Supplementary material

Methodology

To start with, we need to determine the material balance attainable region for the cobalt system. We have come up with three possible material balances given by Eq. (1-3):

$$Co_3O_{4(s)} + 4H_{2(g)} = 3Co_{(s)} + 4H_2O_{(g)} \quad (1)$$

$$Co_3O_{4(s)} + H_{2(g)} = 3CoO_{(s)} + H_2O_{(g)} \quad (2)$$

$$CoO_{(s)} + H_{2(g)} = Co_{(s)} + H_2O_{(g)} \quad (3)$$

This means the system has five components (**N**): Co_3O_4, H_2, Co, H_2O, CoO. We use these to help us find the independent material balances which we define **S**.
Note that S = N-P where P is the number of atomic species present in the system.

N= Co_3O_4, H_2, H_2O, CoO, Co →**5**

P = Co, O, H →**3**

∴ S = 5 – 3

= 2 *(meaning the system has 2 independent material balances).*

To find the two independent material balances we arrange the system into a matrix function and use Gaussian elimination as shown in Table1 and Table 2.

Table 1. Atomic matrix form of the system compounds.

Co	H	O	Compounds
3	0	4	Co_3O_4
1	0	0	Co
0	2	0	H_2
1	0	1	CoO
0	2	1	H_2O

Table 2. Gaussian elimination to get independent balances for the cobalt system.

Co	H	O	Compounds
0	0	0	Co_3O_4-3Co-4(H_2O- H_2)
1	0	0	Co
0	1	0	1/2H_2
0	0	0	CoO-Co-(H_2O- H_2)
0	0	1	H_2O- H_2

The two independent mass balances obtained are given by Equations. (4 and 5)

$$Co_3O_{4(s)} + 4H_{2(g)} = 3Co_{(s)} + 4H_2O_{(g)} \qquad \varepsilon_1 \quad (4)$$

$$CoO_{(s)} + H_{2(g)} = Co_{(s)} + H_2O_{(g)} \qquad \varepsilon_2 \quad (5)$$

Finding the vertices for the AR

The stoichiometric material balances are given below:

$*N_{Co3O4} = N^o_{Co3O4} - \varepsilon_1 \geq 0$

$$\boldsymbol{\varepsilon_1 \leq N^o_{Co3O4}}$$

$*N_{H2} = N^o_{H2} - 4\varepsilon_1 - \varepsilon_2 \geq 0$

$$\mathbf{4\varepsilon_1 + \varepsilon_2 \leq N^o_{H2}}$$

*$N_{Co} = 3\varepsilon_1 + \varepsilon_2 \geq 0$

$$\mathbf{\varepsilon_1 \geq 0}$$

*$N_{H2O} = 4\varepsilon_1 + \varepsilon_2 \geq 0$

$$\mathbf{4\varepsilon_1 + \varepsilon_2 \geq 0}$$

*$N^o_{CoO} - \varepsilon_2 \geq 0$

$$\mathbf{\varepsilon_2 \leq 0}$$

NB: 2 components are specified as feed

$N^o_{Co3O4} = 1$ **$\therefore \varepsilon_1 \leq 1$**

N^o_{H2} = varying (0-1)

Let $\varepsilon_1 = a$, $\varepsilon_2 = b$

We use Matlab '*Mupad*' function to find vertices for the AR for the cobalt system:

The result gives us the three vertices that we use to plot an Attainable region with three boundary sides.

Matlab script to find vertices when N^o_{Co3O4} and $N^o_{H2} = 1$ (Corresponding to Figure 2a)

```
k:=[{a<=1,4*a+b<=4,3*a+b>=0,4*a+b>=0,b<=0},a+b]:linopt::corners(k,[a,b])
```

gives the 3 vertices below

$$\left[\left\{[0,\ 0],\ \left[\frac{1}{4},\ 0\right],\ [1,\ -3]\right\},\ \frac{1}{4},\ \left[\frac{1}{4},\ 0\right]\right]$$

Other vertices for other scenarios were found as above for the respective feed moles.

Defining parameters

First, we define **v** to be the matrix of stochiometric coefficients of the independent mass balances describing the process or the reaction system. So, **v** is defined as:

$$\boldsymbol{v}=\begin{pmatrix} v_{11} & \cdots & v_{1N} \\ \vdots & \ddots & \vdots \\ v_{s1} & \cdots & v_{sN} \end{pmatrix}$$

Where **N** is the number of components in the system, and **S** is the number of independent mass balances for the system. Thus, matrix **v** must be of the size (SxN).

The moles of each component at any point during reaction is given by:

$$\underline{nx} = \underline{n}x^0 + vx^T\underline{\varepsilon x} \qquad (6)$$

where the range of ε is such that all $n_i \geq 0$ and v^T is a transpose of the stoichiometric matrix v with size (NxS) and $\underline{\varepsilon} = \begin{bmatrix} \underline{\varepsilon_1} \\ \vdots \\ \underline{\varepsilon_s} \end{bmatrix}$ column vector of extents,

N = $\begin{bmatrix} \underline{n_1} \\ \vdots \\ \underline{n_N} \end{bmatrix}$ column vector of number of moles at extent S and n^o = $\begin{bmatrix} \underline{n^o}_1 \\ \vdots \\ \underline{n^o}_N \end{bmatrix}$ column vector of initial

The matrices in Equation. (6) are such that the matrix multiplication is

(Nx1) + (NXS) x (SX1) = (NX1)

$\mathbf{v} = \begin{bmatrix} -1 & -4 & 4 & 0 & 3 \\ 0 & -1 & 1 & -1 & 1 \end{bmatrix}$, **(2X5)**

$\underline{\boldsymbol{n}}^{\mathbf{0}} = \begin{bmatrix} Co_3O_4 \\ H_2 \\ H_2O \\ CoO \\ Co \end{bmatrix}$ **(5X1),**

$\underline{\boldsymbol{\varepsilon}} = \begin{bmatrix} \underline{\boldsymbol{\varepsilon}}_1 \\ \underline{\boldsymbol{\varepsilon}}_2 \end{bmatrix}$ (2x1)

Check consistency: (5x1) + (5x2) x (2x1) = (5x1)

Thus, we need to plot the AR for a given feed of Co and H_2, that is find set of extents (***ε***) such that the moles of all components greater or equal to zero. We use a Matlab function *"plotregion"* which plots closed convex regions in 2D/3D. In this case we have 2 independent mass balances hence all plots will be given in 2D.

We write (in Matlab) the inequality in the form $Ax \geq b$ where matrix $A = vx^T$ and $x = \boldsymbol{\varepsilon}x$ and $b = -nox$. This allows us to plot the feasible region also look at cases where we can vary and compare different feeds

Plotting MB-AR using extents

Figure 1

```
nox = [1;0.1;0;0;0];
vx = [-1 -4 4 0 3
      0 -1 1 -1 1];
  figure (1)
subplot(2,2,1,gca)
plotregion(vx',-nox);
title('(a) nox = [1;0.1;0;0;0]')
xlabel('ex1')
ylabel('ex2')

subplot(2,2,2)
nox1 = [1;0.5;0;0;0];
plotregion(vx',-nox1);
title('(b) nox = [1;1;0;0;0]')
xlabel('ex1')
ylabel('ex2')

subplot(2,2,3)
nox3 = [0;0;1;1;0];
plotregion(vx',-nox3);
title('(c) nox [0;0;1;1;0]')
ylabel('ex2')
```

```
xlabel('ex1')

subplot(2,2,4)
nox4 = [1;0;1;0;0];
plotregion(vx',-nox4);
title('(d) nox [1;0;1;0;0]')
ylabel('ex2')
xlabel('ex1')
```

Figure 2

```
figure (x)
Nox1 = [1;10;1;1;0];
[Ex,ind,col] = plotregionmode(vx',-Nox1);



title('Material Balance Attainabe Region')
xlabel('ex1')
ylabel('ex2')
```

```
figure (2)
nox1 = [1;4;0;0;0];
[Ex,ind,col] = plotregionmode(vx',-nox1);

title('Material Balance Attainabe Region')
xlabel('ex1')
ylabel('ex2')
```

Hydrogen, Figure 3

```
nox = [1;0.1;0;0;0];
vx = [-1 -4 4 0 3
        0 -1 1 -1 1];
  figure (1)
subplot(2,2,1,gca)
plotregion(vx',-nox);
title('(a) nox = [1;0.1;0;0;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,2)
nox1 = [1;1;0;0;0];
plotregion(vx',-nox1);
title('(b) nox = [1;1;0;0;0]')
xlabel('ε1')
```

```
ylabel('ε2')

subplot(2,2,3)
nox2 = [1;2;0;0;0];
plotregion(vx',-nox2);
title('(c) nox [1;2;0;0;0]')
ylabel(' ε2')
xlabel(' ε1')

subplot(2,2,4)
nox3 = [1;4;0;0;0];
plotregion(vx',-nox3);
title('(d) nox [1;4;0;0;0]')
ylabel('ε2')
xlabel('ε1')
```

CoO, Figure 4

```
nox = [0;0.1;0;1;0];
vx = [-1 -4 4 0 3
        0 -1 1 -1 1];
   figure (1)
subplot(2,2,1,gca)
plotregion(vx',-nox);
title('(a) nox = [0;0.1;0;1;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,2)
nox1 = [0;0.5;0;1;0];
plotregion(vx',-nox1);
title('(b) nox = [0;0.5;0;1;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,3)
nox2 = [0;1;0;1;0];
plotregion(vx',-nox2);
title('(c) nox [0;1;0;1;0]')
ylabel(' ε2')
xlabel(' ε1')

subplot(2,2,4)
nox3 = [0;2;0;1;0];
plotregion(vx',-nox3);
```

```
title('(d) nox [0;2;0;1;0]')
ylabel('ε2')
xlabel('ε1')
```

All

```
nox = [1;1;0;0;0];
vx = [-1 -4 4 0 3
      0 -1 1 -1 1];
  figure (1)
subplot(2,2,1,gca)
plotregion(vx',-nox);
title('(a) nox = [1;1;0;0;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,2)
nox1 = [0;1;0;1;0];
plotregion(vx',-nox1);
title('(b) nox = [0;1;0;1;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,3)
nox2 = [0;0;1;1;0];
plotregion(vx',-nox2);
title('(c) nox [0;0;1;1;0]')
ylabel(' ε2')
xlabel(' ε1')

subplot(2,2,4)
nox3 = [1;0;1;0;0];
plotregion(vx',-nox3);
title('(d) nox [1;0;1;0;0]')
ylabel('ε2')
xlabel('ε1')
```

MB-AR, Figure 5

```
nox = [1;1;0;1;0];
vx = [-1 -4 4 0 3
      0 -1 1 -1 1];
  figure (1)
```

```
subplot(2,2,1,gca)
plotregion(vx',-nox);
title('(a) nox = [1;1;0;1;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,2)
nox1 = [1;5;0;1;0];
plotregion(vx',-nox1);
title('(b) nox = [1;5;0;1;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,3)
nox2 = [1;10;0;1;0];
plotregion(vx',-nox2);
title('(c) nox = [1;10;0;1;0]')
xlabel('ε1')
ylabel('ε2')

subplot(2,2,4)
nox3 = [1;5;1;1;0];
plotregion(vx',-nox3);
title('(d) nox [1;5;1;1;0]')
ylabel(' ε2')
xlabel(' ε1')
```

Plotting G-H AR

$\underline{nx} = \underline{nx}^0 + vx^T \underline{\varepsilon x}$

$\underline{GHx}^0 = \begin{bmatrix} -910.02 & -774.87 \\ 0.00 & 0.00 \\ -285.51 & -23736 \\ -237.9 & -214.2 \\ 0.00 & 0.00 \end{bmatrix}$ (*Also shows ΔH and ΔG for all species at 25˚C)*

GHx$_R$ = $\boldsymbol{vx}$ x $\underline{\boldsymbol{GHx}}^{\boldsymbol{0}}$ (3x5)(5x2) = (3x2)

GH = $\boldsymbol{\varepsilon x}^{\boldsymbol{T}}$ x **GH$_R$** (1x3)(3x2) =(1x2)

@25degrees, Figure 6

```
GHo = [-910.20 -774.00
0.00 0.00
-241.83 -228.6
-237.90 -214.20
0.00 0.00];

vx = [-1 -4 4 0 3
```

```
0 -1 1 -1 1];

GHR = vx*GHo;
GH = Ex'*GHR;
GH = GH';
figure(6)
plot(1,1); hold on
set(patch(GH(1,ind+1)',GH(2,ind+1)',col),'FaceAlpha',0.5);

title('G-H Attainable Region @ 25 ˚C ')
xlabel('H [kJ/mol]')
ylabel('G [kJ/mol]')
hold off
```

@200 degrees

```
GHo = [-885.86 -778.5
5.04 -1.25
-236.09 -222.24
-228.51 -215.3
4.6 0.00];

vx = [-1 -4 4 0 3
0 -1 1 -1 1];

GHR = vx*GHo;
GH = Ex'*GHR;
GH = GH';
figure(7)
plot(1,1); hold on
set(patch(GH(1,ind+1)',GH(2,ind+1)',col),'FaceAlpha',0.5);

title('G-H Attainable Region @ 200 ˚C ')
xlabel('H [kJ/mol]')
ylabel('G [kJ/mol]')
hold off
```

@320 degrees

```
GHo = [-867.06 -781.87
8.54 -3.26
-231.9 -219.21
-222.07 -216.14
8.04 0.00];

vx = [-1 -4 4 0 3
0 -1 1 -1 1];
```

```
GHR = vx*GHo;
GH = Ex'*GHR;
GH = GH';
figure(8)
plot(1,1); hold on
set(patch(GH(1,ind+1)',GH(2,ind+1)',col),'FaceAlpha',0.5);

title('G-H Attainable Region @ 320 ˚C ')
xlabel('H [kJ/mol]')
ylabel('G [kJ/mol]')
hold off
```

@400 degrees

```
GHo = [-853.71 -784.35
10 -5.00
-229.00 -217.68
-217.74 -216.76
10.45 0.00];

vx = [-1 -4 4 0 3
0 -1 1 -1 1];

GHR = vx*GHo;
GH = Ex'*GHR;
GH = GH';
figure(9)
plot(1,1); hold on
set(patch(GH(1,ind+1)',GH(2,ind+1)',col),'FaceAlpha',0.5);

title('G-H Attainable Region @ 400 ˚C ')
xlabel('H [kJ/mol]')
ylabel('G [kJ/mol]')
hold off
```

@600 degrees

```
GHo = [-817.29 -791.2
16.86 -10.53
-221.4 -215.34
-206.78 -218.4
17.28 0.00];

vx = [-1 -4 4 0 3
0 -1 1 -1 1];
```

```
GHR = vx*GHo;
GH = Ex'*GHR;
GH = GH';
figure(10)
plot(1,1); hold on
set(patch(GH(1,ind+1)',GH(2,ind+1)',col),'FaceAlpha',0.5);

title('(a) G-H Attainable Region @ 600 ˚C ')
xlabel('H [kJ/mol]')
ylabel('G [kJ/mol]')
hold off
```

@800 degrees

```
GHo = [-775.98 -798.8
22.96 -17.46
-213.3 -214.8
-195.57 -220.36
24.54 0.00];

vx = [-1 -4 4 0 3
0 -1 1 -1 1];

GHR = vx*GHo;
GH = Ex'*GHR;
GH = GH';
figure(10)
plot(1,1); hold on
set(patch(GH(1,ind+1)',GH(2,ind+1)',col),'FaceAlpha',0.5);

title('G-H Attainable Region @ 800 ˚C ')
xlabel('H [kJ/mol]')
ylabel('G [kJ/mol]')
hold off
```