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A NEW MATHEMATICAL METHOD FOR THE SOLUTION OF GAS-GAS EQUILIBRIA WITH SPECIAL APPLICATION TO HTGR PRIMARY-COOLANT ENVIRONMENTS

by
Karl Bongartz

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**Prepared under
Contract DE-AT03-76ET35301
for the San Francisco Operations Office
Department of Energy**

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JULY 1983

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***Visiting Scientist, Kernforschungsanlage (Nuclear Research Center), Jülich, West Germany.**

**GA PROJECT 7400
JULY 1983**

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ABSTRACT

A new mathematical method and corresponding computer program have been developed that provide a general method for the numerical solution of an equilibrium problem involving the chemical interactions of gaseous species. The method and computer code were developed to calculate the equilibrium concentrations of impurity gases, such as CO, CO₂, H₂, H₂O, CH₄, and O₂, which may be approached as the result of gaseous chemical reactions occurring within the hot primary coolant helium of a high-temperature gas-cooled reactor (HTGR). The method, however, can be applied to any gas mixture.

The technique developed is based on the solution of several independent equilibrium equations, each corresponding to a chemical equation relating the interaction of gaseous species, and associated with an equilibrium constant or product, and several equations associated with conservation of mass. The equilibrium equations are linearized by means of a Taylor expansion. The resulting system of linear equations is then solved by iteration. An initial guess for the individual impurity concentrations has to be made in order to start the iteration. This implies one fundamental problem: the guess has to be chosen appropriately so that it is already in the range of the desired solution in order to achieve convergence of the iterations. In order to avoid this difficulty, a new method was developed, the main feature of which is the construction of an artificial solution that serves as an initial guess to start the iterations. This solution is constructed by inserting the initial concentrations into the equilibrium product equations (equilibrium constants, K_p). This yields fictitious values for the equilibrium constants, K_p . Together with these K_p 's, the initial concentrations are a solution to the mathematical problem even though not yet at the K_p values given. The K_p 's are then varied in small increments between the fictitious values for which the solution already exists and those given for which the solution is desired. After each increment, a new set of concentrations is calculated by iteration using the previous solution as a guess.

The new model and computer code are described in detail. To test the applicability and correctness of the method, it was applied to recalculate the equilibrium gas compositions of various high-temperature, mixed gas, metal corrosion test environments that have been previously calculated by other authors with different methods. The results were in exact agreement. Especially significant features, such as the strong influence of the initial water and oxygen content on the carbon activity and oxygen potential at equilibrium, become clear.

It should be emphasized that in practical applications such as the helium primary coolant of an HTGR, where coolant flow rates, by design, are very high, and in controlled-impurity helium corrosion experiments simulating an HTGR environment, in which helium flow rates are deliberately maintained at high levels to minimize changes in gas composition via depletion effects, gas-gas interactions, etc., equilibrium conditions will not prevail. The numerical solution to any particular gas equilibrium problem, therefore, represents a condition which may, more than likely, only be approached in actual operating gas environments such as those identified above.

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1. INTRODUCTION

The high-temperature gas-cooled reactor (HTGR) uses graphite as a moderator and helium as a primary coolant at temperatures approaching $\sim 800^{\circ}\text{C}$ (1472°F). Helium, which is itself chemically inert, is contaminated during its circulation through the reactor with small amounts of H_2 , H_2O , CO , CO_2 , CH_4 , and O_2 . These impurities arise from a variety of sources, including outgassing of internal components, inleakage of impurities (e.g., H_2O), and subsequent reaction with the graphite core, etc.

The internal structural materials of the reactor are exposed to this impure helium at elevated temperatures, producing corrosion effects that can degrade the long-term structural integrity or properties of the materials. It has been, therefore, the scope of many investigations to quantitatively determine these effects in order that such degradation in properties can be factored into component design. Tests for this purpose have involved the exposure of alloys at elevated temperatures in helium containing impurities at concentrations simulating the primary coolant environment of an operating HTGR.

Previous studies have shown that oxidation and carburization can occur, depending upon alloy chemistry, helium chemistry, and exposure temperature. Carburization has been identified as the key concern for metallic structural materials. This phenomenon, although produced via interaction between the metal surfaces and the carbon-bearing impurities (e.g., CO , CH_4) in the helium, is strongly affected by oxygen-bearing species such as CO_2 and H_2O . Thus, both carbon and oxygen potentials in the gas are important parameters with regard to material behavior. In general, experimental test gases for studies of the helium compatibility of candidate materials are prepared at room temperature. As chemical reactions, which are temperature dependent, can take place at the test temperature, the gas composition may change. In

the limit of chemical reactivity, the gas composition may approach the state of thermodynamic equilibrium, i.e., constant carbon and oxygen potential. It is in this latter context that the following method for calculating the equilibrium concentrations of gaseous impurities in a helium environment was derived.

2. THE MATHEMATICAL PROBLEM

2.1. THE EQUILIBRIUM REACTIONS OF THE GASES

The gas mixture considered herein is helium containing small and initially specified amounts of H_2 , H_2O , CO , CO_2 , CH_4 , and O_2 , consistent with that contained in an HTGR primary coolant. We will consider the interaction of the various gaseous impurities in this gas mixture using the principles of thermodynamic equilibrium first used by Darken and Gurry (Ref. 1) in their now classic treatment of a similar mixture of gases.

For the system of gases to be treated, several equilibria and corresponding equilibrium constants, K_P , have been chosen, as follows:

K_{P1} , K_{P2} , K_{P3} , and K_{P4} are the equilibrium constants, and P_{H_2O} , P_{H_2} , P_{CH_4} , P_{CO} , P_{CO_2} , and P_{O_2} are the partial pressures of water vapor, hydrogen, methane, carbon monoxide, carbon dioxide and oxygen, respectively. The

activity of carbon is a_C . There are other reactions that occur, but those quoted above suffice to define the problem.

2.2. THE CONSERVATION OF THE GRAM ATOMS OF OXYGEN $\bar{O}$, HYDROGEN $\bar{H}$, AND CARBON $\bar{C}$

The number of gram atoms of each element in the mixture, oxygen $\bar{O}$, hydrogen $\bar{H}$, and carbon $\bar{C}$, is independent of the distribution of concentrations for the individual impurity species. If n_i° denotes the initial molar concentration and n_i the equilibrium concentration at the temperature in question, we have, for mass conservation,

$$\begin{aligned}\bar{O} &= n_{CO}^\circ + 2n_{CO_2}^\circ + n_{H_2O}^\circ + 2n_{O_2}^\circ \\ &= n_{CO} + 2n_{CO_2} + n_{H_2O} + 2n_{O_2}\end{aligned}\quad (2-5)$$

$$\begin{aligned}\bar{H} &= 2n_{H_2}^\circ + 2n_{H_2O}^\circ + 4n_{CH_4}^\circ \\ &= 2n_{H_2} + 2n_{H_2O} + 4n_{CH_4}\end{aligned}\quad (2-6)$$

$$\begin{aligned}\bar{C} &= n_{CH_4}^\circ + n_{CO}^\circ + n_{CO_2}^\circ \\ &= n_{CH_4} + n_{CO} + n_{CO_2}\end{aligned}\quad (2-7)$$

The molar concentrations n_i and partial pressures P_i are given by the relation

$$P_i = \frac{n_i}{n_T} P_T \quad (2-8)$$

where P_T is the total pressure and n_T , the total molar concentration, is given by

$$n_T = n_{H_2O} + n_{H_2} + n_{O_2} + n_{CO} + n_{CO_2} + n_{CH_4} + n_{CG} \quad . \quad (2-9)$$

Here, n_{CG} is the concentration of the inert carrier gas, which in the following cases is helium. It could be the sum of different inert gases as well.

3. THE MATHEMATICAL APPROACH

3.1. THE SETUP OF THE EQUATIONS FOR THE MATHEMATICAL TREATMENT

Equations 2-1 through 2-7 are used for the determination of the equilibrium concentrations of the gases. In order to simplify the mathematical treatment, the nomenclature for the concentrations is changed as follows:

$$\begin{aligned} x_1 &= n_{H_2} & ; & & x_2 &= n_{CO} & ; & & x_3 &= n_{CH_4} & ; \\ x_4 &= n_{H_2O} & ; & & x_5 &= n_{CO_2} & ; & & x_6 &= n_{O_2} & ; \\ x_7 &= n_{CG} & . & & & & & & & & \end{aligned} \quad (3-1)$$

Using Eq. 2-8, the partial pressures P_i in Eqs. 2-1 through 2-4 can be expressed in terms of the molar concentrations n_i or x_i . Furthermore, in practical applications, $P_T = 1$ atm; therefore, for $P_T = 1$, we have

$$K_{P_1} = \frac{x_1^3 x_2}{x_3 x_4} \frac{1}{x_T^2} \quad (3-2)$$

$$K_{P_2} = \frac{x_1^2 x_2^2}{x_3 x_5} \frac{1}{x_T^2} \quad (3-3)$$

$$K_{P_3} = \frac{x_4}{x_1 x_6^{1/2}} x_T^{1/2} \quad (3-4)$$

$$K_{P_4} = \frac{a_C x_1^2}{x_3} \frac{1}{x_T} \quad (3-5)$$

K_{P_1} , K_{P_2} , K_{P_3} , and K_{P_4} are the equilibrium constants given for a certain temperature.

Equations 2-5 through 2-7 and 3-2 through 3-5 are the seven equations that determine $x_1 \rightarrow x_6$ (read " $x_1 \rightarrow x_6$ " as " $x_1, x_2, \dots, x_6$ ") and a_C . a_C appears only in Eq. 3-5; therefore, this equation is left out at first and $x_1 \rightarrow x_6$ are solved using Eqs. 2-5 through 2-7 and 3-2 through 3-4, thus reducing the problem to solving six equations for the six unknowns $x_1 \rightarrow x_6$. a_C can then be calculated using Eq. 3-5. The system to be solved was further simplified by keeping in mind that the oxygen concentration $n_{O_2} = x_6$ is always small because K_{P_3} has relatively high values. x_6 appears in Eqs. 3-4 and 2-5 only. Therefore, Eq. 3-4 was left out of the system to be solved first and x_6 was regarded as a small correction term in Eq. 2-5. This reduces the system of equations to be solved to five, i.e., Eqs. 2-5 through 2-7, 3-2, and 3-3, the unknowns being $x_1 \rightarrow x_5$. The term $2x_6$ in Eq. 2-5 is shifted to the left side of this equation. Since x_6 is considered a small correction term, we denote it as x_6' . Equations 2-5 through 2-7 now take the form

$$\begin{aligned} \bar{O} - 2x_6' &= x_2 + x_4 + 2x_5 \\ &= x_2^\circ + x_4^\circ + 2x_5^\circ \end{aligned} \quad (3-6)$$

$$\begin{aligned} \bar{H} &= 2x_1 + 4x_3 + 2x_4 \\ &= 2x_1^\circ + 4x_3^\circ + 2x_4^\circ \end{aligned} \quad (3-7)$$

$$\begin{aligned} \bar{C} &= x_2 + x_3 + x_5 \\ &= x_2^\circ + x_3^\circ + x_5^\circ \end{aligned} \quad (3-8)$$

The system of Eqs. 3-2, 3-3, and 3-6 through 3-8 is solved by an iterative procedure that will be described later. To start the iteration, x_6' has to be given the value zero. After the solution of the system $x_1 \rightarrow x_5$ is calculated, x_6 can then be calculated using Eq. 3-4. Before the next iteration, x_6' is set equal x_6 and inserted into Eq. 3-6, etc.

3.2. THE LINEARIZATION OF THE NONLINEAR EQUATIONS OF THE SYSTEM TO BE SOLVED

The solution of the system of Eqs. 3-6 through 3-8, 3-2, and 3-3 for the unknowns $x_1 \rightarrow x_5$ is the central problem of this task. Because Eqs. 3-2 and 3-3 are nonlinear in the x_1 , the solution cannot be given straightforward analytically. In order to arrive at an analytical approach, Eqs. 3-2 and 3-3 were linearized using a Taylor expansion.

These two equations can be written in the form

$$Kp_1 = F_1 \text{ with } F_1 = \frac{x_1^3 x_2}{x_3 x_4} \frac{1}{x_T^2} \quad . \quad (3-9)$$

$$Kp_2 = F_2 \text{ with } F_2 = \frac{x_1^2 x_2^2}{x_3 x_5} \frac{1}{x_T^2} \quad . \quad (3-10)$$

Expanding F_1 in a Taylor series and neglecting nonlinear terms in x_1 yields

$$\begin{aligned} F_1(x_1, \dots, x_5) \approx F_1' + \frac{\partial F_1'}{\partial x_1} (x_1 - x_1') + \frac{\partial F_1'}{\partial x_2} (x_2 - x_2') \\ + \dots + \frac{\partial F_1'}{\partial x_5} (x_5 - x_5') \quad . \end{aligned} \quad (3-11)$$

There $x'_1, \dots, x'_5$ are values that have to be near enough to $x_1, \dots, x_5$ that the nonlinear terms in the expansion may be neglected. [F'_1 denotes $F_1(x'_1, \dots, x'_5)$.]

For F_2 we have

$$F_2(x_1, \dots, x_5) \approx F'_2 + \frac{\partial F'_2}{\partial x_1} (x_1 - x'_1) + \frac{\partial F'_2}{\partial x_2} (x_2 - x'_2) + \dots + \frac{\partial F'_2}{\partial x_5} (x_5 - x'_5) \quad (3-12)$$

Using Eqs. 3-9 and 3-10, the derivative terms in Eqs. 3-11 and 3-12 can be written as

$$\frac{\partial F'_1}{\partial x_1} = \frac{3F'_1}{x'_1} - \frac{2F'_1}{x'_T} \quad ; \quad \frac{\partial F'_1}{\partial x_2} = \frac{F'_1}{x'_2} - \frac{2F'_1}{x'_T} \quad ; \text{ etc.} \quad (3-13)$$

$$\frac{\partial F'_2}{\partial x_1} = \frac{2F'_2}{x'_1} - \frac{2F'_2}{x'_T} \quad ; \quad \frac{\partial F'_2}{\partial x_2} = \frac{2F'_2}{x'_2} - \frac{2F'_2}{x'_T} \quad ; \text{ etc.} \quad (3-14)$$

4. THE SYSTEM OF LINEARIZED EQUATIONS AND THEIR SOLUTIONS

4.1. SETUP OF THE SYSTEM OF LINEAR EQUATIONS

Inserting Eq. 3-13 into 3-11 and Eq. 3-14 into 3-12 first, and then Eq. 3-11 into 3-9 and Eq. 3-12 into 3-10, we can rewrite the system of Eqs. 3-6 through 3-10 in a form where all equations are linear:

$$B_1 = \sum_{j=1}^5 \alpha_{1j} x_j \quad . \quad (4-1)$$

$$B_2 = \sum_{j=1}^5 \alpha_{2j} x_j \quad . \quad (4-2)$$

$$B_3 = \sum_{j=1}^5 \alpha_{3j} x_j \quad . \quad (4-3)$$

$$B_4 = \sum_{j=1}^5 \alpha_{4j} x_j \quad . \quad (4-4)$$

$$B_5 = \sum_{j=1}^5 \alpha_{5j} x_j \quad . \quad (4-5)$$

These are the equations to be solved for $x_1 \rightarrow x_5$. The coefficients are derived from Eqs. 3-6 through 3-8 and according to Section 3.2. The coefficients of the system of Eqs. 4-1 through 4-5 are

$$\left. \begin{aligned} B_1 &= \bar{O} - 2x_6' & ; & & B_2 &= \bar{H} & ; & & B_3 &= \bar{C} & ; \\ B_4 &= K_{P1} + F_1' \left(1 - 2 \frac{1}{x_T'} \sum_{j=1}^5 x_j' \right) & ; & & & & & & & & \\ B_5 &= K_{P2} + F_2' \left(1 - 2 \frac{1}{x_T'} \sum_{j=1}^5 x_j' \right) & . & & & & & & & & \end{aligned} \right\} (4-6)$$

$$\left. \begin{aligned} \alpha_{11} &= 0 & , & & \alpha_{12} &= 1 & , & & \alpha_{13} &= 0 & , & & \alpha_{14} &= 1 & , \\ \alpha_{15} &= 2 & , & & \alpha_{21} &= 2 & , & & \alpha_{22} &= 0 & , & & \alpha_{23} &= 4 & , \\ \alpha_{24} &= 2 & , & & \alpha_{25} &= 0 & , & & \alpha_{31} &= 0 & , & & \alpha_{32} &= 1 & , \\ \alpha_{33} &= 1 & , & & \alpha_{34} &= 0 & , & & \alpha_{35} &= 1 & , \\ \alpha_{41} &= \frac{3F_1'}{x_1'} - \frac{2F_1'}{x_T'} & , & & \alpha_{42} &= \frac{F_1'}{x_2'} - \frac{2F_1'}{x_T'} & , & & \alpha_{43} &= -\frac{F_1'}{x_3'} - \frac{2F_1'}{x_T'} & , \\ \alpha_{44} &= -\frac{F_1'}{x_4'} - 2 \frac{F_1'}{x_T'} & , & & \alpha_{45} &= -2 \frac{F_1'}{x_T'} & , & & \alpha_{51} &= 2 \frac{F_2'}{x_1'} - 2 \frac{F_2'}{x_T'} & , \\ \alpha_{52} &= 2 \frac{F_2'}{x_2'} - 2 \frac{F_2'}{x_T'} & , & & \alpha_{53} &= -\frac{F_2'}{x_3'} - 2 \frac{F_2'}{x_T'} & , & & \alpha_{54} &= -2 \frac{F_2'}{x_T'} & , \\ \alpha_{55} &= -\frac{F_2'}{x_5'} - 2 \frac{F_2'}{x_T'} & . & & & & & & & & \end{aligned} \right\} (4-7)$$

4.2. THE ITERATIVE METHOD FOR SOLVING THE EQUATIONS

The coefficients in the linear system of equations depend on $x_1' \rightarrow x_5'$. According to their definition (see Eqs. 3-11 and 3-12), they have to be near the solution of the problem, which is $x_1 \rightarrow x_5$. This leads to an iterative procedure of solution. An assumption has to be made as to where the solution might be, leading to a certain guess for the initial set of values $x_1' \rightarrow x_5'$ ($x_6' = 0$) to be inserted into the coefficients B_1, B_2, α_{ij} , $i = 4, 5$, $j = 1, 5$, in Eqs. 4-6 and 4-7. With these coefficients, the system Eqs. 4-1 through 4-5 can be solved giving a solution $x_1 \rightarrow x_5$. x_6 is calculated from this solution using Eq. 3-4. Then this solution $x_1 \rightarrow x_6$ is used as a guess ($x_1' \rightarrow x_6'$) for the next iteration, etc., until $x_1 \rightarrow x_6$ converge, i.e., the final solution is found.

When the final solution is found, the carbon activity a_C is calculated using Eq. 3-5.

The problem with the procedure described above is that a suitable guess $x_1' \rightarrow x_5'$ must be made near enough to the physical solution of the problem that the iteration converges toward this solution $x_1 \rightarrow x_6$. If the guess is not good enough, the iteration will most likely diverge or may possibly converge to one of the possible mathematical solutions, which is not a physical solution, i.e., a solution with one or more values x_i which are less than zero.

In the following section, the new method is described that avoids this problem. Using this method, no initial guess has to be made for $x_1' \rightarrow x_5'$; the only physical solution $x_1 \rightarrow x_6$ is calculated straightforwardly.

5. THE NEW METHOD AVOIDING THE INITIAL GUESS FOR THE ITERATION

5.1. SOLUTION WITHOUT CONSIDERING THE CARBON POTENTIAL

The special feature of the new method is that a physical solution is constructed for the initial state of the concentration distribution of the gas constituents $n_1 : x_1 \rightarrow x_5$. If $n_{O_2}^0 = 0$, i.e., $x_6^0 = 0$, then $\bar{O}$, $\bar{H}$ and $\bar{C}$ are calculated with Eqs. 2-5 through 2-7. Now fictitious values for K_{p_1} and K_{p_2} are calculated inserting $x_1^0 \rightarrow x_5^0$ into Eqs. 3-2 and 3-3. A high fictitious value of 10^{30} has to be attributed to K_{p_3} . If either of the values $x_1^0 \rightarrow x_5^0$ is zero, a value low enough that it does not significantly contribute to the sums of Eqs. 2-5 through 2-7 has to be assumed for it, thus preventing the products of Eqs. 3-2 and 3-3 from becoming zero or infinite. Now the values $x_1^0 \rightarrow x_5^0$ may be regarded as a solution to the problem for the K_p 's being K_{p_1} and K_{p_2} . In the case that $n_{O_2}^0 \neq 0$ (i.e., $x_6^0 \neq 0$), a different solution has to be constructed since according to Eq. 2-5, the amount $2n_{O_2}^0 \equiv 2x_6^0$ has to be added to give $\bar{O}$. In the simplified system of Eqs. 3-6 through 3-8, x_6^0 no longer appears on the right side and x_6^0 has to be zero at the beginning. Therefore, $2x_6^0$ is added to x_4^0 in Eq. 3-6 to give the proper amount of $\bar{O}$. In order to compensate for this in Eq. 3-7, i.e., leave $\bar{H}$ unchanged, $2x_6^0$ has to be subtracted from x_1^0 . With these new $x_1^0 \rightarrow x_5^0$, the K_{p_1} and K_{p_2} are calculated as described before, such that the new $x_1^0 \rightarrow x_5^0$ are a solution to the system of equations.

In order to arrive at the desired solution for the given $K_{p_1} \rightarrow K_{p_3}$, the three K_p 's are varied in small increments between $K_{p_1} \rightarrow K_{p_3}$ and the given values. After the first increment of the K_p 's an iterative procedure can be started to solve the system of Eqs. 4-1 through 4-5 for the first guess $x_1' \rightarrow x_6'$. The values $x_1^0 \rightarrow x_5^0$ and $x_6' = 0$; i.e., the values of the solution for the previous K_p 's are used. The increment can be made small enough that the iteration converges toward a new solution $x_1 \rightarrow x_6$ for the increased K_p 's. The new solution can then be used as guess $x_1' \rightarrow x_6'$ for the next

increment, etc., until the K_p 's have reached the values given and the desired solution is obtained.

5.2. CONSIDERATION OF THE CARBON POTENTIAL a_C OF THE GAS MIXTURE, CALCULATION OF A POSSIBLE CARBON PLATEOUT, AND THE RESULTING NEW GAS EQUILIBRIUM IF $a_C > 1$

Using the solution for the $x_1 \rightarrow x_6$ derived in the previous section, the carbon activity a_C of the mixture can be calculated with Eq. 3-5. If the calculated carbon activity is lower than 1, the gas mixture is in equilibrium and the solution $x_1 \rightarrow x_6$ obtained in the previous section is the equilibrium solution.

The calculated carbon activity a_C may be higher than one. Then the equilibrium of the mixture is not yet reached because carbon plateout takes place. Due to this, the carbon content $\bar{C}$ of the mixture decreases until the resulting carbon activity is equal to 1. This can be calculated using a procedure similar to the one described in the last section.

In this procedure, the $K_{p_1} \rightarrow K_{p_3}$ are kept constant at the given values and, instead of the K_p 's, the $\bar{C}$ value is decreased in small increments. For first guess $x'_1 \rightarrow x'_6$, the solution $x_1 \rightarrow x_6$ resulting from the calculation in Section 5.1 is used. Then the new solution is calculated for the decreased value of $\bar{C}$. With this solution, the new a_C value is then calculated. This procedure is repeated in a trial/error method until the calculated a_C value is equal to 1. The resulting solution $x_1 \rightarrow x_6$ is considered the equilibrium state of the gas mixture and the integral decrease of $\bar{C}$ ($\Delta\bar{C}$) is the amount of carbon plateout.

6. THE COMPUTER PROGRAM BASED UPON THE MODEL

A computer program has been written which does the calculation of the model described in the previous sections. This program consists of four routines: the MAIN routine and the subroutines CONCEN, LINEQ, and DETERM. The principal routine of the program is the subroutine CONCEN and is therefore described first.

6.1. THE SUBROUTINE CONCEN

CONCEN does the iterative solution of the linearized system of Eqs. 4-1 through 4-5, as described in Section 4. It starts at a guess $x_1' \rightarrow x_6'$ and calculates the solution $x_1 \rightarrow x_6$ for a given set of values $K_{P1} \rightarrow K_{P3}$, $\bar{O}$, $\bar{H}$, and $\bar{C}$. The initial guess $x_1' \rightarrow x_6'$ is created automatically in the MAIN routine.

At the beginning of each iteration, the coefficients α_{4j} , α_{5j} , $j = 1, 5$, B_1 , B_4 , and B_5 given in Eqs. 4-6 and 4-7 are calculated using the initial guess $x_1 \rightarrow x_6$. The coefficients α_{1j} , $i = 1, 3$, $j = 1, 5$ are constant and taken over from the MAIN routine. The coefficients B_2 and B_3 are constant and taken over from MAIN as well. Then the linear system of Eqs. 4-1 through 4-5 is solved for the unknowns $x_1 \rightarrow x_5$ by the subroutine LINEQ, which is described later. x_6 is then calculated using Eq. 3-4. This first solution $x_1 \rightarrow x_6$ is then used as guess $x_1' \rightarrow x_6'$ for the next iteration; the calculation described above is repeated until the solution converges. The precision of the calculation and the convergence is tested in two separate tests:

1. A test is made to show if the solution of the linear system of equations done by the routine LINEQ is precise. This procedure using determinants implies the possibility that the precision of the computer, which for this calculation is set at 10^{-14} , might

not be high enough to give a correct solution in particular cases. For this purpose, a set of values $B_1' \rightarrow B_5'$ is calculated after each iteration using the solution $x_1 \rightarrow x_5$ and inserting it into Eqs. 4-1 through 4-5. Each value B_i' is then compared with its original corresponding value B_i . If the discrepancy of one of the calculated values is higher than 0.01% with respect to its original value, this is indicated by a printout: "Attention Solution of Linear Equations not Exact." The original and the calculated $B_1 \rightarrow B_5$ and the concentration distribution $x_1 \rightarrow x_6$ where this happened are printed out as well.

2. Another test is made to verify if the solution $x_1 \rightarrow x_5$ satisfies the solubility products (Eqs. 3-9 and 3-10). Therefore, after each iteration, the solubility products F_1 and F_2 are calculated by inserting $x_1 \rightarrow x_5$ into Eqs. 3-9 and 3-10 and compared with the values of K_{p_1} and K_{p_2} for the respective calculation step (see Section 5.1). This test determines whether convergence has been reached, i.e., whether the iterations are finished. If the deviations between F_1 and K_{p_1} and between F_2 and K_{p_2} are both smaller than 0.01%, the iterations are stopped and the solution is considered exact within the limits possible. Both tests ensure that after each calculation step (i.e., after the iterations are finished), the resulting $x_1 \rightarrow x_6$ satisfy Eqs. 3-2, 3-3, and 3-6 through 3-8. Equation 3-4 is nevertheless satisfied.

6.2. THE SUBROUTINES LINEQ AND DETERM

The subroutine LINEQ solves the system of linear Eqs. 4-1 through 4-5 for the unknowns $x_1 \rightarrow x_5$. This routine takes over the matrix $[\alpha_{ij}]$ and the vector (B_i) $i = 1, 5$, $j = 1, 5$ which are both calculated in CONCEN. First it calculates the determinant D of the matrix $[\alpha_{ij}]$. Then in the matrix $[\alpha_{ij}]$, the columns $(\alpha_{ij}, j = k)$ are replaced successively by the vector (B_i) for $k = 1, 5$ giving five different matrices for each of which the determinant D_k is calculated with the subroutine DETERM. The unknowns $x_1 \rightarrow x_5$ are then obtained by setting $x_k = d_k/D$ for $k = 1, 5$.

The subroutine DETERM transforms the matrix into its diagonal form, i.e., a transformation such that all coefficients below the diagonal become equal to zero. The product of the diagonal terms of the resulting matrix yields the determinant.

6.3. THE MAIN ROUTINE

The MAIN routine does the following:

1. Handles the input.
2. Constructs the initial fictitious solution necessary to start the iterative solution of the problem (see Section 5.1).
3. Creates the stepwise calculation by varying the K_p values between those calculated for the fictitious solution and those given for the desired solution in small increments (see Section 5.1).
4. Calculates the carbon activity a_C . If $a_C > 1$, it decreases the $\bar{C}$ content of the gas mixture stepwise in small increments in order to determine the equilibrium gas concentration distribution for $a_C = 1$ in a trial/error procedure (see Section 5.2).
5. Provides the printout of intermediate and final results.

6.3.1. The Input of the Program

The input is organized in the following way. Each input card must have eight numbers. There is no format specified. A blank has to be between two different numbers. The maximum number of cards required for the calculation of one case is four. The first number on each card must be one of the integers 0, 1, 2, or 3. These integers specify how the computer is to interpret the remaining numbers on each card.

One input card (usually the first) has to have the initial integer 1. The following number is the temperature for which the gas concentration distribution has to be calculated, e.g., 800°C. Next, four numbers follow, which are the values for the solubility products $K_{p_1} + K_{p_4}$ at the temperature specified in the previous number (e.g., $2.787 \cdot 10^2$, $2.128 \cdot 10^2$, $1.181 \cdot 10^9$, and $2.130 \cdot 10^1$). Since each card must contain eight numbers altogether and the last numbers are not specified here, zeros have to be given as the last numbers.

Another input card has to have the integer 2 in the first place. This integer is followed by the molar concentrations of the constituents of the sample: H_2 , CO , CH_4 , H_2O , CO_2 , O_2 , and the inert carrier gas (which may be helium or any mixture of inert gases). If there is no inert gas in the mixture, the last concentration value has to be set at zero.

An input card with the integer 3 in the first place may be used. The next number on this card specifies the number of steps in the intermediate calculations between a printout. The next number may be zero or one. Zero gives a normal printout of the results; one causes the program to print out all the matrices α_{ij} and the vector B_i it produces during each calculation, which might be needed in case a result cannot be interpreted and in order to make it easier to detect and explain errors or discrepancies in the program in case they should occur. The next input number on this card gives the precision for the intermediate calculations (i.e., the relative agreement between the calculated values of F_1 , K_{p_1} and F_2 , K_{p_2} after each iteration) that must have been reached in order to finish the iteration. Generally this card is not inputted. Then the computer automatically sets the number of intermediate calculations per printout to equal 1. The printout is performed in the regular manner, and the precision is equal to 0.01%.

The last input card of each case to be calculated must have eight zeros. This card advises the computer that no more input is to be expected and the calculation is to be started.

There is one particular option in the input to run a continuation case (i.e., the concentration distribution will then be calculated for more than one temperature). Let us assume the concentration distribution has been calculated for 800°C. The distribution is then to be calculated for 1000°C as well. In this case, only a card with the first index number 2 is inputted, containing 1000°C and the four K_p values at 1000°C. In order to start the calculation, a card with zeros must also be inputted. In that case, the program starts with the concentration distribution calculated in the previous case (i.e., 800°C) and calculates the new distribution for 1000°C. There is no limit to the number of continuation cases.

6.3.2. Construction of the Fictitious Solution Necessary to Start the Iterative Solution Procedure and Rearrangement of the Initial Concentrations if the Initial O_2 Concentration is Greater Than 0

The input values of interest here are $x_1^0 \rightarrow x_6^0$. Several special cases have to be considered.

1. The normal case where all $x_1^0 \rightarrow x_5^0$ are greater than zero and $x_6^0 = 0$. The program calculates the overall oxygen, hydrogen, and carbon concentrations $\bar{O}$, $\bar{H}$, and $\bar{C}$ of the mixture using Eqs. 2-5 through 2-7. Then the fictitious values for K_{p_1} and K_{p_2} , i.e., $K_{p_1}^0$ and $K_{p_2}^0$, are constructed by putting $x_1^0 \rightarrow x_5^0$ into Eqs. 3-2 and 3-3.
2. One or more values of the initial concentrations $x_1^0 \rightarrow x_5^0$ are equal to zero and $x_6^0 = 0$. In this case, the constructed K_{p_1} and K_{p_2} could be either 0 or ∞ , a case which cannot be treated. Therefore, a finite value has to be attributed by the user to the respective concentrations out of $x_1^0 \rightarrow x_5^0$ small enough not to change the resulting $\bar{O}$, $\bar{H}$, and $\bar{C}$ such that K_{p_1} and K_{p_2} become finite.

3. The initial oxygen concentration x_6^0 is greater than zero. In this case, the initial $x_1^0 + x_6^0$ have to be rearranged because the model needs a value $x_6^0 = x_6^1 = 0$ to start the iterations, since x_6 is regarded as a small correction term in the iterative calculation in Section 3. In this case, the program constructs a new value for $x_4^0 \equiv n_{H_2O}^0$ by setting the new x_4^0 equal to the given value x_4^0 plus $2x_6^0$ and setting the new $x_6^0 = 0$. Thus the correct overall oxygen content is calculated in Eq. 2-5. The increased value for x_4^0 would lead to an $\bar{H}$ value being too high in Eq. 2-6. Therefore, a new $x_1^0 \equiv n_{H_2}^0$ has to be constructed as well, being equal to the given value x_1^0 minus 2 times the original value x_6^0 . Thus $\bar{H}$ is not changed by the manipulation in Eq. 2-5. Then the K_{p1} and K_{p2} are constructed using the new x_1^0 and x_4^0 as described above. There is one restriction to the initial x_6^0 : it must be smaller than $x_1^0/2$; otherwise the constructed new x_1^0 will become negative and would therefore not be a physical solution to the problem necessary to start the iterative solution.

6.3.3. The Variation of $K_{p1} \rightarrow K_{p3}$ by Increments

First, the high fictitious value 10^3 is attributed to K_{p3}^0 . Then the three K_p 's have to be varied in small increments according to Section 5.1. The program determines the number of increments by calculating the ratios $K_{p1}^0/K_{p1} = P_1$ and $K_{p2}^0/K_{p2} = P_2$ first. K_{p3}^0/K_{p3} plays no significant role in this context, because K_{p3} determines the O_2 content, which is always very small. The program takes the maximum value of P_1 , P_2 , and sets it equal to P_{max} . Then the number of increments n is determined according to $n = 5.6 \times \ln(P_{max})$. The K_p values are then varied in an exponential function between the initial and final values, the number of increments being n . After each increment, the subroutine CONCEN calculates a new concentration distribution. This has proven to be an optimal procedure as it gave solutions $x_1 + x_6$ after each increment, being 0.01% exact after three iterations. In case the number of iterations needed to obtain the solution with CONCEN is higher than three, the increment is halved for subsequent calculations. As

soon as the K_p 's have reached their final values, the concentration distribution calculated by CONCEN is regarded as a preliminary result. Then the carbon activity a_C is calculated. $x_1 \rightarrow x_6$ and a_C are printed out. If the carbon activity is smaller than one, the calculated $x_1 \rightarrow x_6$ are considered the equilibrium gas distribution and the calculation is finished.

The calculated value for the carbon activity may be higher than one. This means that carbon plateout takes place and the gas mixture has not yet reached the equilibrium state. In this case, the program continues the calculation by decreasing the $\bar{C}$ content of the mixture until the resulting a_C reaches the value one.

6.3.4. Equilibrium Calculation When Carbon Plateout Takes Place

When carbon plateout takes place, the overall carbon content of the mixture $\bar{C}$ can no longer be considered constant. The program decreases $\bar{C}$ in small increments keeping the K_{p1} , K_{p2} , and K_{p3} values constant. $\bar{C}$ is decreased in each step by a certain factor F (explained below). The subroutine CONCEN calculates the new $x_1 \rightarrow x_6$ distribution, a_C is then calculated and the program repeats this procedure in a similar way as described in Section 7.3 until the calculated value a_C is equal to one. The appropriate factor F (i.e., the decrease of $\bar{C}$ in each step yielding a new solution $x_1 \rightarrow x_6$) with no more than three iterations in the subroutine CONCEN is determined experimentally; the factor has the form $F(n) = \sum_{k=1}^n 0.5^k$. The first increment is calculated with $F(1) = 0.5$. Then CONCEN is called, if it needs more than three iterations. The same calculation is repeated with $F(2) = 0.75$, etc., until the number of iterations needed is not more than three. The factor used in this calculation may be applied then for the further decrease of $\bar{C}$ from its initial value in a trial/error method until $a_C = 1$. This state of the gas is considered the equilibrium state. The integral decrease in $\bar{C}$ ($\Delta\bar{C}$) is calculated and printed out together with the concentration distribution of equilibrium $x_1 \rightarrow x_6$.

7. CALCULATIONS PERFORMED WITH THE NEW MODEL

The validity of the model has been verified by recalculation of cases that had been previously calculated with other models and published in the literature (Ref. 2). In this publication, two different programs were used to calculate the equilibrium. One program was used to calculate the equilibrium if no carbon plateout takes place. If it was found that carbon plateout took place, another program had to be used for the calculation of the resulting equilibrium. Both programs need an appropriate initial guess for the concentration distribution to be inputted to start the iterative solution.

7.1. CALCULATION OF THE EQUILIBRIUM OF TWO TEST GASES

Calculations were performed for five material corrosion test environments (gases), each of which was calculated for two different temperatures (800° and 1000°C). In all 10 cases the new model gave results which were in reasonable agreement with those quoted in the publication. Two typical calculations are quoted here. In the first case the gas concentration distribution is such that no carbon plateout takes place; in the second case carbon plateout does take place.

The first case is the DRAGON experimental gas and the second the JAERI-A gas. Table 1 gives the gas concentration distributions at room temperature. The total gas pressure is 1 atm.

The authors who published their calculations quoted values for the constants $K_{p_1} \rightarrow K_{p_4}$ that are slightly different from those that they actually used in their calculations as can be directly shown from their results. The recalculation was done with those values $K_{p_1} \rightarrow K_{p_4}$ which were derived from their results.

TABLE 1
TWO IMPURE HELIUM GASES FOR MATERIAL TESTS

Experimental Gas	Impurities (μ atm)					
	H ₂	H ₂ O	CO	CO ₂	CH ₄	O ₂
DRAGON	30	5	30	2	4	0
JAERI-A	20	2	10	1	5	0

The calculated equilibrium gas concentrations, the carbon plateout ΔC , and the carbon activity are given in Table 2.

The values calculated for the DRAGON gas at 800°C and 1000°C, where carbon plateout did not take place, are in perfect agreement with those quoted in the referenced paper. In the case of the JAERI-A gas where carbon plateout takes place, there was a slight disagreement between the concentrations calculated here with the new method and those quoted in the referenced paper. It is assumed that the disagreement results from the different calculation procedure employed in the referenced calculation in the case of carbon plateout. In that case, reactions different from those leading to the equilibrium Eqs. 2-1 through 2-3 were implied with a different set of K_p 's. A small inconsistency between the K_p 's used in the referenced calculations and the $K_{p_1} \rightarrow K_{p_4}$ used here may account for this discrepancy.

7.2. CALCULATION OF THE INFLUENCE OF THE INITIAL OXYGEN AND WATER CONTENT ON THE CARBON AND OXYGEN POTENTIALS OF THE JAERI-A TEST GAS AT 800° AND 1000°C

In the first calculation, the initial oxygen content of the JAERI-A gas was varied between 0 and 7 μatm and the resulting equilibrium distributions at 800° and 1000°C were calculated. There were two fundamentally different ranges as far as the initial O_2 content is concerned, as shown in Fig. 1. For O_2 values between 0 and $\sim 1 \mu\text{atm}$, carbon plateout takes place and the carbon activity at equilibrium remained 1; the oxygen potentials were $\sim 10^{-30}$ and 10^{-28} for 800° and 1000°C, respectively. As soon as the initial oxygen content exceeds the value $\sim 1 \mu\text{atm}$, there is no more carbon plateout, an almost vertical decrease of the carbon activity over 4 to 5 decades occurs, and an increase of the oxygen potentials over ~ 10 decades takes place. With further increasing initial oxygen content, both potentials level off.

Next the initial H_2O content was varied between 0 and 10 μatm . The resulting carbon and oxygen potentials at equilibrium are plotted in Fig. 2. The water variation has a very similar effect on both potentials as did the oxygen variation. There is carbon plateout in the gas mixture until the

TABLE 2
CALCULATED EQUILIBRIUM GAS CONCENTRATIONS

	H ₂ (μ atm)	H ₂ O (μ atm)	CO (μ atm)	CO ₂ (μ atm)	CH ₄ (μ atm)	O ₂ (μ atm)	Δ C (μ atm)	a _C
DRAGON								
800°C	41.6	1.44	34.4	1.56	6.17×10^{-9}	8.59×10^{-16}	--	7.60×10^{-5}
1000°C	41.1	1.87	34.9	1.13	1.59×10^{-10}	9.53×10^{-12}	--	9.78×10^{-6}
JAERI-A								
800°C	32.0	3.42×10^{-5}	14.0	1.96×10^{-5}	4.81×10^{-5}	8.21×10^{-25}	2	1
1000°C	32.0	5.70×10^{-6}	14.0	1.79×10^{-6}	9.85×10^{-6}	1.47×10^{-22}	2	1

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Fig. 1. Effect of oxygen addition on the carbon activity and oxygen potential in the JAERI-A gas at 800° and 1000°C

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Fig. 2. Effect of water variation on the carbon activity and oxygen potential in the JAERI-A gas at 800° and 1000°C

initial water content reaches $\sim 4 \mu\text{atm}$. Above that value, carbon is no longer plated out and the carbon and oxygen potentials both change very rapidly at first and then level off as before with increasing water content. Both figures show behavior identical to that described in Ref. 2.

8. REFERENCES

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