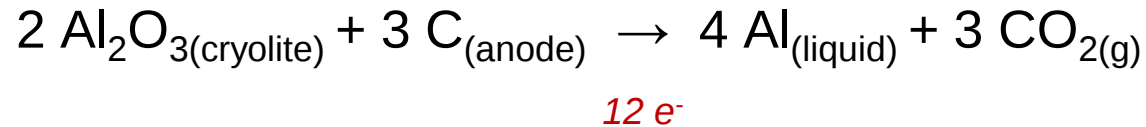


Hall-Heroult Process

- **Electrochemical Process to Reduce Alumina to Aluminum**

- Alumina is dissolved in a molten fluoride solvent called cryolite



$$T = 960^\circ\text{C}$$

Electrical work is needed:

$$I = 200\text{-}400 \text{ kA}$$

$$E \approx 4 \text{ V}$$

Electrolyte (cryolitic bath)



Hall-Heroult Process

- **Electrochemical Process to Reduce Alumina to Aluminum**

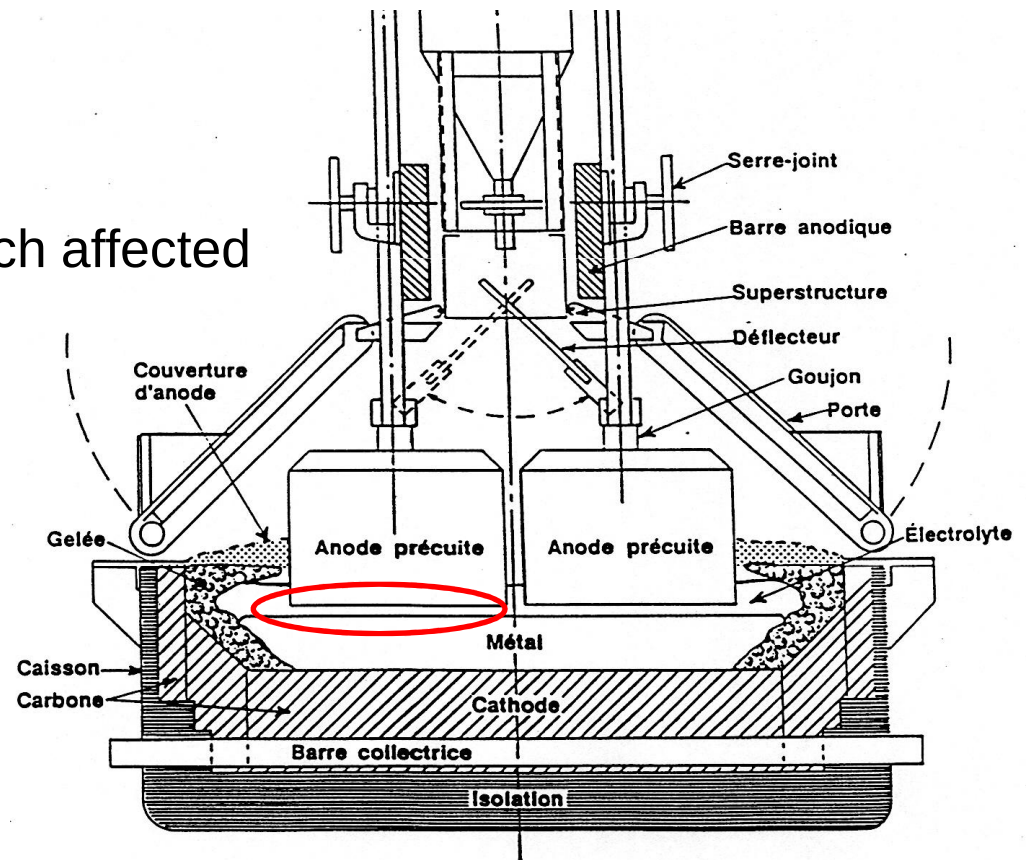
- Alumina is dissolved in a molten fluoride solvent called cryolite

Electrolyte (cryolitic bath)



CR = $\text{NaF} / \text{AlF}_3$ (molar)

Operation T of the cell is much affected by **CR** and $\%\text{Al}_2\text{O}_3$



- **Examples:**

- 1) Create a “stream” for a standard bath
- 2) Phase Diagrams (CR = 2.2; 5% CaF_2)
- 3) Phase Diagrams (% Al_2O_3 vs xs- AlF_3 ; 5% CaF_2)
- 4) Adding reactants to the electrolyte (Al_2O_3)
- 5) Adding reactants to the electrolyte (Na_2CO_3)
- 6) Adding reactants to the electrolyte (AlF_3)
- 7) Carbide formation in the cathode blocks
- 8) Cathode / Collecting Bar / Refractory / $\text{Na}_{(g)}$

Hall-Heroult Process

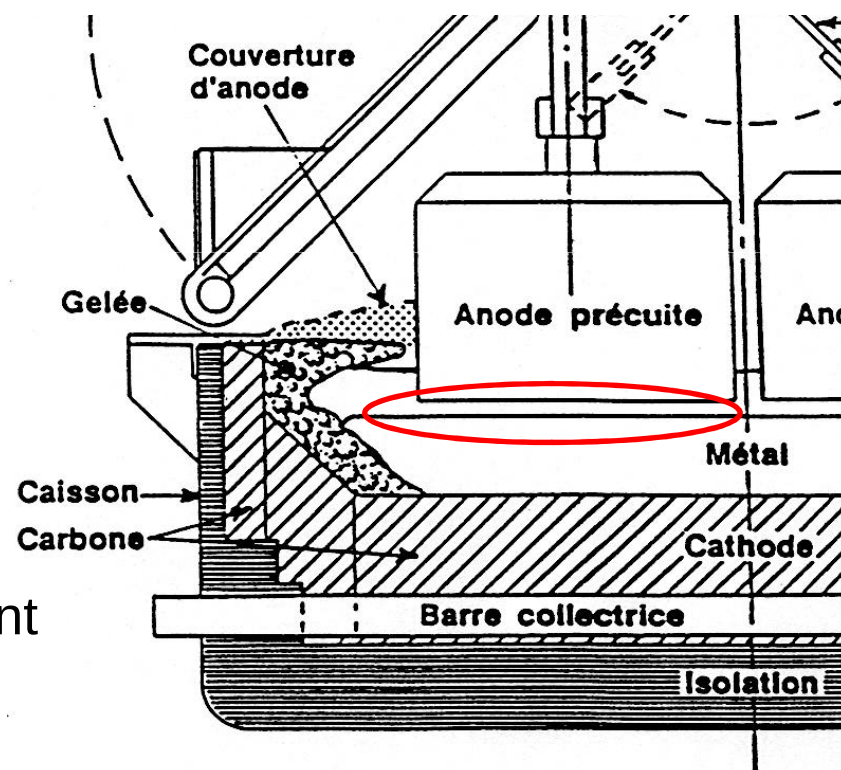
- **Example #1: Create a “stream” for a standard bath**

Create a **stream** of the following **electrolyte**

Na_3AlF_6
+ 12.2 wt.% AlF_3
+ 5.0% CaF_2
+ 3.0% Al_2O_3

The **stream** will be constrained in enthalpy at 960°C.

This **stream** will be used as reactant in several following examples.



Hall-Heroult Process

- Example #1: Create a “stream” for a standard bath

FThall Database

79.8% Na_3AlF_6
+ 12.2 wt.% AlF_3
+ 5.0% CaF_2
+ 3.0% Al_2O_3

Reactants - Equilib

File Edit Table Units Data Search Help

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

1 - 4

Mass(g)	Species	Phase	T(C)	P(total)**	Stream#	Data
79.8	Na3AlF6	solid-1-FThall	25	1	1	FThall
+ 12.2	AlF3	solid-1-FThall perovs	25	1	1	FThall
+ 5	CaF2	solid-1-FThall solid-al	25	1	1	FThall
+ 3	Al2O3	solid-1-FThall gamma	25	1	1	FThall

** 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 >>

FactSage 6.2 beta Compound: 2/24 databases Solution: 1/22 databases

Hall-Heroult Process

- Example #1: Create a “stream” for a standard bath

F Menu - Equilib: HALLHEROULT Standard Bath

File Units Parameters Help

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

Reactants (4)

(gram) 79.8 Na3AlF6	+	12.2 AlF3	+	5 CaF2	+	3 Al2O3
(25C,s1-FThall,#1)		(25C,s1-FThall,#1)		(25C,s1-FThall,#1)		(25C,s1-FThall,#1)

Products

Compound species

☐ gas ☒ ideal ☐ real 0

☐ aqueous 0

☐ pure liquids 0

☐ pure solids 0

☐ suppress duplicates

species: 0

Solution species

*	+	Base-Phase	Full Name
	☒	FThall-BathA	ABath
	☐	FThall-Bath?	?Bath
	☐	FThall-CryL	Na-Cryolite-L
	☐	FThall-CryH	Na-Cryolite-H
	☐	FThall-Liq	Liquid-Alloy
	☐	FThall-FCC	FCC
	☐	FThall-BCC	BCC
	☐	FThall-Mono	Monoxide

Legend
+- selected 1

☒ Show ☒ all ☐ selected

species: 10
solutions: 1

Custom Solutions

☐ fixed activities
☐ ideal solutions
☐ activity coefficients

Pseudonyms

apply ☐

☐ include molar volumes

Total Species (max 1500) 10
Total Solutions (max 40) 1

Target

- none -

Estimate T(K): 1000
Mass(g): 0

Final Conditions

<A>		T(C)	P(atm)	Delta H(J)
		960	1	

10 steps ☐ Table

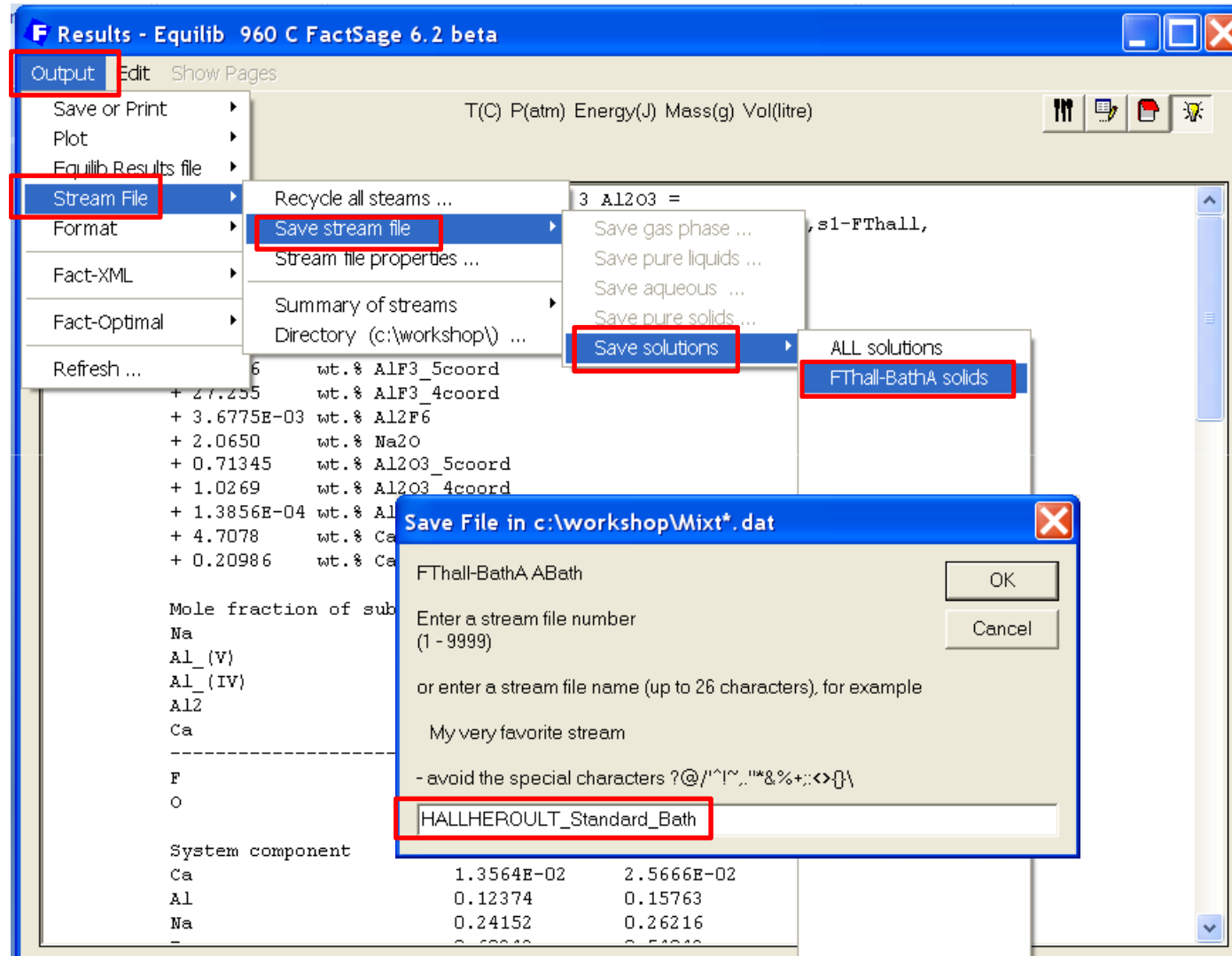
Equilibrium

☒ normal ☐ normal + transitions
☐ transitions only ☐ open
☐ predominant

FactSage 6.2 beta c:\workshop\EquiHALLHEROULT_Standard_Bath.DAT

Hall-Heroult Process

- Example #1: Create a “stream” for a standard bath



Hall-Heroult Process

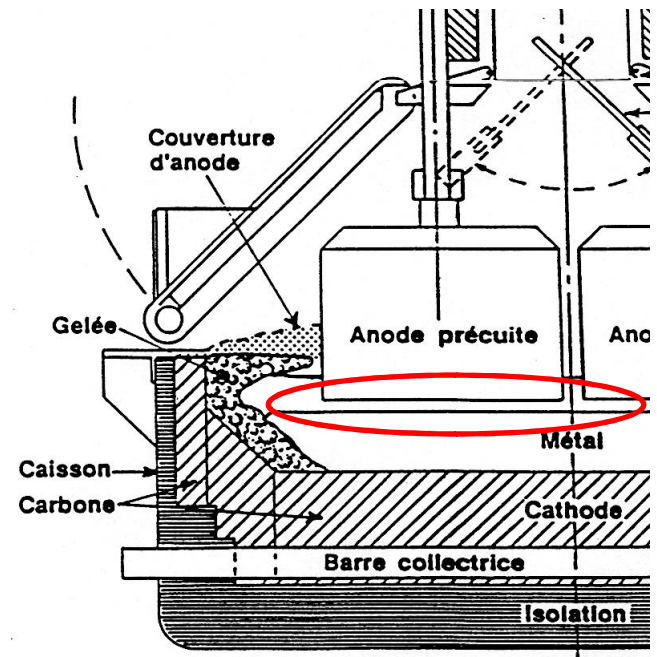
- **Example #2: Phase Diagrams**

The **cryolite (Na_3AlF_6) liquidus** and the **alumina (Al_2O_3) solubility** are **very important** for the cell operation.

The formation of a **side-ledge** protects the cell lining from the corrosive electrolyte.

Alumina has to be transported in the bath to the reaction site under the anode.
So a **high solubility** is better.

A **mapping** of these **phase diagram** features will be useful.



Hall-Heroult Process

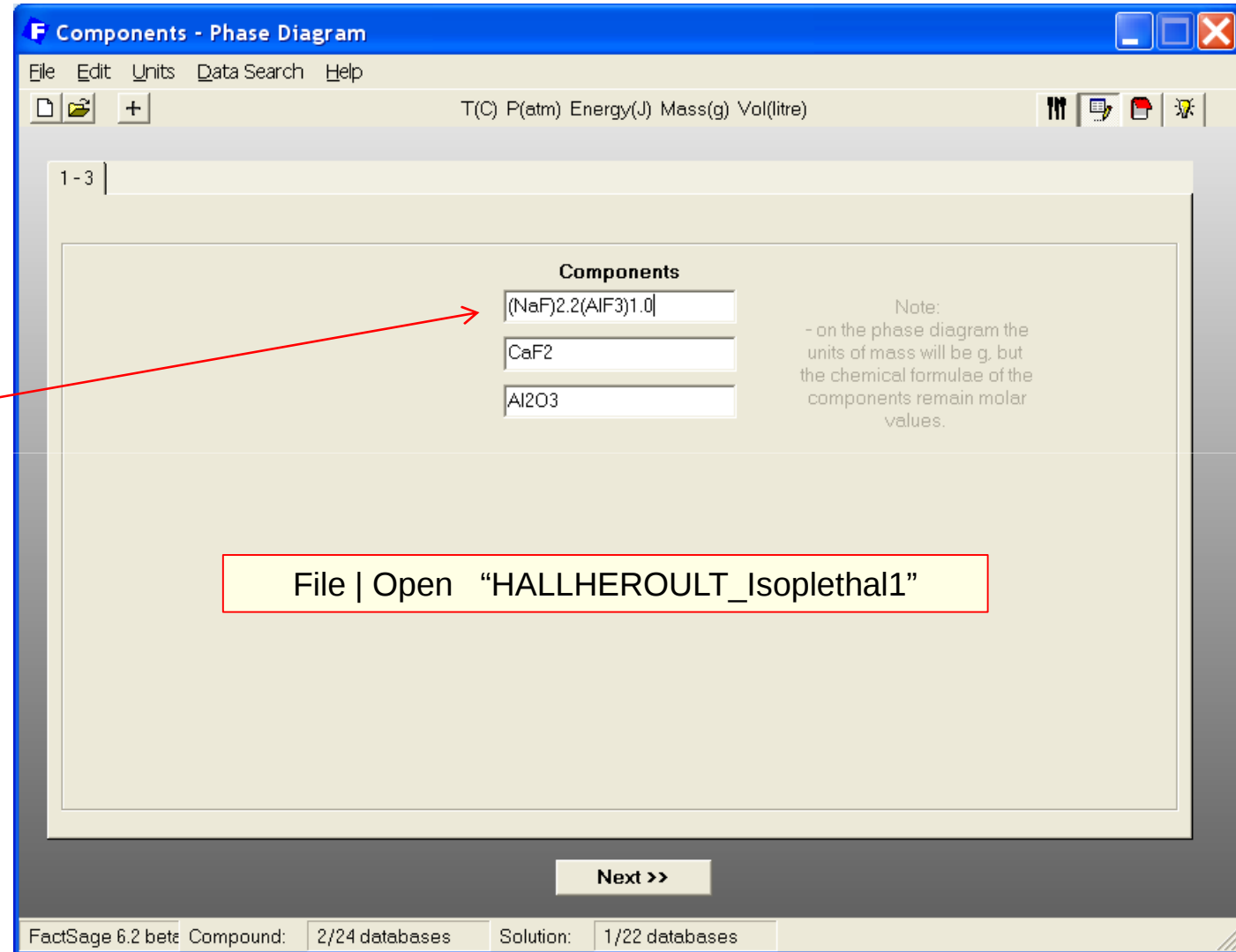
- **Example #2: Phase Diagrams (CR = 2.2; 5% CaF₂)**

FThall database

CR = NaF / AlF₃

CR = 2.2

(NaF)_{2.2}(AlF₃)_{1.0}



Hall-Heroult Process

- Example #2: Phase Diagrams (CR = 2.2; 5% CaF_2)

F Menu - Phase Diagram: (NaF)2.2(AlF3)1.0 - CaF2 - Al2O3

File Units Parameters Variables Help

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

Components (3)

(gram) (NaF)2.2(AlF3)1.0 + CaF2 + Al2O3

Products

Compound species

* ☒ gas ☒ ideal ☐ real 34

☐ aqueous 0

☐ pure liquids 0

* ☒ pure solids 39

☐ suppress duplicates apply

* - custom selection species: 73

Solution species

*	+	Base-Phase	Full Name
	+	FThall-BathA	ABath
		FThall-Bath?	?Bath
	+	FThall-CryL	Na-Cryolite-L
	+	FThall-CryH	Na-Cryolite-H
	I	FThall-Liq	Liquid-Alloy
	+	FThall-FCC	FCC
	I	FThall-BCC	BCC
	I	FThall-Mono	Monoxide

Custom Solutions

0 fixed activities

0 ideal solutions

0 activity coefficients

Details ...

Pseudonyms

apply ☐ List ...

☒ include molar volumes

Total Species (max 1500) 108

Total Solutions (max 40) 10

Default

Target

- none -

Estimate T(K): 1000

Mass(g): 0

Legend

I - immiscible 3

+ - selected 4

☒ Show ☒ all ☐ selected

species: 35

solutions: 10

Select

Variables

T(C)	100CaF2/(L+CaF)	100Al2O3/(L+CaF)		
800 1050	5	0 10		

T(C) vs 100Al2O3/(L+CaF2+Al2O3) - L=(NaF)2.2(AlF3)1.0

Phase Diagram

Y

X

Calculate >>

FactSage 6.2 beta c:\workshop\PhasHALLHEROULT_Isoplethal1.DAT

Hall-Heroult Process

• Example #2: Phase Diagrams (CR = 2.2; 5% CaF₂)

• X-axis

$$\frac{100 \text{ Al}_2\text{O}_3}{1(\text{NaF})_{2.2}(\text{AlF}_3)_{1.0} + 1\text{CaF}_2 + 1\text{Al}_2\text{O}_3} = 0 - 10$$

• Y-axis

$$- T = 800 - 1050^\circ\text{C}$$

• Constants

$$- P = 1 \text{ atm}$$

$$\frac{100 \text{ CaF}_2}{1(\text{NaF})_{2.2}(\text{AlF}_3)_{1.0} + 1\text{CaF}_2 + 1\text{Al}_2\text{O}_3} = 5.0$$

Variables: (NaF)2.2(AlF3)1.0-CaF2-Al2O3 T(C) vs composition #1.

Variables

Y-axis: ☒ compositions
☐ log10(a)
☐ A ☐ B ☐ C

Y steps:
X steps:

T and P

Temperature: ☒ T(C)
☐ 1/TK Max:
Min:

Pressure: ☒ P(atm)
☐ log P

Compositions (mass)

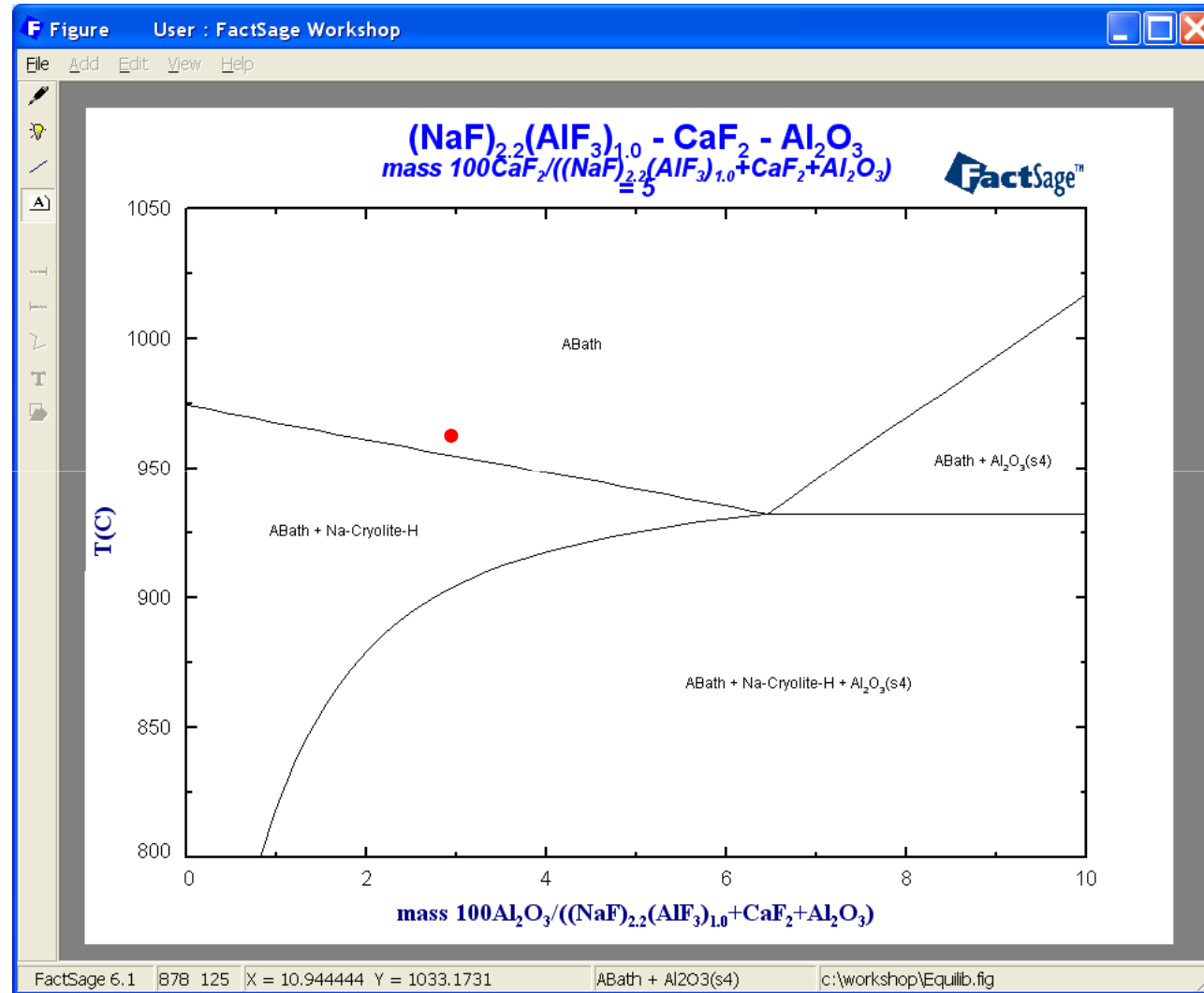
L-(NaF)2.2(AlF3)1.0

#1. L + CaF2 + Al2O3 =
 L + CaF2 + Al2O3 =

#2. L + CaF2 + Al2O3 =
 L + CaF2 + Al2O3 =

Hall-Heroult Process

- Example #2: Phase Diagrams (CR = 2.2; 5% CaF_2)



Hall-Heroult Process

- **Example #3: Phase Diagrams (% Al_2O_3 vs xs- AlF_3 ; 5% CaF_2)**

FThall database

Na_3AlF_6

AlF_3 (excess)

CaF_2

Al_2O_3

$T = 960^\circ\text{C}$

Components - Phase Diagram

File Edit Units Data Search Help

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

1 - 4

Components

Note:
- on the phase diagram the
units of mass will be g, but
the chemical formulae of the
components remain molar
values.

File | Open "HALLHEROULT_Isothermal2"

Next >>

FactSage 6.2 beta Compound: 2/24 databases Solution: 1/22 databases

Hall-Heroult Process

• Example #3: Phase Diagrams (% Al_2O_3 vs xs- AlF_3 ; 5% CaF_2)

• X-axis

$$\frac{100 AlF_3}{1Na_3AlF_6 + 1AlF_3 + 1CaF_2 + 1Al_2O_3} = 0 - 50$$

• Y-axis

$$\frac{100 Al_2O_3}{1Na_3AlF_6 + 1AlF_3 + 1CaF_2 + 1Al_2O_3} = 0 - 10$$

• Constants

– $T = 960^\circ C$

– $P = 1 \text{ atm}$

$$\frac{100 CaF_2}{1Na_3AlF_6 + 1AlF_3 + 1CaF_2 + 1Al_2O_3} = 5.0$$

Variables: Na3AlF6-AlF3-CaF2-Al2O3 composition #2. vs composition #1.

Variables

Y ☒ X ☐ A ☐ B ☐ C ☐

compositions

log10(a)

Y steps:

X steps:

Next >>

T and P

Temperature

☒ T(C)

Pressure

☒ P(atm)

☐ log P

Compositions (mass)

L=Na3AlF6

#1. L + AlF3 + CaF2 + Al2O3 =

L + AlF3 + CaF2 + Al2O3 =

#2. L + AlF3 + CaF2 + Al2O3 =

L + AlF3 + CaF2 + Al2O3 =

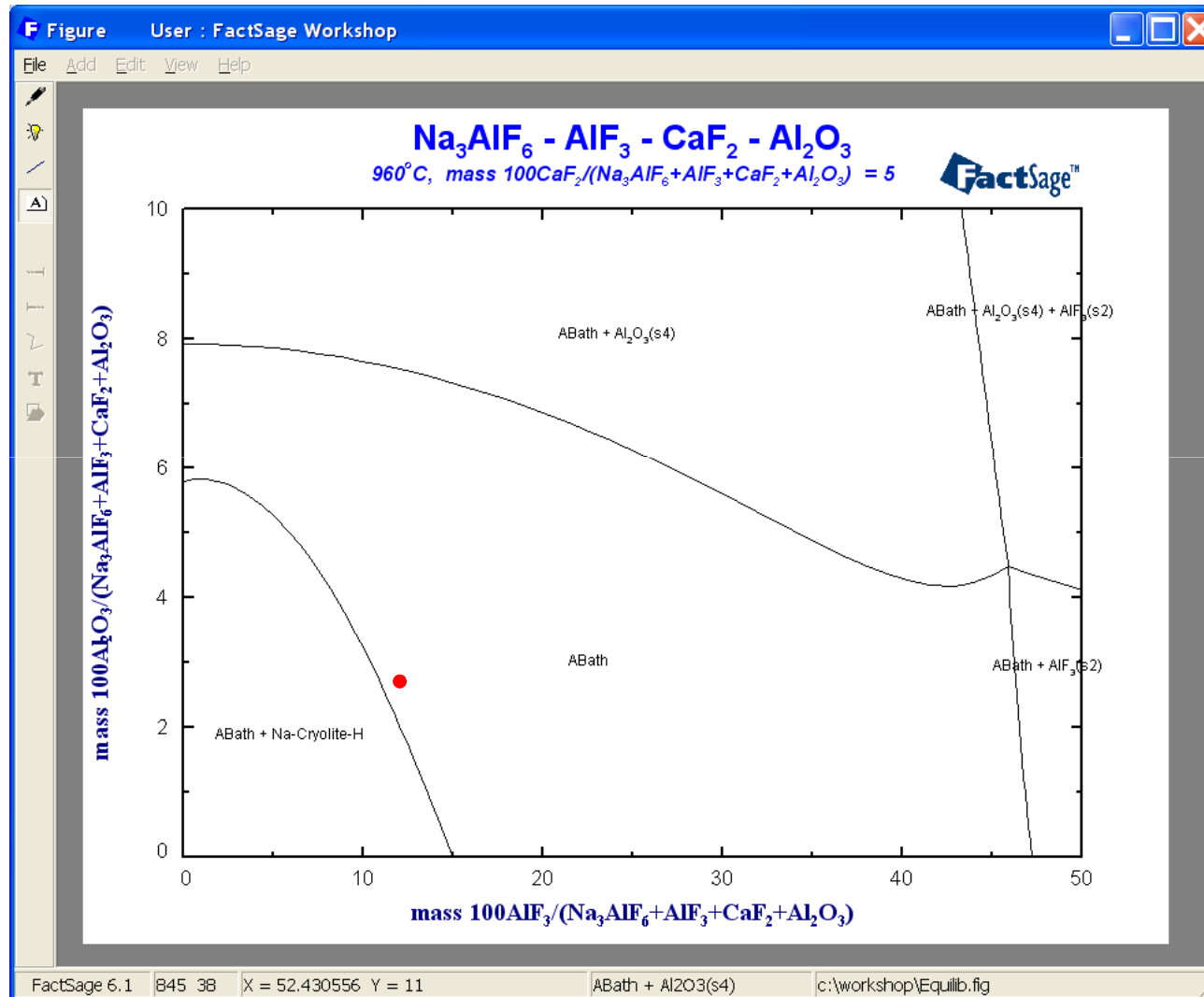
#3. L + AlF3 + CaF2 + Al2O3 =

L + AlF3 + CaF2 + Al2O3 =

Cancel OK

Hall-Heroult Process

- Example #3: Phase Diagrams (% Al_2O_3 vs xs- AlF_3 ; 5% CaF_2)



Hall-Heroult Process

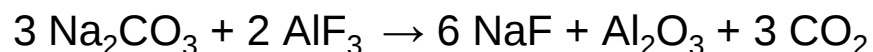
- **Example #4: Adding reactants to the electrolyte**

The **thermal/heat balance** on the electrolytic cell is **very important**

The following additions are frequent:

Al₂O₃ for the reduction reaction

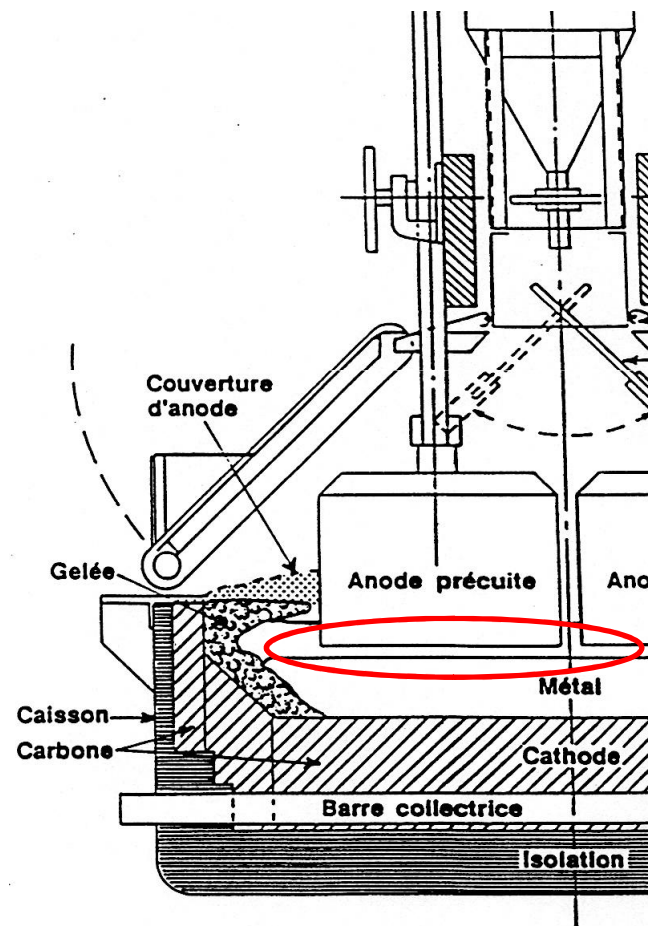
Na₂CO₃ to increase **CR**



AlF₃ to decrease **CR**

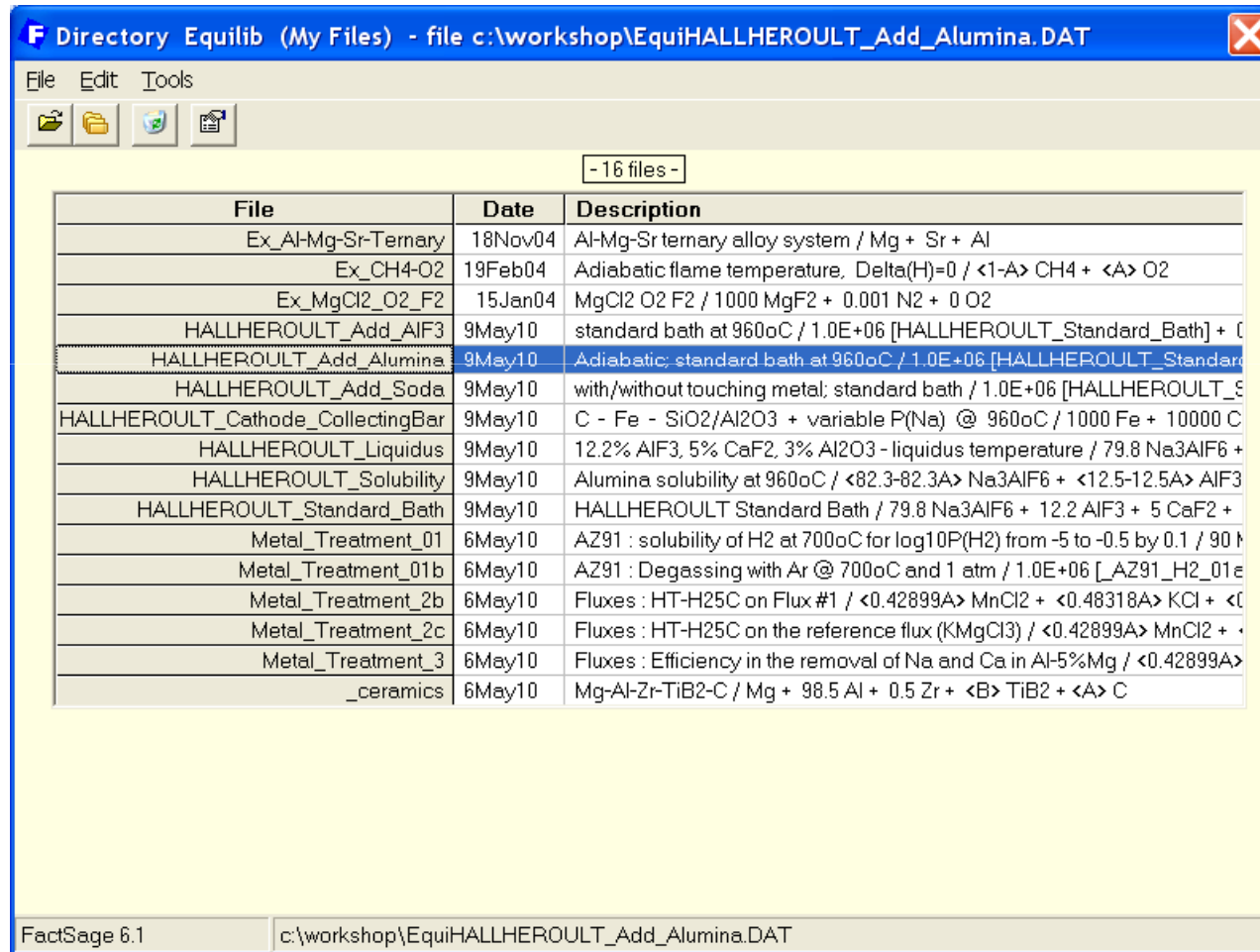
CR = $\text{NaF} / \text{AlF}_3$ (molar)

All these reactants are much **colder** than the cell (10°C – 200°C)



Hall-Heroult Process

- **Example #4: Adding reactants to the electrolyte (Al_2O_3)**
- File | Open “HALLHEROULT_Add_Alumina”



Hall-Heroult Process

• Example #4: Adding reactants to the electrolyte (Al_2O_3)

1.0 ton of **Bath**
(**stream** @ 960°C)

Alumina @ 125°C

$\gamma\text{-Al}_2\text{O}_3$

$\alpha\text{-Al}_2\text{O}_3$

$\text{Al}_2\text{O}_3(\text{H}_2\text{O})$

Na_2CO_3 (s) (@ 20°C)

Al(liq.) (@ 960°C)

AlF_3 (s) (@ 50°C)

The screenshot shows the 'Reactants - Equilib' window in FactSage. The main table lists reactants with columns for Mass(g), Species, Phase, T(C), P(total)**, Stream#, and Data. The 'Species' column has a dropdown menu with '[HALLHEROULT_]' selected. The 'Mass(g)' column has a value of '1.0E+06' for the first row. The 'Phase' column has a dropdown menu with '[Stream]' selected. The 'T(C)' column has a value of '960' for the first row. The 'P(total)**' column has a value of '1' for the first row. The 'Stream#' column has a value of '1' for the first row. The 'Data' column has a value of 'FTHall' for the first row. The 'Edit' menu is open, showing options like 'Add a new Reactant', 'Insert new reactant before [HALLHEROULT_Standard_Bath] ...', 'Delete reactant [HALLHEROULT_Standard_Bath] ...', 'Delete all blank reactants', 'Mixtures and Streams', 'Re-order the reactants', 'Export list of reactants', 'Import list of reactants', 'Clear', and 'Example'. The 'Mixtures and Streams' option is highlighted, and a submenu is open showing 'Import a mixture', 'Import a stream (or single-line mixture)', 'Edit a mixture or stream', and 'Directory (c:\workshop\)'.

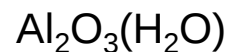
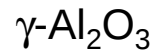
Mass(g)	Species	Phase	T(C)	P(total)**	Stream#	Data
1.0E+06	[HALLHEROULT_]	[Stream]	960	1	1	
+ <925A>	Al2O3	solid-1-FTHall gamma	125	1	2	FTHall
+ <70A>	Al2O3	solid-4-FTHall corund	125	1	2	FTHall
+ <5A>	Al2O3(H2O)	solid-2-FACT53 boeh	125	1	2	FACT53
+ 0	Na2CO3	solid-1-FACT53	20	1	3	FACT53
+ 0	Al	liquid-FTHall	960	1	4	FTHall
+ 0	AlF3	solid-1-FTHall perovs	50	1	5	FTHall

Hall-Heroult Process

• Example #4: Adding reactants to the electrolyte (Al_2O_3)

1.0 ton of **Bath**
(**stream** @ 960°C)

+ 5 kg Alumina



Adiabatic Addition

$$Q = \Delta H = 0$$

F Menu - Equilib: Adiabatic; standard bath at 960oC

File Units Parameters Help

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

Reactants (7)

(gram) 1.0E+06 [HALLHEROULT_Standard_Bath] + <925A> Al2O3 + <70A> Al2O3 + <5A>
(960C,#1) (125C,s1-FThall,#2) (125C,s4-FThall,#2) (125C,s

Products

Compound species

* + gas ☒ ideal ☐ real 110

aqueous 0

pure liquids 0

* + pure solids 67

☐ suppress duplicates

* - custom selection

species: 177

Solution species

*	+	Base-Phase	Full Name
	+	FThall-BathA	ABath
		FThall-Bath?	?Bath
	+	FThall-CryL	Na-Cryolite-L
	+	FThall-CryH	Na-Cryolite-H
	I	FThall-Liq	Liquid-Alloy
	+	FThall-FCC	FCC
	I	FThall-BCC	BCC
	I	FThall-Mono	Monoxide

Legend

I - immiscible 3

+ - selected 4

☒ Show ☒ all ☐ selected

species: 35

solutions: 10

Custom Solutions

0 fixed activities

0 ideal solutions

0 activity coefficients

Pseudonyms

☐ include molar volumes

Total Species (max 1500) 212

Total Solutions (max 40) 10

Final Conditions

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

5 1 0

10 steps ☐ Table 1 calculation

Equilibrium

☒ normal ☐ normal + transitions

☐ transitions only ☐ open

☐ predominant

FactSage 6.2 beta c:\workshop\EquiHALLHEROULT_Add_Alumina.DAT

Hall-Heroult Process

- Example #4: Adding reactants to the electrolyte (Al_2O_3)

Results - Equilib 953.16 C FactSage 6.2 beta

Output Edit Show Pages

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

```
(gram) 1.0E+06 [HALLHEROULT_Standard_Bath] + <925A> Al2O3 + <70A> Al
(960,1,stream,#1) (125,1,s1-FThall,#2) (125,1,s4-FThall,#2) (125,1
(gram) 0 Na2CO3 + 0 Al + 0 AlF3 =
(20,1,s1-FACT53,#3) (960,1,liq-FThall,#4) (50,1,s1-FThall,#5)
```

```
0.24523 mol gas_ideal
(4.6852 gram, 0.24523 mol, 24.677 litre, 1.8986E-04 g/ml)
(953.16 C, 1 atm, a=1.0000)
{ 0.70402 H2O
+ 0.29139 HF
+ 4.2504E-03 NaAlF4
+ 2.2096E-04 Na2AlF5
```

```
+ 7.1324E-05 (NaAlF4)2
+ 2.4232E-05 NaF
+ 7.8358E-06 H2
+ 6.3034E-06 AlF3
+ 3.7294E-06 O2
+ 1.9335E-06 (NaF)2
+ 1.7961E-06 (HF)2
+ 1.6170E-06 NaAl2F7
+ 7.5476E-07 OH
+ 1.3310E-07 NaOH
+ 8.8770E-10 H
+ 5.7273E-10 CaF2
+ 3.4043E-10 (AlF3)2
+ 1.7406E-10 Na
+ 8.2947E-11 O
+ 8.0972E-11 F
+ 4.0619E-11 HOOH
+ 3.6527E-11 HOO
+ 9.4098E-12 H3F3
```

Results - Equilib 953.16 C FactSage 6.2 beta

Output Edit Show Pages

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

```
+ 1.0050E+06 gram ABath
(1.0050E+06 gram, 17398. mol)
(953.16 C, 1 atm, a=1.0000)
{ 44.426 wt.% NaF
+ 18.502 wt.% AlF3_5coord
+ 27.780 wt.% AlF3_4coord
+ 3.6720E-03 wt.% Al2F6
+ 2.3739 wt.% Na2O
+ 0.81323 wt.% Al2O3_5coord
+ 1.2210 wt.% Al2O3_4coord
+ 1.6139E-04 wt.% Al2O3
+ 4.6393 wt.% CaF2
+ 0.24125 wt.% CaO
```

Mole fraction of sublattice constituents:

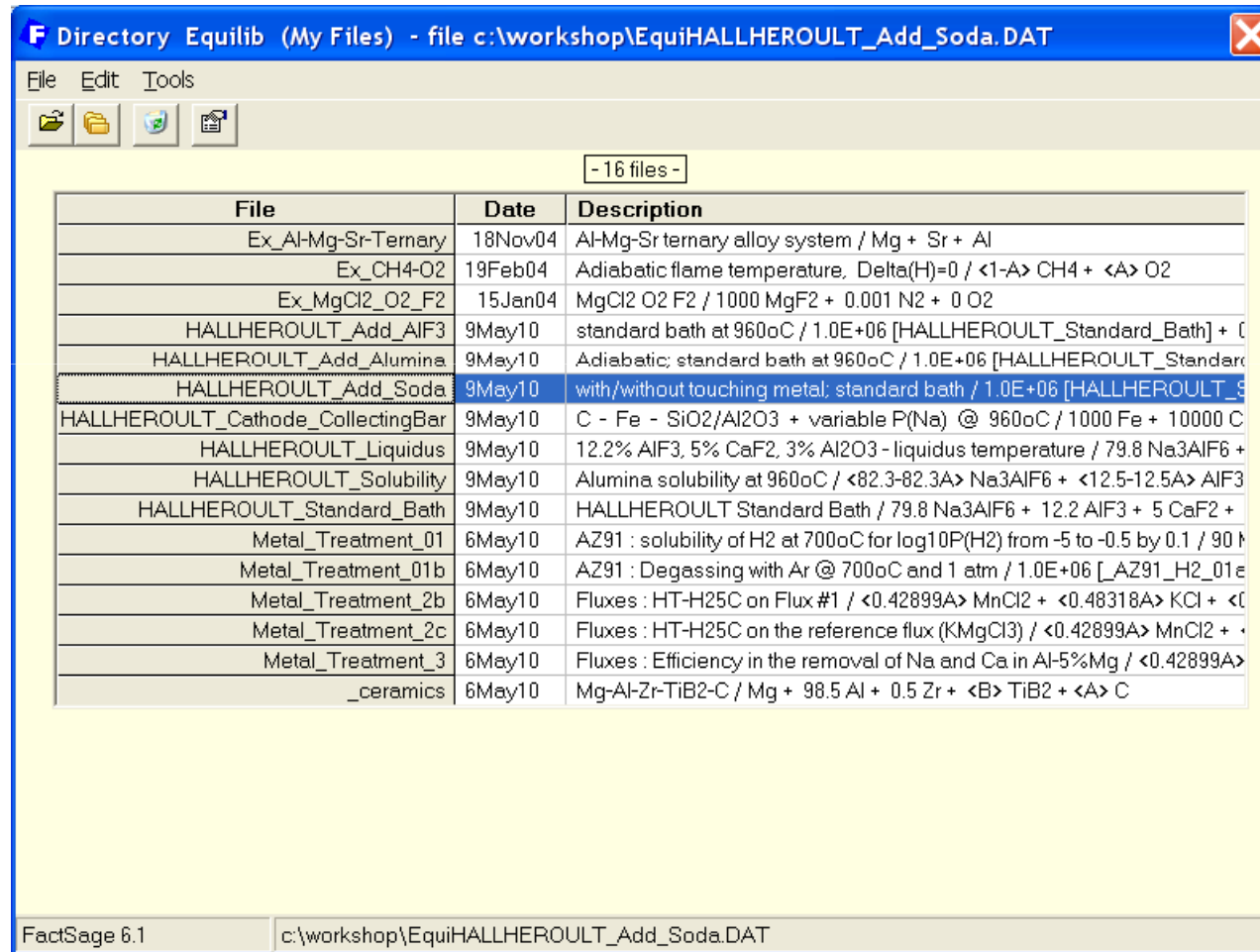
Na	0.63409
Al_(V)	0.13204
Al_(IV)	0.19825
Al2	1.3103E-05
Ca	3.5611E-02

F	0.96506
O	3.4935E-02

System component	Mole fraction	Mass fraction
Ca	1.3494E-02	2.5539E-02
Al	0.12517	0.15948
Na	0.24027	0.26085
F	0.59937	0.53773
O	2.1697E-02	1.6393E-02

Hall-Heroult Process

- **Example #5: Adding reactants to the electrolyte (Na_2CO_3)**
- File | Open “HALLHEROULT_Add_Soda”



Hall-Heroult Process

- **Example #5: Adding reactants to the electrolyte (Na_2CO_3)**

1.0 ton of **Bath**
(**stream** @ 960°C)

$\text{Na}_2\text{CO}_{3(s)}$ (@ 20°C)

$\text{Al}_{(\text{liq.})}$ (@ 960°C)

Bags of Na_2CO_3 can
added manually to the
cell.

A bag can partially
touch the **metal pad**
below the **bath** and
react with it.

Reactants - Equilib

File Edit Table Units Data Search Help

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

1 - 7

Mass(g)	Species	Phase	T(C)	P(total)**	Stream#	Data
1.0E+06	[HALLHEROULT_]	[Stream]	960	1	1	
+ 0	Al2O3	solid-1-FThall gamma	125	1	2	FThall
+ 0	Al2O3	solid-4-FThall corund	125	1	2	FThall
+ 0	Al2O3(H2O)	solid-2-FACT53 boeh	125	1	2	FACT53
+ <1000B>	Na2CO3	solid-1-FACT53	20	1	3	FACT53
+ <1000A>	Al	liquid-FThall	960	1	4	FThall
+ 0	AlF3	solid-1-FThall perovs	50	1	5	FThall

☒ Initial Conditions

Next >>

FactSage 6.2 beta Compound: 2/24 databases Solution: 1/22 databases

Hall-Heroult Process

• Example #5: Adding reactants to the electrolyte (Na_2CO_3)

1.0 ton of **Bath**
(**stream** @ 960°C)

$\text{Na}_2\text{CO}_{3(s)}$ (@ 20°C)

$\text{Al}_{(liq.)}$ (@ 960°C)

Bags of Na_2CO_3 can
added manually to the
cell ** = 10 kg**

A bag can partially
touch the **metal pad**
below the **bath** and
react with it

<A> = 0 or 2 kg

Menu - Equilib: with/without touching metal; standard bath

File Units Parameters Help

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

Reactants (7)

(gram) 1.0E+06 [HALLHEROULT_Standard_Bath] (960C.#1)	+	0 Al2O3 (125C.s1-FThall,#2)	+	0 Al2O3 (125C.s4-FThall,#2)	+	0 Al (125C.s)
--	---	-----------------------------	---	-----------------------------	---	---------------

Products

Compound species

- ☒ gas ☒ ideal ☐ real 110
- ☐ aqueous 0
- ☐ pure liquids 0
- ☒ pure solids 67
- ☐ suppress duplicates
- * - custom selection species: 177

Target: - none -

Estimate T(C): 900

Mass(g): 0

Solution species

*	+	Base-Phase	Full Name
	+	FTball-BathA	ABath
		FTball-Bath?	?Bath
	+	FTball-CryL	Na-Cryolite-L
	+	FTball-CryH	Na-Cryolite-H
	I	FTball-Liq	Liquid-Alloy
	+	FTball-FCC	FCC
	I	FTball-BCC	BCC
	I	FTball-Mono	Monoxide

Legend

I - immiscible 3

+- selected 4

☒ Show ☒ all ☐ selected

species: 35

solutions: 10

Custom Solutions

0 fixed activities

0 ideal solutions

0 activity coefficients

Pseudonyms

☐ include molar volumes

Total Species (max 1500) 212

Total Solutions (max 40) 10

Final Conditions

<A>		T(C)	P(atm)	Delta H(J)
0	2		1	0

Equilibrium

☒ normal ☐ normal + transitions

☐ transitions only ☐ open

☐ predominant

FactSage 6.2 beta c:\workshop\EquiHALLHEROULT_Add_Soda.DAT

Hall-Heroult Process

• Example #5: Adding reactants to the electrolyte (Na_2CO_3)

Bags of Na_2CO_3
 = 10 kg

metal pad
<A> = 0 kg

Result

$T < 960^\circ\text{C}$

4.2 kg gas
(9.5 m³ gas)
986.7 kg bath
19.1 kg Na_3AlF_6

Results - Equilib 954.35 C, A=0 (page 1/2) FactSage 6.2 beta

Output Edit Show Pages

954.35 C, A=0 964.33 C, A=2

(gram) 1.0E+06 [HALLHEROULT_Standard_Bath] +
(960,1,stream,#1) (125,1,s1-FThall,#2) (125
(gram) <1000(10)> Na2CO3 + <1000A> Al + 0
(20,1,s1-FACT53,#3) (960,1,liq-FThall,#4) (

94.765 mol gas_ideal
(4206.0 gram, 94.765 mol, 9545.3 litre, 4.
(954.35 C, 1 atm, a=1.0000)
(0.99560 CO2
+ 4.0538E-03 NaAlF4
+ 2.2367E-04 Na2AlF5
+ 6.3598E-05 (NaAlF4)2
+ 2.6410E-05 NaF
+ 1.2678E-05 CO
+ 6.3388E-06 O2
+ 5.6895E-06 AlF3
+ 2.2416E-06 (NaF)2
+ 1.3530E-06 NaAl2F7
+ 5.7454E-10 CaF2
+ 2.7207E-10 (AlF3)2
+ 2.5504E-10 COF2
+ 1.7412E-10 Na
+ 1.1079E-10 O
+ 9.2387E-11 F
+ 2.5207E-12 OAlF
+ 1.7625E-13 AlF2
+ 1.7420E-13 NaO
+ 1.4534E-15 COF
+ 2.0224E-16 AlOF2
+ 4.3389E-17 OF
+ 3.4397E-18 O3

Results - Equilib 954.35 C, A=0 (page 1/2) FactSage 6.2 beta

Output Edit Show Pages

954.35 C, A=0 964.33 C, A=2

+ 2.8016E-59 C3
+ 1.2961E-60 Al2
+ 9.8670E+05 gram ABath
(9.8670E+05 gram, 17160. mol)
(954.35 C, 1 atm, a=1.0000)
(45.095 wt.% NaF
+ 18.948 wt.% AlF3_5coord
+ 26.775 wt.% AlF3_4coord
+ 3.2159E-03 wt.% Al2F6
+ 2.3315 wt.% Na2O
+ 0.80580 wt.% Al2O3_5coord
+ 1.1387 wt.% Al2O3_4coord
+ 19097. gram Na-Cryolite-H
(19097. gram, 92.816 mol)
(954.35 C, 1 atm, a=1.0000)
(88.390 wt.% Na3AlF6
+ 3.2304 wt.% Na3AlF4[2+]
+ 0.13218 wt.% AlF4[-]
+ 4.0552 wt.% AlF6[3-]
+ 4.0213 wt.% Ca3AlF6[3+]
+ 0.17066 wt.% Ca3AlF4[5+]

Mole fraction of sublattice constituents:
Na[+] 0.90492
Va 6.1828E-02
Ca[2+] 3.3249E-02

AlF6[3-] 0.95699
AlF4[-] 4.3012E-02

Hall-Heroult Process

• Example #5: Adding reactants to the electrolyte (Na_2CO_3)

Bags of Na_2CO_3
 = 10 kg

metal pad
<A> = 2 kg

Result

$T > 960^\circ\text{C}$

2.2 kg gas
(7.8 m³ gas)
1009.6 kg bath
0.2 kg C

F Results - Equilib 964.33 C, A=2 (page 2/2) FactSage 6.2 beta

Output Edit Show Pages

T(C) P(atm)

954.35 C, A=0 - 964.33 C, A=2 -

(gram) 1.0E+06 [HALLHEROULT_Standard_Bath] + (960,1,stream,#1) (125,1,s1-FThall,#2) (125,1,stream,#3) <1000(10)> Na2CO3 + <1000A> Al + 0 Al

(20,1,s1-FACT53,#3) (960,1,liq-FThall,#4) (50

77.021 mol gas_ideal
(2209.9 gram, 77.021 mol, 7821.1 litre, 2.82
(964.33 C, 1 atm, a=1.0000)
(0.98372 CO
+ 1.1328E-02 CO2
+ 4.5852E-03 NaAlF4
+ 2.5164E-04 Na2AlF5
+ 6.8989E-05 (NaAlF4)2
+ 3.2724E-05 NaF
+ 6.7124E-06 AlF3
+ 2.8147E-06 (NaF)2
+ 1.4270E-06 NaAl2F7
+ 5.9682E-07 Na
+ 7.7844E-10 CaF2
+ 6.2683E-10 AlF2
+ 3.2301E-10 (AlF3)2
+ 3.6450E-12 AlF
+ 3.6237E-12 OAlF
+ 3.2125E-12 COF2
+ 1.9440E-12 C3O2
+ 5.3327E-14 COF
+ 4.8969E-14 F
+ 3.0305E-14 Na2
+ 1.9898E-15 CaF
+ 8.5765E-16 C2O
+ 1.0736E-16 NaO

F Results - Equilib 964.33 C, A=2 (page 2/2) FactSage 6.2 beta

Output Edit Show Pages

T(C) P(atm) Energy(J) Mass(g) Vo

954.35 C, A=0 - 964.33 C, A=2 -

+ 1.0096E+06 gram ABath
(1.0096E+06 gram, 17526. mol)
(964.33 C, 1 atm, a=1.0000)
(44.782 wt.% NaF
+ 18.194 wt.% AlF3_5coord
+ 27.514 wt.% AlF3_4coord
+ 3.4791E-03 wt.% Al2F6
+ 2.5290 wt.% Na2O
+ 0.84515 wt.% Al2O3_5coord

F Results - Equilib 964.33 C, A=2 (page 2/2) FactSage 6.2 beta

Output Edit Show Pages

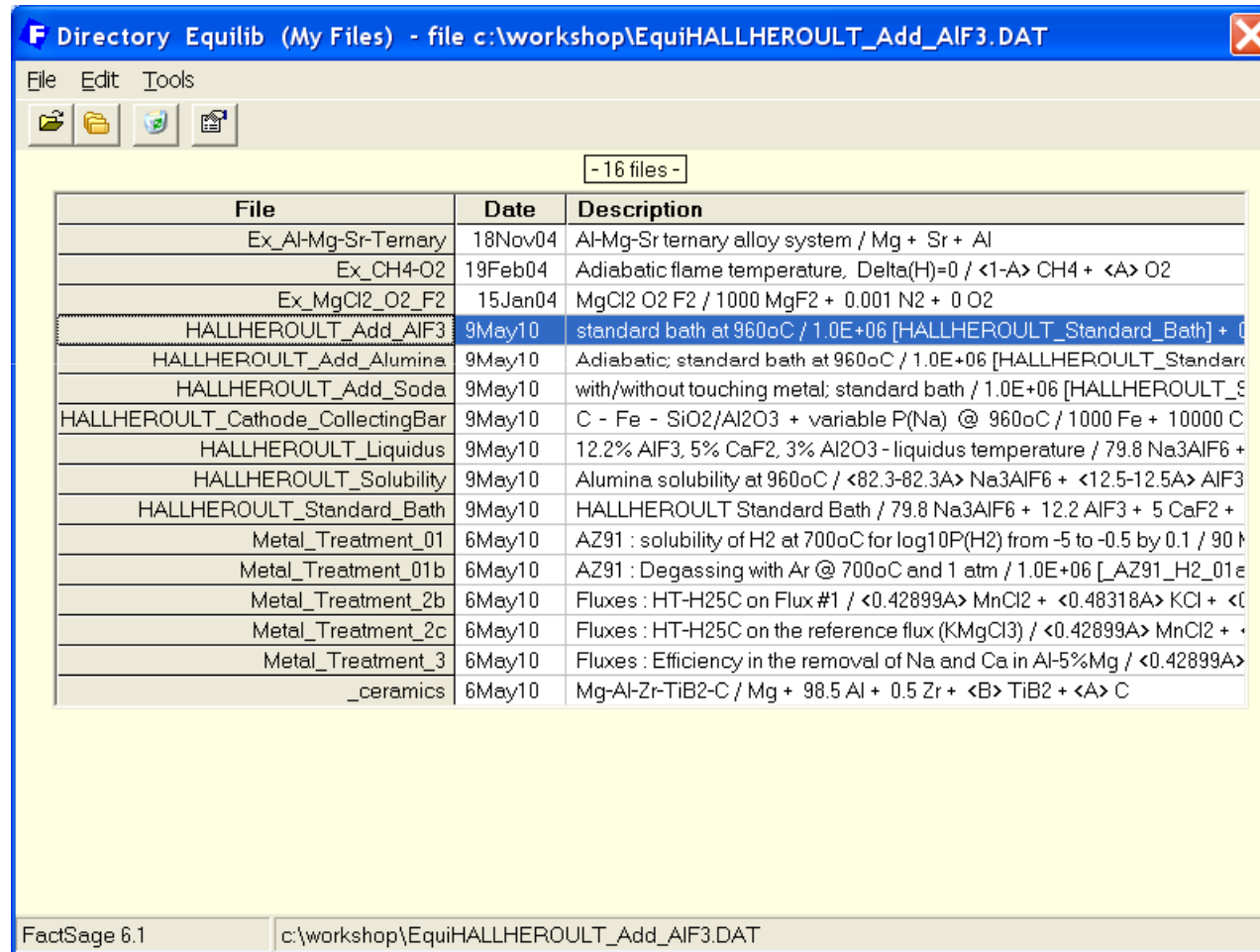
T(C) P(atm) Ener

954.35 C, A=0 - 964.33 C, A=2 -

+ 212.71 gram C_graphite
(212.71 gram, 17.710 mol)
(964.33 C, 1 atm, S1, a=1.0000)
+ 0.00000 gram Na3AlF6_solid_beta
(964.33 C, 1 atm, S2, a=0.64662)
+ 0.00000 gram Na3AlF6_solid_alpha
(964.33 C, 1 atm, S1, a=0.57647)

Hall-Heroult Process

- **Example #6: Adding reactants to the electrolyte (AlF_3)**
- File | Open “HALLHEROULT_Add_AIF3”



Hall-Heroult Process

- Example #6: Adding reactants to the electrolyte (AlF_3)

1.0 ton of Bath
(stream @ 960°C)

$\text{AlF}_{3(s)}$ (@ 50°C)

Reactants - Equilib

File Edit Table Units Data Search Help

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

1 - 7

	Mass(g)	Species	Phase	T(C)	P(total)**	Stream#	Data
	1.0E+06	[HALLHEROULT_]	[Stream]	960	1	1	
+	0	Al ₂ O ₃	solid-1-FThall gamma	125	1	2	FThall
+	0	Al ₂ O ₃	solid-4-FThall corund	125	1	2	FThall
+	0	Al ₂ O ₃ (H ₂ O)	solid-2-FACT53 boeh	125	1	2	FACT53
+	0	Na ₂ CO ₃	solid-1-FACT53	20	1	3	FACT53
+	0	Al	liquid-FThall	960	1	4	FThall
+	<1000A>	AlF ₃	solid-1-FThall perovs	50	1	5	FThall

☒ Initial Conditions

Next >>

FactSage 6.2 beta Compound: 2/24 databases Solution: 1/22 databases

Hall-Heroult Process

• Example #6: Adding reactants to the electrolyte (AlF_3)

1.0 ton of **Bath**
(**stream** @ 960°C)

+ 5 kg $\text{AlF}_{3(s)}$ (@ 50°C)

Adiabatic Addition

$$Q = \Delta\Delta H = 0$$

F Menu - Equilib: standard bath at 960oC

File Units Parameters Help

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

Reactants (7)

(gram) 1.0E+06 [HALLHEROULT_Standard_Bath]	+	0 Al2O3	+	0 Al2O3	+	0 Al
(960C,#1)		(125C,s1-FThall,#2)		(125C,s4-FThall,#2)		(125C,s

Products

Compound species

* + gas ☒ ideal ☐ real	110
aqueous	0
pure liquids	0
* + pure solids	67

☐ suppress duplicates

* - custom selection
species: 177

Target
- none -
Estimate T(C): 900
Mass(g): 0

Solution species

*	+	Base-Phase	Full Name
	+	FThall-BathA	ABath
		FThall-Bath?	?Bath
	+	FThall-CryL	Na-Cryolite-L
	+	FThall-CryH	Na-Cryolite-H
	I	FThall-Liq	Liquid-Alloy
	+	FThall-FCC	FCC
	I	FThall-BCC	BCC
	I	FThall-Mono	Monoxide

Legend
I - immiscible 3
+ - selected 4

☒ Show ☒ all ☐ selected

species: 35
solutions: 10

Custom Solutions

0 fixed activities
0 ideal solutions
0 activity coefficients

Pseudonyms

apply ☐

☐ include molar volumes
Total Species (max 1500) 212
Total Solutions (max 40) 10

Final Condition

<A>		T(C)	P(atm)	Delta H(J)
5			1	0

10 steps ☐ Table

Equilibrium

☒ normal ☐ normal + transitions
☐ transitions only ☐ open
☐ predominant

FactSage 6.2 beta c:\workshop\EquiHALLHEROULT_Add_AIF3.DAT

Hall-Heroult Process

- Example #6: Adding reactants to the electrolyte (AlF_3)

1.0 ton of Bath
(stream @ 960°C)

+ 5 kg $\text{AlF}_{3(s)}$ (@ 50°C)

T = 956.00°C

1005.0 kg Bath

F Results - Equilib 956 C FactSage 6.2 beta

Output Edit Show Pages

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

+ 1.0050E+06 gram ABath
(1.0050E+06 gram, 17443. mol)
(956.00 C, 1 atm, a=1.0000)

(44.874	wt.% NaF	FThall
+ 18.959	wt.% AlF_3 _5coord	FThall
+ 27.487	wt.% AlF_3 _4coord	FThall
+ 3.8431E-03	wt.% Al_2F_6	FThall
+ 2.0426	wt.% Na ₂ O	FThall
+ 0.70987	wt.% Al_2O_3 _5coord	FThall
+ 1.0292	wt.% Al_2O_3 _4coord	FThall
+ 1.4389E-04	wt.% Al_2O_3	FThall
+ 4.6861	wt.% CaF ₂	FThall
+ 0.20758	wt.% CaO	FThall

Mole fraction of sublattice constituents:

Na	0.63545
Al_(V)	0.13424
Al_(IV)	0.19462
Al ₂	1.3605E-05
Ca	3.5687E-02

F	0.97009
O	2.9915E-02

System component	Mole fraction	Mass fraction
Ca	1.3496E-02	2.5539E-02
Al	0.12437	0.15845
Na	0.24031	0.26085
F	0.60322	0.54111
O	1.8602E-02	1.4052E-02

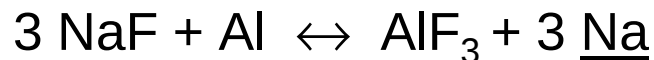
Hall-Heroult Process

- **Example #7: Carbide formation in the cathode blocks**

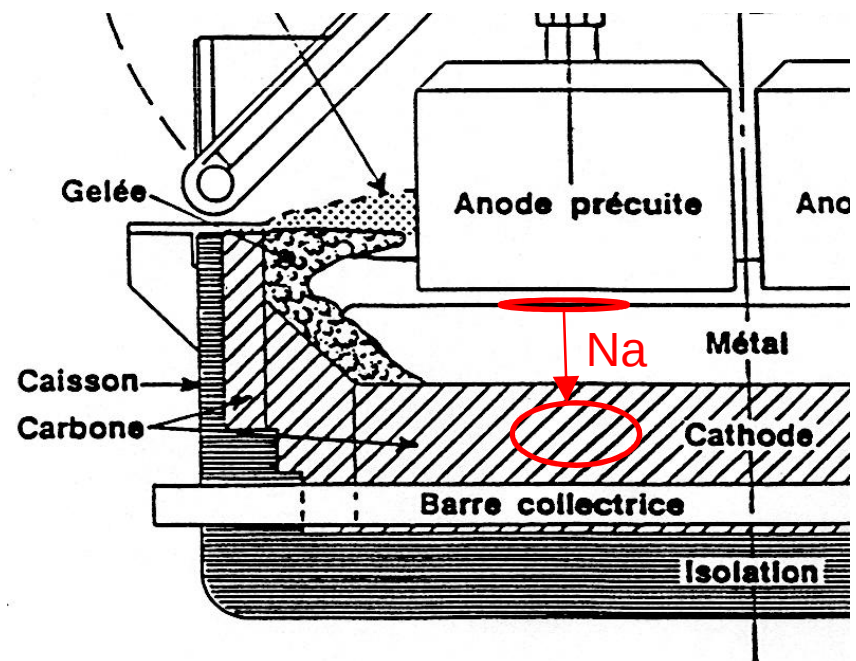
The **lifetime** of the cell is **very dependent** on the cathode block (graphite) lifetime.

The cathode blocks can be degraded by mechanical erosion, but also by chemical reactions with the penetrating **sodium vapors** and **liquid electrolyte**.

Sodium is generated at the metal bath interface with

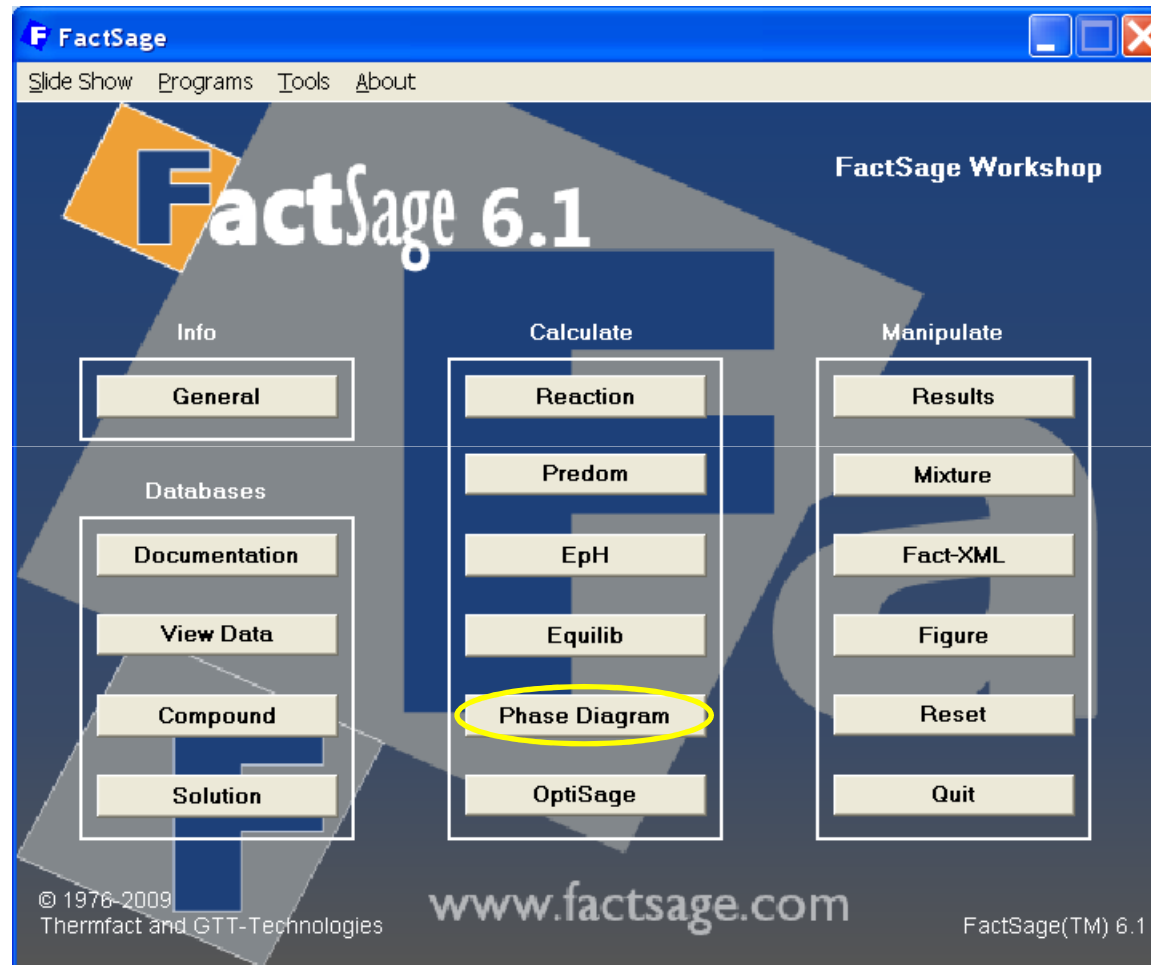


Residual N_2 and CO can be present in the carbon pores init.



Hall-Heroult Process

- **Example #7: Carbide formation in the cathode blocks**



Hall-Heroult Process

- Example #7: Carbide formation in the cathode blocks

C with small amounts of N & O

Bath; CR=2.2

Penetrating Na

Components

(NaF)2.2(AlF3)1.0
CaF2
Al2O3
(C)0.9998(N)0.0001(O)0.000
Na

Note:
- on the phase diagram the units of mass will be g, but the chemical formulae of the components remain molar values.

File | Open "HALLHEROULT_Cathode1"

Next >>

FactSage 6.2 beta Compound: 2/24 databases Solution: 1/22 databases

Hall-Heroult Process

• Example #7: Carbide formation in the cathode blocks

- FACT53
 - Gas species
 - $\text{NaCN}_{(\text{liq.})}$
 - C
- Fthall
 - Bath
 - Metal

F Menu - Phase Diagram: last system

File Units Parameters Variables Help

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

Components (5)

(gram) (NaF)2.2(AlF3)1.0 + CaF2 + Al2O3 + (C)0.9998(N)0.0001(O)0.0001 + Na

Products

Compound species

- * ☒ gas ☒ ideal ☐ real 88
- ☐ aqueous 0
- * ☒ pure liquids 1
- * ☒ pure solids 60
- ☐ suppress duplicates **apply**
- * - custom selection species: 149

Target

- none -

Estimate T(K): 1000

Mass(g): 0

Solution species

*	+	Base-Phase	Full Name
		FThall-BathA	ABath
	+	FThall-Bath?	?Bath
	+	FThall-CryL	Na-Cryolite-L
	+	FThall-CryH	Na-Cryolite-H
		FThall-Liq	Liquid-Alloy
	+	FThall-FCC	FCC
		FThall-BCC	BCC
		FThall-Mono	Monoxide

Legend

| - immiscible 3

+ - selected 4

☒ Show ☒ all ☐ selected

species: 40

solutions: 10 **Select**

Custom Solutions

0 fixed activities

0 ideal solutions

0 activity coefficients

Details ...

Pseudonyms

apply ☐ **List ...**

☐ include molar volumes

Total Species (max 1500) 189

Total Solutions (max 40) 10

Default

Variables

T(C)	100CaF2/(L+CaF)	100Al2O3/(L+CaF)	M/(L+CaF2+Al2O)	Na/(L+CaF2+Al2O)
960	5	0.10	5	0.0.01

100Al2O3/(L+CaF2+Al2O3) vs Na/(L+CaF2+Al2O3) - L=(NaF)2.2(AlF3)1.0 M=(C)0.9998(N)0.0001

Phase Diagram

Y

X

Calculate >>

FactSage 6.2 beta

Hall-Heroult Process

• Example #7: Carbide formation in the cathode blocks

• X-axis

$$\frac{1 \text{ Na}}{1 (NaF)_{2.2} (AlF_3)_{1.0} + 1 CaF_2 + 1 Al_2O_3} = 0..0.01$$

0–0.01 kg Na / kg of bath

• Y-axis

$$\frac{100 Al_2O_3}{1 (NaF)_{2.2} (AlF_3)_{1.0} + 1 CaF_2 + 1 Al_2O_3} = 0..10$$

0 – 10% Al_2O_3 in the bath

• Constants

– T = 960°C & P = 1 atm

$$\frac{100 CaF_2}{1 (NaF)_{2.2} (AlF_3)_{1.0} + 1 CaF_2 + 1 Al_2O_3} = 5$$

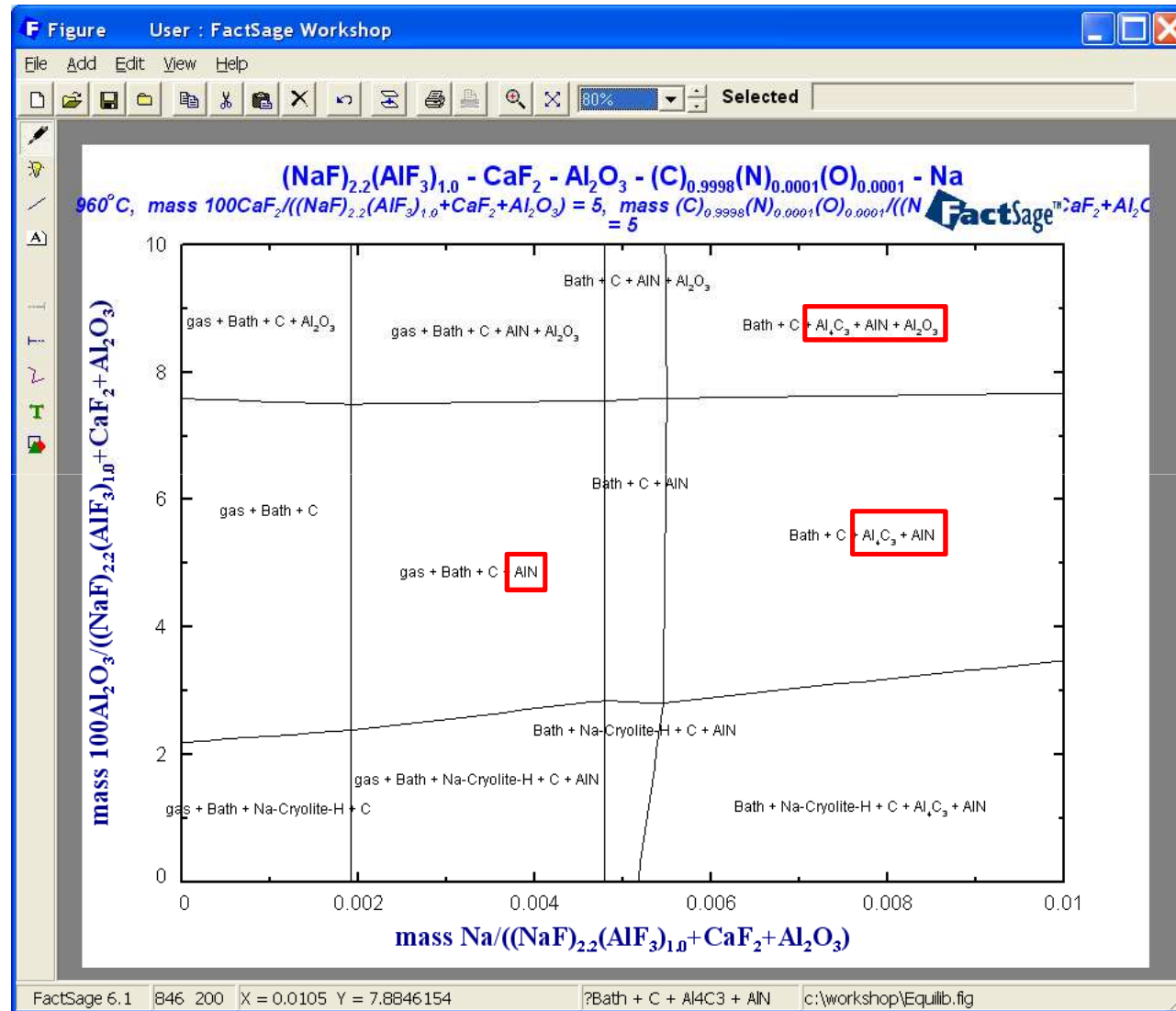
← CaF_2 is 5% of the mass of the bath

$$\frac{1 C}{1 (NaF)_{2.2} (AlF_3)_{1.0} + 1 CaF_2 + 1 Al_2O_3} = 5$$

← The carbon to bath mass ratio is fixed at 5.0 (arbitrary)

Hall-Heroult Process

- Example #7: Carbide formation in the cathode blocks



Hall-Heroult Process

- Example #8: Cathode / Collecting Bar / Refractory / Na_(g)**

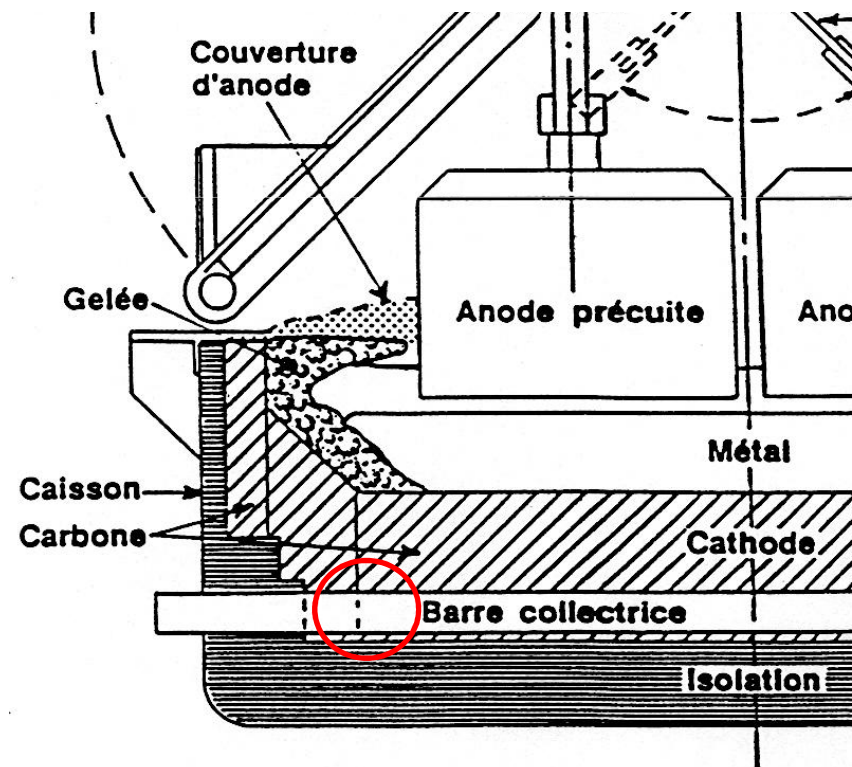
The current collecting bar (steel) entrapped inside the cathode block (C-graphite);

a SiO₂/Al₂O₃ layer is beneath it;

Na(vapors) percolated through the Cathode block from the metal pad;

Unwanted reaction products can increase the electrical resistivity
→ \$\$

T ≈ 900-960°C



Hall-Heroult Process

- **Example #8: Cathode / Collecting Bar / Refractory / Na_(g)**

- FACT53
 - Gas species
- FToxid
 - Refractory Mat.
- FSstel
 - Steel

The screenshot shows the 'Reactants - Equilib' window in FactSage. The 'File' menu is highlighted with a red box. The input table is as follows:

Mass(g)	Species	Phase	T(C)	P(total)**	Stream#	Data
1000	Fe	s			1	
+ 10000	C	s			1	
+ <800A>	SiO2	s			1	
+ <200A>	Al2O3	s			1	
+ 0	Na	s			1	

Below the table, a red box highlights the text: 'File | Open "HALLHEROULT_Cathode_CollectingBar"'. At the bottom right, there is a checkbox for 'Initial Conditions'.

Next >>

FactSage 6.2 beta Compound: 3/24 databases Solution: 2/22 databases

Hall-Heroult Process

- **Example #8: Cathode / Collecting Bar / Refractory / Na_(g)**

F Menu - Equilib: C - Fe - SiO2/Al2O3 + variable P(Na) @ 960oC

File Units Parameters Help

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

Reactants (5)

(gram) 1000 Fe + 10000 C + <800A> SiO2 + <200A> Al2O3 + 0 Na

Products

Compound species

☐ gas ☒ ideal ☐ real 32

☐ aqueous 0

☐ pure liquids 0

☒ pure solids 71

☐ suppress duplicates apply

* - custom selection species: 103

Solution species

*	+	Base-Phase	Full Name
	+	FSstel-DIAM	DIAMOND_A4
	+	FSstel-FCC	FCC_A1:Me(C,N)
	+	FSstel-BCC	BCC_A2
	+	FSstel-AL52	Al5Fe4
	+	FSstel-ALFE	AlFeSi_ALPHA
	+	FSstel-AL13	Al13Fe4
	+	FSstel-FE-L	Fe-LIQUID
	+	FSstel-ALM1	ALMNSI_ALPHA

Legend

I - immiscible 2

+ - selected 19

☒ Show ☒ all ☐ selected

species: 109

solutions: 23

Select

Custom Solutions

1 fixed activities

0 ideal solutions

0 activity coefficients

Details ...

Pseudonyms

apply ☐ List ...

☐ include molar volumes

Total Species (max 1500) 212

Total Solutions (max 40) 23

Default

Target

- none -

Estimate T(K): 1000

Mass(g): 0

Final Conditions

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

0.5 950 1

10 steps Table 91 calculations

Equilibrium

☒ normal ☐ normal + transitions

☐ transitions only ☐ open

☐ predominant

Calculate >>

FactSage 6.2 beta c:\workshop\EquiHALLHEROULT_Cathode_CollectingBar.DAT

Hall-Heroult Process

• Example #8: Cathode / Collecting Bar / Refractory / Na_(g)

P_{Na} is varied
from 10^{-10} atm to
 10^{-1} atm

Menu - Equilib: C - Fe - SiO2/Al2O3 + variable P(Na) @ 960oC

Reactants (5)

(gram) 1000 Fe

Products

Compound species

gas ideal real 32

13 Na(g)

- clear

✓ + - select

- standard stable phase

! - dormant (metastable) phase

F - formation target phase

P - precipitate target phase

S - Scheil cooling gas phase

C - composition target ...

Ideal Solution

a Activity

log10(activity)

Fixed Partial Pressure

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

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

-10.0 -1.0 0.10

OK

Cancel

Final

0.5

950

10 steps

Table

91 calculations

predominant

Calculate >>

FactSage 6.2 beta

c:\workshop\EquiHALLHEROULT_Cathode_CollectingBar.DAT

Hall-Heroult Process

- Example #8: Cathode / Collecting Bar / Refractory / Na_(g)

Extract & Plot Results

The screenshot displays the FactSage 6.2 beta interface. The main window shows the 'Results - Equilib a=1.00E-10 (page 1/91) FactSage 6.2 beta' window. The 'Output' menu is open, and the 'Plot' option is selected, leading to the 'Plot Results ...' dialog box. The 'Results Processor: c:\workshop\Equi0.res' window is also open, showing the chemical reaction: 1000 Fe + 10000 C + <800A> SiO2 + <200A> Al2O3 +. The 'Axes' dialog box is open, showing the Y-axis as log10(gram) and the X-axis as log10(activity). The Y-axis has a maximum of 5, a minimum of -3, and a tick every 0.5. The X-axis has a maximum of 0, a minimum of -10, and a tick every 1. The 'Na(g)' label is visible in the X-axis section. The 'Axes' button in the 'Results Processor' window is highlighted. The 'Plot >>' button is also visible.

FactSage 6.1 | c:\workshop\Equi0.res | 9May10 | 91 sets

Hall-Heroult Process

- Example #8: Cathode / Collecting Bar / Refractory / Na_(g)

X-axis : $\log_{10}(P_{\text{Na}})$

Na_(g) is species #13

Y-axis : $\log_{10}(\text{grams})$

Select all species with
"Mole (max)" > 0

Species Selection - EQUILIB Results: log10(gram) vs log10(activity)

+	#	Species	Mole (min)	Mole (max)	Fract. (min)	Fract. (max)	Act. (min)	Act. (max)
	208	Fe2SiO4(s)	0	0	0	0	1.0309E-16	8.5157E-03
	209	Fe2SiO4(s2)	0	0	0	0	8.9169E-18	7.3660E-04
	210	Fe2SiO4(s3)	0	0	0	0	8.9869E-18	7.4238E-04
	211	Fe2Al4Si5O18(s)	0	0	0	0	3.6473E-37	2.5390E-02
	212	Fe3Al2Si3O12(s)	0	0	0	0	1.9822E-33	6.5999E-04
		SOLUTIONS						
+	213	GAS	0	1.0699E-05	0	0	7.6539E-04	1.
	214	DIAM	0	0	0	0	0.502257	0.502257
+	215	FCC	0	19.714	0	0	0.990296	1.
+	216	BCC	0	20.449	0	0	0.928947	1.
	217	AL52	0	0	0	0	0.423855	0.54455
	218	ALFE	0	0	0	0	0	1.1714E-257
	219	AL13	0	0	0	0	0	1.5071E-207
	220	FE-L	0	0	0	0	0.734095	0.849108
	221	ALM1	0	0	0	0	1.9427E-251	2.3756E-137
	222	HCP	0	0	0	0	0.706783	0.736318
	223	BCC2	0	0	0	0	0.850103	0.996067
+	224	SLAGA#1	0	9.9486	0	0	0.786151	1.
	225	SLAGA#2	0	0	0	0	0.786151	1.

Y: log10(gram) select species - use "+" Clear

X: log10(activity) enter one species # 13 Na(g)

Mass ☒ mole ☐ gram ☐ source

Order ☒ integer # ☐ mass (max) ☐ fraction (max) ☐ activity (max)

Select Top 15 11 species selected Refresh OK

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

Hall-Heroult Process

• Example #8: Cathode / Collecting Bar / Refractory / Na_(g)

At low $\log_{10}(P_{\text{Na}})$

C
+ Austenite(fcc)
+ Refractory (SiO₂ + mullite)

At intermediate $\log_{10}(P_{\text{Na}})$

C
+ Austenite(fcc)
+ Albite (NaAlSi₃O₈) + SiO₂

Higher:
+ Slag
+ Nepheline (NaAlSiO₄)

At high $\log_{10}(P_{\text{Na}})$

C
+ Ferrite(bcc)
+ Slag (Na₂SiO₃ + NaAlO₂-NaAlSiO₄(s.s.))

