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A COMPUTER CODE SIMULATING MULTISTAGE CHEMICAL EXCHANGE COLUMN  
UNDER WIDE RANGE OF OPERATING CONDITIONS

September 1996

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A Computer Code Simulating Multistage Chemical Exchange Column  
under Wide Range of Operating Conditions

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A computer code has been developed to simulate a multistage CECE(Combined Electrolysis Chemical Exchange) column. The solution of basic equations can be found out by the Newton-Raphson method. The independent variables are the atom fractions of D and T in each stage for the case where H is dominant within the column. These variables are replaced by those of H and T under the condition that D is dominant. Some effective techniques have also been developed to get a set of solutions of the basic equations: a setting procedure of initial values of the independent variables; and a procedure for the convergence of the Newton-Raphson method. The computer code allows us to simulate the column behavior under a wide range of the operating conditions. Even for a severe case, where the dominant species changes along the column height, the code can give a set of solutions of the basic equations.

Keywords: Fusion Reactor, Isotope Separation, Water Detritiation, Tritium, Chemical Exchange, Multistage, Newton-Raphson, Convergence, Initial Value, Independent Variable

多様な運転条件下における多段型化学交換塔挙動を  
シミュレーションする計算コード

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山西 敏彦・奥野 健二

(1996年 8月 7日 受理)

多段型CECE（化学交換塔）の挙動をシミュレーションするために、計算コードを開発した。導かれた基礎式の解は、ニュートン-ラフソン法で求めることができる。式の独立変数は、塔内の主成分がHの場合、充填部各段のDとTの原子分率である。この独立変数は、塔内の主成分がDである場合、充填部格段のHとTの原子分率に置き換えられる。更に基礎式の解を得るために、独立変数の初期値の与え方、ニュートン-ラフソン法の収束手法に関して、効果的な方法をコードに導入した。計算コードは、多様な運転条件下での塔挙動をシミュレーションすることができる。主成分が塔の高さ方向で変化するという、計算上極めて厳しい条件においても、コードは塔挙動の解を与えることができる。

## Contents

1. Introduction .....	1
2. Mathematical Simulation Procedure .....	2
2.1 Basic Equations for the Catalyst Bed .....	3
2.2 Basic Equations for the Scrubbing Trays .....	9
2.3 Basic Equations for the Electrolysis Cell .....	12
2.4 Bubble Point Calculation .....	13
2.5 Physical Properties .....	13
2.6 Simulation Procedure .....	14
2.7 Application of Broyden's Method .....	17
3. Numerical Example .....	18
4. Convergence Technique .....	19
5. Conclusion .....	21
Acknowledgement .....	22
References .....	23
Nomenclature .....	25

## 目 次

1. 緒 言 .....	1
2. 数学的シミュレーション手法 .....	2
2.1 触媒層に対する基礎式 .....	3
2.2 充填部に対する基礎式 .....	9
2.3 電解セルに対する基礎式 .....	12
2.4 沸点計算 .....	13
2.5 物 性 .....	13
2.6 シミュレーション手法 .....	14
2.7 プロイデンの方法の適用 .....	17
3. 解析例 .....	18
4. 収束手法 .....	19
5. 結 論 .....	21
謝 辞 .....	22
参考文献 .....	23
記号表 .....	25

## 1. INTRODUCTION

A CECE(Combined Electrolysis Chemical Exchange) column<sup>1,2</sup> is one of the most attractive processes for the separation of water isotopes. The column is composed of an electrolysis cell, a liquid phase catalytic exchange section, and a recombiner. The hydrogen gas produced by the electrolysis cell at the bottom of the column flows in the liquid phase catalytic exchange section, and is oxidized to water by the recombiner. The water drops to the electrolysis cell again. A high separation factor can thus be obtained by a single column. However, it has been known that the catalysts which cause the water/hydrogen exchange reactions often lose the activity; where the surface of the catalyst is covered with liquid water<sup>3,4</sup>. A multistage type column has been proposed to overcome this problem. A liquid-vapor scrubbing step proceeds in a sieve tray; while a vapor-hydrogen exchange step is separately caused in a hydrophobic catalyst bed (See Fig. 1)<sup>5,6</sup>. This type of column is expected to be promising for the system of tritium recovery from the tritiated waste water in fusion reactors and from the heavy water in fission reactors.

The multistage CECE column has been designed and operated for the enrichment of D<sub>2</sub>O in a fission reactor in Japan. However, the characteristics of the column have not yet been understood. The authors have previously developed a simulation code dealing with all the twelve molecular species of hydrogen gas and water for the multistage CECE column<sup>7</sup>. The equilibrium of the atomic elements in the liquid phase is also taken into account. The Murphree-type factors are introduced in the code to consider the efficiencies of scrubbing trays and catalysts beds. The atom fractions of

D and T on the scrubbing trays are the independent variables of the code. By using this code, the characteristics of the column have been studied in detail<sup>8</sup>. However, a serious problem was found for the code: the solution was not obtained for the case where H is not a dominant species within the column. To overcome this problem, it is strongly required to improve our previous code.

This paper describes the simulation code which is improved from our previously proposed code<sup>7</sup>. The improved code allows us to simulate the column behavior under a wide range of the operating conditions. Even for a severe case, where the dominant species changes along the column height, the improved code can give a set of solutions of the basic equations.

## 2. MATHEMATICAL SIMULATION PROCEDURE

The model column is illustrated in Fig. 2. The column has the recombiner at the top and the electrolysis cell at the bottom. The liquid phase catalytic exchange section is composed of N sieve trays and (N-1) catalyst beds. The model can accept multiple feed streams and multiple withdrawal streams of liquid water and hydrogen gas. The differences in latent heat of vaporization can be neglected for the isotopes of water. An operating temperature is slightly higher than the room temperature, and a hot water jacket is attached to the column. Hence, the heat transfer through the column wall is expected to be negligible. As a consequence, the heat balance equations are not required to taken into account. The flow rates of liquid, vapor, and hydrogen gas are input variables. The bottom product is either a hydrogen gas or a water stream.



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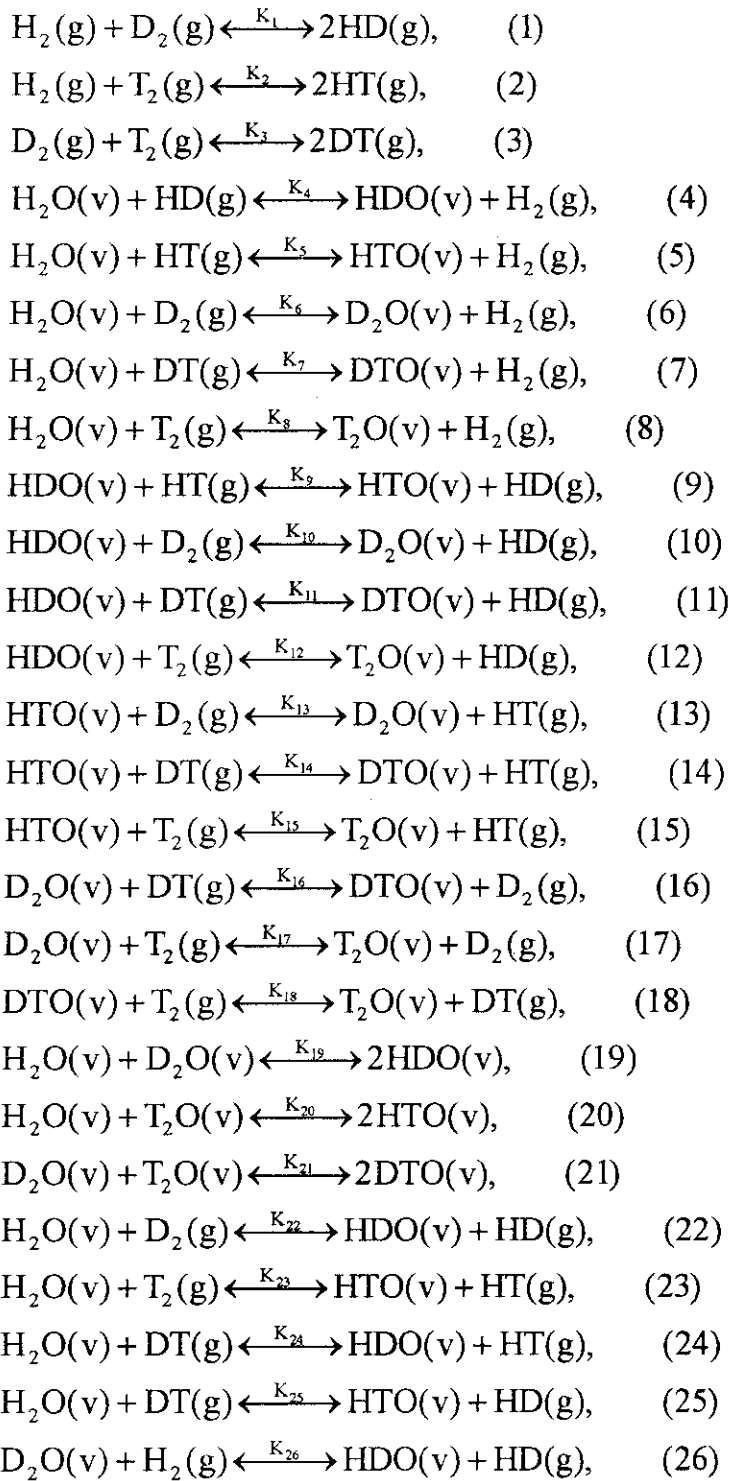
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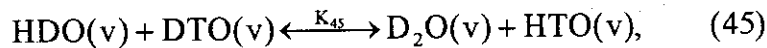
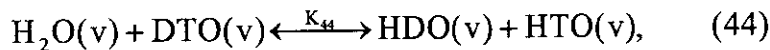
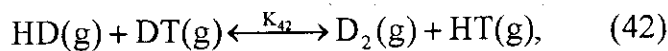
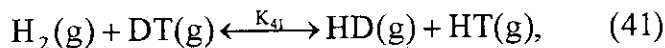
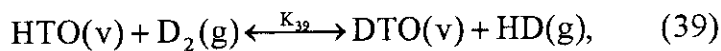
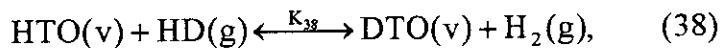
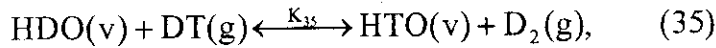
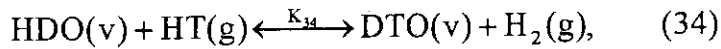
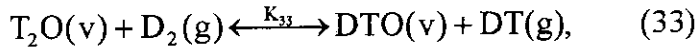
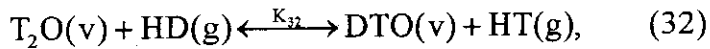
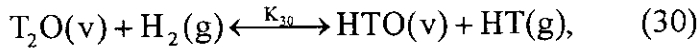
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## 2.1 Basic equations for the catalyst bed

There are twelve molecular species of hydrogen gas and water vapor. The following 45 reactions can be described between the water vapor and the hydrogen gas:





From the stoichiometric matrix of the reactions of (1)~(45), it can be shown that the rank of the matrix is eight. In other words, among 45 reactions, only eight reactions are independent. For instance, the equilibrium constants of the reactions of (9)~(45) can be described by using those of the reactions of (1)~(8):

$$\begin{aligned}
K_9 &= K_5/K_4, & K_{10} &= K_6/K_4, & K_{11} &= K_7/K_4, & K_{12} &= K_8/K_4, \\
K_{13} &= K_6/K_5, & K_{14} &= K_7/K_5, & K_{15} &= K_8/K_5, & K_{16} &= K_7/K_6, \\
K_{17} &= K_8/K_6, & K_{18} &= K_8/K_7, & K_{19} &= K_1 K_4^2 / K_6, & K_{20} &= K_2 K_5^2 / K_8, \\
K_{21} &= K_3 K_7^2 / (K_6 K_8), & K_{22} &= K_4 K_1, & K_{23} &= K_5 K_2, \\
K_{24} &= K_4 \sqrt{K_1 K_2 / K_3}, & K_{25} &= K_5 \sqrt{K_1 K_2 / K_3}, & K_{26} &= K_1 K_4 / K_6, \\
K_{27} &= K_4 / (K_6 \sqrt{K_2 / K_1 K_3}), & K_{28} &= K_7 / (K_6 \sqrt{K_2 / K_1 K_3}), & K_{29} &= K_3 K_7 / K_6, \\
K_{30} &= K_2 K_5 / K_8, & K_{31} &= K_5 \sqrt{K_2 K_3 / K_1} / K_8, & K_{32} &= K_7 \sqrt{K_2 K_3 / K_1} / K_8, \\
K_{33} &= K_7 K_3 / K_8, & K_{34} &= K_7 \sqrt{K_1 K_2 / K_3} / K_4, & K_{35} &= K_5 \sqrt{K_2 / K_1 K_3} / K_4, \\
K_{36} &= K_7 \sqrt{K_2 K_3 / K_1} / K_4, & K_{37} &= K_5 \sqrt{K_2 K_3 / K_1} / K_4, \\
K_{38} &= K_7 / (K_5 \sqrt{K_1 K_2 / K_3}), & K_{39} &= K_7 / (K_5 \sqrt{K_2 / K_1 K_3}), & K_{40} &= \sqrt{K_2 K_3 / K_1}, \\
K_{41} &= \sqrt{K_1 K_2 / K_3}, & K_{42} &= \sqrt{K_2 / K_1 K_3}, & K_{43} &= K_5 K_7 \sqrt{K_2 K_3 / K_1} / (K_4 K_8), \\
K_{44} &= K_4 K_5 \sqrt{K_1 K_2 / K_3} / K_7, & K_{45} &= K_5 K_6 \sqrt{K_2 / K_1 K_3} / K_7
\end{aligned}
\tag{46}$$

On the assumption that compositions of the input streams,  $y_{i,j+1}^{\text{out}}$ 's and  $z_{i,j+1}$ 's, are all known, there are ten unknown variables for the output streams:  $y_{i,j}^{\text{in}}$ , and  $z_{i,j}$ . Eight equations can be described from the eight reactions among the 45 reactions. From the mass balances for atomic elements of the catalyst bed, two equations can be obtained. Thus, ten equations are prepared.

It has been known that the rates of the three reactions (1)~(3) are very rapid<sup>9</sup>. It can be assumed that the equilibrium for the three reactions is readily achieved at the outlet of the catalyst bed. The bed performance is not a monotone increasing function of  $\gamma$ . It may be better to introduce a factor for each hydrogen-water exchange reaction. However, there has been no experimental data for the efficiency of catalyst bed; and it is quite difficult to give a reasonable value for the factor of each reaction. For these reasons, we introduce the Murphree-type factors to take the efficiency of the catalyst bed

into account :

$$\gamma = \frac{y_{i,j}^{\text{in}} - y_{i,j+1}^{\text{out}}}{y_{i,j}^{\text{in,eq}} - y_{i,j+1}^{\text{out}}} \quad (47)$$

As described in the precede section, the CECE column would be used for the tritium recovery systems from waste water in the fusion reactor and from the heavy water in the fission reactor<sup>3,6</sup>. From viewpoint of radiological hazard, it is not desired to concentrate the tritium as a form of water. A stream containing T is sent to a ISS(Hydrogen Isotope Separation) system, and a high purity tritium stream is produced from the ISS system. This means that the dominant species within the column is either H or D. In the case where the dominant species is H, the reactions of (1)~(8) are chosen, and the mass balances are taken for D and T. Consequently, four equations are derived for four unknown variables of  $z_{2,j}$ ,  $z_{3,j}$ ,  $z_{4,j}$ ,  $z_{6,j}$ <sup>7</sup> :

$$F_1 = z_{2,j}^2 - K_1 z_{4,j} (1.0 - z_{2,j} - z_{3,j} - z_{4,j} - \sqrt{K_3 z_{6,j} z_{4,j}} - z_{6,j}) = 0$$

$$F_2 = z_{3,j}^2 - K_2 z_{6,j} (1.0 - z_{2,j} - z_{3,j} - z_{4,j} - \sqrt{K_3 z_{6,j} z_{4,j}} - z_{6,j}) = 0$$

$$F_3 = G_j a_2 + V_{j+1} b_2 - G_j \left( \frac{z_{2,j}}{2} + z_{4,j} + \frac{\sqrt{K_3 z_{4,j} z_{6,j}}}{2} \right) -$$

$$V_{j+1} \gamma \left\{ \left( \frac{K_4 z_{2,j}}{2} + K_6 z_{4,j} + \frac{K_7 \sqrt{K_3 z_{4,j} z_{6,j}}}{2} \right) / \text{xx} \right\} - V_{j+1} (1 - \gamma) b_2 = 0$$

$$F_4 = G_j a_1 + V_{j+1} b_1 - G_j \left( \frac{z_{3,j}}{2} + z_{6,j} + \frac{\sqrt{K_3 z_{4,j} z_{6,j}}}{2} \right) -$$

$$V_{j+1} \gamma \left\{ \left( \frac{K_5 z_{3,j}}{2} + K_8 z_{6,j} + \frac{K_7 \sqrt{K_3 z_{4,j} z_{6,j}}}{2} \right) / \text{xx} \right\} - V_{j+1} (1 - \gamma) b_1 = 0$$

$$\text{xx} = (K_4 - 1)z_{2,j} + (K_5 - 1)z_{3,j} + (K_6 - 1)z_{4,j} +$$

$$(K_7 - 1)\sqrt{K_3 z_{4,j} z_{6,j}} + (K_8 - 1)z_{6,j} + 1.0$$

$$\begin{aligned}
a_1 &= \frac{z_{5,j+1}}{2} + z_{6,j+1} + \frac{z_{3,j+1}}{2} \\
a_2 &= \frac{z_{2,j+1}}{2} + z_{4,j+1} + \frac{z_{5,j+1}}{2} \\
b_1 &= \frac{y_{5,j+1}^{\text{out}}}{2} + y_{6,j+1}^{\text{out}} + \frac{y_{3,j+1}^{\text{out}}}{2} \\
b_2 &= \frac{y_{2,j+1}^{\text{out}}}{2} + y_{4,j+1}^{\text{out}} + \frac{y_{5,j+1}^{\text{out}}}{2} \\
z_{i,j+1} &= (z_{i,j+1} G_{j+1} + z z_{i,j} F z_j) / (G_{j+1} + F z_j)
\end{aligned} \tag{48}$$

For the case where D is dominant, the mass balances should be taken for H and T. In addition, the equations should not be derived for  $z_{4,j}$ . We use the reactions of (1)~(3), (6), (10), (13), (16), and (17), and obtain the four equations for  $z_{1,j}$ ,  $z_{2,j}$ ,  $z_{5,j}$ , and  $z_{6,j}$ :

$$\begin{aligned}
F_5 &= z_{2,j}^2 - K_1 z_{1,j} (1.0 - z_{1,j} - z_{2,j} - z_{5,j} - \sqrt{K_2 z_{6,j} z_{1,j}} - z_{6,j}) = 0 \\
F_6 &= z_{5,j}^2 - K_3 z_{6,j} (1.0 - z_{1,j} - z_{2,j} - z_{5,j} - \sqrt{K_2 z_{6,j} z_{1,j}} - z_{6,j}) = 0 \\
F_7 &= G_j a_3 + V_{j+1} b_3 - G_j \left( \frac{z_{2,j}}{2} + z_{1,j} + \frac{\sqrt{K_2 z_{1,j} z_{6,j}}}{2} \right) - \\
&V_{j+1} \gamma \left\{ \left( \frac{z_{2,j}}{2K_{10}} + \frac{z_{1,j}}{K_6} + \frac{\sqrt{K_2 z_{1,j} z_{6,j}}}{2K_{13}} \right) / \text{xx} \right\} - V_{j+1} (1 - \gamma) b_3 = 0 \\
F_8 &= G_j a_4 + V_{j+1} b_4 - G_j \left( \frac{z_{5,j}}{2} + z_{6,j} + \frac{\sqrt{K_2 z_{1,j} z_{6,j}}}{2} \right) - \\
&V_{j+1} \gamma \left\{ \left( \frac{K_{16} z_{5,j}}{2} + K_{17} z_{6,j} + \frac{\sqrt{K_2 z_{1,j} z_{6,j}}}{2K_{13}} \right) / \text{xx} \right\} - V_{j+1} (1 - \gamma) b_4 = 0 \\
\text{xx} &= (1/K_6 - 1) z_{1,j} + (1/K_{10} - 1) z_{2,j} + (K_{16} - 1) z_{5,j} + \\
&(1/K_{13} - 1) \sqrt{K_2 z_{1,j} z_{6,j}} + (K_{17} - 1) z_{6,j} + 1.0
\end{aligned}$$

$$\begin{aligned}
 a_3 &= \frac{z_{2,j+1}}{2} + z_{1,j+1} + \frac{z_{3,j+1}}{2} \\
 a_4 &= \frac{z_{3,j+1}}{2} + z_{6,j+1} + \frac{z_{5,j+1}}{2} \\
 b_3 &= \frac{y_{2,j+1}^{out}}{2} + y_{1,j+1}^{out} + \frac{y_{3,j+1}^{out}}{2} \\
 b_4 &= \frac{y_{3,j+1}^{out}}{2} + y_{6,j+1}^{out} + \frac{y_{5,j+1}^{out}}{2} \\
 z_{i,j+1} &= (z_{i,j+1} G_{j+1} + z z_{i,j} F z_j) / (G_{j+1} + F z_j)
 \end{aligned} \tag{49}$$

The equations of (48) and (49) can be solved by the Newton-Raphson method.

$$z^{k+1} = z^k + \Delta z^k,$$

$$\Delta z^k = -J_F^{-1} F,$$

$$z = \begin{pmatrix} z_{2,j} \\ z_{3,j} \\ z_{4,j} \\ z_{6,j} \end{pmatrix} \text{ or } z = \begin{pmatrix} z_{1,j} \\ z_{2,j} \\ z_{5,j} \\ z_{6,j} \end{pmatrix}, \quad F = \begin{pmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \end{pmatrix} \text{ or } \begin{pmatrix} F_5 \\ F_6 \\ F_7 \\ F_8 \end{pmatrix}, \tag{50}$$

$$J_F = \begin{pmatrix} \partial F_1 / \partial z_{2,j} & \dots & \partial F_1 / \partial z_{6,j} \\ \dots & \dots & \dots \\ \partial F_4 / \partial z_{2,j} & \dots & \partial F_4 / \partial z_{6,j} \end{pmatrix} \text{ or } \begin{pmatrix} \partial F_5 / \partial z_{1,j} & \dots & \partial F_5 / \partial z_{6,j} \\ \dots & \dots & \dots \\ \partial F_8 / \partial z_{1,j} & \dots & \partial F_8 / \partial z_{6,j} \end{pmatrix}$$

## 2.2 Basic equations for the scrubbing trays

The mass balance equations for atomic element of H can be derived as follows:

$$\begin{pmatrix} B_1 & C_1 & \dots & \dots & \dots & \dots \\ A_2 & B_2 & C_2 & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & A_{N-1} & B_{N-1} & C_{N-1} \\ \dots & \dots & \dots & \dots & A_N & B_N \end{pmatrix} \begin{pmatrix} X_{H,1}^{out} \\ \dots \\ \dots \\ \dots \\ X_{H,N}^{out} \end{pmatrix} = \begin{pmatrix} E_1 \\ \dots \\ \dots \\ \dots \\ E_N \end{pmatrix}, \tag{51}$$



where

$$\begin{aligned}
 A_j &= -L_{j-1}, & B_j &= L_j + U_j + \kappa_{H,j} V_j, & C_j &= -V_{j+1} \kappa_{H,j+1}, \\
 E_1 &= (V_1 + G_1 - D) X_{H,1}^{\text{in}} + V_2 \beta_{H,1} + F_1 Z f_{H,1}, \\
 E_j &= V_{j+1} \beta_{H,j} + F_j Z f_{H,j}, \\
 E_N &= v Y_{H,N}^{\text{in}} + F_N Z f_{H,N}, \\
 \beta_{H,j} &= \frac{y_{2,j}^{\text{in}} - y_{2,j+1}^{\text{out}}}{2} + y_{1,j}^{\text{in}} - y_{1,j+1}^{\text{out}} + \frac{y_{3,j}^{\text{in}} - y_{3,j+1}^{\text{out}}}{2}, \\
 \kappa_{H,j} &= \left( \frac{y_{2,j}^{\text{out}}}{2} + y_{1,j}^{\text{out}} + \frac{y_{3,j}^{\text{out}}}{2} \right) / \left( \frac{x_{2,j}^{\text{out}}}{2} + x_{1,j}^{\text{out}} + \frac{x_{3,j}^{\text{out}}}{2} \right), \\
 X_{H,j}^{\text{in,out}} &= \frac{x_{2,j}^{\text{in,out}}}{2} + x_{1,j}^{\text{in,out}} + \frac{x_{3,j}^{\text{in,out}}}{2}, & Y_{H,j}^{\text{in,out}} &= \frac{y_{2,j}^{\text{in,out}}}{2} + y_{1,j}^{\text{in,out}} + \frac{y_{3,j}^{\text{in,out}}}{2}, \\
 Z f_{H,j} &= \frac{z f_{2,j}}{2} + z f_{1,j} + \frac{z f_{3,j}}{2}, & x_{i,j}^{\text{in}} &= x_{i,j-1}^{\text{out}}
 \end{aligned} \tag{52}$$

The distributions of L, G, and V within the column can be calculated by

$$\begin{aligned}
 G_j &= G_{j+1} + F z_j, \\
 V_j &= V_{j+1} + F z_j \delta_j / (1 - \delta_j), \\
 \delta_j &= p_{ii}^*(T_{av}) / P_j, \\
 L_j &= G_1 - D + V_{j+1} + SF - SU, \\
 SF &= \sum_{j=1}^j F_j, \\
 SU &= \sum_{j=1}^j U_j,
 \end{aligned} \tag{53}$$

Similar equations are derived for atomic elements of D and T also.

The Murphree-type factor is introduced for the efficiency of the scrubbing trays also<sup>9</sup>:

$$\alpha = \frac{y_{i,j}^{\text{out}} - y_{i,j}^{\text{in}}}{y_{i,j}^{\text{out,eq}} - y_{i,j}^{\text{in}}}, \quad y_{i,j}^{\text{out,eq}} = \frac{(V_j + G_j) p_i^*(T_j) x_{i,j}^{\text{out}}}{V P_j} \tag{54}$$

For the liquid water phase, the three equilibrium reactions are described by



The equilibrium compositions can be obtained by

$$\begin{aligned}
 Q_1 x_{2,j}^{\text{out}^4} + Q_2 x_{2,j}^{\text{out}^3} + Q_3 x_{2,j}^{\text{out}^2} + Q_4 x_{2,j}^{\text{out}} + Q_5 &= 0, \\
 Q_1 &= q_1^2 q_6 + q_1 q_4 q_8, \\
 Q_2 &= 2q_1 q_2 q_6 + q_2 q_4 q_8 + q_1 q_5 q_8 + q_1 q_4 q_7 + q_4^2 q_9, \\
 Q_3 &= 2q_1 q_3 q_6 + q_2^2 q_6 + q_1 q_5 q_7 + q_2 q_5 q_8 + q_2 q_4 q_7 + q_3 q_4 q_8 \\
 &\quad + 2q_4 q_5 q_9 + q_4^2 q_{10}, \\
 Q_4 &= 2q_2 q_3 q_6 + q_2 q_5 q_7 + q_3 q_5 q_8 + q_3 q_4 q_7 + q_5^2 q_9 + 2q_4 q_5 q_{10}, \\
 Q_5 &= q_3^2 q_6 + q_3 q_5 q_7 + q_5^2 q_{10}, \\
 q_1 &= 2 - \frac{K_{46}}{2}, \quad q_2 = K_{46}(1 - X_{\text{T},j}^{\text{out}}), \quad q_3 = -2K_{46} X_{\text{D},j}^{\text{out}} X_{\text{T},j}^{\text{out}} \\
 q_4 &= \frac{K_{46}}{2} - \sqrt{K_{46} K_{47} / K_{48}}, \quad q_5 = -K_{46} X_{\text{H},j}^{\text{out}}, \quad q_6 = 2 - \frac{K_{48}}{2}, \\
 q_7 &= K_{48}(1 - X_{\text{H},j}^{\text{out}}), \quad q_8 = \sqrt{K_{47} K_{48} / K_{46}} - \frac{K_{48}}{2}, \quad q_9 = K_{48} X_{\text{T},j}^{\text{out}}, \\
 q_{10} &= -2K_{48} X_{\text{T},j}^{\text{out}} X_{\text{D},j}^{\text{out}}, \quad x_{5,j}^{\text{out}} = (q_1 x_{2,j}^{\text{out}^2} + q_2 x_{2,j}^{\text{out}} + q_3) / (q_4 x_{2,j}^{\text{out}} + q_5), \\
 x_{4,j}^{\text{out}} &= X_{\text{D},j}^{\text{out}} - \frac{x_{2,j}^{\text{out}}}{2} - \frac{x_{5,j}^{\text{out}}}{2}, \quad x_{6,j}^{\text{out}} = \frac{x_{5,j}^{\text{out}^2}}{K_{48} x_{4,j}^{\text{out}}}, \\
 x_{3,j}^{\text{out}} &= 2 \left( X_{\text{T},j}^{\text{out}} - x_{6,j}^{\text{out}} - \frac{x_{5,j}^{\text{out}}}{2} \right), \quad x_{1,j}^{\text{out}} = 1 - x_{2,j}^{\text{out}} - x_{3,j}^{\text{out}} - x_{4,j}^{\text{out}} - x_{5,j}^{\text{out}} - x_{6,j}^{\text{out}}
 \end{aligned} \tag{56}$$

In the case where D is dominant species, it is better to replace the last two equations in Eq. (56) by the following equations.

$$x_{3,j}^{\text{out}} = \sqrt{K_{47} x_{1,j}^{\text{out}} x_{6,j}^{\text{out}}} \quad \text{and} \quad x_{1,j}^{\text{out}} = \frac{x_{2,j}^{\text{out}^2}}{K_{46} x_{4,j}^{\text{out}}} \tag{57}$$

### 2.3 Basic equations for the electrolysis cell

Two factors are introduced to consider the separation efficiency of the electrolysis cell.

$$\begin{aligned}\eta_D &= \left\{ (1 - Z_{D,N}) / Z_{D,N} \right\} / \left\{ (1 - Y_{D,N}^{in}) / Y_{D,N}^{in} \right\}, \\ \eta_T &= \left\{ (1 - Z_{T,N}) / Z_{T,N} \right\} / \left\{ (1 - Y_{T,N}^{in}) / Y_{T,N}^{in} \right\}, \\ Z_{D,N} &= z_{4,N} + \frac{z_{2,N}}{2} + \frac{z_{5,N}}{2}, \quad Z_{T,N} = z_{6,N} + \frac{z_{3,N}}{2} + \frac{z_{5,N}}{2}\end{aligned}\quad (58)$$

From the mass balances of atomic elements of D and T around the electrolysis cell, we obtain

$$\begin{aligned}Y_{D,N}^{in} &= \left( \sqrt{o_1^2 - 4o_2o_3} - o_1 \right) / 2o_2, \\ Y_{T,N}^{in} &= \left( \sqrt{o_4^2 - 4o_5o_6} - o_4 \right) / 2o_5, \\ o_1 &= v\eta_D + o_7 - L_N X_{D,N}^{out} (1 - \eta_D), \\ o_2 &= v(1 - \eta_D), \quad o_3 = -L_N X_{D,N}^{out} \eta_D, \\ o_4 &= v\eta_T + o_7 - L_N X_{T,N}^{out} (1 - \eta_T), \\ o_5 &= v(1 - \eta_T), \quad o_6 = -L_N X_{T,N}^{out} \eta_T,\end{aligned}\quad (59)$$

$o_7 = G_N + W$  (Bottom product is hydrogen.) or  $= G_N$  (Bottom product is water.)

In liquid phase, the equilibrium reactions of (55) must be considered:

$$\begin{aligned}y_{2,N}^{in} / (y_{1,N}^{in} y_{4,N}^{in}) &= K_{46} \left\{ (p_2^*(T_e))^2 / p_1^*(T_e) p_4^*(T_e) \right\}, \\ y_{3,N}^{in} / (y_{1,N}^{in} y_{6,N}^{in}) &= K_{47} \left\{ (p_3^*(T_e))^2 / p_1^*(T_e) p_6^*(T_e) \right\}, \\ y_{5,N}^{in} / (y_{6,N}^{in} y_{4,N}^{in}) &= K_{48} \left\{ (p_5^*(T_e))^2 / p_6^*(T_e) p_4^*(T_e) \right\}\end{aligned}\quad (60)$$

The values of  $y_{i,N}^{in}$  can be calculated by Eq. (56), where  $x_{i,j}^{out}$ ,  $X_{D,j}^{out}$ , and  $X_{T,j}^{out}$  are replaced by  $y_{i,N}^{in}$ ,  $Y_{D,N}^{in}$ , and  $Y_{T,N}^{in}$ , respectively. The constants of  $K_{46,47,48}$  are replaced by the right sides of Eq. (60). Also in gas phase, the equilibrium reactions of (1)~(3) must

be considered. In Eq. (56),  $x_{i,j}^{\text{out}}$ ,  $X_{D,j}^{\text{out}}$ , and  $X_{T,j}^{\text{out}}$  are replaced by  $z_{i,N}$ ,  $Z_{D,N}$ , and  $Z_{T,N}$ , respectively. The constants of  $K_{46,47,48}$  are replaced by  $K_{1,2,3}$ . Hence, if the atom fractions of D and T in the water stream to the electrolysis cell are given,  $y_{i,N}^{\text{in}}$ 's and  $z_{i,N}$ 's can be calculated from Eqs. (56)~(60).

## 2.4 Bubble point calculation

The temperatures of sieve trays,  $T_j$ 's, can be calculated by the Newton method:

$$\begin{aligned} f(T_j) &= \sum_{i=1}^m y_{i,j}^{\text{out,eq}} - 1 = 0, \\ T_j^{k+1} &= T_j^k + \Delta T_j^k, \\ \Delta T_j^k &= -f(T_j^k) / \frac{df(T_j^k)}{dT_j^k} \end{aligned} \quad (61)$$

## 2.5 Physical properties

The vapor pressure of water and equilibrium constants of the reactions are needed as the physical properties. The vapor pressure of the six isotopic species of water can be calculated by the equations reported by Van Hook<sup>10</sup>.

$$p_i^*(T_j) = 1.013 \times 10^5 \exp \left[ \phi_{1,i}/T_j^2 + \phi_{2,i}/T_j + \phi_{3,i}/(T_j + \phi_{4,i}) + \phi_{5,i} \right]. \quad (62)$$

We describe the equilibrium constants as a function of temperature from the values at several temperatures listed in Ref. 11.

$$\ln(K) = \lambda_1/T + \lambda_2 \quad (63)$$

The parameters of Eqs. (62) and (63) are presented in Tables 1 and 2, respectively.

## 2.6 Simulation procedure

The basic equations derived in preceding sections can be solved by the Newton-Raphson method. The simulation procedure is as follows.

- (i) Calculate the distributions of L, G, and V from Eq. (53).
- (ii) Assume the atom fractions of D and T in liquid water streams leaving the sieve trays,  $X_{D,j}^{out}$ 's and  $X_{T,j}^{out}$ 's for the case where H is dominant species within the column. The independent variables are the atom fractions of H and T,  $X_{H,j}^{out}$ 's and  $X_{T,j}^{out}$ 's for the case where D is dominant. A practical method is that all the atom fractions of D and T or H and T are equal to the average values of all the water feed streams:

$$\begin{aligned} X_{D,j}^{out} &= \sum_{j=1}^N \left( z f_{4,j} + \frac{z f_{2,j}}{2} + \frac{z f_{5,j}}{2} \right) / \sum_{j=1}^N F_j, \quad \text{or} \\ X_{H,j}^{out} &= \sum_{j=1}^N \left( z f_{1,j} + \frac{z f_{2,j}}{2} + \frac{z f_{3,j}}{2} \right) / \sum_{j=1}^N F_j, \\ X_{T,j}^{out} &= \sum_{j=1}^N \left( z f_{6,j} + \frac{z f_{5,j}}{2} + \frac{z f_{3,j}}{2} \right) / \sum_{j=1}^N F_j \end{aligned} \quad (64)$$

- (iii) Assume the temperatures of the sieve trays. From Eqs. (56) and (57),  $x_{i,j}^{out}$ 's are calculated.

- (iv) By the bubble point calculation, Eqs. (61) and (62),  $T_j$ 's and  $y_{i,j}^{out,eq}$ 's become all known. If the temperatures assumed in step (iii) are not equal to the values calculated by the bubble point calculation, return to step (iii).

- (v) Since  $x_{i,N}^{out}$ 's are known,  $y_{i,N}^{in}$ 's and  $z_{i,N}$ 's can be calculated from Eqs. (56)~(60) and (63).

- (vi) By accounting for the scrubbing efficiencies for the N'th tray,  $y_{i,N}^{out}$ 's are calculated from Eq. (54).

(vii) Then, the catalyst beds are treated. From  $y_{i,N}^{out}$ 's and  $z_{i,N}$ 's,  $y_{i,N-1}^{in}$  and  $z_{i,N-1}$ 's can be calculated with the efficiency of the catalyst bed by Eqs. (47)~(50) and (63).

(viii) Steps (vi) and (vii) are sequentially carried out from  $j=N-1$  to 1. Thus,  $y_{i,j}^{out}$ 's,  $y_{i,j}^{in}$ 's, and  $z_{i,j}$ 's for  $j=1$  to  $N$  become known.

(ix) Now we can evaluate all the values of  $A_j$ 's,  $B_j$ 's,  $C_j$ 's, and  $E_j$ 's in Eq. (52). The new values of  $X_{H,j}^{out}$ 's,  $X_{D,j}^{out}$ 's, and  $X_{T,j}^{out}$ 's are obtained by solving the tridiagonal equations of Eq. (51) three times. Normarize the new atom fractions of H, D and T.

(x) Denote the value of  $X_{D,j}^{out}$ 's and  $X_{T,j}^{out}$ 's or  $X_{H,j}^{out}$ 's and  $X_{T,j}^{out}$ 's assumed at step (ii) by  $(X_{D,j}^{out})_0$  and  $(X_{T,j}^{out})_0$  or  $(X_{H,j}^{out})_0$  and  $(X_{T,j}^{out})_0$ . The values of  $X_{D,j}^{out}$ 's and  $X_{T,j}^{out}$ 's or  $X_{H,j}^{out}$ 's and  $X_{T,j}^{out}$ 's are not equal to  $(X_{D,j}^{out})_0$  and  $(X_{T,j}^{out})_0$  or  $(X_{H,j}^{out})_0$  and  $(X_{T,j}^{out})_0$ .

The functions of  $S_j$ 's are defined by

$$\begin{aligned} S_j &= (X_{D,j}^{out})_0 - X_{D,j}^{out} = 0 \quad (j = 1, N), \quad \text{or} \\ S_j &= (X_{H,j}^{out})_0 - X_{H,j}^{out} = 0 \quad (j = 1, N), \\ S_{j+N} &= (X_{T,j}^{out})_0 - X_{T,j}^{out} = 0 \quad (j = 1, N) \end{aligned} \tag{65}$$

The simulation can be understood to find out the solution of Eq. (65). This is carried out by the 2N-variable Newton-Raphson method.

$$\mathbf{X}^{k+1} = \mathbf{X}^k + \Delta\mathbf{X}^k,$$

$$\Delta\mathbf{X}^k = -\mathbf{J}_S^{-1}\mathbf{S},$$

$$\mathbf{X} = \begin{pmatrix} X_{D,1}^{\text{out}} \\ \vdots \\ X_{D,N}^{\text{out}} \\ X_{T,1}^{\text{out}} \\ \vdots \\ X_{T,N}^{\text{out}} \end{pmatrix}, \quad \text{or} = \begin{pmatrix} X_{H,1}^{\text{out}} \\ \vdots \\ X_{H,N}^{\text{out}} \\ X_{T,1}^{\text{out}} \\ \vdots \\ X_{T,N}^{\text{out}} \end{pmatrix}, \quad \mathbf{S} = \begin{pmatrix} S_1 \\ \vdots \\ S_N \\ S_{N+1} \\ \vdots \\ S_{2N} \end{pmatrix},$$

$$\mathbf{J}_S = \begin{pmatrix} \partial S_1 / \partial (X_{D,1}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{D,1}^{\text{out}})_0 \\ \partial S_1 / \partial (X_{D,N}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{D,N}^{\text{out}})_0 \\ \partial S_1 / \partial (X_{T,1}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{T,1}^{\text{out}})_0 \\ \vdots & \ddots & \vdots \\ \partial S_1 / \partial (X_{T,N}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{T,N}^{\text{out}})_0 \end{pmatrix}, \quad \text{or}$$

$$= \begin{pmatrix} \partial S_1 / \partial (X_{H,1}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{H,1}^{\text{out}})_0 \\ \vdots & \ddots & \vdots \\ \partial S_1 / \partial (X_{H,N}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{H,N}^{\text{out}})_0 \\ \partial S_1 / \partial (X_{T,1}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{T,1}^{\text{out}})_0 \\ \vdots & \ddots & \vdots \\ \partial S_1 / \partial (X_{T,N}^{\text{out}})_0 & \cdots & \partial S_{2N} / \partial (X_{T,N}^{\text{out}})_0 \end{pmatrix}. \quad (66)$$

The partial derivatives are numerically calculated. For instance,

$$\partial S_j / \partial (X_{T,k}^{\text{out}})_0 = \left( S_j |_{(X_{T,k}^{\text{out}})_0} - S_j |_{(X_{T,k}^{\text{out}})_0 - \Delta(X_{T,k}^{\text{out}})_0} \right) / \Delta(X_{T,k}^{\text{out}})_0 \quad (67)$$

Each  $S_j$  in Eq. (67) is calculated from Eqs. (47)~(52), (54), (56)~(63).

(xi) Return to step (iii). If  $S_j$ 's are equal to zero, the variables in steps (i) through (xi) satisfy all the basic equations derived. The simulation problem is considered solved once

$$\sum_{j=1}^{2N} |S_j| / 2N \leq \varepsilon, \quad \varepsilon \approx 10^{-10} \quad (68)$$

is satisfied.

The simulation procedure thus described is illustrated in Fig. 3.

## 2.7 Application of Broyden's method

The order of Jacobian matrix is only twice the number of sieve trays in the present simulation code. However, if the number of sieve trays is large, long computation time is expected for evaluation of the Jacobian matrix and its inversion. To overcome this problem, Broyden's method<sup>12</sup> is applied in the code. The evaluation of the Jacobian matrix and its inversion are needed only once in his method.

The Jacobian matrix  $J_s$  is given in Eq. (66). Expressing  $-J_s^{-1}$  by  $H$ , the simulation procedure can be summarized as follows:

- (i) Obtain an initial estimate  $X^0$ .
- (ii) Calculate  $J_s$  and invert it. Thus  $H^0$  is obtained. Also calculate  $S^0$ .
- (iii) Compute  $\Delta X^0 = H^0 S^0$ .
- (iv) Calculate  $X^1 = X^0 + \tau \Delta X^0$ . In the case of  $\varphi^1 \leq \varphi^0$ ,  $\tau$  is set at unity. In the case of  $\varphi^1 \geq \varphi^0$ ,  $\tau$  is calculated from

$$\tau = \left\{ (1 + 6\theta)^{1/2} - 1 \right\} / 3\theta, \quad \theta = \varphi^1 / \varphi^0,$$

$$\varphi^1 = \sum_{j=1}^{2N} (S_j|_{X^0 + \Delta X^0})^2, \quad \varphi^0 = \sum_{j=1}^{2N} (S_j|_{X^0})^2 \quad (69)$$

Thus,  $X^1$  and  $S^1$  are calculated.

- (v) If the convergence has not been achieved yet, calculate  $H^1$  from



$$\mathbf{H}^1 = \mathbf{H}^0 - \left\{ \mathbf{H}^0 (\mathbf{S}^1 - \mathbf{S}^0) + \tau \Delta \mathbf{X}^0 \right\} (\Delta \mathbf{X}^0)^T \mathbf{H}^0 / \left\{ (\Delta \mathbf{X}^0)^T \mathbf{H}^0 (\mathbf{S}^1 - \mathbf{S}^0) \right\}, \quad (70)$$

$$(\mathbf{X})^T = (X_1, \dots, X_{2N})$$

(vi) The values of  $\mathbf{X}^1, \mathbf{S}^1, \mathbf{H}^1$  are substituted for  $\mathbf{X}^0, \mathbf{S}^0, \mathbf{H}^0$ , and repeat from step (iii).

For the second iteration or later, the Jacobian matrix can be calculated by Eqs. (69) and (70) instead of Eq. (67). The simulation procedure incorporating Broyden's method is also illustrated in Fig. 3.

### 3. NUMERICAL EXAMPLE

Our previous code could give a set of solutions in the case where H is dominant species within the column. No difficulty for the convergence was observed<sup>7</sup>. However, for the case where D is dominant, the difficulty for the convergence is sometimes observed. The improvement of the code has been carried out to overcome this problem. The basic equations and simulation procedure which should be used for the case where D is dominant are shown in sections of 2.1, 2.2, and 2.6. To evaluate the improvement of the code, a simulation was carried out for an example case. The input specifications and calculated results of the example case are presented in Tables 3 and 4 as Case 1. Heavy water containing T is supplied to the column. A small amount of D gas containing T is also supplied to the column. The situation of Case 1 can be expected for the system

$$\mathbf{H}^1 = \mathbf{H}^0 - \left\{ \mathbf{H}^0 (\mathbf{S}^1 - \mathbf{S}^0) + \tau \Delta \mathbf{X}^0 \right\} (\Delta \mathbf{X}^0)^T \mathbf{H}^0 / \left\{ (\Delta \mathbf{X}^0)^T \mathbf{H}^0 (\mathbf{S}^1 - \mathbf{S}^0) \right\}, \quad (70)$$

$$(\mathbf{X})^T = (X_1, \dots, X_{2N})$$

(vi) The values of  $\mathbf{X}^1, \mathbf{S}^1, \mathbf{H}^1$  are substituted for  $\mathbf{X}^0, \mathbf{S}^0, \mathbf{H}^0$ , and repeat from step (iii).

For the second iteration or later, the Jacobian matrix can be calculated by Eqs. (69) and (70) instead of Eq. (67). The simulation procedure incorporating Broyden's method is also illustrated in Fig. 3.

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recovering T from the heavy water of a fission reactor<sup>13</sup>. A hydrogen gas of D stream is withdrawn as the bottom product, whose DT mole fraction is increased by ~20 times in comparison with that of the feed water. The previous code could not give us the convergence for Case 1, since D is dominant within the column. However, the improved code gets the convergence with only 4 iterations (See Table 4). The effectiveness of the basic equations newly derived in this paper has thus been verified for the case where D is dominant within the column also.

#### 4. CONVERGENCE TECHNIQUE

The improved code can simulate the column behavior for the case where H or D is dominant within the column. As a strict condition, there is the possibility that the dominant species differs between the top and bottom of the column. For instance, we now consider the CECE column processing the waste water of the fusion reactor. The top product is an H stream free from T. The CECE column can produce a D stream as a bottom product even for this case. The composition within the column greatly varies along the column height. Some special techniques are required to get the convergence of the Newton-Raphson method for this case. As the first technique, we propose a procedure for preparing a set of initial values of the independent variables.

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(i) Assume the atom fractions of H, D, and T at the top and bottom of the column,

$$X_{H,1}^{out}, X_{H,N}^{out}, X_{D,1}^{out}, X_{D,N}^{out}, X_{T,1}^{out}, X_{T,N}^{out}.$$

The values of  $X_{H,j}^{out}, X_{D,j}^{out}, X_{T,j}^{out}$  do not vary linearly within the column.

(ii) Assume the atom fractions of H, D, and T at Nm-th tray,  $X_{H,Nm}^{out}, X_{D,Nm}^{out}, X_{T,Nm}^{out}$ .

(iii) Set the initial values of  $X_{H,j}^{out}, X_{D,j}^{out}, X_{T,j}^{out}$  by

$$\begin{aligned} X_{HorDorT,j}^{out} &= X_{HorDorT,Nm}^{out} + (j - Nm) \left( X_{HorDorT,N}^{out} - X_{HorDorT,Nm}^{out} \right) / (n - Nm), \\ (j &= Nm, N) \\ \ln(X_{HorDorT,j}^{out}) &= \ln(X_{HorDorT,1}^{out}) + (j - 1) \left\{ \ln(X_{HorDorT,Nm}^{out}) - \ln(X_{HorDorT,1}^{out}) \right\} / (nm - 1), \\ (j &= 1, Nm - 1) \end{aligned} \quad (71)$$

(iv) Normalize  $X_{H,j}^{out}, X_{D,j}^{out}, X_{T,j}^{out}$ .

(v) Evaluate all the values in Eq. (52) in accordance with the procedures of (i)~(viii) in the section of 2.6.

(vi) Solve the tridiagonal equations of Eq. (51) three times. Normalize H, D, and T.

The values thus calculated are used for the initial values of the iterations. As the second technique, a simple procedure is applied to modify the independent variables.

$$\mathbf{X}^{k+1} = \mathbf{X}^k + \eta \Delta \mathbf{X}^k, \quad \Delta \mathbf{X}^k = -\mathbf{J}_s^{-1} \mathbf{S} \quad (72)$$

The value of  $\eta$  is usually set at 0.1~0.2. Several procedures have been reported to get the convergence of the Newton-Raphson method stable<sup>14</sup>. The authors tried these procedures, however, the convergence was not greatly improved in comparison with that of Eq. (72).

The column behavior is simulated for an example case, Case 2 in Table 3, to discuss the convergence techniques described above. An H<sub>2</sub>O stream containing D and

T is supplied to the column. A small amount of hydrogen stream of HD and D<sub>2</sub> is also supplied to the column. For Case 2, a water stream from the recombiner is a H<sub>2</sub>O stream free from T. The top product is discarded to environment. This means that the water vapor and hydrogen streams are not necessarily required to be converted to the water. The water stream from the recombiner can be replaced by a stream of natural water. The recombiner is thus excluded for Case 2 (See Table 3). The simulation results are shown in Table 4. The top product is an H stream free from T, while the bottom product is a stream of D<sub>2</sub>. The code could not give the convergence without the techniques described above. Although 72 iterations are required, a set of solutions could be obtained for this strict example case by using Eqs. (71) and (72).

## 5. CONCLUSION

A simulation code for the multistage chemical exchange column has been developed<sup>7</sup>. The code has further be improved to simulate the column behavior under a wide range of operating conditions.

(1) The code can deal with all the twelve molecular species of hydrogen gas and water. The equilibrium of atomic elements of H, D and T in the liquid phase is also considered in the code. The separation factor between the isotopic species depends on the temperature and composition. This dependency is fully taken into account.

T is supplied to the column. A small amount of hydrogen stream of HD and D<sub>2</sub> is also supplied to the column. For Case 2, a water stream from the recombiner is a H<sub>2</sub>O stream free from T. The top product is discarded to environment. This means that the water vapor and hydrogen streams are not necessarily required to be converted to the water. The water stream from the recombiner can be replaced by a stream of natural water. The recombiner is thus excluded for Case 2 (See Table 3). The simulation results are shown in Table 4. The top product is an H stream free from T, while the bottom product is a stream of D<sub>2</sub>. The code could not give the convergence without the techniques described above. Although 72 iterations are required, a set of solutions could be obtained for this strict example case by using Eqs. (71) and (72).

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(2) The Murphree-type factors are introduced in the code to evaluate the efficiencies for both of the sieve trays and catalyst beds.

(3) The main calculation loop is based on the Newton-Raphson iteration. The order of the Jacobian matrix is only twice the number of the sieve trays.

(4) The code can accept multiple feed streams and multiple withdrawal streams of liquid water and hydrogen gas.

(5) The code chooses the independent variables for the operating conditions of the column: D and T or H and T for the case where H or D is dominant species within the column, respectively.

(6) An effective method has been introduced into the code to get the convergence of the basic equations.

The most significant features of the improvement of the code are (4)~(6). By these improvements, the code allows us to simulate the column behavior under a wide range of conditions: either H or D is dominant species within the column; and the dominant species varies along the column height.

#### **ACKNOWLEDGMENT**

The authors wish to express their sincere thanks and appreciation to Assoc. Prof. Dr. M. Kinoshita (Kyoto Univ.) for his guidance in developing the simulation code.



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**NOMENCLATURE**

$D$  : Flow rate of top product (mol/h)

$F$  : Flow rate of feed water (mol/h)

$F_z$  : Flow rate of feed hydrogen (mol/h)

$G$  : Flow rate of hydrogen gas (mol/h)

$J$  : Jacobian matrix (-)

$K$  : Equilibrium constant of reaction (-)

$L$  : Flow rate of liquid water (mol/h)

$N$  : Total number of sieve trays (-)

$N_F$  : Feed water tray number (-)

$N_z$  : Feed hydrogen tray number (-)

$P$  : Total pressure (Pa)

$p^*$  : Vapor pressure of pure component for water (Pa)

$R$  : Reflux ratio =  $(V_1 + G_1 - D)/D$  (-)

$T$  : Temperature (K)

$T_{av}$  : Temperature of hot-water bath (operating temperature) (K)

$T_e$  : Temperature at electrolysis cell (K)

$U$  : Flow rate of side stream of water (mol/h)

$V$  : Flow rate of water vapor stream (mol/h)

$W$  : Flow rate of bottom product (mol/h)

$v$  : Flow rate of water vapor stream from electrolysis cell (mol/h)

$X$  : Atomic fraction of element in liquid water (-)

- x : mole fraction of component in liquid water (-)
- Y : Atomic fraction of element in water vapor (-)
- y : Mole fraction of component in water vapor (-)
- Z : Atomic fraction of element in hydrogen gas (-)
- z : Mole fraction of component in hydrogen gas (-)
- Zf : Atomic fraction of element in feed water (-)
- zf : Mole fraction of component in feed water (-)
- ZZ : Atomic fraction of element in feed hydrogen (-)
- zz : Mole fraction of component in feed hydrogen (-)
- $\alpha$  : Murphree-type scrubbing efficiency (-)
- $\gamma$  : Murphree-type catalytic efficiency (-)

#### Subscripts

- i : Component or element index
- ii : Dominat component at j-th tray
- 1 : H<sub>2</sub>O, H<sub>2</sub>O; 2 : HD, HDO; 3 : HT, HTO; 4 : D<sub>2</sub>, D<sub>2</sub>O; 5 : DT, DTO; 6 : T<sub>2</sub>, T<sub>2</sub>O
- H : Hydrogen; D : Deuterium; T : Tritium
- j : Tray index

#### Superscripts

- eq : Equilibrium composition
- k : Iteration number
- in : Entering

out : Leaving

For Instance,

$x_{1,j}^{\text{out}}$  : Mole fraction of HDO in liquid water stream leaving j-th tray

$Y_{D,j}^{\text{in}}$  : Atomic fraction of deuterium in water vapor stream entering j-th tray

$z_{6,j}$  : Mole fraction of  $T_2$  in hydrogen gas leaving j-th catalyst bed and going through j-th tray

In Eqs. (1)~(45) and (55), l means liquid phase, g means hydrogen gas phase, and v means vapor phase.

Table 1 Parameters of equation (62)

	$\phi_1$	$\phi_2$	$\phi_3$	$\phi_4$	$\phi_5$
H <sub>2</sub>	0.0	0.0	-3578.5	-54.15	11.20
HD	-26398.8	89.6065	-3578.5	-54.15	11.124198
HT	-37813.2	136.751	-3578.5	-54.15	11.075904
D <sub>2</sub>	-49314.9	164.266	-3578.5	-54.15	11.059951
DT	-59313.4	204.941	-3578.5	-54.15	11.017314
T <sub>2</sub>	-68702.3	244.687	-3578.5	-54.15	10.975612

Table 2 Parameters of equation (63)

	$\lambda_1$	$\lambda_2$
K <sub>1</sub>	-77.5	1.441
K <sub>2</sub>	-176.0	1.528
K <sub>3</sub>	-20.2	1.406
K <sub>4</sub>	472.0	-0.297
K <sub>5</sub>	673.0	-0.434
K <sub>6</sub>	923.0	-0.667
K <sub>7</sub>	1072.0	-0.7354
K <sub>8</sub>	1189.0	-0.669
K <sub>10</sub>	415.0	-0.277
K <sub>13</sub>	211.0	-0.109
K <sub>16</sub>	170.0	-0.132
K <sub>17</sub>	291.0	-0.102
K <sub>46</sub>	-13.0	1.419
K <sub>47</sub>	-71.7	1.469
K <sub>48</sub>	-35.6	1.397

Table 3 Input specifications for example cases

	Case 1	Case 2 <sup>*1</sup>
N	69	66
N <sub>F</sub>	30	25
N <sub>Z</sub>	60	80
F	40 mol/h	20 mol/h
F <sub>Z</sub>	1.928 mol/h	0.04 mol/h
D	40 mol/h	119.04 mol/h
W	1.928 mol/h	0.2 mol/h
P	101.3 kPa	101.3 kPa
Pressure drop	66 Pa per tray	66 Pa per tray
R	3.0	5.0 <sup>*2</sup>
T <sub>av</sub>	348.15 K	330.15 K
Feed water Composition	H <sub>2</sub> O:3.3x10 <sup>-11</sup> HDO:1.1x10 <sup>-5</sup> HTO:2.5x10 <sup>-8</sup> D <sub>2</sub> O:0.9999 DTO:4.4x10 <sup>-5</sup> T <sub>2</sub> O:5.4x10 <sup>-10</sup>	H <sub>2</sub> O:0.9817 HDO:1.8x10 <sup>-2</sup> HTO:3.3x10 <sup>-6</sup> D <sub>2</sub> O:8.5x10 <sup>-5</sup> DTO:3.1x10 <sup>-8</sup> T <sub>2</sub> O:3.2x10 <sup>-12</sup>
Feed Hydrogen Composition	H <sub>2</sub> :1.2x10 <sup>-17</sup> HD:6.3x10 <sup>-9</sup> HT:2.9x10 <sup>-12</sup> D <sub>2</sub> :0.9995 DT:5.0x10 <sup>-4</sup> T <sub>2</sub> :6.6x10 <sup>-8</sup>	H <sub>2</sub> :2.0x10 <sup>-2</sup> HD:0.270 HT:4.6x10 <sup>-5</sup> D <sub>2</sub> :0.710 DT:3.8x10 <sup>-8</sup> T <sub>2</sub> :3.0x10 <sup>-15</sup>

The values of  $\alpha$  and  $\gamma$  are unity.

\*1: The recombiner is not used. Natural water (99.2 mol/h) is supplied from top of the column.

\*2: The reflux ratio is calculated by  $R=(V_1+G_1-D')/D'$ , where  $D'=F+Fz-W$ .

Table 4 Calculated results for the example cases

	Case 1	Case 2
Top Product Composition	H <sub>2</sub> O:3.4x10 <sup>-11</sup> HDO:1.1x10 <sup>-5</sup> HTO:1.6x10 <sup>-10</sup> D <sub>2</sub> O:0.99997 DTO:2.0x10 <sup>-5</sup> T <sub>2</sub> O:1.0x10 <sup>-10</sup>	mixture of water vapor and hydrogen gas; H:0.9997, D:3x10 <sup>-4</sup> , and T:4x10 <sup>-11</sup>
Bottom Product Composition	H <sub>2</sub> :1.2x10 <sup>-17</sup> HD:6.2x10 <sup>-9</sup> HT:2.9x10 <sup>-12</sup> D <sub>2</sub> :0.9990 DT:1.0x10 <sup>-3</sup> T <sub>2</sub> :2.7x10 <sup>-7</sup>	H <sub>2</sub> :1.3x10 <sup>-3</sup> HD:6.3x10 <sup>-2</sup> HT:1.0x10 <sup>-5</sup> D <sub>2</sub> :0.935 DT:3.3x10 <sup>-4</sup> T <sub>2</sub> :3.1x10 <sup>-8</sup>
Iteration Number	4	72
v	2.80 mol/h	3.17 mol/h
V <sub>1</sub>	57.5 mol/h	20.8 mol/h
G <sub>1</sub>	102.5 mol/h	98.2 mol/h



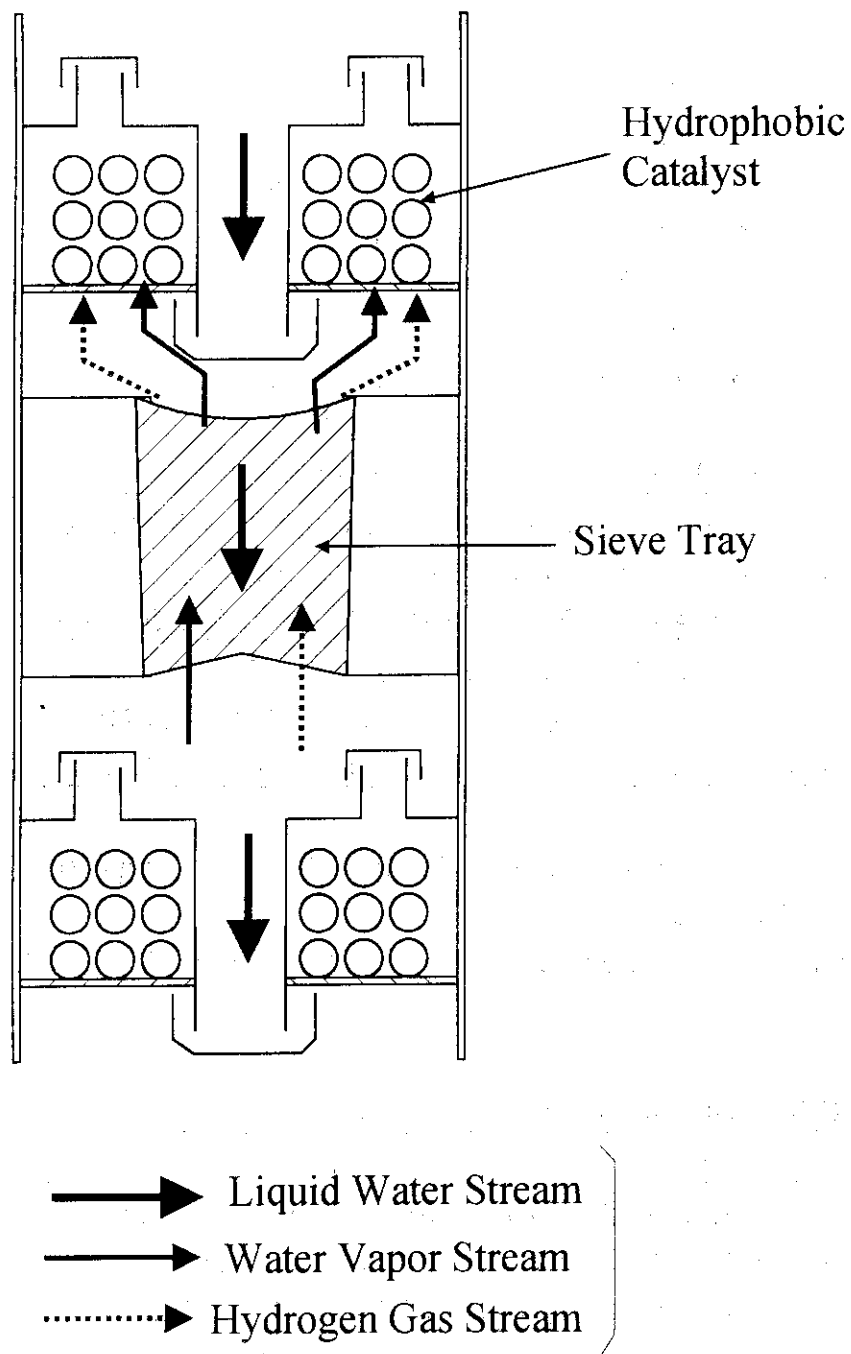


Figure 1 Structure of multistage water/hydrogen exchange column.

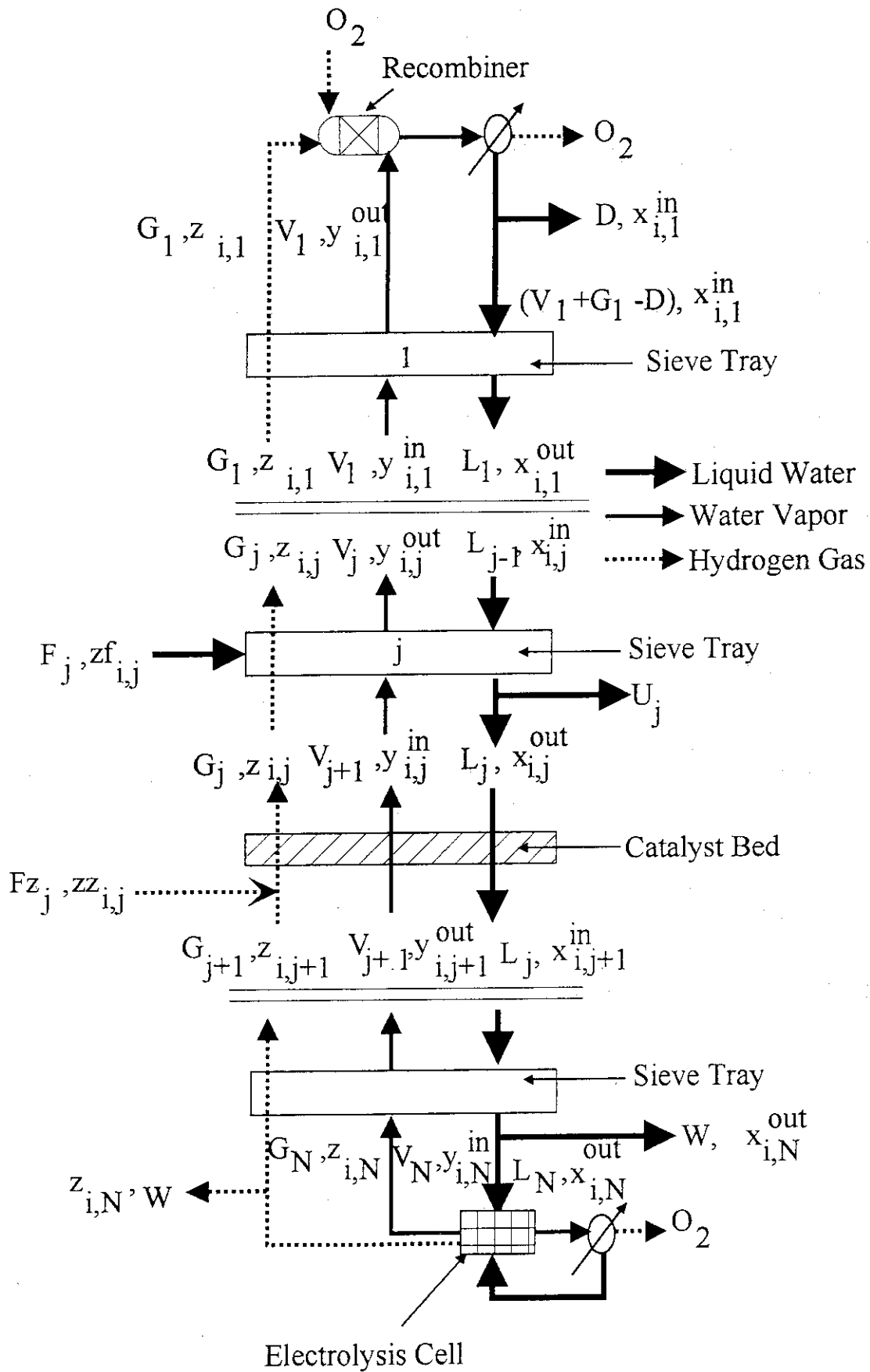


Figure 2 Model column for simulation on digital computers.

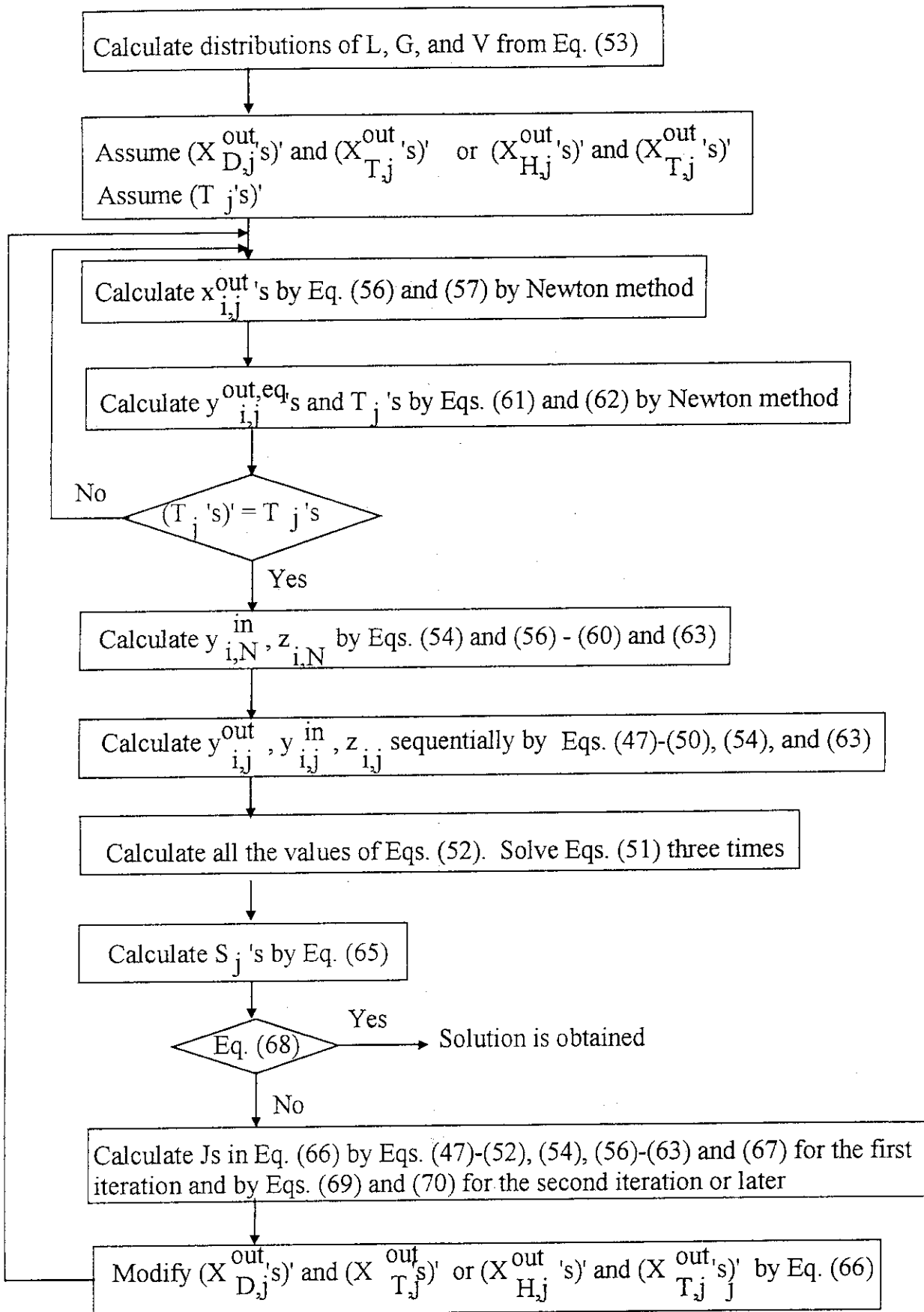


Figure 3 Flow chart of simulation procedure.