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RESEARCH ARTICLE

On Application of the Newton-Raphson's Fixed Point Iterative Method in the Solution of Chemical Equilibrum Problems

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ABSTRACT

In this work, we discussed the solution of a chemical equilibrium problem aiming to obtain it's fixed point. To do this, the preliminary and basic ideas introducing the fixed point theory were X-rayed and the Newton-Raphson's iterative method for solving the system of non-linear equations discussed; then, the problem of the chemical equilibrium involving principal reactions in the production of synthesis gas by partial oxidation of methane with oxygen was stated. Using a computer program, the O reactant ratio that produces an adiabatic equilibrium temperature was obtained by developing a system of seven simultaneous non-linear equations that have the form which we now solve using the Newton-Raphson's method described in section 2.2 and hence the desired fixed point of the chemical equilibrium problem.

Key words: Banach contraction principle, Chemical equilibrium, Fixed point, Fortran subroutine, Newton-Raphson's iteration method, Non-linear equations

2020 Mathematics Subject Classification ÷ 65K10

INTRODUCTION

(The Netwon's Method, A Preliminary to the Newton-Raphson's Iterative Method)

Let T be an operator mapping a set X into itself, a apoint $x \in X$ is called a fixed point of T if

$$x = Tx \tag{1.1}$$

By (1.1), we achieve a natural construction of the method of successive approximations

$$x_{n+1} = T(x_n), n \geq 0 \in X \tag{1.2}$$

And if the sequence $(x_n), n \geq 0$ converges to some point $x = x^* \in X$ for some initial guess $x_0 \in X$, where T is a continuous operator in a Banach space X, we have

$$x^* = lim\{limTx_n\}$$

That is x^* a fixed point the operator T. Hence, we now state without proof the following important results that make easy the understanding of the Newton-Raphson's method used in this work.

Theorem 1.1A: [1,2] If T is a continuous operator in a Banach X, $\{x_n\}$ $(n \geq 0)$ generated by (1.2) converges to some point $x^* \in X$ for some initial guess $x_0 \in X$ and we say that x^* is a fixed point of the operator T.

To investigate the uniqueness property, we introduce the concept of contraction mapping as follows. Let (X, d) be a metric space and T a mapping of X into itself. The operator T is said to be a contraction if there exists a real number k, $0 \leq k \leq 1$ such that

$$\|F(x)-F(y)\| \leq k \|x-y\|, \text{ for all } x, y \in X \tag{1.3}$$

Hence, every contraction mapping T is uniformly continuous. Indeed T is Lipschitz continuous with a Lipschitz constant k which may also be called the contraction constant for T. With the above, we now discuss the Banach fixed point extensively as related to the target of this research.

Theorem 1.1B: (Banach fixed point theorem (1922). Suppose[3,4] that

- We are given an operator $T: M \subseteq X \rightarrow M$, that is, M is mapped into itself by T
- M is a closed non empty set in a complete metric space (X,d);
- T is k-contractive, that is, $d(T_x, T_y) \leq k$

Then the following hold:

- Existence and uniqueness: T has exactly one fixed point on M

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- Convergence of the iteration: The sequence $\{x_n\}$ of successive approximations converges to the solution, x for an arbitrary choice of initial point x_0 in M
- Error estimate: For all $n = 0,1,2,\ldots$ we have the prior error estimate $d(x_n, x) \leq k^n (1-k)^{-1} d(x_0,x)$ and the posterior error estimate $d(x_{n+1},x) \leq k(1-k)^{-1} d(x_n,x_{n+1})$
- Rate of convergence: For all $n = 0,1,2,\ldots$ we have $d(x_{n+1},x) \leq kd(x_n,x)$

Definition 1.1:[5,6] An operator $T: M \subseteq X \to X$ on a metric space (X,d) is called k-contractive if (1.3) holds for all $x,y \in M$ with fixed $k, 0 \leq k < 1$, T is called Lipschitz continuous and if

$$d(T_x,T_y) < d(x,y) \quad (1.4)$$

For all $x,y \in M$ with $x \neq y$. T is called contractive for T and we obviously have the implications:

k- Contractive → Contractive → no expansive → Lipschitz continuous

Every Banach space $(X,\|.\|)$ is also a complete metric space (X,d) as (X,d) under $d(X,y)=\|x-y\|$

On a Banach space, (1.3) therefore becomes

$\|Tx-Ty\| \leq k\|x-y\|$

Thus, the following follows

- $\{x_n\}$ is a Cauchy sequence. This follows from

$$d(x_n,x_{n+1}) = d(Tx_{n-1},Tx_n) \leq kd(x_{n-1},x_n) \leq k^2 d(x_{n-2},x_{n-1}) \leq \cdots \leq k^n d(x_0,x_1) \quad (1.6)$$

Since X is complete, the Cauchy sequence converges, that is, as.[3] Equation (1.5) follows by letting $m \to \infty$.

- The error estimate (1.6) follows by letting $m \to \infty$ in

$$d(x_{n+1},x_{n+m+1}) \leq d(x_{n+1},x_{n+2}) + \cdots + d(x_{n+m-1},x_{n+m+1})$$

$$(k+k^2+\cdots+k^m)\, d(x_n,x_{n+1}) \leq k(1-k)^{-1} d(x_n,x_{n+m}) \quad (1.7)$$

- The point x is a solution of (1.1) for T is continuous by (1.4). Since $T(M) \subseteq M$ and $x_0 \in M$, we have $x_n \in M$ also, for all n. Since M is closed and $x_n \to x$ as $n \to \infty$, we get $x \in M$. Equation (1.2) implies that $Tx = x$ for $n \to \infty$.
- Equation (1.6) follows $d(x_{n+1},x) = d(Tx_n,T_x) \leq kd(x_n,x)$
- Uniqueness of solution. Suppose $x = Tx$ and $y = Ty$, the $d(x,y) = d(Tx, Ty) \leq k\, d(x,y)$ which forces $d(x,y) = 0$, that is, $x = y$
- Continuous dependence on a parameter

It is important to note that in many applications, T depends on an additional parameter P, then is replaced by the equation

$$x_p = T_p x_p, x_p \in M \quad (1.8)$$

Where $p \in P$.

Proposition 1.2. (Corollary to the Theorem 1.1A) Let[3,4] the following

- p is a metric space, called the parameter space
- For each p, the operator T_p satisfies the hypotheses of Theorem (1A) but with k in (1.3) independent of p
- For a fixed $p_0 \in P$, and for all $x \in M, \lim_{p \to p_0} p p_0$

Then, for each $p \in P$, (1.8) has exactly one solution $x_p \in M, \lim_{p \to p_0} p_p 0$

Proof. Let x_p be the solution of (1.8) given by theorem 1.1A, then

$d(x_p,x_{p0}) = d(T_p x_p, T_{p0} x_{p0})$

$\leq d(T_p x_p, T_{p0} x_{p0}) + d(T_p x_{p0}), T_{p0} x_{p0})$

$\leq kd(x_p,x_{p0}) + d(T_p x_{p0}, T_{p0} x_{p0})$

and $d(x_p,x_{p0}) < (1-k)^{-1} d(T_p x_{p0}, T_{p0} x_{p0}) \to 0$ as $p \to p0$ by (iii).[9]

Accelerated Convergence and Newton's Method

We[9,10] begin with the insight which underlines the acceleration of iterative methods. Let x be a solution of the real equation $X=F(x)$, and suppose the sequence of iterations (x) where

$$x_{n+1} = f(x_n) \quad (1.9)$$

And $x_n \in [a,b]$ for all n, converges to x as $n \to \infty$.

Now for the key: Suppose further that f is m-times differentiable on $[a,b]$, with

$$f'(x) = f^{(2)}(x) = f^{(m-1)} = 0 \quad (1.10)$$

Since $x_{n+1}=f(x_n)$ and $x = f(x)$, we have

$$\left|x_{n+1} - x\right| \leq \sup_{a<\xi<b}^{(m)}(\xi) x_n - x \quad (1.11)$$

If the supremum in (1.11) is finite, we obtain the convergence of order m, as opposed to the linear convergence ($m = 1$) of (1.9).

Example 1.1.[10] The trick to Newton's method consists of rewriting the equation $f(x) = 0$ in the equivalent form $X=F(x)$, where $f(x) = x - \frac{f(x_n)}{f(x_n)}$ then the iterative method becomes

$$x_{n+1} = x_n - \frac{f(x_n)}{f(x_n)}$$

We assume that $f'(x_n) \neq 0$ for all n then, $f'(x) = f(x) - \frac{f^n(x)}{f'(x)^2}$. So that, if x is a solution of $f(x) = 0$ with $f'(x) \neq 0$, then $f'(x) = 0$. Thus, we have a method with $m = 2$ in (1.1.9), that is, we have quadratic convergence.

We apply this to the equation $x = T(x)$ in (1.1.1), that is, $f(x) = T(x)$. Computing, we obtain the iterative values x_n with linear convergences.

The geometric interpretation of Newton's methods. To find a zero, x of f, take the initial value, x_0, and determine the corresponding functional value, $f(x_0)$. The next iterative value, x_1 is the intersection of the tangent line at $(x_0,f(x_0))$ and the x-axis. Keep repeating the process, it is typical of Newton's method that it converges very rapidly if the initial value x_0 is already in the vicinity of the zero, but shows a better of this.

However, we know that the above-discussed fixed point method is just the traditional fixed point method that is restricted to the solution of only linear systems and for the purpose of this research, we advance onto the modified Newton's method which is the Newton-Raphson's iterative method here below generated for use in section three.

NEWTON-RAPHSON'S METHOD

Sections 2 and 3 are concerned with finding the solution, or solutions, of the system

$$\begin{aligned} f_1(x_1,x_2.,x_n) &= 0,\\ f_2(x_1,x_2.,x_n) &= 0,\\ f_n(x_1,x_2.,x_n) &= 0, \end{aligned} \tag{2.1}$$

Involving n real functions of the n real variables $x_1,x_2,\ldots,x_n$. Following the previous notation, $x = \{x_1,x_2,\ldots,x_n\}^t$, we shall write $f_i(x)=f_i(x_1,x_2,\ldots,x_n)$ here, and in the subsequent development, $1 \le i \le n$. Then let $a = [a_1,a_2,\ldots,a_n]^t$ be a solution of (2.1), that is, let $f_i(a) = 0$.

Let the n functions $f_i(x)$ be such that

$$x_i = F_i(x) \tag{2.2}$$

implies $f_i(x) = 0, 1 \le j \le n$. Basically, the n equations (2.2) will constitute a suitable rearrangement of the original system (2.1). In particular, let

$$\alpha_i = f_i(\alpha) \tag{2.3}$$

Let the starting vector $x_0 = [x_{10},x_{20},\ldots,x_{n0}]^t$ be an approximation to a. Define successive new estimates of the solution vector, $x_k = [x_{1k},x_{2k}\ldots,x_{nk}]^t$, $k = 1,2,\ldots$, by computing the individual elements from the recursion relations.

$$x_{ik} = F_i(x_{1,k-1}, x_{2,k-1},\ldots,x_{n,k-1}) \tag{2.4}$$

Suppose there is starting R describable as $|x_j - a_j| \le h, 1 \le j \le n$, and for x in R there is a positive number μ, less than one, such that

$$\Sigma_{j=1}^{n} \left| \frac{\partial F_i(x)}{\partial x_j} \right| \le \mu \tag{2.5}$$

Then, if the starting vector x_0 lies in R, we show that the iterative method expressed by (2.4) converges to a solution of the system (2.1), that is,

$$\lim_{k\to\infty} x_k = \alpha \tag{2.6}$$

Using the mean-value theorem, the truth of (2.1) is established by first noting from (2.3) and (2.4), that]

$$\begin{aligned} x_{ik} - a_i &= F_i\left(x_{k-1}\right) - F_i(a)\\ &= \sum_{n}^{j=1} (x_{j,k-1} - \alpha_j) \frac{\partial F_i\left[\alpha + \xi_{i,k-1}\left(x_{k-1} - \alpha\right)\right]}{\partial x_j} \end{aligned} \tag{2.7}$$

In which $0 < \xi_{i,k-1} < 1$. that is,

$$\left|x_{ik} - \alpha\right| \le h \sum_{n}^{j=1} \left| \frac{\partial F_i}{\partial x_j} \right| \le \mu h < h \tag{2.8}$$

Showing that the points x_k lie in R. Furthermore, by induction, from (2.5) and (2.7),

$$\left|x_{ik} - a\right| \le \mu \, max\left(\left|x_{j,k-1} - a_j\right|\right) \le \mu^k h \tag{2.9}$$

Therefore, (2.6) is true, and the procedure converges to a solution of (2.1). Note that if $F_i(x)$ are linear, we have the Newton's method, and the sufficient conditions of (2.5) are the same as the second set of sufficient conditions controlling the Newton's iteration.

For the non-linear equations, there is also a counterpart to the Newton's method, previously discussed for the linear case. We proceed as before, except that some replacements are made by

$$X_{ik} = F_i\left(x_{ik}, x_{2k},\ldots, x_{i-1,k}, x_{i,k-1},\ldots, x_{n,k-1}\right) \tag{2.10}$$

That is, the most recently computed elements of the solution vector are always used in evaluating the F_i. The proof of convergence according to (2.10) is much the same as for the Jacobi-type iteration. We have

$$x_{ik} - \alpha_i = \sum_{n}^{j=1} (x_{j,k-1} - \alpha_j) \frac{\partial F_i(\Sigma_{ik})}{\partial x_j}$$

Where

$$\sum x_{ik} - \alpha = \begin{bmatrix} \alpha_1 + \xi_{ik}(x_{1,k-1} - \alpha),\ldots,\alpha_n + \xi_{ik} \\ \left(x_{n,k-1}\right) - \alpha_n \end{bmatrix}^t$$

It will appear inductively that the above is true, because the various points concerned remain in R. If e_{k-1} is the largest of the numbers $|x_{j,k-1}-\alpha_j|$, then

$$|x_{ik}-\alpha_1| \le \mu, e_{k-1} < e_{k-1} < \mathrm{h}$$

It follows that

$$x_{2k}-\alpha_2=(x_{ik}-\alpha_1)\frac{\partial F_2(\Sigma_{2k})}{\partial x_j}+\overset{j=2}{\underset{n}{\Sigma}}\left(x_{j,k-1}-\alpha_j\right)$$

$$\frac{\partial F_2(\Sigma_{2k})}{\partial xj}$$

Where

$$e_{2k}=\begin{bmatrix}\alpha_1+\xi_{2k}\left(x_{1k}-\alpha_1\right),\alpha_2+\xi_{2k}\left(x_{2,k-1}-\alpha_2\right),\\ \ldots,\alpha_n+\xi_{2k}\left(x_{n,k-1}-\alpha_n\right)\end{bmatrix}^t$$

that is, $\left|x_{2k}-\alpha_2\right|\le\mu e_{k-1}<e_{k-1}<h$

Therefore, $\left|x_{ik}-\alpha_i\right|\le\mu^k h$, and convergence according to (2.1) is again established.

Observe that the first of the sufficiency conditions of the same (2.10) has been reaffirmed under slightly general circumstance.

Newton-Raphson's Iteration for Nonlinear Equations

The equations to be solved are again those of (2.1), and we retain the nomenclature of the previous section. The Newton-Raphson process, to be described, is once more iterative in character. We first define.

$$f_{ij}(x)=\frac{\partial f_i(x)}{\partial x_j}\qquad(2.11)$$

Next define the matrix $\phi(x)$ as

$$\phi(x)=\left(f_i(x)\right),1\le I\le n,1\le j\le n\qquad(2.12)$$

Thus det $(\phi(x))$ is the Jacobian of the system (2.1) for the vector $x=[x_1,x_2,\ldots,x_n]^t$. Now define the vector $f(x)$ as

$$f(x)=\left[f_i(x),f_2(x),\ldots,f_n(x)\right]^t\qquad(2.13)$$

With these definitions in mind, and with the starting vector $x_0=[x_{10},x_{20},\ldots,x_{n0}]^t$, let

$$x_{k+1}=x_k+\delta_k\qquad(2.14)$$

The fundamental theorem concerning convergence is much less restrictive than those of the previous sections. We have the result that if the components of $\phi(x)$ are continuous in a neighborhood of a point α such that $f(\alpha)=0$, if det $(\phi(\alpha))\neq 0$, and if x_0 is "near" α, then $\lim_{x\to\infty}^{k}$.

An outline for a method of proof follows. By (2.13) and (2.14), since

$$f_i(\alpha)=0,\delta_k=\phi^{-1}(x_k)\left[f(\alpha)\right]\qquad(2.15)$$

By the mean – value theorem,

$$f_i(x_k)-f_i(\alpha)=\overset{j=1}{\underset{n}{\Sigma}}\int ij\left(\alpha+\xi_{ik}\left(x_k-\alpha\right)\right)(x_{jk}-\alpha),$$

$$where 0<\xi_{ik}<1$$

For the i throw of a matrix ψ use $\left[f_{i1}\left(a+\xi_{ik}\left(x_k-a\right)\right),\ldots,f_{in}\left(\alpha+\xi_{ik}\left(x_k-\alpha\right)\right)\right]$

Then

$$x_{k+1}-\alpha=x_k-\alpha+\delta_k=\phi^{-1}(x_k)\left[\phi(x_k)-\psi\right](x_k-\alpha)$$

Since the entries in the matrix $\phi(x_k)$–ψ are differences of the type $f_{ij}(x_k)$–$f_{ij}(\alpha+\xi_{ik}(x_k-\alpha))$, they can be kept uniformly small if the starting vector x_0 lies in an initially chosen region R describable as $|x_i-\alpha_i|\le h,1\le i\le n$ concurrent with this is the fact that since det $(\phi(x_k))$ can be bounded from zero. The net result is that, for $0<\mu<1,|x_{ik}-\alpha_j|\le h\mu^k,1\le i\le n$. Thus, the sequence $[x_k]$ converges to α.[6]

Example 2.1:[7-10] To illustrate the procedure, we use the example below, namely;

$$f_1(x_1,x_2)=\frac{1}{2}\sin(x_1,x_2)-\frac{x_2}{4\pi}-\frac{x_1}{2}=0$$

$$f_2(x_1,x_2)=\left(1-\frac{1}{4\pi}\right)(e^{2x1}-e)+\frac{ex_2}{\pi}-2ex1=0$$

$$\frac{\partial f_1}{\partial x_1}=-\frac{1}{2}\frac{x_2\cos(x_1,x_2)}{2},\frac{\partial f_1}{\partial x_1}=-\frac{1}{4\pi}+\frac{x_1\cos(x_1,x_2)}{2}$$

$$\frac{\partial f_2}{\partial x_1}=-2e+\left(2-\frac{1}{2\pi}\right)e^{2x1},\frac{\partial f_2}{\partial x_2}=\frac{e}{\pi}\qquad(2.16)$$

The increments Δx_1 and Δx_2 in x_1 and x_2 are determined by

$$\frac{\partial f_1}{\partial x_1}\Delta x_1+\frac{\partial f_1}{\partial x_2}\Delta x_2=-f_1,\frac{\partial f_2}{\partial x_1}\Delta x_1+\frac{\partial f_2}{\partial x_2}\Delta x_2=-f_2$$

Or, writing the determinant D of the coefficient matrix (the Jacobian),

$$D=\frac{\partial f_1}{\partial x_1}\frac{\partial f_2}{\partial x_2}-\frac{\partial f_1}{\partial x_2}\frac{\partial f_2}{\partial x_1}$$

Then

$$\left(\frac{f_2\frac{\partial f_1}{\partial x_2}-f_1\frac{\partial f_2}{\partial x_2}}{D}\right),\Delta x_2\left(\frac{f_1\frac{\partial f_2}{\partial x_1}-f_1\frac{\partial f_1}{\partial x_1}}{D}\right)$$

For case in verification, detailed results are tabulated in Table 1, and moreover, calculations

Table 1: Component enthalpies in BTU/b mole

Component	1000° *F*	2200° *F*
CH4	−13492	8427
H_2O	−90546	−78213
CO_2	−154958	−139009
CO	−38528	−28837
H_2	10100	18927
O_2	10690	20831

were carried out using slide rule and the entries 0.00000 showed tiny negative values.

APPLICATION OF NEWTON-RAPHSON'S METHOD IN SOLVING THE CHEMICAL EQUILIBRUIM PROBLEM

The principal reactions in the production of synthesis gas by partial oxidation of methane with oxygen are

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad (3.1)$$

$$CH_4 + H_2 0 \rightarrow CO + 3H_2 \quad (3.2)$$

$$H_2 + CO_2 \rightarrow CO + H_2O \quad (3.3)$$

Write a program that finds the 0 reactant ratio that will produce an adiabatic equilibrium temperature of 2200° *F* at an operating pressure of 20 atmospheres, when the reactant gases are preheated to an entering temperature of 1000° *F*. Assuming that the gases behave ideally, so that the component activities are identical with component partial pressures, the equilibrium constants at 2200° *F* for the three equations are, respectively:

$$K_1 = \frac{P_{CO}P^2{}_{H_2}}{P_{CH}P\frac{1/2}{O_2}} = 1.3\times10^{11} \quad (3.4)$$

$$K_2 = \frac{P_{CO}P^3{}_{H_2}}{P_{CH_4}P_{H_2O}} = 1.7837\times10^5 \quad (3.5)$$

$$K_3 = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2O}} = 2.6058 \quad (3.6)$$

Here, P_{CO}, P_{CO2}, P_{H2O}, $P_{CH4,}$ and P_{O2} are the partial pressured of *CO* (carbon monoxide), CO_2 (carbon dioxide), H_2O (water vapor), H_2 (hydrogen), CH_4 (methane), and O_2 (oxygen), respectively. Enthalpies of the various components at 1000°*F* and 2200°*F* are listed in (Table 1).

A fourth reaction may also occur at high temperatures: $C+ CO_2=2CO$ (3.1) at 2200°*F*, any carbon formed would be deposited as a solid; the equilibrium constant is given by

$$K_4 = \frac{P^2{}_{CO}}{a_c P_{CO_2}} = 1.7837\times10^5$$

Where a_c is the activity of carbon in the solid state. Do not include reaction (3.7) in the equilibrium analysis. After establishing the equilibrium composition, considering only the homogeneous gaseous reactions given by (3.1), (3.2), and (3.3), determine the thermodynamic likelihood that solid carbon would appear as a result of reaction (3.7). Assume that the activity of solid carbon is unaffected by pressure and equals unity.

The use the Newton-Raphson method to solve the system of simultaneous non-linear equations developed as the result of the equilibrium analysis.

METHOD OF SOLUTION

Due to the magnitude of *K*, the equilibrium constant for reactions, the first reaction can be assumed to go to completion at 2200° *F*, that is, virtually no unrelated oxygen which will remain in the product gases at equilibrium.

Let the following nomenclature be used.

x_1	Mole fraction of *CO* in the equilibrium mixture
x_2	Mole fraction of CO_2 in the equilibrium mixture
x_3	Mole fraction of H_2O in the equilibrium mixture
x_4	Mole fraction of H_2 in the equilibrium mixture
x_5	Mole fraction of CH_4 in the equilibrium mixture
x_6	Number of moles of O_2 per mole of CH_2 in the feed gas
x_7	Number of moles of product gases in the equilibrium mixture per Mole of in the feed gases

Then, a system of seven simultaneous equations may be generated from three atom balances an energy balance, a mole fraction constraint, and two equilibrium relations.

Atom conservation balances: The number of atoms of each element entering equals the number of atoms of each clement in the equilibrium mixture.

$$Oxygen: x_6 = \left(\frac{1}{2x_1} + x_2 + \frac{1}{2x_3}\right) \quad (3.9)$$

$$Hydrogen: 4 = \left(2x_3 + 2x_4 + 4x_2\right) \quad (3.10)$$

$$Carbon: 1 = \left(x_1 + x_2 + x_5\right) \quad (3.11)$$

Since the reaction is to be conducted adiabatically, that is, no energy is added to or removed from the reacting gases, the enthalpy (H) of the reactants must equal the enthalpy of the products.

$$\left[HCH_4 + x_6 H0_2\right]_{1000^0 F} = x_7\left[x_1 HC0_2 + x_3 H_2 0 + x_4 H_2 + x_5 HCH_2\right]_{2200^0 F} \quad (3.12)$$

Mole fraction constraint.

$$x_1 + x_2 + x_4 + x_5 + \cdots = 1 \quad (3.13)$$

Equilibrium relations

$$K_2 = \frac{p^2 X_1 X^3{}_4}{x_3 x_5} = 1.7837 \times 10^5 \quad (3.14)$$

$$K_3 = \frac{X_1 X_3}{X_2 X_4} = 2.6058 \quad (3.15)$$

The relationships (3.14) and (3.15) follow directly from (3.5) and (3.6), respectively, where P is the total pressure and $P_{CO} = Px_1$, etc. In addition, there are five side conditions.

$$x_i \geq 0, i = 1, 2, 5, \ldots \quad (3.16)$$

These C ions more that all mole fractions in the equilibrium mixture are nonnegative, that is, any solution of equation (3.9) to 3.15) that contains negative mole fractions is physically meaningless from physical-chemical principle, there is one and only one solution of the equation that satisfies conditions (3.16). Any irrelevant solutions may be detected easily.

The seven equations may be rewritten in the form

$$f_i(x) = 0,\ i = 1, 2, \ldots, 7 \quad (3.17)$$

Where

$$x = \left[x_1, x_2, x_3, x_4, x_5, x_6, x_7\right]^t \quad (3.18)$$

As follows:

$$f_1(x) = \frac{1}{2}x_1 + x_2 + \frac{1}{2}x_3 - \frac{x_6}{x_7} = 0 \quad (3.19a)$$

$$f_2(x) = x_3 + x_4 + 2x_5 - \frac{2}{x_7} = 0 \quad (3.19b)$$

$$f_3(x) = x_1 + x_2 + x_5 - \frac{1}{x_7} = 0 \quad (3.19c)$$

$$f_4(x) = -28837x_1 - 139009x_2 - 78213x_3 + 18927x_4 + 8427x_5 + \frac{13492}{x_7} - 10690\frac{x_6}{x_7} = 0 \quad (3.19d)$$

$$f_5(x) = x_1 x_2 x_3 x_4 x_5 - 1 = 0 \quad (3.19e)$$

$$f_6(x) = P^2 x_1 x_4 - 1.7837 \times 10^5 x_3 x_5 = 0 \quad (3.19f)$$

$$f_7(x) = x_1 x_3 - 2.6058 x_2 x_4 = 0 \quad (3.19g)$$

The system of simultaneous nonlinear equations has the form (2.1) and will be solved using the Newton-Raphson method, described in section 2.2. The partial derivatives of above may be found by partial differentiation of the seven functions, f_i (x) with respect to each of the seven variables. For example,

$$\frac{\partial f_1}{\partial x_1} = \frac{1}{2}, \frac{\partial f_1}{\partial x_4} = 0, \frac{\partial f_1}{\partial x_7} = \frac{x_6}{x_7}$$

$$\frac{\partial f_1}{\partial x_{21}} = 1, \frac{\partial f_1}{\partial x_5} = 0,$$

$$\frac{\partial f_1}{\partial x_3} = \frac{1}{2}, \frac{\partial f_1}{\partial x_6} = -\frac{1}{x_7},$$

The Newton-Raphson method may be summarized as follows:

- Choose a starting vector $x_k = x_0 = [x_{10}, x_{20}, \ldots, x_{70}]$, where x_0 is hopefully near a solution
- Solve the system of linear equations (2.14), $\phi(x_k)\ \delta_k = -f(x_k)$ where

$$\phi_{ij}\left(x_k\right) = \frac{\partial f_1}{\partial x_j}\left(x_k\right), {}^{i=1,2,\ldots,7}_{j=1,2,\ldots,7} \quad (3.20)$$

And

$$f\left(x_k\right) = f_1\left(x_k\right), f_2\left(x_k\right), \ldots, f_7\left(x_k\right)^t \quad (3.21)$$

For the increment vector

$$\delta_k = \left[\delta_{1k}\delta_{2k,\ldots\ldots,\delta_{7k}}\right]^t \quad (3.22)$$

- Update the approximation to the root for the next iteration $x_{k+1} = x_k + \delta_k$
- Check for possible convergence to a root α. One such test might be

$$\left|\delta_{ik}\right| < \varepsilon_2, i = 1, 2, \ldots, 7 \quad (3.23)$$

If (3.23) is true for all i, then x_{k+1} is taken to be the root. If test (3.23) is failed for any 1, then the process is repeated starting with step 2. The iterative process is continued until test (3.23) is passed for some k, or when k exceeds some specified upper limit. In the programs that follow, the elements of the augments matrix

$$A = \left[\phi\left(x_k\right), -f\left(x_k\right)\right] \quad (3.24)$$

Are evaluated by a subroutine named CALCN. The system of linear equations (3.24) is solved by calling on the function SIMUL, described in detail in example (2.1).

The main program is a general one, in that, it is not specifically written to solve only the seven equations of interest. By properly defining the subroutine CALCN, the main program could be used to solve any system of n simultaneous non-linear equations. The main program reads data values for itmax, iprint, n, $\sum 1$, $\sum 2$ and $x_1, x_2, \ldots, x_n$ here, itmax is the maximum number of Newton-Raphson's iterations, print is a variable that controls printing of intermediate output, n is the number of nonlinear equations, $\sum 1$, is the minimum pivot magnitude allowed in the Gauss-Jordan reduction algorithm, $\sum 2$, is a small positive number used in test (3.23), and $x_1, x_{20}, \ldots, x_{n0}$, that is, the elements of x_0.

We, then, apply the FORTRAN implementation program as below and the underlisted computer outputs were generated.

FORTRAN Implementation

List of principle various program symbol (Main)	
A	Augmented matrix of coefficients, A (see (3.22).
DETER	d, determinant of the matrix (the Jacobian).
EPS1	1, minimum pivot magnitude permitted in subroutine SIMUL
EPS2	2, small positive number, used in convergence test (3.23).
	subscript, *i*.
IPRINT	Print control variable, if iprint=1, intermediate solutions are printed after each iteration.
ITCON	Used in convergence test (3.23). ITCON 1 if (3.23) is passed for all i, i=1, 2,…., n: otherwise ITCON=0.
ITER	Iteration counter, k.
ITMAX	Maximum number of iterations permitted, itmax.
N	Number of nonlinear equations, n.
XINC	Vector of increments, $_{ik}$, i=1, 2, …., n.
XOLD	Vector of approximations to the solution, $_{xik}$.
SIMUL	Function developed in Example (2.1) solves the system of n linear equations (2.15) for the increments,. $_{ik}$ i=1, 2,…, n.
(subroutine CALCN)	
DXOLD	Same as XOLD. Used to avoid an excessive number of reference to subroutine arguments in CALCN.
I, J,	i and j, row and column subscript, respectively.
NRC	N, dimension of the matrix A in the calling program. A is assumed to have the same number of rows and columns.
P	Pressure, P, atm.

Computer Output

Results for the 1st Data Set		
ITMAX	=	50
IPRINT	=	1
N	=	7
EPS1	=	1.0E - 10
EPS2	=	1. 0E - 05

XOLD (1)	XOLD (7)			
5.000000E −01		0.0	0.0	5.000000E −01
0.0		5.000000E −01	2.000000E 00	
ITER	=	1		
DETER	=	−0.97077E −07		
XOLD (1)	XOLD (7)			
2.210175E −01		2.592762E −02	6.756210E −02	4.263276E −01
2.591652E −01		3.3432350E −01	1.975559E −00	
ITER	=	2		
DETER	=	−0.10221E −10		
XOLD (1)	XOLD (7)			
3.101482E −01		7.142063E −03	5.538273E −02	5.791981E −01
4.812878E −02		4.681466E −01	2.524948E −00	
ITER	=	3		
DETER	=	−0.41151E −09		
XOLD (1)	XOLD (7)			
3.202849E −01		9.554777E −03	4.671279E −02	6.129664E −01
1.048106E −02		5.533223E −01	2.880228E −00	
ITER	=	4		
DETER	=	−0.22807E −09		
XOLD (1)	XOLD (7)			
3.228380E −01		9.22480E −03	4.603060E −02	6.180951E −01
3.811378E −03		5.758237E−01	2.974139E −00	
ITER	=	5		
DETER	=	−0.20218E −09		
XOLD (1)	XOLD (7)			
3.228708E −01		9.223551E −03	4.601710E −02	6.181716E −01
3.716873E −03		5.767141E −01	2.977859E −00	
ITER	=	6		
DETER	=	−0.20134E −09		
XOLD (1)	XOLD (7)			
3.228708E −01		9.223547E −03	4.601710E −02	6.181716E −01
3.716847E − 03		5.767153E − 01	2.977863E − 00	

Computer Output

SUCCESSFUL CONVERGENCE				
ITER	=	6		
XOLD (1)	XOLD (7)			
3.228708E −01		9.223547E −03	4.601710E −02	6.181716E −01
3.716847E − 03		5.767153E − 01	2.97863E − 00	

Results for the 3rd Data Set				
ITMAX	=	50		
IPRINT	=	1		
N	=	7		
EPS1	=	1.0E −10		
EPS2	=	1. 0E −05		
XOLD (1)	XOLD (7)			
2.200000E −01		7.499999e −02	9.999999e −04	5.800000E −01
1.250000e −01		4.360000e −01	2.349999e 00	
ITER	=	1		
DETER	=	−0.61808E −08		
XOLD (1)	XOLD (7)			
6.9514955E −01		−8.022028E −02	1.272939E −02	1.217132E −00
−8.447912E −01		1.314754E −00	5.969404E −00	
ITER	=	2		
DETER	=	0.12576E −09		
XOLD (1)	XOLD (7)			
4.958702E −01		−1.698154E −02	5.952045E −03	9.518250E −01
−3.65007E −01		2.379797E −00	1.043425E −01	
ITER	=	3		
DETER	=	0.77199E 07		
XOLD (1)	XOLD (7)			
4.559822E −01		−9.799302E −04	−7.583648E −04	9.107630E −01
−3.650070E −01		2.509821E −00	1.107038E −01	
ITER	=	1		
DETER	=	0.53378−07		
XOLD (1)	XOLD (7)			
4.569673E −01		−4.071472E −04	−2.142648E −03	9.152630E −01
−3.696806E −01		2.608933E 00	1.149338E −01	
ITER	=	5		
DETER	=	0.49739E −07		
XOLD (1)	XOLD (7)			
4.569306E −01		−4.071994E −04	−2.125205E −03	9.151721E −01
−3.695704E −01		2.610552E −00	1.150046E −01	
ITER	=	6		
DETER	=	0.49611E 07		
XOLD (1)	XOLD (7)			
4.569306E −01		−4.071984E −04	−2.125199E −03	9.151720E −01
−3.695703R −01		2.610549E − 00	1.150045E − 01	

DISCUSSION OF RESULTS

Results are shown for the first and third data set only for the first two data sets, the Newton-Raphson iteration converged to the same solution, one that satisfies the side conditions (3.26). Results for the third data set cannot be physically meaningful because the solution has negative mole function for CO_2, H_20, and CH_4. The equilibrium compositions, reaction ratio O_2/CH_4 in the feed gases, and the total numbers of moles of product per mole of HC_4 in the feed are tabulated in (Table 2).

Thus, the required feed ratio is 0.5767 moles of oxygen per moles of methane in the feed gases.

To establish if carbon is likely to be formed according to reaction (5.5.7) at 2200°F for a gas of the computed composition, it is necessary to calculate the magnitude of

$$\bar{K} = \frac{P^2_{CO}}{a_c P_{CO_2}} = \frac{P x_1^2}{a_c x_2} \tag{3.25}$$

If $\bar{K}$ is larger than k_4 from (3.25), then there will be a tendency for reaction (3.24) to shift toward the left; carbon will be formed. Assuming that $a_c = 1$,

$$\bar{k} = \frac{20 \times (0.322871)^2}{1 \times 0.009224} = 226.03 < k_4 = 1329.5 \tag{3.26}$$

Therefore, there will be no tendency for carbon to form.

CONCLUSION

Results obtained from our experiment on the chemical equilibrium problem indicates that the

Tables 2: Equilibrium gas mixture

x_1	Mole fraction CO	0.322871
x_2	Mole fraction CO_2	0.009224
x_3	Mole fraction $H2_O$	0.046017
x_4	Mole fraction $H2$	0.618172
x_5	Mole fraction CH_4	0.003717
x_6	Mole fraction O_2/CH_4	0.576715
x_7	Total moles of product	2.977863

Newton-Raphson's iteration method is perfectly a non-linear Newton's fixed point iteration method in the solution of the chemical equilibrium problem as demonstrated in section three.

REFERNCES

1. Alefeld G, Potra FA, Shen Z. On the existence theorems of Kontorovich, more and Mirands, Comput Suppl 2001;15:21-8.
2. Ames W. Nonlinear Ordinary Differential Equations in Transport Processes. New York: Academic Press; 1968.
3. Agyros IK. On an interative algorithon for solving non linear equations beritrage zir. Numerschen Math 19981;1:83-92.
4. Agyros IK. Some generalized projection methods for solving operator equations. J Comput Appl Math 1992;39:1-6.
5. Ralston A, Wilf HS. Mathematical Methods for Digital Computers. New York: Wiley; 1960.
6. Carnahan B, Luther HA, James WO. Applied Numerical Methods. Sydney, Toronto: John Wiley and Sons in Cooperated;1975.
7. Jenkins FA, White HE. Fundamentals of Optics. 2nd ed. United States: McGraw-Hill Education; 1951.
8. Traub RF. Iterative Methods for the Solution of Equations. New Jessey: Prentice-Hall, Eagle Wood Cliffa; 1964.
9. Ortega JM, Rheinboldt WC. Iterative Solution of non Linear Equations in Several Variable. New York: Academic Press; 1970.
10. Rall LB. Computational Solution of non Linear Operator Egns. New York: Wiley; 1968.