Chemical Equilibrium by Gibbs Energy Minimization on Spreadsheets

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Chemical Equilibrium by Gibbs Energy Minimization on Spreadsheets*

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This paper describes the use of Solver function, contained in the Microsoft Excel spreadsheet package, in computing the chemical equilibrium of known substances in either an ideal or non-ideal gas phase by the method of direct Gibbs energy minimization. Apart from some deficiency of Solver in applying the generalized reduced gradient method for this type of problem, the approach is simple to understand and apply and provides a direct solution procedure whereas the traditional approach often employs a high-level programming language. The results are compared with those obtained by a Fortran program, and found to be in satisfactory agreement.

SUMMARY OF EDUCATIONAL ASPECTS OF THE PAPER

1. The paper discusses materials/software for courses in Chemical Engineering Thermodynamics and Physical Chemistry.
2. Course levels are 3rd year in a 4-year program and 4th or 5th year in a 5–6-year program of regular undergraduate courses.
3. Mode of presentation is by computer and lecture.
4. Class hours required to cover the material is 3 semester-hours.
5. Student homework hours required for the course: maximum 4 hours for initial preparation of a general spreadsheet model; maximum 1–2 hours for modification to suit particular problems.
6. Novel aspects presented in this paper: use of spreadsheets in direct minimization of Gibbs energy to determine the chemical equilibrium concentrations. A way is described to smoothly run the spreadsheet Solver in solving this type of optimization problems.

NOMENCLATURE

a_{ji} Number of gram atoms of element j in a mole of species i
$\mathbf{a_{ji}}$ Matrix of a_{ji}'s
b_j Total number of gram atoms of element j in the reaction mixture
$\hat{f}_i$ Fugacity of species i in the gas mixture
f_i^0 Fugacity of species i at its standard state
G_i Gibbs free energy of species i in the gas mixture
G_i^0 Gibbs free energy of species i at its standard state
G_i Gibbs free energy of pure species i at operating conditions
ΔG_{fi}^0 Standard Gibbs free energy of formation of species i
K Total number of atomic elements
k_{ij} Binary interaction parameters
N Total number of species in the reaction mixture
n_i Number of moles of species i
nG Total Gibbs free energy of the system
P Total pressure of the system
P_c Critical pressure
R Gas constant
T Temperature of the system
T_c Critical temperature
y_i Mole fraction of species i
Z Compressibility factor
$\hat{\phi}_i$ Fugacity coefficient of species i in the gas mixture
ω Acentric factor

INTRODUCTION

IN THE engineering education literature, a number of papers concerning the use of spreadsheets as teaching/learning tools have been described. They involved flowsheeting, database development, material and energy balance calculations, solving algebraic and differential equations, process optimization, curve fitting, modeling and simulation, etc.

The usefulness of spreadsheets as a teaching/learning tool underlies in its:

    simplicity and user-friendliness;
    built-in graphics capabilities;
    flexibility in changing the model parameters;
    universal availability;
    ability to be used as or combined with a word-processor.

This paper presents a use of Solver function of the spreadsheet in solving nonlinear programming problems with an example of Gibbs energy minimization in chemical equilibrium calculations.

Chemical equilibrium calculations have traditionally been made through the use of equilibrium constants of known reactions – a procedure still useful for simple problems. However, when the equilibrium composition is determined by a number of simultaneous reactions, the computations required become complex and tedious. A more direct and general method for solving these complicated problems is the direct minimization of the Gibbs function of the system, given by:

$$nG = \sum_{i=1}^{N} n_i \bar{G}_i = \sum n_i G_i^0 + RT \sum n_i \ln \frac{\hat{f}_i}{f_i^0} \quad (1)$$

For gas phase reactions, $\hat{f}_i = \hat{\phi}_i y_i P$. Since the standard state is taken as the pure ideal gas state at 1 bar (100 kPa), $f_i^0 = 1$ bar. And since G_i^0 is set equal to zero for each chemical element in its standard state, $G_i^0 = \Delta G_{fi}^0$ for each component. Substituting these into equation (1) gives:

$$nG(n_i s, T, P) = \sum n_i \Delta G_{fi}^0 + \sum n_i RT \ln P$$
$$+ \sum n_i RT \ln y_i + \sum n_i RT \ln \hat{\phi}_i \quad (2)$$

The problem now is to find the set of $n_i s$ which minimizes nG at constant T and P, subject to the constraints of elemental balances:

$$\sum_{i=1}^{N} n_i a_{ji} = b_j, \quad j = 1, \ldots, K \quad (3)$$

The nonlinear programming model, comprising the objective function (2) to be minimized and the constraints (3), is traditionally solved by the Lagrange multiplier method. Advances in computational techniques allow the direct solution of such models by the sequential or successive quadratic programming (SQP) (e.g. [1]) and the generalized reduced gradient (GRG) methods.

To solve such models numerically, one usually develops a computer program which requires considerable testing and debugging before results can be obtained. Moreover, the model is usually obscured from the user unless relevant documentation is provided, and cannot be modified without recompilation. Instead of developing computer programs, one can also use commercial scientific computing libraries. However they still require driver programs and are usually not particularly user friendly and often are machine or software specific. Although there are commercial software packages for solving chemical equilibrium problems, the calculation steps are hidden from the user, and hence they are not suitable to use as teaching and learning aids.

Using the spreadsheet offers some unique features which the conventional approach does not usually provide, such as graphics capability and flexibility in experimenting by changing input data or independent variables. It is also available universally on nearly all personal computers. Although preparing the spreadsheet models may take some time, for most students it is easier than writing computer programs. The spreadsheet allows the naming of cells which enables the users to readily understand the model.

Among the variety of scientific and engineering problems that have been solved using spreadsheets, several chemical engineering applications have been reported [2–9]. Most of the papers are concerned with using the ability of the spreadsheet for entering formulas and solving simultaneous equations, using built-in solving capabilities.

In his paper on the use of spreadsheets in undergraduate thermodynamic calculations, Savage [3] has described the chemical equilibrium calculations of single chemical reactions occurring in either an ideal or non-ideal fluid phase by the stoichiometric method. The method is based on the reaction equilibrium constants. This paper will describe how the optimization feature of the spreadsheet Solver can be used to perform chemical equilibrium calculations for known substances in either an ideal or non-ideal gas phase by the method of direct Gibbs energy minimization.

METHOD

The minimization model consisting of the objective function (2) and the constraints (3), can be directly solved by using Microsoft Excel Spreadsheet's Solver feature. This feature allows the user to specify a cell or set of cells whose numerical values are to be varied such that another cell gets a specified value or optimized subject to the cells that are constrained to constant values. The Solver applies the Generalized Reduced Gradient (GRG) method to solve nonlinear programming problems.

The spreadsheet shown in Fig. 1 gives a solution to the example problem appearing in [10, 11].

The problem statement is as follows:

Calculate the equilibrium compositions at 1000 K and 1 bar (100 kPa) of a gas-phase system containing the species CH_4, H_2O, CO, CO_2, and H_2. In the initial unreacted state, there are present 2 mol of CH_4 and 3 mol of H_2O.

The problem is solved as an example in these references [10, 11] by using the Lagrange multiplier method on the model (2)–(3). To solve the problem on the spreadsheet, the user supplies the chemical identities, starting moles, temperature and pressure of the system, atomic matrix a_{ji}, critical constants (Tc, Pc, ω) and the ideal gas standard Gibbs free energy of formation of each species at T, binary interaction parameters (k_{ij}), and initial estimates of moles of components and compressibility factor (Z) of the mixture. The initial estimate for Z is unity. On the spreadsheet given in Fig. 1, the cells

	A	B	C	D	E	F	G	H	I
1		Chemical Equilibrium by Gibbs Energy Minimization (S-R-K EOS is used)							
2									
3	Starting components	CH4	H2O	CO	CO2	H2			
4	Starting moles		2	3	0	0	0		
5	T, K	1000							
6	P, bar	1		elements in the system:			C	H	O
7	R, kJmol⁻¹K⁻¹	8.31E-03		moles of elements in system (bⱼ)			2	14	3
8	RT, kJmol⁻¹	8.314							
9	Ideal gas (y/n)?		n	Use binary interaction parameters (y/n)?				y	
10									
11		CH4	H2O	CO	CO2	H2			
12	initial est.	0.180101	0.854677	1.494475	0.325424	5.785121	Σ ni		
13	ni, moles	0.180101	0.854677	1.494475	0.325424	5.785121	8.6397981		
14	yi	0.0208455	0.098923	0.172976	0.037666	0.66959		Input data	
15	ΔG°fi, kJ mol⁻¹	19.401348	-192.809	-200.235	-396.271	0			
16	Tci, K	190.55	647.15	132.8	303.95	33.3		Estimates	
17	Pci, bar	45.8	218.4	35	73	12.8			
18	ωi	0.012	0.345	0.048	0.224	-0.216		Linked	
19	ai	0.0234255	0.056662	0.014889	0.037395	0.00256	b=Σyi_bi_		
20	bi	0.0029969	0.002134	0.002733	0.002999	0.001874	0.0021141		
21	α_i	0.1267688	0.572169	0.001009	0.108638	0.167707			
22	aα_i	0.0029696	0.03242	1.5E-05	0.004063	0.000429			
23	B_i	0.0003605	0.000257	0.000329	0.000361	0.000225			
24									
25	Atomic Matrix (aⱼᵢ)								
26		CH4	H2O	CO	CO2	H2			
27	C	1	0	1	1	0			
28	H	4	2	0	0	2			
29	O	0	1	1	2	0			
30									
31	binary interaction parameters, kij:								
32		CH4	H20	CO	CO2	H2			
33	CH4	0	0	0.03	0.09	0			
34	H2O	0	0	0	0	0			
35	CO	0.03	0	0	0.3	0			
36	CO2	0.09	0	0.3	0	0			
37	H2	0	0	0	0	0			
38								Σyj_aα_ij	yiΣyj_aα_ij
39	(aα)ij:							0.0019431	4.05E-05
40		0.00296962	0.009812	0.000205	0.003161	0.001129		0.0064627	0.0006393
41		0.00981204	0.0324203	0.000698	0.011476	0.003731		0.0001362	2.356E-05
42		0.00020488	0.0006979	1.5E-05	0.000173	8.03E-05		0.0022684	8.544E-05
43		0.00316077	0.0114765	0.000173	0.004063	0.001321		0.0007437	0.000498
44		0.0011291	0.0037307	8.03E-05	0.001321	0.000429	aα = ΣΣyi*yj*(aα)ij		0.0012868
45									
46	A_	B_		Z	F(Z)		C-balance		2
47	1.8616E-05	0.0002543		1.000236	4.4E-10		H-balance		14
48							O-balance		3
49	ln φi:						Σ(niΔG°fi)		-589.4985
50	ln φ1	ln φ2	ln φ3	ln φ4	ln φ5		nRT ln P		0
51	0.00032288	8.841E-05	0.000343	0.000314	0.000222		RTΣ(ni ln yi)		-72.19839
52							RTΣ(ni ln φi)		0.0169291
53							nG		-661.68

Fig. 1. Spreadsheet solution of the chemical equilibrium problem given in [10, 11].

for input data and those for initial estimates are shown in double outlines and thick outlines, respectively. Chemical equilibrium occurring in an ideal gas phase can be so indicated. For the Gibbs energy of formation, the temperature-dependent equation $(\Delta G_f^0 = a + bT + cT^2)$, if available, can be directly entered as cell formulas to the respective cells (B15:F15). Alternatively, it can be calculated, on the same spreadsheet or a separate sheet and then linked, from the standard Gibbs energy of formation at 298 K

and the temperature-dependent equation for standard enthalpy of formation. On the spreadsheet the linked cells are shown in thick broken outlines.

The spreadsheet then uses the data to calculate the terms in the right-hand side of equation (2). The fugacity coefficient of each species in the mixture is calculated via the Soave-Redlich-Kwong (S-R-K) equation of state [12]. Finally the Gibbs function of the system, the left-hand side of equation (2), is computed.

The fugacity coefficients are calculated as follow [13]:

$$\ln \hat{\phi}_i = \frac{B_i}{B}(Z-1) - \ln(Z-B)$$

$$+ \frac{A}{B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_j y_j(a\alpha)_{ij}\right]\ln\left(1+\frac{B}{Z}\right) \quad (4)$$

where Z is given by S-R-K equation of state:

$$f(Z) = Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \quad (5)$$

The parameters A, B, B_i, $(a\alpha)_{ij}$, and $a\alpha$ of these equations are calculated by the formulas given in [13]. On the spreadsheet shown in Fig. 1, nG occupies the target cell (H53) that is to be minimized. The moles of the species and the compressibility factor occupy the set of cells (B13:F13,D47) whose values are to be varied (change cells). The constrained cells include the atomic balances of C, H and O given by (3) (H46:H48), the function of Z representing the equation of state given by (5) (E47), and the non-negativity constraints of the change cells. Because the computation involves the logarithmic function of the decision variables, the lower limits of the non-negativity constraints must not be zero.

Once these have been defined and put in the Solver Parameters dialogue, and the Use Automatic Scaling box in the Solver Options dialogue has been checked to minimize the effects of poorly scaled models, the problem can be solved. The search conditions and solution parameters, contained in the Solver Options dialogue, give control over the time, precision and structure of the solution. Once a solution has been generated, Solver permits the user to keep or reject the solution found. Additionally, Solver can create reports that summarize the sensitivity, answer and limits of the solution found.

One drawback of the current GRG spreadsheet solver, especially in solving this type of model, is that it seems to violate the non-negativity constraints. This may be due to the fact that the GRG algorithm can reach at nonfeasible points in trying to get to the optimal solution [14, 15], combined with the involvement of logarithmic functions of the variables. In order to avoid the error message generated by this deficiency of the Solver, one can use the MAX function available in Excel spreadsheet to replace the non-negativity constraints. Accordingly, the change cells for mole numbers are replaced by the cells B12:F12 labeled as Initial Estimates. The MAX function will return the positive values to B13:F13 from whatever values of B12:F12 before subsequent calculations so that the Solver can run continuously without being interrupted by the

error message. Copies of the spreadsheets, including the equations used, are available from the author.

When the Solver completion message 'Solver found a solution, all constraints and optimality conditions are satisfied' appears, it means that a locally optimal solution has been found. The solver should be run from several sets of initial estimates for the decision variables to increase the chances that the globally optimal solution has been found. For details about the GRG Solver stopping conditions and completion messages, refer to a Microsoft Excel reference manual or online help.

Although the original example contained in [10, 11] assumes the ideal gas phase because of the low pressure and high temperature, the spreadsheet model was developed to include non-ideal gas phase systems. The results are compared with the solution of the example problem and those obtained by the Fortran program developed by [1], and found to be in satisfactory agreement.

To consider the non-ideality of the mixture, the same problem for 20 bar pressure is also solved by the Solver. The results are compared with the solutions of the Fortran program [1] and the Lagrange multiplier method, and found to be in good agreement.

This approach of using Solver can be applied to solve general nonlinear programming and other problems encountered in many engineering and thermodynamic computations such as nonlinear regression, calculation of adiabatic flame temperature of reversible and irreversible reactions, entropy maximization and Gibbs energy minimization in solution thermodynamics, vapor-liquid equilibrium calculations, etc.

SUMMARY

The use of spreadsheet Solver in solving nonlinear programming problems is presented with an example of direct Gibbs energy minimization for computing the chemical equilibrium of known substances in either an ideal or non-ideal gas phase. A method to run the Solver continuously without error messages being generated due to the violation of non-negativity constraints is described. The approach is simple to understand and apply, and provides a direct solution procedure. The results are compared with those obtained by using conventional Fortran programs and found to be in good agreement.

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