Nonlinear Programming (Optimization) with Equity Constraints

The nonlinear programming problem with equity constrains is defined by:

$$\begin{aligned} &\text{Minimize} \quad f(\mathbf{x}) \\ &\text{Subject to} \quad \mathbf{h}(\mathbf{x}) = \mathbf{0} \end{aligned}$$

where f is a function, $\mathbf{x}$ is an n – vector of variables and $\mathbf{h}$ is an m-vector (m<n) of functions.

For example:

$$\min_{n_i} F = \sum_{i=1}^{c} n_i \left(\frac{G_i^0}{RT} + \ln \frac{n_i}{\sum n_i} \right)$$

Subject to:

$$g_1 = 2n_4 + n_5 + 2n_6 + n_7 - 4 = 0$$

$$g_2 = 4n_1 + 4n_2 + 2n_3 + 2n_7 + 2n_8 + 6n_9 - 14 = 0$$

$$g_3 = n_1 + 2n_2 + 2n_3 + n_4 + n_5 + 2n_9 - 2 = 0$$

$$n_1 \geq 0;\ n_2 \geq 0;\ \ldots\ n_9 \geq 0;$$

Complex Chemical Equilibrium by Gibbs Energy Minimization – Problem Definition

Ethane is steam cracked to form hydrogen over a cracking catalyst at temperature T = 1000 K and pressure of P = 1 atm. The feed contains 4 moles of H_2O per mole of CH_4.

No.	Component	Gibbs energy kcal/g-mol	Feed g-mol	Effluent Init. Estimate
1	CH_4	4.61		0.001
2	C_2H_4	28.249		0.001
3	C_2H_2	40.604		0.001
4	CO_2	-94.61		0.993
5	CO	-47.942		1
6	O2	0		0.007
7	H_2	0		5.992
8	H_2O	-46.03	4	1
9	C_2H_6	26.13	1	0.001

Note very small amounts

Compounds in the effluent

Gibbs energy at 1000 K

Using the data above calculate the effluent equilibrium composition

Formulate the problem as a constrained minimization problem

The objective function to be minimized is the total Gibbs energy:

$$\min_{n_i} \frac{G}{RT} = \sum_{i=1}^{c} n_i \left(\frac{G_i^0}{RT} + \ln \frac{n_i}{\sum n_i} \right)$$

where n_i is the number of moles of component i, c is the total number of compounds, R is the gas constant and is the Gibbs energy of pure component i at temperature T.

Minimization is carried out subject to atom balance constrains:

CH_4 C_2H_4 C_2H_2 CO_2 CO O2 H_2 H_2O C_2H_6

Oxygen balance $g_1 = 2n_4 + n_5 + 2n_6 + n_7 - 4 = 0$

Hydrogen Balance $g_2 = 4n_1 + 4n_2 + 2n_3 + 2n_7 + 2n_8 + 6n_9 - 14 = 0$

Carbon Balance $g_3 = n_1 + 2n_2 + 2n_3 + n_4 + n_5 + 2n_9 - 2 = 0$

Introduce the constraints into the objective function using Lagrange multipliers and differentiate this function to obtain a system of nonlinear algebraic equations.

The constraints are introduced into the objective functions using Lagrange multipliers: λ_1, λ_2 and λ_3.

$$\min_{n_i, \lambda_j} F = \sum_{i=1}^{c} n_i \left(\frac{G_i^0}{RT} + \ln \frac{n_i}{\sum n_i} \right) + \sum_{j=1}^{3} \lambda_j g_j$$

The condition for minimum of this function at a particular point is that all the partial derivatives of F with respect to n_i and λ_j vanish at this point. The partial derivative of F with respect to n_1, for example, is:

Preferred form if n_i is very small

$$\frac{\partial F}{\partial n_1} = \frac{G_1^0}{RT} + \ln \frac{n_1}{\sum n_i} + 4\lambda_2 + \lambda_3 = 0 \quad \text{or} \quad n_1 - \sum n_i \exp\left(\frac{G_1^0}{RT} + 4\lambda_2 + \lambda_3 \right) = 0$$

Use the Polymath “Constrained” Algorithm to Find the Solution

```
R = 1.9872
sum = H2 + O2 + H2O + CO + CO2 + CH4 + C2H6 + C2H4 + C2H2
f(lamda1) = 2 * CO2 + CO + 2 * O2 + H2O - 4 # Oxygen balance
f(lamda2) = 4 * CH4 + 4 * C2H4 + 2 * C2H2 + 2 * H2 + 2 * H2O + 6 * C2H6 - 14 # Hydrogen
balance
f(lamda3) = CH4 + 2 * C2H4 + 2 * C2H2 + CO2 + CO + 2 * C2H6 - 2 # Carbon balance
f(H2) = ln(H2 / sum) + 2 * lamda2
f(H2O) = -46.03 / R + ln(H2O / sum) + lamda1 + 2 * lamda2
f(CO) = -47.942 / R + ln(CO / sum) + lamda1 + lamda3
f(CO2) = -94.61 / R + ln(CO2 / sum) + 2 * lamda1 + lamda3
f(CH4) = 4.61 / R + ln(CH4 / sum) + 4 * lamda2 + lamda3
f(C2H6) = 26.13 / R + ln(C2H6 / sum) + 6 * lamda2 + 2 * lamda3
f(C2H4) = 28.249 / R + ln(C2H4 / sum) + 4 * lamda2 + 2 * lamda3
f(C2H2) = C2H2 - exp(-(40.604 / R + 2 * lamda2 + 2 * lamda3)) * sum
f(O2) = O2 - exp(-2 * lamda1) * sum
H2(0) = 5.992
O2(0) = 0.0001 > 0
H2O(0) = 1
CO(0) = 1
CH4(0) = 0.001 > 0
C2H4(0) = 0.001 > 0
C2H2(0) = 0.001 > 0
CO2(0) = 0.993
C2H6(0) = 0.001 > 0
lamda1(0) = 10
lamda2(0) = 10
lamda3(0) = 10
```

Variables defined as “Absolutely Positive”

Positive and negative values are allowed

Polymath Solution for Equilibrium Composition

	Variable	Value	f(x)	Initial Guess
1	lamda1	24.41966	0	10
2	lamda2	0.253059	0	10
3	lamda3	1.559832	0	10
4	H2	5.345225	1.11E-16	5.992
5	H2O	1.521646	-1.67E-15	1
6	CO	1.388517	2.44E-15	1
7	CO2	0.544918	-1.11E-15	0.993
8	CH4	0.066564	0	0.001
9	C2H6	1.67E-07	-1.69E-13	0.001
10	C2H4	9.54E-08	-2.58E-13	0.001
11	C2H2	3.16E-10	7.24E-25	0.001
12	O2	5.46E-21	-5.69E-27	0.0001
13	R	1.9872		
14	sum	8.866871		

Compounds of trace amounts

Polymath Entry of the Objective Function Value for Excel Solver Solution

The problem can be solved using the Excel "Solver" by entering the objective function and the constraints only.

The objective function:

```
1   G_O2 = O2 * ln(abs(O2 / sum))
2   G_H2 = H2 * ln(H2 / sum)
3   G_H2O = H2O * (-46.03 / R + ln(H2O / sum))
4   G_CO = CO * (-47.942 / R + ln(CO / sum))
5   G_CO2 = CO2 * (-94.61 / R + ln(CO2 / sum))
6   G_CH4 = CH4 * (4.61 / R + ln(abs(CH4 / sum)))
7   G_C2H6 = C2H6 * (26.13 / R + ln(abs(C2H6 / sum)))
8   G_C2H4 = C2H4 * (28.249 / R + ln(abs(C2H4 / sum)))
9   G_C2H2 = C2H2 * (40.604 / R + ln(abs(C2H2 / sum)))
10  ObjFun = G_H2 + G_H2O + G_CO + G_O2 + G_CO2 + G_CH4 + G_C2H6 + G_C2H4 + G_C2H2
```

Note the use of "abs" to prevent errors in case n_i becomes negative during the iterations

Objective Function, Constraints and Initial Estimates in Excel

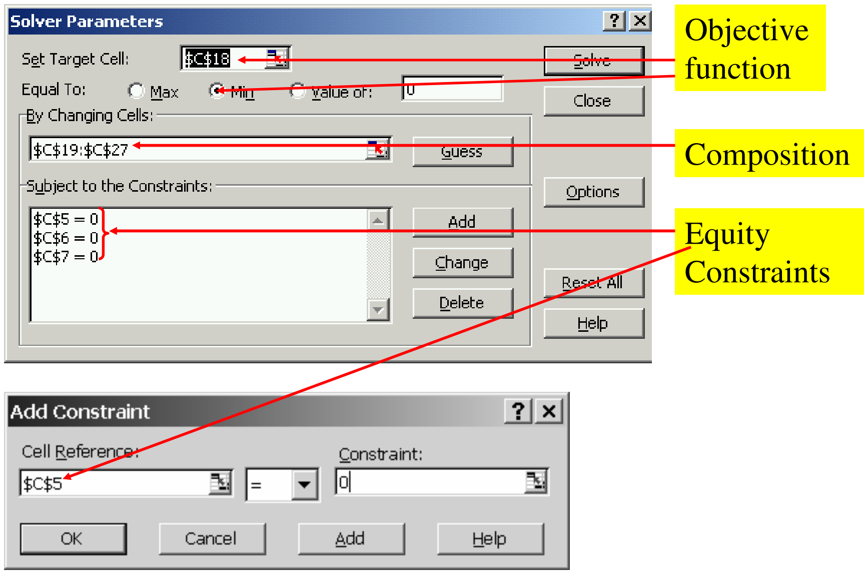
Variable	Value	Polymath Equation
R	1.9872	*R=1.9872*
sum	8.996	*sum=H2 + H2O + CO + O2 + CO2 + CH4 + C2H6 + C2H4 + C2H2*
OxBal	-4.441E-16	*OxBal=2 * CO2 + CO + 2 * O2 + H2O - 4*
HydBal	0	*HydBal=4 * CH4 + 4 * C2H4 + 2 * C2H2 + 2 * H2 + 2 * H2O + 6 * C2H6 - 14*
CarBal	0	*CarBal=CH4 + 2 * C2H4 + 2 * C2H2 + CO2 + CO + 2 * C2H6 - 2*
eps	1E-21	*eps=0.1e-20*
G_O2	-0.0501104	*G_O2=O2 * ln(abs(O2 + eps / sum))*
G_H2	-2.4348779	*G_H2=H2 * ln(H2 / sum)*
G_H2O	-25.360025	*G_H2O=H2O * (-46.03 / R + ln(H2O / sum))*
G_CO	-26.322183	*G_CO=CO * (-47.942 / R + ln(CO / sum))*
G_CO2	-49.464812	*G_CO2=CO2 * (-94.61 / R + ln(CO2 / sum))*
G_CH4	-0.0067847	*G_CH4=CH4 * (4.61 / R + ln(CH4 / sum))*
G_C2H6	0.00404462	*G_C2H6=C2H6 * (26.13 / R + ln(abs(C2H6 + eps / sum)))*
G_C2H4	0.00511094	*G_C2H4=C2H4 * (28.249 / R + ln(abs(C2H4 + eps / sum)))*
G_C2H2	0.01132823	*G_C2H2=C2H2 * (40.604 / R + ln(abs(C2H2 + eps / sum)))*
ObjFun	-103.61831	*ObjFun=G_H2 + G_H2O + G_CO + G_O2 + G_CO2 + G_CH4 + G_C2H6 + G_C2H4 + G_C2H*
O2	0.007	*O2=0.007*
H2	5.992	*H2=5.992*
H2O	1	*H2O=1*
CO	1	*CO=1*
CH4	0.001	*CH4=0.001*
C2H4	0.001	*C2H4=0.001*
C2H2	0.001	*C2H2=0.001*
CO2	0.993	*CO2=0.993*
C2H6	0.001	*C2H6=0.001*

Equity constraints

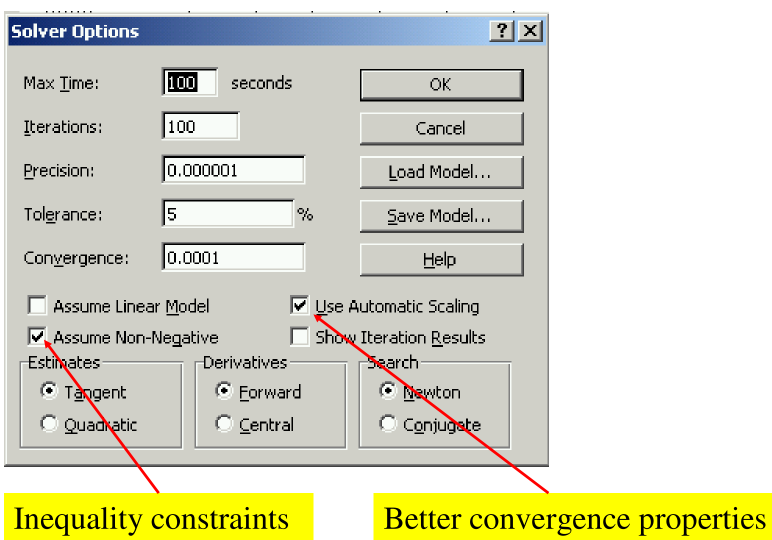
Objective function

Initial guesses

Solver Parameters for the Free Energy Minimization Problem



Solver Parameters for the Free Energy Minimization Problem



Comparison of Polymath and Excel Results

No.	Component	Initial Estimate	Solution: Polymath	Solution: Excel Solver	Solution: Balzisher et. al[1]
1	CH4	0.001	0.066564	0.00149444	0.066456
2	C2H4	0.001	9.54E-08	1.0112E-06	9.41E-8
3	C2H2	0.001	3.16E-10	2.9847E-07	3.15E-10
4	CO2	0.993	0.544918	0.53441967	0.544917
5	CO	1	1.388517	1.46396259	1.3886
6	O2	0.007	5.46E-21	0	3.704E-21
7	H2	5.992	5.345225	5.52962977	5.3455
8	H2O	1	1.521646	1.46719804	1.5215
9	C2H6	0.001	1.67E-07	6.0332E-05	1.572E-7
	Gibbs Energy	-103.61831	-104.34	-104.27612	