates selected. X denotes species excluded by default

- no results -

	Code	Species	Data	Phase	T	V	Activity	Minimum	Maximum
+	9	Fe(s)	FactPS	bcc		V			
+	10	Fe(s2)	FactPS	fcc		V			
X	11	FeO(s)	FactPS	Wustite		V			
X	12	Fe2O3(s)	FactPS	hematite		V			
X	13	Fe2O3(s2)	FactPS	High-Pressure-H		V			
X	14	Fe2O3(s3)	FactPS	High-Pressure-H		V			
X	15	Fe3O4(s)	FactPS	Magnetite		V			
X	16	Fe3O4(s2)	FactPS	Magnetite		V			
X	17	Fe3O4(s3)	FactPS	High-Pressure-m		V			
X	18	Fe3O4(s4)	FactPS	High-Pressure-m		V			
+	19	Fe2O3(s)	FToxid	hematite		V			
+	20	Fe2O3(s2)	FToxid	High-Pressure-H		V			
+	21	Fe2O3(s3)	FToxid	High-Pressure-H		V			

Right Click

FeO is excluded because FToxid\_MeO (solution, wustite) is a better model; Fe2O3 is excluded because FToxid\_Fe2O3 is used; Fe3O4 is excluded because FToxid\_SPINA (solution, spinel) is a better model.

All pure solids are selected with the suppression of duplicates.

# Equilib Module: Oxidation of Iron

## Menu Window: Select Solution Phases

Equilib Menu last system

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

Reactants (2)

Fe + 0 O2

Products

Compound species

- gas  ideal  real 5
- aqueous 0
- pure liquids 0
- pure solids 5
- \* - custom selection species: 10

Solution phases

*	+	Base-Phase	Full Name
	+	FTmisc-FeLQ	Fe-liq
		FToxid-SLAGA	A-Slag-liq all oxides + S
	+	FToxid-SPINA	A-Spinel
	+	FToxid-MeO_A	A-Monoxide

Custom Solutions

1 fixed activities **Details ...**

0 ideal solutions

Pseudonyms

apply  Edit ...

Volume data

- assume molar volumes of solids and liquids = 0
- include molar volume data and physical properties data

Target

- none -

Estimate T(K): 1000

Quantity(mol): 0

Final Conditions

<A>	<B>	T(C)	P(atm)	Product H(J)
		2500	1	

Equilibrium

- normal
- normal + transitions
- transitions only
- open

Calculate >>

FactSage 7.3

Custom Solutions

Fixed Activity: 1 Species

2: O2(g): Log10(a) = -12 -0.1 0.1 (i.e. 120 values)

Ideal Solutions: 0 Phases

OK

Select all the solution phases: two liquid solutions and two solid solutions.



# Equilib Module: Oxidation of Iron

## Menu Window: Set Final Conditions

Equilib - Menu last system

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

**Reactants (2)**

Fe + 0 O<sub>2</sub>

**Products**

Compound species

- gas  ideal  real 5
- aqueous 0
- pure liquids 0
- pure solids 5
- \* - custom selection species: 10

Solution phases

*	+	Base-Phase	Full Name
	+	FTmisc-FeLQ	Fe-liq
		FToxid-SLAGA	A-Slag-liq all oxides + S
	+	FToxid-SPINA	A-Spinel
	+	FToxid-MeO_A	A-Monoxide

Custom Solutions

1 fixed activities Details ...

0 ideal solutions

Pseudonyms

apply  Edit ...

Volume data

- assume molar volumes of solids and liquids = 0
- include molar volume data and physical properties data

Target

- none -

Estimate T(K): 1000

Quantity(mol): 0

Legend

| - immiscible 1

+ - selected 3

Total Phases (max 1500) 11

**Final Conditions**

<A> <B> T(C) P(atm) Product H(J)

10 steps  Table 120+ calculations

**Equilibrium**

- normal
- normal + transitions
- transitions only
- open

Calculate >>

FactSage 7.3

This option permits us to find all the transition temperatures between different oxidation products.

The oxidation of iron occurs at 1400 °C.

# Equilib Module: Oxidation of Iron

Results: When  $P_{O_2} = 10^{-4}$  atm

Equilib Results a=1.00E-04 (page 87/128)

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

a=7.94E-06 | a=1.00E-05 | a=1.26E-05 | a=1.58E-05 | a=2.00E-05 | a=2.51E-05 | a=3.16E-05 | a=3.98E-05 | a=5.01E-05

a=0.0005 | a=0.0006 | a=0.0008 | a=0.001 | a=0.0013 | a=0.0016 | a=0.002 | a=0.0025 | a=0.00316

a=6.31E-05 | a=7.94E-05 | a=1.00E-04 | a=0.000126 | a=0.000158 | a=0.0002 | a=0.000251 | a=0.000316

Let us view the result when  $P_{O_2} = 10^{-4}$  atm.

T = 1400 C  
P = 1 atm  
V = 0 dm3

STREAM CONSTITUENTS	AMOUNT/mol
Fe	1.0000E+00
O2	0.0000E+00
*O2/gas_ideal/	6.669E-01

This is the amount of O<sub>2</sub> that is automatically calculated, which gives the required partial pressure of O<sub>2</sub>.

PHASE: gas_ideal	EQUIL AMOUNT mol	MOLE FRACTION	FUGACITY atm
O2	0.0000E+00	9.9660E-01	1.0000E-04
O	0.0000E+00	3.3149E-02	3.3262E-07
FeO	0.0000E+00	7.0002E-05	7.0241E-09
Fe	0.0000E+00	1.4343E-05	1.4392E-09
O2	0.0000E+00	9.343E-11	9.3755E-15
TOTAL:	0.0000E+00	1.0000E+00	1.0000E-04

The solid solution "Spinel" is the oxidation product because its activity is 1.0. The composition can be expressed as Fe<sub>0.42847</sub>O<sub>0.57153</sub>.

PHASE: Spinel	mol	MOLE FRACTION	ACTIVITY
Fe3O4	7.4695E-02	2.2399E-01	1.9232E-01
Fe3O4[1-]	7.3320E-02	2.1986E-01	9.1896E-02
Fe3O4[1+]	1.4832E-01	4.4478E-01	2.6459E-01
Fe3O4[2-]	3.6923E-02	1.1072E-01	2.1362E-02
Fe1O4[5-]	1.442E-04	4.3260E-04	3.9150E-07
Fe1O4[6-]	7.2650E-05	2.1786E-04	9.1019E-08
TOTAL:	3.2348E-01	1.0000E+00	1.0000E+00

System component	Amount/mol	Amount/gram	Mole fraction	Mass fraction
Fe	1.0000	55.845	0.42847	0.72350
O	1.3229	21.342	0.57153	0.27650

Site fraction of sublattice constituents:

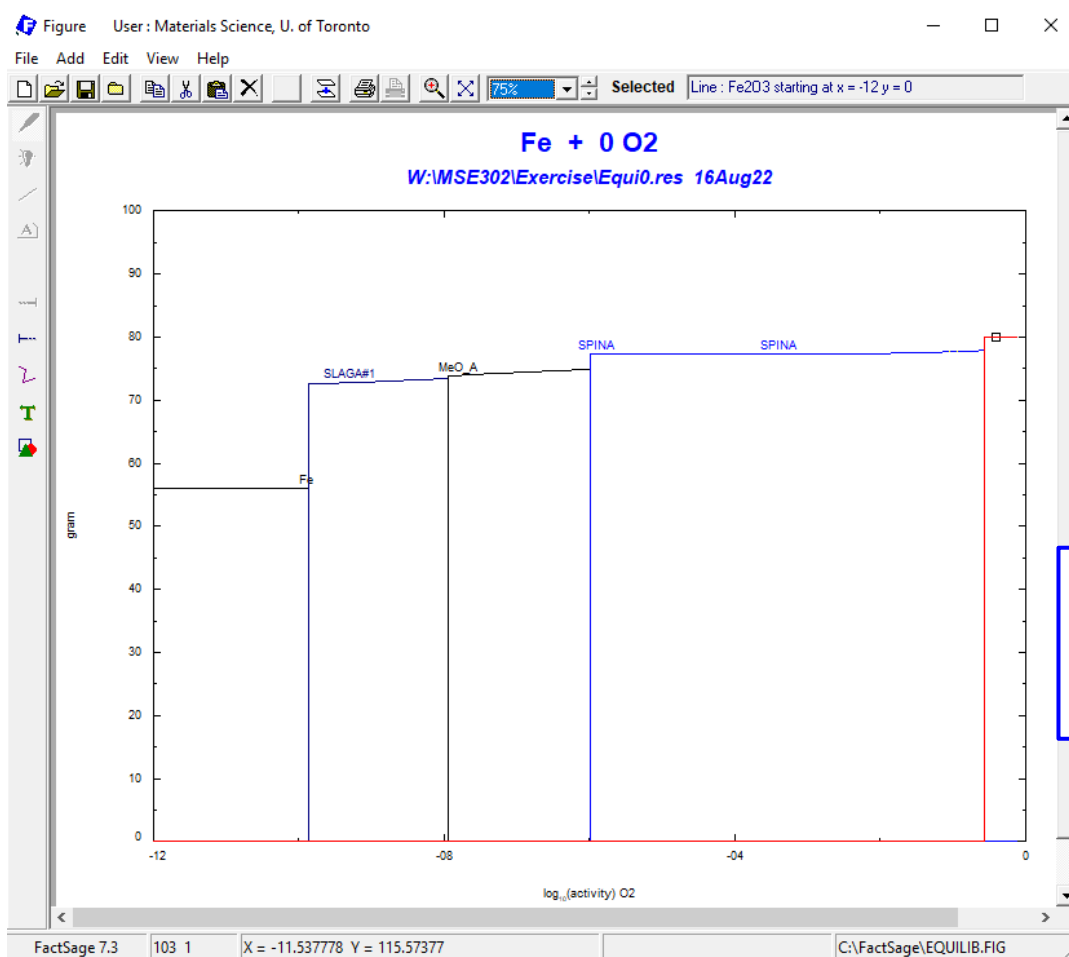
Sublattice	Amount/mol	Stoichiometry
Fe[2+]T	0.33493	1
Fe[3+]T	0.66507	1
Fe[2+]O	0.33059	2
Fe[3+]O	0.66876	2

Curie temperature = 571.87 C  
Average magnetic moment/atom = 44.383



# Equilib Module: Oxidation of Iron

**Results: Plot the masses of oxidation products, i.e.,  $\text{gram} \sim P_{\text{O}_2}$ .**



This graph shows that the oxidation products at 1400 °C are affected by the oxygen partial pressure.

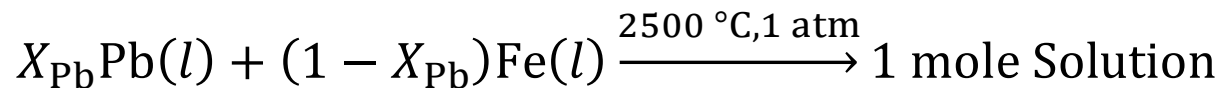
# Equilib Module: Mixing Properties

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Recall we studied the **solution** properties by looking at an **isothermal mixing process** (Chapter 4.3). Now let us calculate some mixing properties using the Equilib Module.

Say we would like to mix varying amounts of liquid Pb and liquid Fe at 2500 °C and 1 atm. We assume the total amount of Pb and Fe is 1 mole.

The mixing process can be described as the following:



# Equilib Module: Mixing Properties

## Reactants Window: Define Reactants

Equilib Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(g) Vol(litre)

1-2

Don't forget the Directory.

Quantity(g)	Species	Phase	T(C)	P(total)**	Stream#	Data
1	Pb				1	
+ 1	Fe					

Species that are being mixed.

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 1/15 databases

# Equilib Module: Mixing Properties

## Reactants Window: Database(s)

The screenshot displays the Equilib software interface. The main window is titled "Equilib Reactants" and has a menu bar with "File", "Edit", "Table", "Units", "Data Search", "Data Evaluation", and "Help". The "Data Search" window is open, showing a list of databases under "Databases - 17/14 compound databases, 17/15 solution databases". The "FTlite" checkbox is checked. A search results window titled "Search Results - FactSage Browser - [search\_results.htm]" is also open, showing search results for "Pb Fe". The search results window has a menu bar with "File", "View", and "About...". The search results window shows a list of phase diagrams, with "FTlite" highlighted in the "List of Phase Diagrams" section. A red box highlights the "FTlite" checkbox in the Reactants window and the "FTlite" entry in the search results window. A red arrow points from the "FTlite" entry in the search results window to a text box below.

We use the Documentation Module to find which databases contain the optimized parameters for the Pb-Fe system. FTlite is selected.

# Equilib Module: Mixing Properties

## Reactants Window: Choose Units and Input the Quantity of Species

Equilib - Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 2

Choose the units. Use mol for quantity.

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
<A>	Pb				1	
+ <1-A>	Fe				1	

We have variable amounts of Pb and Fe.

Initial Conditions

Next >>

FactSage 7.3 Compound: 1/14 databases Solution: 1/15 databases



# Equilib Module: Mixing Properties

## Reactants Window: Specify the Initial Conditions

Equilib Reactants

File Edit Table Units Data Search Data Evaluation Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

1 - 2

Quantity(mol)	Species	Phase	T(C)	P(total)**	Stream#	Data
<A>	Pb	liquid	2500	1.0	1	
+ <1-A>	Fe	liquid	2500	1.0	2	

Choose the units.

We are mixing liquid Pb and liquid Fe.

Both liquid Pb and liquid Fe are initially at 2500 °C and 1 atm.

\*\* P(total) is the hydrostatic pressure above the phase. For a gaseous stream this is the sum of the partial pressures of the species in that stream.

Initial Conditions

Next >>

Check "Initial Conditions"

FactSage 7.3 Compound: 1/14 databases Solution: 1/15 databases

# Equilib Module: Mixing Properties

## Menu Window: Select Products and Define Final Conditions

The screenshot shows the FactSage Equilib Menu window. The title bar reads "Equilib - Menu last system". The menu bar includes "File", "Units", "Parameters", and "Help". The main window displays the following information:

- Reactants (2):** <A> Pb (2500C.liq.#1) + <1-A> Fe (2500C.liq.#2)
- Products:** A table with columns for "Base-Phase" and "Full Name". The first row is highlighted in yellow and contains "FTlite-Liqu" and "Liquid".
- Final Conditions:** A table with columns for "<A>", "<B>", "T(C)", "P(atm)", and "Delta H(J)". The first row contains "0.1", "0.005", "2500", "1", and "0".

Red boxes and arrows highlight specific elements in the interface, corresponding to the text boxes below.

*	+	Base-Phase	Full Name
1		FTlite-Liqu	Liquid
		FTlite-A1	FCC-A1

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.1	0.005	2500	1	0

Choose FTlite-Liqu only, and use the default [I]-option. From the Pb-Fe phase diagram (Documentation), it is seen that the immiscibility exists for liquid Pb and liquid Fe.

We would like to perform the calculations from pure Fe to pure Pb using the step of 0.005.

The mixing process is isothermal.

# Equilib Module: Mixing Properties

## Results

Equilib Results A=0.015 (page 4/201)

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

A=0.12

A=0.06 | A=0.065 | A=0.07 | A=0.075 | A=0.08 | A=0.085 | A=0.09 | A=0.095 | A=0.1 | A=0.105 | A=0.11 | A=0.115 |

A=0 | A=0.005 | A=0.01 | **A=0.015** | A=0.02 | A=0.025 | A=0.03 | A=0.035 | A=0.04 | A=0.045 | A=0.05 | A=0.055 |

T = 2500 C  
P = 1 atm  
V = 0 dm3

**Final conditions.**

Thermodynamic properties before mixing.

Two stable immiscible liquids: Liquid#1 is Fe-rich and Liquid#2 is Pb rich. However, these two liquids are described using the same model, but the possibility of immiscibility was considered.

STREAM	CONSTITUENTS	AMOUNT/mol	TEMPERATURE/C	PRESSURE/atm	STREAM
Pb_liquid		1.5000E-02	2500.00	1.0000E+00	1
Fe_liquid		9.8500E-01	2500.00	1.0000E+00	2

	Cp_INI J.K-1	H_INI J	S_INI J.K-1	G_INI J	V_INI dm3
	4.57555E+01	1.16132E+05	1.19645E+02	-2.15660E+05	0.00000E+00

PHASE: Liquid#1	EQUIL	AMOUNT	MOLE FRACTION	ACTIVITY
Fe		9.8485E-01	9.8793E-01	9.8941E-01
Pb		1.2032E-02	1.2069E-02	9.6014E-01
TOTAL:		9.9688E-01	1.0000E+00	1.0000E+00
System component	Amount/mol	Amount/gram	Mole fraction	Mass frac
Pb	1.2032E-02	2.4929	1.2069E-02	4.2361E-02
Fe	0.98485	54.999	0.98793	0.95664

PHASE: Liquid#2	EQUIL	AMOUNT	MOLE FRACTION	ACTIVITY
Fe		1.4845E-04	4.7626E-02	9.8941E-01
Pb		2.9685E-03	9.5237E-01	9.6014E-01
TOTAL:		3.1169E-03	1.0000E+00	1.0000E+00
System component	Amount/mol	Amount/gram	Mole fraction	Mass fraction
Pb	2.9685E-03	0.61507	0.95237	0.98670
Fe	1.4845E-04	8.2900E-03	4.7626E-02	1.3299E-02

DELTA Cp	DELTA H	DELTA S	DELTA G	DELTA V
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# Equilib Module: Mixing Properties

## Results (Cont'd)

Equilib Results A=0.015 (page 4/201)

Output Edit Show Pages Final Conditions

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

A=0.12

A=0.06 | A=0.065 | A=0.07 | A=0.075 | A=0.08 | A=0.085 | A=0.09 | A=0.095 | A=0.1 | A=0.105 | A=0.11 | A=0.115

A=0 | A=0.005 | A=0.01 | **- A=0.015 -** | A=0.02 | A=0.025 | A=0.03 | A=0.035 | A=0.04 | A=0.045 | A=0.05 | A=0.055

Fe	0.98485	54.999	0.98793	0.95664
PHASE: Liquid#2	mol	MOLE FRACTION	ACTIVITY	
Fe	1.4845E-04	4.7626E-02	9.8941E-01	
Pb	2.9685E-03	9.5227E-01	9.6014E-01	
TOTAL:	3.1169E-03	1.0000E+00	1.0000E+00	
System component	Amount/mol	Amount/gram	Mole fraction	
Pb	2.9685E-03	0.61507	0.95237	
Fe	1.4845E-04	8.2900E-03	4.7626E-02	1.3299E-02

DELTA Cp	DELTA H	DELTA S	DELTA G	DELTA V
J.K-1	J	J.K-1	J	dm3
2.18358E+00	1.22689E+02	5.35522E-01	-2.58194E+02	0.00000E+00

Cp	H	S	G	V
J.K-1	J	J.K-1	J	dm3
4.79290E+01	1.17359E+05	1.20180E+02	-2.15918E+05	0.00000E+00

	Cp	H	S	G
	J.K-1	J	J.K-1	J
Liquid#1	4.78298E+01	1.17103E+05	1.19750E+02	-2.14981E+05
Liquid#2	1.09266E-01	2.56742E+02	4.30406E-01	-9.36840E+02

Cut-off limit for phase activities = 1.00E-75

Databases: FTLite 7.3

Data Search options: exclude gas ions; organic CxHy.. X(max) = 2; min soln cpts = 2

Final conditions: <A> = 0 1 0.005, T(C) = 2500, P(atm) = 1

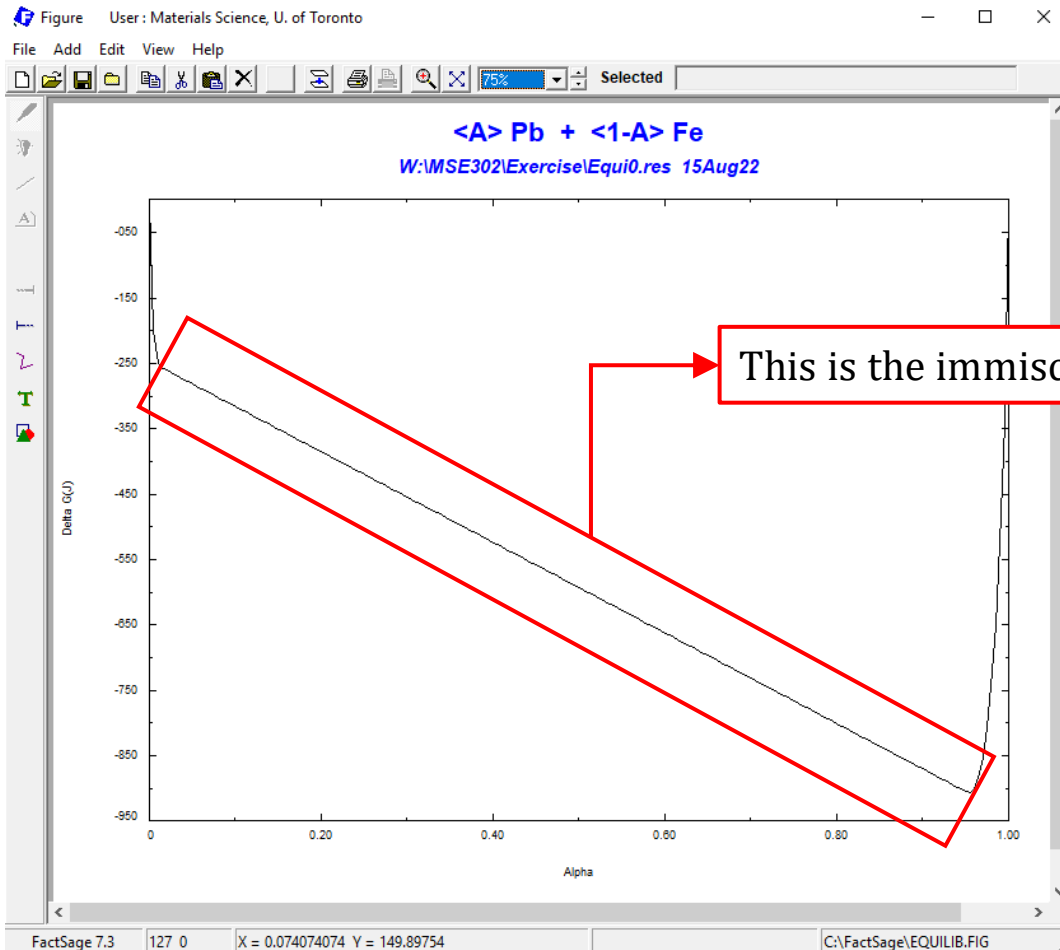
These are the changes in thermodynamic properties of mixing during the isothermal mixing.

These are the thermodynamic properties of the **system** after mixing.

These are the thermodynamic properties of the stable phases after mixing.

# Equilib Module: Mixing Properties

## Results: Make Plots $\Delta_{\text{mix}}g_{2500\text{ }^\circ\text{C}} \sim X_{\text{Pb}}$



This is the immiscibility region.

You might ask, what if liquid Pb and liquid Fe are completely miscible and form a single liquid solution?

# Equilib Module: Mixing Properties

## Menu Window: Select Products and Define Final Conditions

Equilib Menu last system

File Units Parameters Help

T(C) P(atm) Energy(J) Quantity(mol) Vol(litre)

**Reactants (2)**

<A> Pb + <1-A> Fe  
(2500C.liq.#1) (2500C.liq.#2)

**Products**

Compound species

gas  ideal  real 0  
aqueous 0  
pure liquid 0  
pure solid 0

species: 0

Target  
- none -  
Estimate T(K): 1000  
Quantity(mol): 0

Legend  
+ - selected 1  
 Show  all  selected  
species: 2  
solutions: 1

*	+	Base-Phase	Full Name
	<input checked="" type="checkbox"/>	FTlite-Liqu	Liquid
	<input type="checkbox"/>	FTlite-A1	FCC-A1

Custom Solutions  
0 fixed activities  
0 ideal solutions

Pseudonyms

solids and liquids = 0  
 include molar volume data and physical properties data

paraequilibrium & Gmin

Virtual species: 1  
Total Species (max 5000) 2  
Total Solutions (max 200) 1  
Total Phases (max 1500) 1

**Final Conditions**

<A>	<B>	T(C)	P(atm)	Delta H(J)
0.1	0.005	2500	1	

10 steps  Table 201 calculations

**Equilibrium**

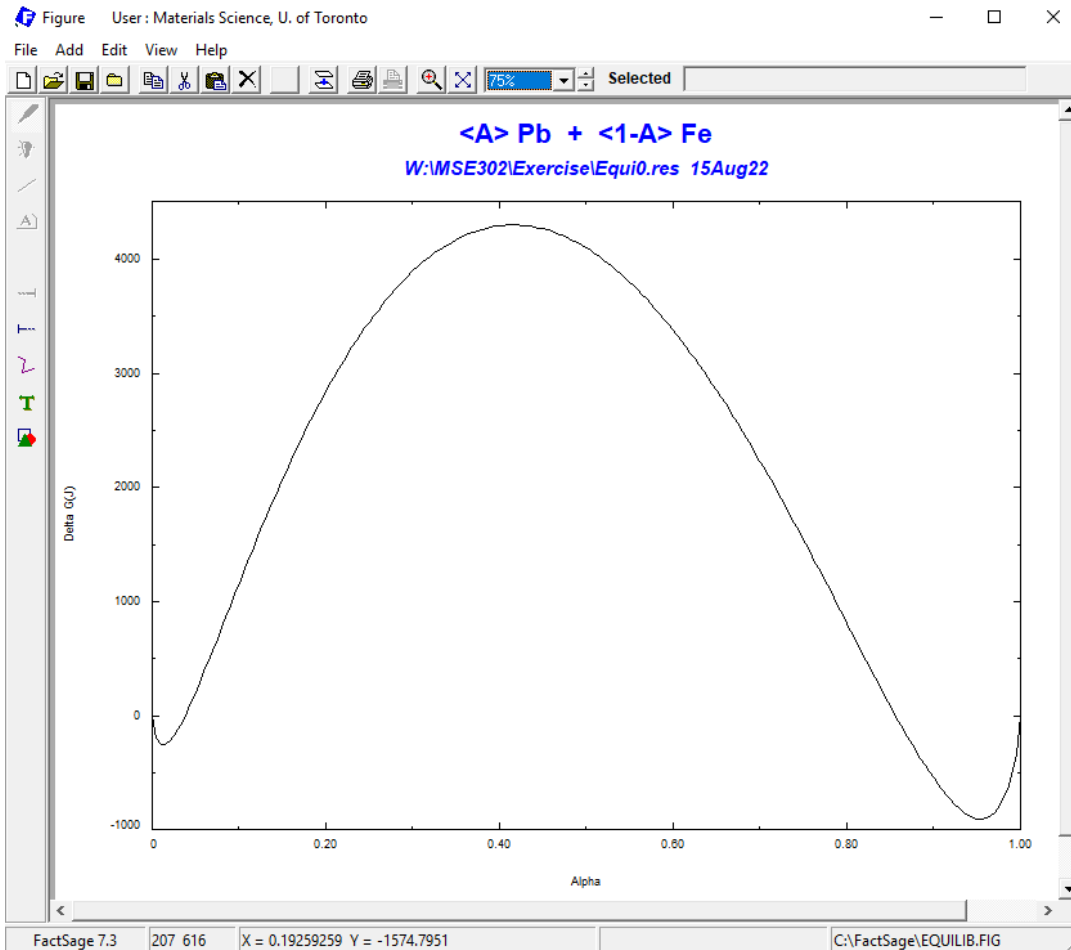
normal  normal + transitions  
 transitions only  
 open

FactSage 7.3

This time, we do not consider the immiscibility. The single-phase setting is chosen.

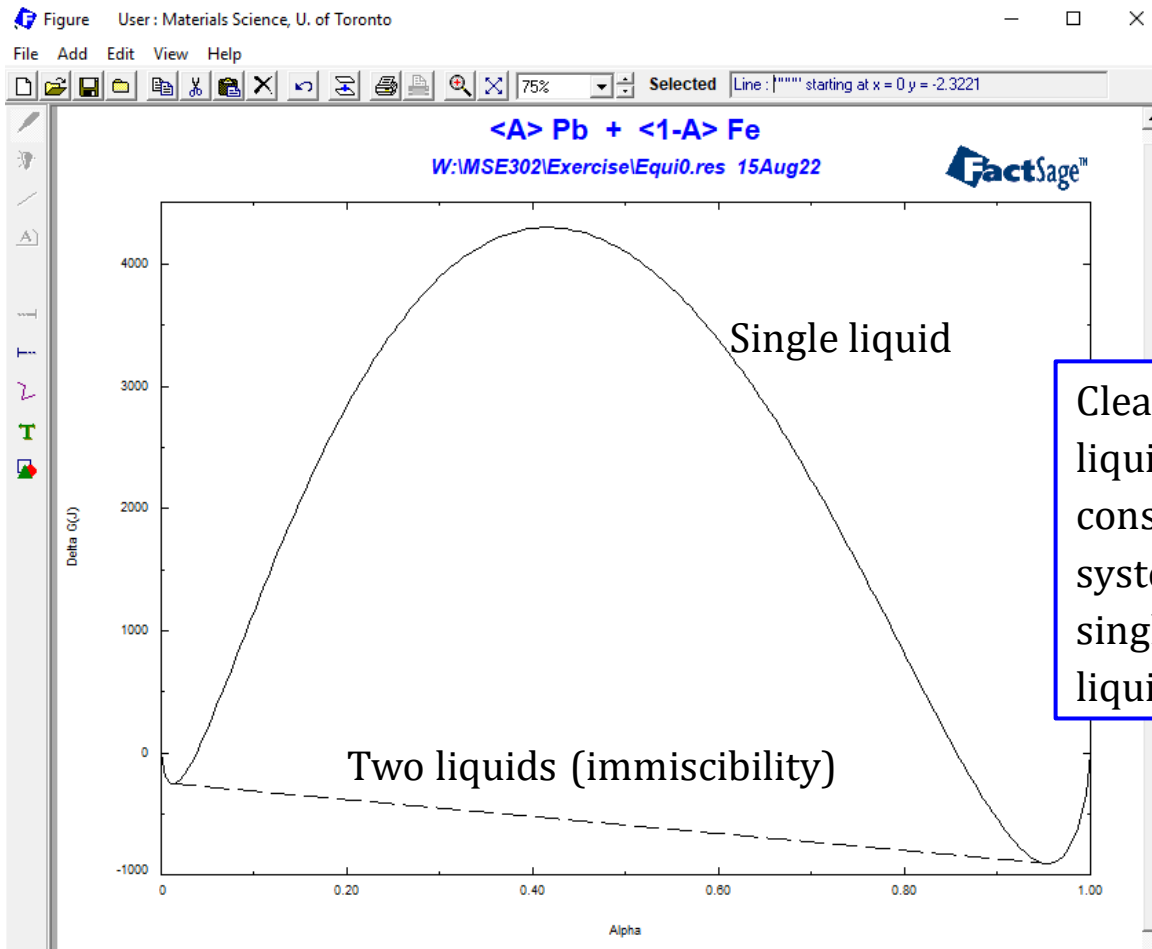
# Equilib Module: Mixing Properties

Results: Make Plots  $\Delta_{\text{mix}}g_{2500\text{ }^\circ\text{C}} \sim X_{\text{Pb}}$



# Equilib Module: Mixing Properties

**Results: Use the Figure Module to superimpose the two figures**



Clearly, if the system exists as two liquids, that is, immiscibility is considered, the Gibbs energy of the system would be much lower than if single liquid exists. Therefore, two liquids are more stable.



# Equilib Module: Mixing Properties

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## Results

Use the [I]-option for FTlite-Liqu, please plot other mixing properties

$$\Delta_{\text{mix}}h_{2500\text{ }^{\circ}\text{C}} \sim X_{\text{Pb}} \text{ and } \Delta_{\text{mix}}s_{2500\text{ }^{\circ}\text{C}} \sim X_{\text{Pb}}.$$

Then, please go back to the Menu Window, and save the solution properties for FTlite-Liqu.

(It is also recommended that you use Fact-XML to plot all the solution properties)

# Equilib Module: General Tips

---

**Some general tips for the Equilib Module are summarized in a Q&A format**

**Q1:** How to perform calculations when the mass of the reactant changes?

**A1:** You can use  $\langle A \rangle$  or  $\langle aA + b \rangle$  or  $\langle a + bA \rangle$  where “a” and “b” are constants and  $\langle A \rangle$  (alpha) is a variable to represent the quantities of the reactants.

**Q2:** How to calculate the adiabatic flame temperature?

**A2:** After inputting the initial temperature, you can leave the final temperature blank, and set 0 for the Enthalpy change .

**Q3:** I saw in the FToxid database, the slag is modeled as SLAGA, SLAGB, SLAG?, which one should I select?.

**A3:** On the Menu window, right click on FToxid-SLAGA, FToxid-SLAGB, FToxid-SLAG?, and then check the phase information. You should find the description which details the elements that are considered in the phase model, and then choose the model which contains the elements of interest.

# Equilib Module: General Tips

---

**Some general tips for the Equilib Module are summarized in a Q&A format**

**Q4:** I want to perform some calculations about high-temperature treatment of solid wastes (slag, fly ash, mine tailings, municipal solid wastes...)?

**A4:** Since the solid wastes are mostly high-order systems, trial-and-error calculations are required to find the optimal phase selection. If the molten oxide slag is expected, “FToxid-SLAG?” can be used for preliminary calculations; if you are interested in the chlorine behavior, you should select the FTsalt database.

**Q5:** How to control the oxygen partial pressure?

**A5:** You need to use the FactPS database. Right click on the gas (Compound species on the Menu Window), then right click on the “+” column of O<sub>2</sub> to set the activity which is numerally identical to partial pressure of O<sub>2</sub> in the ideal gas mixture. The oxygen input amount will be automatically calculated.

# Equilib Module: General Tips

---

**Some general tips for the Equilib Module are summarized in a Q&A format**

**Q6:** How to calculate the equilibrium composition of slag by specifying the activity of the slag components?

**A6:** Right click on the FToxid-SLAGA, and use the [C]-option. This will permit us to specify the activity of the slag component.

**Q7:** How to determine the solidus temperature and liquidus temperature?

**A7:** Right click on the liquid phase (e.g., FTlite-Liqu), and use the [P]-option for the calculation of liquidus temperature and [F]-option for the calculation of solidus temperature. Also, you need to leave the temperature (Final Conditions) blank. However, for a complicated system, these two temperatures may not be obtained by this approach. In this case, it is suggested to activate the “normal + transitions” option, and generate the graph to find these two temperatures (We will discuss this in the advanced applications).

# Equilib Module: General Tips

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**Some general tips for the Equilib Module are summarized in a Q&A format**

**Q8:** What should I do if the solution model does not contain the species I want to calculate? For example,  $\text{TiO}_2$  is not included in the FToxid-SLAG.

**A8:** If the amount of the species is low, we can consider using the dilute solution model. Instructions can be found in the help file (Select/Slide Show/Advanced Features).

**Q9:** Based on the information shown in the Documentation Module, the system I am investigating has not been optimized by any of the available FactSage databases? What should I do?

**A9:** Please consider building a private database for the system of interest using the assessment papers that have been published.

# Equilib Module: General Tips

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**Some general tips for the Equilib Module are summarized in a Q&A format**

**Q10:** I want to analyze a system containing metastable phases, for example, Fe-C system. What should I do?

**A10:** Do not select C(s) (Graphite), but select Fe<sub>3</sub>C(s) (Cementite), and then perform the calculation.

**Q11:** I am experiencing “Abort” issue (no solution) even though it is a simple problem?

**A11:** You can try to add a small amount of argon (e.g., 1E-6) to the list of reactants.

# In-Class Exercise

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**Question 1.** Use the Equilib Module to solve the following questions.

- (1) 1 mole of  $\text{H}_2\text{O}$  becomes a gas mixture at  $2500\text{ }^\circ\text{C}$  and 1 atm. Calculate the equilibrium partial pressure of  $\text{H}_2$  in the gas mixture.
- (2) For a gas mixture containing 2 mole of  $\text{H}_2\text{O}$ , 0.79 mole of  $\text{N}_2$ , and 0.21 mole of  $\text{O}_2$ , calculate at  $25\text{ }^\circ\text{C}$  and 1 atm the equilibrium partial pressure of  $\text{H}_2\text{O}$ .
- (c) Heating of LVDS 3 ( $\text{NaHCO}_3$ ) results in the formation of  $\text{Na}_2\text{CO}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , find the minimum temperature for this reaction.
- (d) Find the Enthalpy for 1 mole of  $\text{H}_2\text{O}$  (s), 1 mole of  $\text{H}_2\text{O}$  (l), and 1 mole of  $\text{H}_2\text{O}$  (g) when the temperature is  $150\text{ }^\circ\text{C}$  and the pressure is 1 atm.
- (e) Find the composition and temperature of the system when 10 J of energy is supplied to 1 gram of water at  $25\text{ }^\circ\text{C}$ .
- (f) Calculate the final temperature when 1 gram of ice ( $0\text{ }^\circ\text{C}$ ) and 2 gram of hot water ( $90\text{ }^\circ\text{C}$ ) are mixed. Assume no heat exchange with the surroundings.

# In-Class Exercise

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## Question 2. Mixing Properties

- (1) Use FTLite database to calculate the Al-Mg phase diagram.  $T(^{\circ}\text{C}) \sim X_{\text{Mg}}$
- (2) From the diagram, you should see that at 800 °C, the system exists as liquid over the entire composition range, i.e.,  $X_{\text{Mg}}$  varies from 0 to 1. Calculate and plot for the liquid phase  $\Delta_{\text{mix}}g_{800\text{ }^{\circ}\text{C}} \sim X_{\text{Mg}}$  and  $\Delta_{\text{mix}}h_{800\text{ }^{\circ}\text{C}} \sim X_{\text{Mg}}$ .
- (3) From the diagram, you should see that at 500 °C, the system may exist as two coexisting phases or single phase over the entire composition range. Calculate and plot the molar Gibbs energy of the system when  $X_{\text{Mg}}$  varies from 0 to 1.