4.5 COMPLEX CHEMICAL EQUILIBRIUM BY GIBBS ENERGY MINIMIZATION

4.5.1 Concepts Demonstrated

Formulation of a chemical equilibrium problem as a Gibbs energy minimization problem with atom balance constraints. Use of Lagrange multipliers to introduce the constraints into the objective function. Conversion of the minimization problem into a system of nonlinear algebraic equations.

4.5.2 Numerical Methods Utilized

Solution of a system of nonlinear algebraic equations with constraints.

4.5.3 Excel Options and Functions Demonstrated

Use of the Excel Add-In Solver for constrained minimization.

4.5.4 Problem Definition

Ethane reacts with steam to form hydrogen over a cracking catalyst at a temperature of $T = 1000$ K and pressure of $P = 1$ atm. The feed contains 4 moles of H_2O per mole of CH_4. Balzisher et al.[1] suggest that only the compounds shown in Table 4–10 are present in the equilibrium mixture (assuming that no carbon is deposited). The Gibbs energies of formation of the various compounds at the temperature of the reaction (1000 K) are also given in Table 4–10. The equilibrium composition of the effluent mixture is to be calculated using these data.

Table 4–10 Compounds Present in Effluent of Steam Cracking Reactor[1]

No.	Component	Gibbs Energy kcal/gm-mol	Feed gm-mol	Effluent Initial 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		0.0001[a]
7	H_2	0		5.992
8	H_2O	-46.03	4	1
9	C_2H_6	26.13	1	0.001

[a] This initial estimate is more realistic and useful than the original published estimate of 0.007.

(a) Formulate the problem as a constrained minimization problem. Introduce the constraints into the objective function using Lagrange multipliers and differentiate this function to obtain a system of nonlinear algebraic equations.
(b) Use the POLYMATH "Constrained" solution algorithm to find the solution to this system of nonlinear equations. Start the iterations from the initial estimates shown in Table 4–10.
(c) Use Excel's "Solver" to solve the problem as a constrained minimization problem without the use of Lagrange multipliers and without differentiation of the objective functions. Compare the results with those obtained in (b).

4.5.5 Solution

The objective function to be minimized is the total Gibbs energy given by

$$\min_{n_i} \frac{G}{RT} = \sum_{i=1}^{c} n_i \left(\frac{G_i^0}{RT} + \ln \frac{n_i}{\sum n_i} \right) \tag{4-49}$$

where n_i is the number of moles of component i, c is the total number of compounds, R is the gas constant and G_i^0 is the Gibbs energy of pure component i at temperature T. The minimization of Equation (4-49) must be carried out subject to atomic balance constraints

Oxygen Balance $$g_1 = 2n_4 + n_5 + 2n_6 + n_7 - 4 = 0 \tag{4-50}$$

Hydrogen Balance $$g_2 = 4n_1 + 4n_2 + 2n_3 + 2n_7 + 2n_8 + 6n_9 - 14 = 0 \tag{4-51}$$

Carbon Balance $$g_3 = n_1 + 2n_2 + 2n_3 + n_4 + n_5 + 2n_9 - 2 = 0 \tag{4-52}$$

The identification of the various components is given in Table 4–10.

These three constraints can be introduced into the objective functions using Lagrange multipliers: λ_1, λ_2 and λ_3. The extended objective function is

$$\min_{n_i, \lambda_j} F = \sum_{i=1}^{c} n_i \left(\frac{G_i^0}{RT} + \ln \frac{n_i}{\sum n_i} \right) + \sum_{j=1}^{3} \lambda_j g_j \tag{4-53}$$

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

$$\frac{\partial F}{\partial n_1} = \frac{G_1^0}{RT} + \ln \frac{n_1}{\sum n_i} + 4\lambda_2 + \lambda_3 = 0 \tag{4-54}$$

The other partial derivatives with respect to n_i can be obtained similarly. If it is

expected that the amount of a particular compound at equilibrium is very close to zero, it is preferable to rewrite the equation in a form that does not require calculation of the logarithm of a very small number. Rearranging Equation (4-54), for example, yields

$$n_1 - \sum n_i \exp\left(\frac{G_1^0}{RT} + 4\lambda_2 + \lambda_3\right) = 0 \qquad \textbf{(4-55)}$$

The partial derivatives of F with respect to λ_1, λ_2 and λ_3 are g_1, g_2 and g_3 respectively.

(b) The complete set of nonlinear equations, as entered into the POLYMATH Nonlinear Algebraic Equation Solver, is shown in Table 4–11. There are 12 implicit equations associated with the 12 unknowns. In the POLYMATH input, the amount (moles) of a compound (n_i) is represented by the formula of the compound, for clarity. The equations associated with O_2 and C_2H_2 are written in the form of Equation (4-55) as preliminary tests have shown difficulty in convergence of the solution algorithm when the equations that contain logarithms of the amount of those compounds are used.

Table 4–11 Equation Input to the POLYMATH Nonlinear Equation Solver Program - File **P4-05B1.POL**

No.	Equation, # Comment
1	R = 1.9872
2	sum = H2 + O2 + H2O + CO + CO2 + CH4 + C2H6 + C2H4 + C2H2
3	f(lamda1) = 2 * CO2 + CO + 2 * O2 + H2O - 4 # Oxygen balance
4	f(lamda2) = 4 * CH4 + 4 * C2H4 + 2 * C2H2 + 2 * H2 + 2 * H2O + 6 * C2H6 - 14 # Hydrogen balance
5	f(lamda3) = CH4 + 2 * C2H4 + 2 * C2H2 + CO2 + CO + 2 * C2H6 - 2 # Carbon balance
6	f(H2) = ln(H2 / sum) + 2 * lamda2
7	f(H2O) = -46.03 / R + ln(H2O / sum) + lamda1 + 2 * lamda2
8	f(CO) = -47.942 / R + ln(CO / sum) + lamda1 + lamda3
9	f(CO2) = -94.61 / R + ln(CO2 / sum) + 2 * lamda1 + lamda3
10	f(CH4) = 4.61 / R + ln(CH4 / sum) + 4 * lamda2 + lamda3
11	f(C2H6) = 26.13 / R + ln(C2H6 / sum) + 6 * lamda2 + 2 * lamda3
12	f(C2H4) = 28.249 / R + ln(C2H4 / sum) + 4 * lamda2 + 2 * lamda3
13	f(C2H2) = C2H2 - exp(-(40.604 / R + 2 * lamda2 + 2 * lamda3)) * sum
14	f(O2) = O2 - exp(-2 * lamda1) * sum
15	H2(0) = 5.992
16	O2(0) = 0.0001 > 0
17	H2O(0) = 1
18	CO(0) = 1
19	CH4(0) = 0.001 > 0
20	C2H4(0) = 0.001 > 0
21	C2H2(0) = 0.001 > 0
22	CO2(0) = 0.993
23	C2H6(0) = 0.001 > 0
24	lamda1(0) = 10
25	lamda2(0) = 10
26	lamda3(0) = 10

The initial estimates suggested by Balzisher et al.[1] (shown in Table 4–10) are entered in lines 15 through 23 of the input to POLYMATH. Note that the initial estimate `O2(0)=0.0001>0`, for example, indicates that this variable is constrained to be always positive ("absolutely positive") during the problem solution. For this problem, only the "constrained" POLYMATH solution algorithm converges to the solution from the given initial estimates, while the other algorithms stop with the error message that the calculation of the logarithm of a negative number is attempted. The constrained algorithm also allows definition of some or all of the unknowns to be positive at the solution ("physically positive"). For O_2 in this problem, the corresponding "physically positive" format as specified in the initial estimate would `O2(0)=0.0001>=0`. This format was not used in this problem.

The variables for which the initial estimates are specified in lines 16, 19, 20, 21 and 23 in Table 4–10 are marked as "absolutely positive". The rest of the variables do not approach zero so as to obtain negative values during the solution process (lines 15, 17, 18 and 19), or they are allowed to have both negative and positive values (lines 24, 25 and 26).

The POLYMATH solution for the equilibrium composition of the effluent mixture is shown in Table 4–12. These results indicate that the effluent contains

Table 4–12 POLYMATH Results for Equilibrium Composition of Effluent Stream - File **P4-05B1.POL**

	Variable	Value	f(x)	Initial Guess
1	C2H2	3.157E-10	7.238E-25	0.001
2	C2H4	9.541E-08	-2.58E-13	0.001
3	C2H6	1.671E-07	-1.688E-13	0.001
4	CH4	0.0665638	0	0.001
5	CO	1.388517	2.442E-15	1.
6	CO2	0.5449182	-1.11E-15	0.993
7	H2	5.345225	1.11E-16	5.992
8	H2O	1.521646	-1.665E-15	1.
9	lamda1	24.41966	0	10.
10	lamda2	0.2530591	0	10.
11	lamda3	1.559832	0	10.
12	O2	5.459E-21	-5.687E-27	0.0001
13	R	1.9872		
14	sum	8.866871		

significant amounts of H_2 (5.345 moles per mole of C_2H_6 feed), H_2O, CO, CO_2 and CH_4 and contains only trace amounts of C_2H_6, C_2H_4, C_2H_2 and O_2. All the function values are smaller by several orders of magnitude than the respective variable values, indicating that the solution is correct. The same values were obtained also by Balzisher et al.[1], who used a dedicated FORTRAN program to solve the same problem.

The value of the objective function at this point may be added to the POLYMATH problem by including Equation (4-49). The additional equations comprising Equation (4-49) are summarized in Table 4–13. The objective function value at the solution is -104.34, and this can be used to compare the POLYMATH solution with the Excel solution in part (c).

Table 4–13 Equations for Calculation of the Gibbs Energy Function - File **P4-05B2.POL**

Line	Equation
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

(c) The use of the Excel Add-In "Solver"* to solve this problem requires only the Gibbs Energy objective function of Equation (4-49) as presented in Table 4–13 and the atomic material balance constraints given by Equations (4-50), (4-51) and (4-52). It is convenient to enter these needed equations into Excel via POLYMATH. The resulting equations from POLYMATH as exported to Excel are given in Table 4–14. Note that the Gibbs Energy objective function is in line 4, and the atomic constraints are in lines 5, 6 and 7. The equations in line 4 and lines 9 through 18 are components of the objective function (Equation (4-49). Lines 19 through 27 provide the initial estimates for the nine problem variables.

Table 4–14 Gibbs Energy Minimization with Atom Balance Constraints as Exported from POLYMATH to Excel - Files **P4-05C.POL** and **P4-05C.XLS**

	A	B	C	D	E
1	POLYMATH NLE Migration Document				
2		Variable	Value		Polymath Equation
3	Explicit Eqs	R	1.9872		R=1.9872
4		sum	8.996		sum=H2 + H2O + CO + O2 + CO2 + CH4 + C2H6 + C2H4 + C2H2
5		OxBal	-4.441E-16		OxBal=2 * CO2 + CO + 2 * O2 + H2O - 4
6		HydBal	0		HydBal=4 * CH4 + 4 * C2H4 + 2 * C2H2 + 2 * H2 + 2 * H2O + 6 * C2H6 - 14
7		CarBal	0		CarBal=CH4 + 2 * C2H4 + 2 * C2H2 + CO2 + CO + 2 * C2H6 - 2
8		eps	1E-21		eps=0.1e-20
9		G_O2	-0.0501104		G_O2=O2 * ln(abs((O2 + eps) / sum))

* The Excel Add-In "Solver" may require special installation from Microsoft Excel or the Microsoft Office. If this Add-In is not available from the drop-down Tools/Add-Ins menu in Excel, please consult the Microsoft instructions to install this software.

Table 4–14 Gibbs Energy Minimization with Atom Balance Constraints as Exported from POLYMATH to Excel - Files **P4-05C.POL** and **P4-05C.XLS**

	A	B	C	D	E
10		G_H2	-2.4348779		G_H2=H2 * ln(H2 / sum)
11		G_H2O	-25.360025		G_H2O=H2O * (-46.03 / R + ln(H2O / sum))
12		G_CO	-26.322183		G_CO=CO * (-47.942 / R + ln(CO / sum))
13		G_CO2	-49.464812		G_CO2=CO2 * (-94.61 / R + ln(CO2 / sum))
14		G_CH4	-0.0067847		G_CH4=CH4 * (4.61 / R + ln(CH4 / sum))
15		G_C2H6	0.00404462		G_C2H6=C2H6 * (26.13 / R + ln(abs((C2H6 + eps) / sum))
16		G_C2H4	0.00511094		G_C2H4=C2H4 * (28.249 / R + ln(abs((C2H4 + eps) / sum))
17		G_C2H2	0.01132823		G_C2H2=C2H2 * (40.604 / R + ln(abs((C2H2 + eps) / sum))
18		ObjFun	-103.61831		ObjFun=G_H2 + G_H2O + G_CO + G_O2 + G_CO2 + G_CH4 + G_C2H6 + G_C2H4 + G_C2H2
19		O2	0.007		O2=0.007
20		H2	5.992		H2=5.992
21		H2O	1		H2O=1
22		CO	1		CO=1
23		CH4	0.001		CH4=0.001
24		C2H4	0.001		C2H4=0.001
25		C2H2	0.001		C2H2=0.001
26		CO2	0.993		CO2=0.993
27		C2H6	0.001		C2H6=0.001

It should be noted that the "Solver" Add-In cannot find the minimum when Equation (4-49) is entered in its original form. Excel execution stops with error messages indicating that there is an attempt to calculate logarithm of a negative number. In order to prevent calculation of logarithm of a negative number or logarithm of zero, the expressions for calculating the partial Gibbs energy of some of the compounds have been changed according to

$$\frac{G_i}{RT} = n_i\left\{\frac{G_i^0}{RT} + \ln\left[\text{abs}\left(\frac{n_i+\varepsilon}{\sum n_i}\right)\right]\right\} \qquad \textbf{(4-56)}$$

where ε is a very small number ($\varepsilon = 1\times10^{-21}$). This equation is used only for the compounds which present in trace amounts in the effluent: O_2, C_2H_2, C_2H_4 and C_2H_6.

The use of the Excel "Solver" Add-In for the solution of this minimization problem is best explained with reference to Figures 4–51, 4–52 and 4–53. After the "Solver" interface is requested within the Excel "Tools" drop-down menu as shown in Figure 4–51, the "Target Cell" to be minimized should be entered as cell C18 which contains the formula for the objective function (see Table 4–14). Next the "Equal to:" option should be set to "Min". The cells to be changed are the cells which contain the numbers of moles of the various compounds which is indicated in Excel by $C$19:$C$27. The three constraint equations from the atomic material balance constraints given by Equations (4-50), (4-51) and (4-52) are entered by reference to the Excel cell containing each equation as shown in Figure 4–51. These balances should all be equal to zero at the solution. Addition of the first

constraint is shown in Figure 4–52.

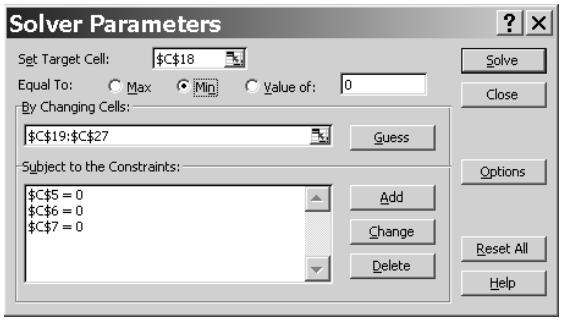

Figure 4–51 Solver Parameters for the Gibbs Energy Minimization Problem - File **P4-05C.XLS**

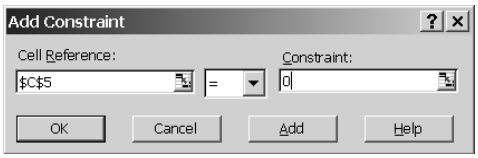

Figure 4–52 Addition of First Constraint for Solver Minimization - File **P4-05C.XLS**

The constraints regarding the positive value of the compounds can be specified in the "Options" communication box shown in Figure 4–53. Two default options must be changed with the "Options" button to obtain a solution. First, "Assume Non-Negative" must be selected; otherwise the "Solver" converges to a solution where some of the mole numbers are negative. Second, "Use Automatic Scaling" must also be selected in order to obtain a feasible solution. The Excel Solver solution is partially shown in Figure 4–54.

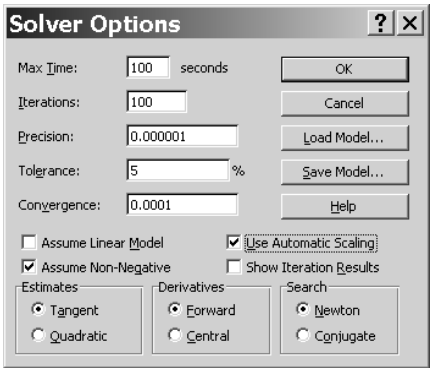

Figure 4–53 Solver Options for the Gibbs Energy Minimization Problem

18	ObjFun	-104.2757	*ObjFun=G_H2 + G_H2O + G_CO + G_O2 + G_CO2 + G_CH4 + G_C2*
19	O2	0	*O2=1e-20*
20	H2	5.5304163	*H2=5.992*
21	H2O	1.466646	*H2O=1*
22	CO	1.4636555	*CO=1*
23	CH4	0.001396	*CH4=0.001*
24	C2H4	3.117E-06	*C2H4=0.001*
25	C2H2	0	*C2H2=0.001*
26	CO2	0.5348493	*CO2=0.993*
27	C2H6	4.651E-05	*C2H6=0.001*

Figure 4–54 Partial Excel Spreadsheet Showing Solver Minimization Solution

The results obtained by the POLYMATH constrained Nonlinear Equation Solver, the Excel Solver constrained minimization algorithm and the values reported by Balzisher et al.[1] are summarized in Table 4–15. Examination of the various results indicates that the minimum Gibbs energy obtained by POLYMATH is slightly lower than the value obtained by the Solver. The composition values obtained by POLYMATH are almost identical to those reported by Balzisher et al.[1]. There are considerable differences between those values from POLYMATH and those obtained by the Excel Solver Add-In. There may be other optimization routines that can be used with Excel to achieve a closer agreement in the solution.

Table 4–15 Effluent Composition and Minimum of Gibbs Energy by Various Solution Techniques

No.	Component	Initial Estimate	POLYMATH	Excel Solver	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	

The problem solution files are found in directory CHAPTER 4 and designated **P4-05B1.POL**, **P4-05B2.POL**, **P4-05C.POL**, and **P4-05C.XLS**.