

Estimation of Concentrations in Chemical Systems at Equilibrium Using Geometric Programming

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Abstract

Geometric programming is a mathematical technique, which has been developed for nonlinear optimization problems. This technique is based on the dual program with linear constraints. Determination of species concentrations in chemical equilibrium conditions is one of its applications in chemistry and chemical engineering fields. In this paper, the principles of geometric programming and its computational method are presented. Also, for a chemical equilibrium, as an example, the concentrations of species for the ammonia synthesis reaction are determined. The obtained results are compatible with the experimental data available in the literature. This leads to the application of the geometric programming to estimate the concentrations in the equilibrium conditions for reactions where the experimental data are not available.

Keywords

Chemical equilibrium;
Gibbs free Energy;
Mathematical modeling;
Optimization.

1. Introduction

Nowadays, optimization models and operation research methods have been extensively used in solving many real and complex problems in almost all aspects of science and engineering. Operations research methods deal with the assignment of limited resources to competitor activities to achieve some pre-defined goals in different areas such as economics, business, industry, and health care. Geometric Programming (GP) is a technique developed for solv-

ing algebraic nonlinear programming problems subject to nonlinear constraints. This technique was first proposed in 1961 by Zener, a director of science at Westinghouse Corporation. He discovered that many engineering design problems consisting of a sum of component costs could sometimes be minimized under suitable conditions [1]. The original mathematical development of the method used the arithmetic-geometric mean inequality relationship between sums and products of positive numbers. In exact words, minimizing a posynomial¹ function subject to posynomial ine-

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¹A posynomial is a function of the form:

$$f(x_1, x_2, \dots, x_n) = \sum_{k=1}^K c_k x_1^{a_{1k}} \dots x_n^{a_{nk}}$$

quality constraints and monomial equality constraints is called a geometric program in standard form [2].

Solving the dual problem with the linear constraints, instead of the primal nonlinear problem with nonlinear constraints, is the preference of the GP, which has revealed its vast applications in many engineering design problems. The GP has been applied for the chemical equilibrium condition in engineering design applications [3]. There are two major approaches to determining the composition of a chemical system at equilibrium: the thermodynamic and the kinetic approach. The thermodynamic approach is based on the idea that at equilibrium, the chemical system achieves the state of minimum free energy with these constraints at which mass cannot be created or destroyed in a chemical reaction and charge balance must be conserved. The kinetic approach focuses on two kinds of reactions taking place in any chemical system. One type of reaction involves the conversion of reactants into products, and the other involves the conversion of products into reactants. Chemical equilibrium can be defined as the condition under which the rates of production and consumption of any component in the equilibrium are equal, i.e., the composition of the overall chemical system is no longer changing with time. Selection of chemical reaction conditions is important in chemical industries in order to design the process systems and to determine the amount of the interfered materials (and undesirable by-products) in the reactions at the equilibrium situation. Gibbs free Energy is an appropriate thermodynamical function used to illustrate the equilibrium conditions at constant temperature and pressure [4]. The definition of Gibbs free Energy (G) is:

$$G = U + PV - TS \quad (1)$$

where U is internal energy, P is pressure, V is volume, T is temperature, and S is entropy. In conventional methods, the equilibrium constant has to be known for estimation of the composition of a chemical equilibrium system. The computation is based on solving a set of nonlinear equations corresponding to thermodynamical conditions, and mass and energy balances. The equilibrium

constant is calculated using Eq. (2), where constants α , β , γ , and I must be found through expensive and time-consuming experiments [4]:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\alpha}{R} \ln T + \frac{\beta}{2R} T + \frac{\gamma}{6R} T^2 + I \quad (2)$$

White et al. [5] calculated the equilibrium concentration in ideal gas phase using the minimization of Gibbs free Energy method. They converted the logarithmic form for Gibbs free Energy of system into a quadratic function using the Taylor expansion method. Akbari et al. [6] studied the equilibrium chemical reactions taking place in a converter reactor of the KHORASAN Petrochemical Ammonia plant using the minimization of Gibbs free Energy method by the Davidon-Fletcher-Powell optimization procedure and the penalty terms.

Traditional methods of computing equilibrium compositions involve the simultaneous solutions to the appropriate set of equations, including the physical equilibrium equations. Recently, new methods, such as computer simulation, element balance approach, or, in a more systematic way, building a residue curve map, have been reported for solving the chemical equilibrium problem, including the simultaneous determination of both physical and chemical equilibrium. New algorithms for the computation of the simultaneous chemical and physical equilibrium involve simulations of reactive flash operations and the calculations of phase diagrams [7].

Meta-heuristic methods have also been applied in phase stability and equilibrium calculations for global minimization of the tangent plane distance function and the Gibbs Energy function. Bonilla and Segovia [8] showed the effectiveness of the classical particle swarm optimization and Tabu search methods for the equilibrium calculations in multi-component reactive and non-reactive systems.

This paper presents a theoretical method for determining species concentrations at chemical equilibrium conditions and only one-phase reaction. It is based on the application of geometric programming principles to solve the corresponding systems of nonlinear equations.

where all the coordinates x_i and coefficients c_k are positive real numbers, and the exponents a_{ik} are real numbers. Posynomials are closed under addition, multiplication, and nonnegative scaling.

2. Geometric Programming

The basic approach in GP modeling is to express a practical problem, such as an engineering analysis or design problem, in GP format. In the best case, this formulation is precise; when this is not possible, we settle for an approximate formulation. The general form of GP is [9]:

$$\text{Minimize } y_0(x) = \sum_{l=1}^{L_0} \sigma_{0l} C_{0l} \prod_{n=1}^N x_n^{a_{0n}} \quad (3)$$

$$\text{s.t. } y_m(x) = \sum_{l=1}^{L_m} \sigma_{ml} C_{ml} \prod_{n=1}^N x_n^{a_{mn}} \leq \delta_m, \quad m=1,2,\dots,M \quad (4)$$

$$x_n > 0, \quad n = 1, 2, \dots, N$$

where,

$$c_{0l} > 0, \quad c_{ml} > 0, \quad \delta_m = \pm 1, \quad \sigma_{0l} = \pm 1, \quad \sigma_{ml} = \pm 1.$$

L_m is the number of the terms in the m^{th} constraint and L_0 is the number of terms in the objective function. In engineering of expensive and time-consuming experiments design formulations, C_{ml} is called the economic coefficient (representing the effect of each decision on objective or constraints terms), x_n is a design decision variable, and a_{mn} is a technological exponent of the design variables. If all σ s are positive, the program is called a posynomial GP as:

$$y = y(x) = \sum C_l p_l(x) \quad (5)$$

with:

$$p_l(x) = \prod_{n=1}^N x_n^{a_{ln}} \quad (6)$$

If we define:

$$w_l = \frac{C_l p_l(x^*)}{y^*} \quad (7)$$

then, y^* will be determined [1] as:

$$y^* = \prod_{l=1}^L \left(\frac{C_l}{w_l} \right)^{w_l} \quad (8)$$

The conditions $\sum_{l=1}^L w_l = 1$ and $\sum_{l=1}^L a_{ln} w_l = 0$ are called the normality conditions and the orthogonality conditions, respectively. They are valid for W_l . Given C_l and optimal W_l , y^* can be determined.

The optimization problem (3)-(4) (and (5)) is reduced to find the optimal values of W_l . The above conditions are a system containing $N+1$ equations and L variables. The posynomial function is defined as:

$$y = \sum_{l=1}^L w_l \left(\frac{C_l p_l}{w_l} \right) \quad (9)$$

Using the arithmetic-geometric mean inequality and orthogonality conditions results in:

$$\sum_{l=1}^L C_l p_l \geq \prod_{l=1}^L \left(\frac{C_l}{w_l} \right)^{w_l} \quad (10)$$

where, W_l is the dual variable and the right-hand side term is called the dual function. In GP, the optimal values of W_l are obtained first. Then, their corresponding dual objective values are calculated, which are equal to the primal objective values. Finally, the optimal values of X_n are obtained according to Eqs. (5) and (6).

The degree of difficulty is defined as $L-(N+1)$, where L is the number of terms in all concerned posynomials and N is the number of independent variables. If the problem has zero degree of difficulty, then its unique optimal solution is determined by solving a system of linear equations. Determining the optimal solution becomes harder as the degree of difficulty increases. There are many practical engineering design problems with low degrees of difficulty, although considering the normality and orthogonality conditions reveals some useful properties.

3. Ammonia Reaction and its GP Model

It has been revealed that there are similarities between Gibbs free Energy and the GP dual objective functions [10]. Duffin et al. pointed out that the theory of GP proves properties of chemical systems. On the other hand, the chemical model suggests lines of research in mathematical programming [11]. To bring out the significant correspondence between chemical equilibrium theory and GP, they considered the equilibrium state of a homogeneous mixture of hydrogen, iodine, and hydriodic acid, all in gaseous state, and presented the associated GP.

Now, consider the chemical reaction for production of ammonia as $3H_2 + N_2 \rightleftharpoons 2NH_3$ in gaseous state. Gibbs free Energy function is:

$$G = G(T, P, \delta_2, \delta_3, \delta_4) \quad (11)$$

where δ_2 , δ_3 , and δ_4 are the mole numbers of hydrogen, nitrogen, and ammonia, respectively. To get an explicit form for the function G , it is assumed that the pressure P is sufficiently low so that the gas components obey the perfect gas law, $PV = RT$. Gibbs free Energy for a simple substance satisfies the relation:

$$dG = VdP - SdT \quad (12)$$

where S is entropy. In particular, for one mole of a perfect gas:

$$\left(\frac{\partial G}{\partial P}\right)_T = V = \frac{RT}{P} \quad (13)$$

Integration of this differential equation gives:

$$G = RT \ln P + G^0 \quad (14)$$

where G^0 is Gibbs free Energy per mole at temperature T and 1atm of pressure. Different gases have different values for G^0 and it is important in experimental chemistry to evaluate these values.

According to Dalton law for partial pressures, P_t can be calculated from the following equation:

$$P_t = \sum_{i=1}^n P_i = P_1 + P_2 + P_3 + \dots \quad (15)$$

where P_t is the total pressure and P_i is the partial pressure of each gas. Therefore, P_i can be calculated based on the portion of concentration i as follows:

$$P_i = \frac{\delta_i}{\delta_2 + \delta_3 + \delta_4} \times P_t, \quad i=2,3,4 \quad (16)$$

or, from Eq. (14), and getting the summation on the elements i , we have:

$$\frac{G}{RT} = \sum \delta_i \left(\ln P_i + \frac{G_i^0}{RT} \right) \quad (17)$$

Then, substituting P_i from Eq. (16) and defining $\lambda = \delta_2 + \delta_3 + \delta_4$ result in:

$$\frac{G}{RT} = \sum \delta_i (C_i + \ln \delta_i) - \lambda \ln \lambda \quad (18)$$

where, $C_i = \frac{G_i^0}{RT} + \ln P_t$. Let A be Avogadro number, then Ae_1 is the number of Hydrogen atoms and Ae_2 is the number of nitrogen atoms. The mass balance equations are:

$$\left. \begin{aligned} 2\delta_2 + 3\delta_4 &= e_1 \\ 2\delta_3 + \delta_4 &= e_2 \\ \delta_2, \delta_3, \delta_4 &\geq 0 \end{aligned} \right\} \quad (19)$$

According to Gibbs variational principle, the equilibrium values of $\delta_2, \delta_3, \delta_4$ are obtained by minimizing $G(\delta_2, \delta_3, \delta_4)$ subject to constraint (19). Clearly, the values of $\delta_2, \delta_3, \delta_4$ are calculated equally by maximizing the following function [10]:

$$v_1 = e^{-G/RT} = \prod_{i=2}^4 \left(\frac{c_i}{\delta_i} \right)^{\delta_i} \lambda^\lambda \quad (20)$$

in which $c_i = e^{-C_i}$, $i=2,3,4$. To maximize v_1 , let a function v be defined as:

$$v = \prod_{i=1}^4 \left(\frac{c_i}{\delta_i} \right)^{\delta_i} \lambda^\lambda \quad (21)$$

where $c_1 = 1$. Consider the dual geometric program that requires maximizing $v(\delta)$ subject to the following (normality and orthogonality) constraints [10, 11]:

$$\left. \begin{aligned} \delta_1 &= 1 \\ -e_1\delta_1 + 2\delta_2 + 3\delta_4 &= 0 \\ -e_2\delta_1 + 2\delta_3 + \delta_4 &= 0 \\ \delta_i &\geq 0 \quad i=1,2,3,4 \end{aligned} \right\} \quad (22)$$

Since $\delta_1 = 1$, it follows that $v = v_1$, and that the orthogonality constraints are same as the mass balance in Eq. (19). Thus, the equilibrium mole numbers can be found by solving the dual GP (21)-(22) [12]. Also, Gibbs free Energy function at equilibrium is $G = -RT \ln v$ and corresponding primal program is [11]:

$$\min \quad g_0(t) = t_1^{-e_1} t_2^{-e_2} \quad (23)$$

$$\text{s.t.} \quad g_1(t) = c_2 t_1^2 + c_3 t_2^2 + c_4 t_1 t_2 \leq 1$$

$$t_1 > 0 \quad t_2 > 0$$

The geometric mean inequality is:

$$\ln v(\delta) \leq -\frac{G}{RT} \leq \ln g_0(t) \quad (24)$$

where G is the equilibrium free energy. If $(\delta_1, \delta_2, \delta_3, \delta_4)$ solves the dual program and (t_1, t_2) solves the primal program, then Eq. (24) is an equality. Moreover, from conditions for equality of the geometric mean inequality, it is known that:

$$\left. \begin{aligned} \varepsilon_2 &= \frac{\delta_2}{\lambda} = c_2 t_1^2 \\ \varepsilon_3 &= \frac{\delta_3}{\lambda} = c_3 t_2^2 \\ \varepsilon_4 &= \frac{\delta_4}{\lambda} = c_4 t_1 t_2 \end{aligned} \right\} \quad (25)$$

where $\varepsilon_2, \varepsilon_3$, and ε_4 are the equilibrium mole fractions and give the relative composition of the equilibrium mixture.

4. Computational Results

In practice, the ammonia reaction occurs at a high pressure (300 atm) and at high temperatures (450-500 °C). To solve the chemical equilibrium optimization problem more appropriately, the mixture is assumed to be ideal. Let the reaction conditions be at the temperature of 200°C and the pressure of 100 atm. Gibbs free energy of each component for the given enthalpy and entropy was extracted from [12]. The GP dual problem is:

$$\text{Max } v = \left(\frac{1}{\delta_1}\right)^{\delta_1} \left(\frac{0.015}{\delta_2}\right)^{\delta_2} \left(\frac{0.016}{\delta_3}\right)^{\delta_3} \left(\frac{0.017}{\delta_4}\right)^{\delta_4} \lambda^2$$

s.t.

$$\left. \begin{aligned} \delta_1 &= 1 \\ -e_1 \delta_1 + 2\delta_2 &+ 3\delta_4 = 0 \\ -e_2 \delta_1 &+ 2\delta_3 + \delta_4 = 0 \\ \delta_i &\geq 0 \quad i=1,2,3,4 \end{aligned} \right\}$$

It is observed that the system of equations has 3 equations and 4 variables and, hence, its degree of difficulty is one. Letting $\delta_4 = r$ gives:

$$\begin{cases} 2\delta_2 + 3r = e_1 \\ 2\delta_3 + r = e_2 \end{cases}$$

If we assume that there is one mole of nitrogen for each 3 moles of hydrogen at first, then:

$$\delta_2 = \frac{3-3r}{2}, \delta_3 = \frac{1-r}{2}, \delta_4 = r$$

Since $0 \leq r \leq 1$, direct search procedure as suggested in Fig. 1, $r = 0.898$ is chosen and $\delta_2 = 0.153, \delta_3 = 0.051, \delta_4 = 0.898$, and $\lambda = 1.102$. The dual function is $v = 0.02086$ and $\frac{G}{RT} = 3.868$. Solving the system

$$\left. \begin{aligned} \varepsilon_2 &= \frac{0.153}{1.102} = 0.13875 = 0.015 t_1^2 \\ \varepsilon_3 &= \frac{0.051}{1.102} = 0.04625 = 0.016 t_2^2 \\ \varepsilon_4 &= \frac{0.898}{1.102} = 0.815 = 0.017 t_1 t_2 \end{aligned} \right\}$$

gives: $t_1 = 3.0414$ and $t_2 = 1.7002$. Then, we have

$$g_0(t) = 0.0209 \quad \text{and} \quad -3.8699 \leq -\frac{G}{RT} \leq -3.8677$$

Since $\frac{G}{RT} = 3.868$, the difference would be less than 0.05%.

Finally, the mole fractions will be:

$$\left. \begin{aligned} \varepsilon_2 &= \varepsilon_{H_2} = 0.13875 \\ \varepsilon_3 &= \varepsilon_{N_2} = 0.04625 \\ \varepsilon_4 &= \varepsilon_{NH_3} = 0.815 \end{aligned} \right\}$$

These results are compatible with the experimental results obtained from Fig. 2. The compatibility of the results proposes the application of the GP to determine the concentrations at the equilibrium condition for the reactions where the experimental data are not available.

5. Discussion

For the reaction which has been studied in this paper, it is observed that the concentration of ammonia is very low at the pressure of 1atm. It

will increase as the pressure increases; in the pressure of 100atm and temperature of 200 °C, its concentration becomes 80%. This verifies the value calculated by the proposed method, i.e., 81.5%. This reaction is simple but important enough to be considered for further research from this point of view. On the other hand, the main contribution of this work is extending a previous application of GP in chemistry. Previous works were on a simpler reaction, which was equi-molar (hydriodic acid), whereas the selected reaction for this research is different in the number of the molecularity of the reactant in the reaction. The objective of this work is to use GP as a tool for the optimization problem in chemistry and to advertise for it. The comparison has been done to validate the application, although the method theoretically finds the optimal solution; but, in the case of application in some chemical reaction concentrations, there is some kind of approximation sub-procedure in the related system of equations. Considering high cost of the experimental method, the accuracy of the result is encouraging enough to study other reactions to find out a suitable domain for the application of GP.

1. Choose an arbitrary value $0 \leq r \leq 1$,
2. Compute δ_i and then $\nu(\delta)$,
3. Compute the mole fractions \mathcal{E}_i and the value of t_i and then $g_0(t)$,
4. Compute the difference between primal and dual objective functions using the geometric mean inequality,
5. If the difference is small enough, then stop, compute the Gibbs free energy and the mole fractions,
6. Otherwise, improve the value of r and then go back to 2.

Figure 1. Direct Search algorithm for finding the mole fractions

6. Conclusion

Geometric programming provides a systematic method for formulating a class of nonlinear optimization problems in engineering design, which generally involves nonconvex functions. The method always produces a global minimum [12]. The minimum of the primal objective function is

equal to the maximum of a corresponding dual problem whose constraints are linear. If the primal problem has zero degree of difficulty, the solution to the dual problem is obtained by solving a system of linear equations. If the problem has a degree of difficulty greater than zero, the corresponding system of linear equations has no single solution, but can be solved in terms of basic variables. The dual problem can then be reformulated in terms of the basic variables, with the linear constraints, that is easier to solve rather than the primal problem with nonlinear constraints. Indeed, each value of the dual function provides a lower bound on the minimum value of the primal function and their optimal values are equal, which lead to finding the optimal values for the variables [15].

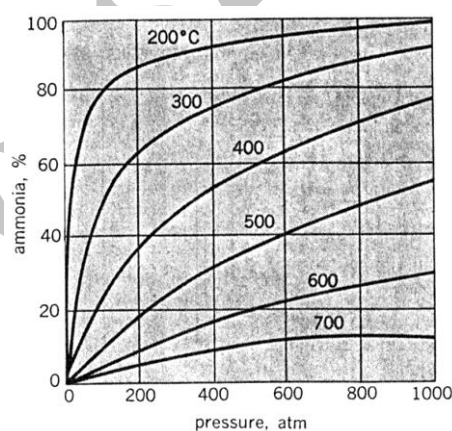


Figure 2. The effects of the temperature and pressure on the Ammonia reaction [14]

Applying GP to determine the concentration of the components in a chemical reaction seems to be more appropriate than the usual experimental methods in Eq. (2). Since the proposed method does not need the experimental data for determining the equilibrium constant K , it only requires some thermodynamical data, such as the standard reaction's heat and the change in the Gibbs Energy. The usual experimental measurement methods are hard, time-consuming, and costly.

It is necessary to note that GP model is based on Eqs. (13) and (14), which is applicable to ideal gases (in low pressure). To be more precise, it is recommended to substitute P in the equations with f , which is the fugacity [13], $dG_i = RT \ln f_i$. Fu-

gacity is the attribute which is used instead of pressure in nonideal cases. There are different ways to determine the fugacity factor based on the other known properties of gases [14]. The multipliers of primal and dual functions will be corrected, accordingly. But, this may cause a higher degree of difficulty and, therefore, the solving procedure becomes more complex. The method proposed in this paper is more suitable for determining the concentrations in equilibrium for those reactions where the experimental data are not available, especially when the degree of difficulty is zero or one. On the other hand, several industrial processes involve reactive systems with several phases. Formulating the physical equilibrium conditions as additional constraints to the set of models (21)-(22) and further research are required to extend the method for the modeling of simultaneous chemical and phase equilibrium problem. It is proposed for future studies to select an actual gas for the estimation of concentrations in chemical systems at equilibrium using geometric programming.

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