Analytical Calculation of Equilibrium Gas Composition in a C-H-O-Inert System

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Various industrial processes and devices, such as combustion, gasification, and fuel cells, often involve carbon-hydrogen-oxygen-inert (CHOI) systems; species, chemically inactive under the conditions of interest, e.g., nitrogen and helium, are collectively defined as inert. This work presents an analytic method for calculating the equilibrium gas composition of a heterogeneous CHOI system with carbon as the solid phase. Although equilibrium is rarely achieved in practice, the equilibrium composition of a CHOI system serves as an important benchmark for the design of industrial processes involving CHOI systems.

While a great deal of research effort has been spent on it, the calculation of the equilibrium composition for a CHOI system still remains a tedious and time consuming task. Of the two major approaches available, one resorts to minimization of free energy, and the other to the numerical solution of the simultaneous mass balance and equilibrium equations. Mohnot and Kyle (1978) have employed the former, for temperatures ranging from 500 to 1,500 K, pressures ranging from 1 to 25 atm, and nitrogen-to-oxygen (N/O) atom ratios ranging from 0 to 20. Cairns and Tevebaugh (1964) have employed the latter (without an inert species) over the temperature range from 298 to 1,500 K, at a pressure of 1 atm. Baron et al. (1976) have also employed the latter, for temperatures ranging from 297.8 to 1,644.4 K, pressures ranging from 1 to 100 atm, and hydrogen-to-oxygen (H/O) atom ratios ranging from 1 to 3. Their work has also included equilibrium in the presence of nitrogen at a H/O atom ratio of unity.

All prior methods have resorted to numerical solution, in which stability and convergence problems are often involved. The present method employs an analytic scheme to solve the simultaneous mass balance and equilibrium equations. The computing time is drastically reduced and the ease of application is greatly enhanced, as compared to prior methods.

Thermodynamic Considerations

The chemical species present in significant amounts (e.g., greater than a molar fraction of 10^{-5}) in a heterogeneous CHO system under equilibrium are carbon, hydrogen, water, carbon dioxide, carbon monoxide, and methane, for a temperature range of 298 to 1,500 K, and a pressure range of 1 to 100 atm (Cairns and Tevebaugh, 1964; Baron et al., 1976). Three independent chemical reactions, collectively involving all these chemical species, are necessary and sufficient to describe the system's chemical behavior. The following reactions are employed (see, e.g., Cairns and Tevebaugh, 1964):

$$C + 2H_2 = CH_4 \tag{1}$$

$$C + CO_2 = 2CO \tag{2}$$

$$C + H_2O = CO + H_2 \tag{3}$$

Note that the elimination of carbon from Eqs. 2 and 3 gives rise to the homogeneous water-gas shift reaction. If ideal gas behavior is assumed, the equilibrium constants for these reactions, which are functions of temperature, can be expressed as:

$$K_1 = y_{CH_4}/(y_{H_2}^2 P) \tag{4}$$

$$K_2 = P y_{CO}^2 / y_{CO_2} \tag{5}$$

$$K_3 = y_{CO} y_{H_2} P / y_{H_2O} \tag{6}$$

where P is the total pressure, and y_i, the molar fraction of species, i. By definition, the fractions of all species *in the gas phase* have a sum of unity, i.e.,

$$y_{H_2} + y_{H_2O} + y_{CO} + y_{CO_2} + y_{CH_4} + y_{N_2} = 1 \tag{7}$$

The presence of an inert species, in this case N_2, does not affect

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the chemical behavior of the system (see, e.g., Mohnot, 1977).

Applying the phase rule:

$$\begin{aligned} F = {} & \text{number of chemical species} \\ & - \text{number of independent reactions} \\ & - \text{number of stoichiometric constraints} \\ & + 2 - \text{number of phases} \end{aligned}$$

to the system under consideration yields a degree of freedom, F, of four for the heterogeneous CHOI system containing an inert gas. The present case involves no stoichiometric constraints. Therefore, four independent constraints need be specified to fully define the present heterogeneous CHOI system. While the choice of these constraints is entirely arbitrary, those chosen here are temperature, total pressure, H/O atom ratio, and N/O atom ratio. The two atom ratios are designated as a and b, respectively. Thus,

$$(2y_{H_2} + 2y_{H_2O} + 4y_{CH_4})/(y_{H_2O} + y_{CO} + 2y_{CO_2}) = H/O = a \qquad (8)$$

$$2y_{N_2}/(y_{H_2O} + y_{CO} + 2y_{CO_2}) = N/O = b \qquad (9)$$

Mathematical Derivations

Equations 4 through 9 are the six fundamental equations to be solved for the equilibrium compositions. With T, P, a, and b given, the six unknowns remaining are: y_{H_2}, y_{H_2O}, y_{CO}, y_{CO_2}, y_{CH_4}, and y_{N_2}. An analytic scheme, developed to solve this set of coupled nonlinear algebraic equations, is delineated below.

The first step is to reduce the six equations into two equations in terms of two unknowns. Let

$$X = y_{H_2} \qquad (10)$$

$$Y = y_{CO} \qquad (11)$$

Then, y_{CH_4}, y_{CO_2}, and y_{H_2O} are expressed in terms of X and Y. By letting

$$k_1 = K_1P \qquad (12)$$

we have, from Eq. 4,

$$y_{CH_4} = (K_1P)y_{H_2}^2 = k_1X^2 \qquad (13)$$

Similarly, by defining

$$k_2 = P/K_2 \qquad (14)$$

we have, from Eq. 5,

$$y_{CO_2} = (P/K_2)y_{CO}^2 = k_2Y^2 \qquad (15)$$

and by defining

$$k_3 = P/K_3 \qquad (16)$$

we have, from Eq. 6,

$$y_{H_2O} = (P/K_3)y_{H_2}y_{CO} = k_3XY \qquad (17)$$

Then, eliminating y_{N_2} from Eq. 7 by using Eq. 9, and rewriting the resultant expression in terms of X and Y, gives

$$k_1X^2 + (1 + b/2)k_3XY + (1 + b)k_2Y^2 + X + (1 + b/2)Y = 1 \qquad (18)$$

Also, rewriting Eq. 8 in terms of X and Y leads to

$$4k_1X^2 + (2 - a)k_3XY - 2ak_2Y^2 + 2X - aY = 0 \qquad (19)$$

The problem becomes one of solving a pair of simultaneous conical equations, Eqs. 18 and 19, for the two unknowns, X and Y.

The second step is to reduce the two equations into a single fourth-order polynomial equation. Eliminating the XY term from Eq. 18 by resorting to Eq. 19 yields

$$a_1X^2 + c_1Y^2 + d_1X + e_1Y + f_1 = 0 \qquad (20)$$

where

$$a_1 = k_1 \qquad (21)$$

$$c_1 = -k_2 \qquad (22)$$

$$d_1 = (a + b)/(a + 2b + 2) \qquad (23)$$

$$e_1 = -(b + 2)/(a + 2b + 2) \qquad (24)$$

$$f_1 = (-a + 2)/(a + 2b + 2) \qquad (25)$$

Then, eliminating the Y^2 term from Eq. 19 by using Eq. 20 gives

$$a_2X^2 + b_2XY + d_2X + e_2Y + f_2 = 0 \qquad (26)$$

where

$$a_2 = k_1 \qquad (27)$$

$$b_2 = 0.5k_3 \qquad (28)$$

$$d_2 = (a + b + 1)/(a + 2b + 2) \qquad (29)$$

$$e_2 = 0.5a/(a + 2b + 2) \qquad (30)$$

$$f_2 = -a/(a + 2b + 2) \qquad (31)$$

Elimination of the first-order terms from Eq. 20 is accomplished through a translation of the coordinates. Let

$$X' = X - h \qquad (32)$$

$$Y' = Y - k \qquad (33)$$

where

$$h = -d_1/2a_1 \qquad (34)$$

$$k = -e_1/2c_1 \tag{35}$$

Consequently, expressing Eqs. 20 and 26 in terms of X' and Y' gives, respectively,

$$a_1X'^2 + c_1Y'^2 + f'_1 = 0 \tag{36}$$

and

$$a_2X'^2 + b_2X'Y' + d'_2X' + e'_2Y' + f'_2 = 0 \tag{37}$$

where

$$f'_1 = a_1h^2 + c_1k^2 + d_1h + e_1k + f_1 \tag{38}$$

$$d'_2 = 2a_2h + b_2k + d_2 \tag{39}$$

$$e'_2 = b_2h + e_2 \tag{40}$$

$$f'_2 = a_2h^2 + b_2hk + d_2h + e_2k + f_2 \tag{41}$$

Writing Y' in terms of X' via Eq. 36, and substituting the resultant expression into Eq. 37, gives rise to the following fourth-order polynomial equation:

$$X'^4 + g_3X'^3 + g_2X'^2 + g_1X' + g_0 = 0 \tag{42}$$

where

$$g_3 = (2c_1a_2d'_2 + 2a_1b_2e'_2)/m \tag{43}$$

$$g_2 = (c_1d'^2_2 + 2c_1a_2f'_2 + a_1e'^2_2 + f'_1b^2_2)/m \tag{44}$$

$$g_1 = (2c_1d'_2f'_2 + 2f'_1b_2e'_2)/m \tag{45}$$

$$g_0 = (c_1f'^2_2 + f'_1e'^2_2)/m \tag{46}$$

$$m = c_1a^2_2 + a_1b^2_2 \tag{47}$$

Equation 42, a fourth-order polynomial equation with real coefficients, can be solved analytically (see, e.g., Mishina and Proskuryakov, 1965). Of the four roots of Eq. 42, the only physically feasible solution can be located by the constraint that molar fractions of all gas species lie between zero and one.

Implementation and Comparison

The present method has been extensively tested against some prior methods. Nearly 4,000 sets of solutions have been obtained and found to be in exact agreement with the corresponding values generated by Mohnot (1977), through free energy minimization, over the range of 500 to 1,500 K, 1 to 25 atm, 0.1 to 100 for H/O, and 0 to 20 for N/O. In our calculations, we adopted the same equilibrium constants (Zwolinski et al., 1960) used by Mohnot in this verification. The "exact agreement" implies that both solutions agree to 5 decimal places. Also, 84 sets of solutions have been produced and found to be in good agreement with the corresponding values from Cairns and Tevebaugh (1964), obtained by numerical solution at 1 atm, for temperatures ranging from 298 to 1,500 K. Equilibrium constants are slightly different for this comparison, due to different sources of data.

Comparison of the computational speeds has also been made for the following methods:

1. The present analytic method (for which a Fortran77 program is available as supplementary material)
2. Numerical solution of Eq. 42
3. Cairns and Tevebaugh's (1964) method
4. Mohnot and Kyle's (1978) method.

Computer programs were written for these methods and were run on the same computer, using the same compiler. It has been found that method 1 is approximately six times as fast as method 2, 30 times as fast as method 3, and 80 times as fast as method 4. The present method is capable of producing more than 200 sets of solutions per second on an NAS-6630 mainframe computer (an IBM-370 equivalent).

Theoretically, accuracy of the solution can be as high as needed. To achieve this, high precision must be maintained in all steps of computation. As a rule of thumb, double precision (14 significant digits) is required in all computational steps to achieve a five-significant-digit accuracy for the solution.

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