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A Thermodynamic Investigation into Steam-Methane Reforming and the Synthesis of Methane from Carbon Monoxide and Hydrogen

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SYNTHESIS OF METHANE FROM CARBON MONOXIDE AND HYDROGEN

Li-hua Wu and M. H. Lietzke

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A THERMODYNAMIC INVESTIGATION INTO STEAM-METHANE REFORMING AND THE
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ABSTRACT

In this study the steam-methane equilibrium reaction was investigated by considering both methane synthesis from hydrogen and carbon monoxide and by considering steam-methane reforming from methane and steam. A FORTRAN computer program was written to carry out all the calculations over a wide range of temperatures, pressures, and initial compositions. The products of each process as a function of pressure, temperature, and starting ratio of reactant gases were calculated, as well as the heats involved. In both processes the minimum ratios above which no carbon precipitates were determined as a function of temperature and pressure.

INTRODUCTION

The steam, methane, hydrogen, carbon monoxide equilibrium has a number of interesting and important applications, since the equilibrium may be approached starting either with hydrogen and carbon monoxide or with steam and methane. The catalytic reaction between hydrogen and carbon monoxide is exothermic and may be used to synthesize methane. Moreover, by using different catalysts and operating conditions other organic compounds such as methanol may be directly synthesized in a similar manner. Experience gained in modelling the methane synthesis may be useful in investigating the synthesis of other organic compounds. The catalytic reaction between steam and methane, on the other hand, is endothermic and results in the production of a mixture of hydrogen and carbon monoxide, a process known as steam-methane reforming. One promising application of this process is to use the hydrogen-carbon monoxide mixture in the direct reduction of iron ore. Another possibility is to use the

reaction for the chemical storage of energy, since heat must be supplied to drive the reaction. This heat may partially be recovered later by allowing the reverse exothermic reaction to take place.

In utilizing the methane-steam equilibrium system in any practical application, the formation of elemental carbon by disproportionation of carbon monoxide must be avoided. Carbon formed in this way causes catalyst inactivation as well as plugging and fouling of equipment. Hence it is necessary to define the range of operating conditions under which no deposition of carbon occurs. In this study we have considered the effects of temperature, pressure, and initial compositions on final yields both for the synthesis of methane and for steam-methane reforming. Detailed models of both of these processes have been developed and a computer program written to carry out the calculations. Provision is made in the program for the deposition of carbon either as β -graphite or as "Dent" carbon.¹ "Dent" carbon has apparently not been characterized except that it is a non-graphite form of carbon. The conditions favoring either β -graphite or "Dent" carbon precipitation are not known. However, equilibrium constants as a function of temperature are available for the disproportionation of carbon monoxide to yield either β -graphite or "Dent" carbon. In general, when "Dent" carbon is precipitated, the mole fraction of carbon is lower than when β -graphite is precipitated.

PREVIOUS INVESTIGATIONS

The synthesis of methane has previously been investigated by M. Greyson and co-workers² for the temperature range 500-900°K, for pressures of 1, 10, and 25 atmospheres and for hydrogen-carbon monoxide

ratios from 0.50 to the limiting ratio above which the deposition of carbon does not occur. These authors did not have the benefit of a modern high speed computer and hence did not make as complete a study as that reported in the present work. They did not compute any sensible heats.

Gruber^{3a} also studied the methane synthesis system and considered that carbon may be deposited either as graphite or as "Dent" carbon.¹ In this work all possible starting compositions are considered over a temperature range of 600°K and 2000°K and a pressure range of 30 atm to 300 atm. Again no sensible heats were computed and the results of the calculations are presented graphically in a way that is not easy to interpret.

P. Wellman and S. Katell⁴ studied the effect of pressure and temperature on steam-methane reforming over a temperature range of 1200°F to 1900°F, a pressure range of 5 to 31 atmospheres, and a steam-to-methane ratio range of 2 to 6. However, they did not consider the deposition of carbon in their calculations.

DESCRIPTION OF THE MODELS

The discussion of the methane-steam equilibrium will be broken into two parts. The first part will deal with the synthesis of methane from carbon monoxide and hydrogen, while the second part will deal with the reforming of methane by steam to produce hydrogen and carbon monoxide.

A. Methane Synthesis

In considering the synthesis of methane from hydrogen and carbon monoxide, the following reactions are sufficient to describe the system:

Let the initial mole fractions of H_2 and CO be $\underline{a}$ and $1 - \underline{a}$, respectively, and the final yields of CH_4 , CO_2 , and C be $\underline{x}$, $\underline{y}$, and $\underline{z}$ moles per mole input. From the equilibrium relationships of Eqs. (1) to (3), the final moles of H_2O , H_2 , and CO can be expressed in terms of $\underline{a}$, $\underline{x}$, $\underline{y}$, and $\underline{z}$ as

$$\text{H}_2\text{O} = x - y + z, \quad (4)$$

$$\text{H}_2 = a - 3x + y - z, \quad (5)$$

$$\text{CO} = 1 - a - x - y - z. \quad (6)$$

The total number of moles of gas is then $1 - 2\underline{x} - \underline{z}$. Thus, the equilibrium constants for Eqs. (1) through (3) may be written as

$$\begin{aligned} K_{p,1} &= \frac{p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^3 \cdot p_{\text{CO}}} \\ &= \frac{\frac{x}{1 - 2x - z} p \cdot \frac{x - y + z}{1 - 2x - z} p}{\frac{(a - 3x + y - z)^3}{(1 - 2x - z)^3} p^3 \cdot \frac{1 - a - x - y - z}{1 - 2x - z} p} \\ &= \frac{x(x - y + z)(1 - 2x - z)^2}{(a - 3x + y - z)^3 (1 - a - x - y - z) p^2}, \end{aligned} \quad (7)$$

$$\begin{aligned}
K_{p,2} &= \frac{p_{\text{CO}_2} \cdot p_{\text{H}_2}}{p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}} \\
&= \frac{\frac{y}{1-2x-z} p \cdot \frac{a-3x+y-z}{1-2x-z} p}{\frac{1-a-x-y-z}{1-2x-z} p \cdot \frac{x-y+z}{1-2x-z} p} \\
&= \frac{y(a-3x+y-z)}{(1-a-x-y-z)(x-y+z)}, \tag{8}
\end{aligned}$$

$$\begin{aligned}
K_{p,3} &= \frac{p_{\text{CO}_2}}{p_{\text{CO}}^2} \\
&= \frac{\frac{y}{1-2x-z} p}{\frac{(1-a-x-y-z)^2}{(1-2x-z)^2} p^2} \\
&= \frac{y(1-2x-z)}{(1-a-x-y-z)^2 p}, \tag{9}
\end{aligned}$$

where p_i is the partial pressure of component i , and p is the total pressure of the system. Values of the logarithms of these constants were calculated at a number of temperatures using thermodynamic data from the literature.⁵ These values were then fitted by the method of least squares to yield the following expressions.

$$\begin{aligned}
\log K_{p,1} &= 2.15530 \times 10 - 3.33134 \times 10^{-2} t + 1.59845 \times 10^{-5} t^2 \\
&\quad - 2.94297 \times 10^{-9} t^3, \tag{10}
\end{aligned}$$

$$\begin{aligned}
\log K_{p,2} &= 4.09775 - 5.89713 \times 10^{-3} t + 2.90724 \times 10^{-6} t^2 \\
&\quad - 5.33920 \times 10^{-10} t^3, \tag{11}
\end{aligned}$$

$$\log K_{p,3} = 1.72556 \times 10 - 2.51018 \times 10^{-2}t + 1.18293 \times 10^{-5}t^2 - 2.12805 \times 10^{-9}t^3, \quad (12)$$

while for "Dent" carbon^{3b}

$$\log K_{p,3} = 3.35280 + 8.36512 \times 10^{-3}t - 1.63599 \times 10^{-5}t^2 + 6.05889 \times 10^{-9}t^3. \quad (13)$$

In these equations t refers to the temperature expressed in degrees Fahrenheit.

Thus, for each temperature, pressure, and value of a , equations (1) through (3) must be solved simultaneously to yield values of the three unknowns x , y , and z . This calculation is conveniently carried out using the first-order Newton-Raphson method.⁶ First we define three functions $f_1(x, y, z)$, $f_2(x, y, z)$, and $f_3(x, y, z)$ as

$$f_1(x, y, z) = K_{p,1} (a - 3x + y - z)^3 (1 - a - x - y - z)p^2 - x(x - y + z)(1 - 2x - z)^2 \quad (14)$$

$$f_2(x, y, z) = K_{p,2} (1 - a - x - z)(x - y + z) - y(a - 3x + y - z) \quad (15)$$

$$f_3(x, y, z) = K_{p,3} (1 - a - x - y - z)^2 p - y(1 - 2x - z). \quad (16)$$

The derivatives of these functions with respect to x , y , and z are given by

$$\begin{aligned} \frac{\partial f_1}{\partial x} = & -9K_{p,1} (a - 3x + y - z)^2 (1 - a - x - y - z)p^2 \\ & - K_{p,1} (a - 3x + y - z)^3 p^2 - (x - y + z)(1 - 2x - z)^2 \\ & - x(1 - 2x - z)^2 + 4x(x - y + z)(1 - 2x - z) \end{aligned} \quad (17)$$

$$\begin{aligned}\frac{\partial f_1}{\partial y} &= 3K_{p,1}(a - 3x + y - z)^2(1 - a - x - y - z)p^2 \\ &\quad - K_{p,1}(a - 3x + y - z)^3p^2 + x(1 - 2x - z)^2\end{aligned}\quad (18)$$

$$\begin{aligned}\frac{\partial f_1}{\partial z} &= -3K_{p,1}(a - 3x + y - z)^2(1 - a - x - y - z)p^2 \\ &\quad - K_{p,1}(a - 3x + y - z)^3p^2 - x(1 - 2x - z)^2 \\ &\quad + 2x(x - y + z)(1 - 2x - z)\end{aligned}\quad (19)$$

$$\frac{\partial f_2}{\partial x} = -K_{p,2}(x - y + z) + K_{p,2}(1 - a - x - y - z) + 3y \quad (20)$$

$$\begin{aligned}\frac{\partial f_2}{\partial y} &= -K_{p,2}(x - y + z) - K_{p,2}(1 - a - x - y - z) \\ &\quad - (a - 3x + y - z) - y\end{aligned}\quad (21)$$

$$\frac{\partial f_2}{\partial z} = -K_{p,2}(x - y + z) + K_{p,2}(1 - a - x - y - z) + y \quad (22)$$

$$\frac{\partial f_3}{\partial x} = -2K_{p,3}(1 - a - x - y - z)p + 2y \quad (23)$$

$$\frac{\partial f_3}{\partial y} = -2K_{p,3}(1 - a - x - y - z)p - (1 - 2x - z) \quad (24)$$

$$\frac{\partial f_3}{\partial z} = -2K_{p,3}(1 - a - x - y - z)p + y \quad (25)$$

Hence, in starting the calculations, for each initial set of guesses $\underline{x}$, $\underline{y}$, and $\underline{z}$ we can obtain another set of values α , β , and γ by using the equations:

$$\begin{aligned}f_1(\alpha, \beta, \gamma) &= f_1(x, y, z) + (\alpha - x) \frac{\partial f_1}{\partial x} + (\beta - y) \frac{\partial f_1}{\partial y} \\ &\quad + (\gamma - z) \frac{\partial f_1}{\partial z},\end{aligned}\quad (26)$$

where $\underline{i} = 1, 2, 3$. Equation (26) can be written in matrix form as

$$\begin{pmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} & \frac{\partial f_1}{\partial z} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} & \frac{\partial f_2}{\partial z} \\ \frac{\partial f_3}{\partial x} & \frac{\partial f_3}{\partial y} & \frac{\partial f_3}{\partial z} \end{pmatrix} \begin{pmatrix} \alpha - x \\ \beta - y \\ \gamma - z \end{pmatrix} = \begin{pmatrix} -f_1(x, y, z) \\ -f_2(x, y, z) \\ -f_3(x, y, z) \end{pmatrix} \quad (27)$$

The inverse of the 3 x 3 matrix in Eq. (27) may be obtained by using the Gauss-Jordan method.⁷ Pre-multiplying both sides of Eq. (27) by the inverse matrix we get α , β , and γ , which are equated to $\underline{x}$, $\underline{y}$, and $\underline{z}$, respectively. The procedure is repeated until the differences between two sets of values are smaller than some pre-defined criterion value (in our case 1×10^{-5}).

If γ happens to be zero for a given set of conditions, i.e., if no carbon precipitation is indicated, then equation (3) is dropped and $\underline{z}$ is removed from all the terms in equations (1) and (2). Consequently equation (27) is reduced to

$$\begin{pmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{pmatrix} \begin{pmatrix} \alpha - x \\ \beta - y \end{pmatrix} = \begin{pmatrix} -f_1(x, y) \\ -f_2(x, y) \end{pmatrix} \quad (28)$$

B. Steam-Methane Reforming

In considering the steam-methane reforming process, the following reactions are sufficient to describe the system:

In this model the first equation (1') is just the inverse of Eq. (1), while the other two equations are the same as in the methane synthesis model. Let the initial mole fractions of steam and methane be $\underline{a}$ and $1 - \underline{a}$, and let $\underline{x}$ represent the number of moles of methane reacted. Further let $\underline{y}$ and $\underline{z}$ be the final yields of CO_2 and C per mole input, respectively. From the equilibrium relationships of Eqs. (1) to (3), the final moles of H_2O , CH_4 , CO , and H_2 can then be expressed in terms of $\underline{a}$, $\underline{x}$, $\underline{y}$, and $\underline{z}$ as

$$\text{H}_2\text{O} = a - x - y + z \quad (29)$$

$$\text{CH}_4 = 1 - a - x \quad (30)$$

$$\text{CO} = x - y - z \quad (31)$$

$$\text{H}_2 = 3x + y - z. \quad (32)$$

The total number of moles of gas is then $1 + 2\underline{x} - \underline{z}$. Thus, the equilibrium constants of reactions (1) to (3) may be written as

$$\begin{aligned} K_{p,1} &= \frac{p_{\text{CO}} \cdot p_{\text{H}_2}^3}{p_{\text{H}_2\text{O}} \cdot p_{\text{CH}_4}} \\ &= \frac{\frac{x - y - z}{1 + 2x - z} p \cdot \frac{(3x + y - z)^3}{(1 + 2x - z)^3} p^3}{\frac{a - x - y + z}{1 + 2x - z} p \cdot \frac{1 - a - x}{1 + 2x - z} p} \end{aligned}$$

$$= \frac{(x - y - z)(3x + y - z)^3 p^2}{(a - x - y + z)(1 - a - x)(1 + 2x - z)^2} \quad (33)$$

$$\begin{aligned} K_{p,2} &= \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} \\ &= \frac{\frac{y}{1 + 2x - z} p \cdot \frac{3x + y - z}{1 + 2x - z} p}{\frac{x - y - z}{1 + 2x - z} p \cdot \frac{a - x - y + z}{1 + 2x - z} p} \\ &= \frac{y(3x + y - z)}{(x - y - z)(a - x - y + z)} \quad (34) \end{aligned}$$

$$\begin{aligned} K_{p,3} &= \frac{P_{CO_2}}{P_{CO}} \\ &= \frac{\frac{y}{1 + 2x - z} p}{\frac{(x - y - z)^2}{(1 + 2x - z)^2} p^2} \\ &= \frac{y(1 + 2x - z)}{(x - y - z)^2 p} \quad (35) \end{aligned}$$

In these expressions p_i is the partial pressure of the component i and p is the total pressure of the system.

As in the case of methane synthesis the equilibrium constants are functions of temperature and have been calculated from the same equations used in that system except that $\log K_{p,1} = -\log K_{p,1}$ as given by Eq. (10).

The method of calculation is similar to that used in the methane synthesis. For each temperature and pressure we have three equations (1') to (3), and three unknowns, $\underline{x}$, $\underline{y}$, and $\underline{z}$. These are solved by the first-

order Newton-Raphson method. We define $f_1(x, y, z)$, $f_2(x, y, z)$, and $f_3(x, y, z)$ as

$$f_1(x, y, z) = K_{p,1}(a - x - y + z)(1 - a - x)(1 + 2x - z)^2 - (x - y - z)(3x + y - z)^3 p^2 \quad (36)$$

$$f_2(x, y, z) = K_{p,2}(x - y - z)(a - x - y + z) - y(3x + y - z) \quad (37)$$

$$f_3(x, y, z) = K_{p,3}(x - y - z)^2 p - y(1 + 2x - z). \quad (38)$$

The derivatives of these functions with respect to $\underline{x}$, $\underline{y}$, and $\underline{z}$ are

$$\begin{aligned} \frac{\partial f_1}{\partial x} = & -K_{p,1}(1 - a - x)(1 + 2x - z)^2 - K_{p,1}(a - x - y + z) \\ & (1 + 2x - z)^2 + 4K_{p,1}(a - x - y + z)(1 - a - x) \\ & (1 + 2x - z) - (3x + y - z)^3 p^2 - 9(x - y - z) \\ & (3x + y - z)^2 p^2 \end{aligned} \quad (39)$$

$$\begin{aligned} \frac{\partial f_1}{\partial y} = & -K_{p,1}(1 - a - x)(1 + 2x - z)^2 + (3x + y - z)^3 p^2 \\ & - 3(x - y - z)(3x + y - z)^2 p^2 \end{aligned} \quad (40)$$

$$\begin{aligned} \frac{\partial f_1}{\partial z} = & K_{p,1}(1 - a - x)(1 + 2x - z)^2 - 2K_{p,1}(1 - a - x) \\ & (a - x - y + z)(1 + 2x - z) + (3x + y - z)^3 p^2 \\ & + 3(x - y - z)(3x + y - z)^2 p^2 \end{aligned} \quad (41)$$

$$\frac{\partial f_2}{\partial x} = K_{p,2}(a - x - y + z) - K_{p,2}(x - y - z) - 3y \quad (42)$$

$$\begin{aligned} \frac{\partial f_2}{\partial y} = & -K_{p,2}(a - x - y + z) - K_{p,2}(x - y - z) \\ & - (3x + y - z) - y \end{aligned} \quad (43)$$

$$\frac{\partial f_2}{\partial z} = -K_{p,2}(a - x - y + z) + K_{p,2}(x - y - z) + y \quad (44)$$

$$\frac{\partial f_3}{\partial x} = 2K_{p,3}(x - y - z)p - 2y \quad (45)$$

$$\frac{\partial f_3}{\partial y} = -2K_{p,3}(x - y - z)p - (1 + 2x - z) \quad (46)$$

$$\frac{\partial f_3}{\partial z} = -2K_{p,3}(x - y - z)p + y \quad (47)$$

For each initial set of guesses, $\underline{x}$, $\underline{y}$, and $\underline{z}$ we can get another set of values α , β , and γ by using the equations:

$$\begin{aligned} f_1(\alpha, \beta, \gamma) = f_1(x, y, z) + (\alpha - x) \frac{\partial f_1}{\partial x} + (\beta - y) \frac{\partial f_1}{\partial y} \\ + (\gamma - z) \frac{\partial f_1}{\partial z} \end{aligned} \quad (48)$$

where $\underline{i} = 1, 2, 3$. Equation (48) can be written in matrix form as

$$\begin{pmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} & \frac{\partial f_1}{\partial z} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} & \frac{\partial f_2}{\partial z} \\ \frac{\partial f_3}{\partial x} & \frac{\partial f_3}{\partial y} & \frac{\partial f_3}{\partial z} \end{pmatrix} \begin{pmatrix} \alpha - x \\ \beta - y \\ \gamma - z \end{pmatrix} = \begin{pmatrix} -f_1(x, y, z) \\ -f_2(x, y, z) \\ -f_3(x, y, z) \end{pmatrix} \quad (49)$$

and solved by pre-multiplying both sides by the inverse of the 3 x 3 matrix. α , β , and γ are then equated to $\underline{x}$, $\underline{y}$, and $\underline{z}$, respectively. The procedure is repeated until the differences between two successive sets of values are smaller than 10^{-5} .

As in the case of methane synthesis, Eq. (49) reduces to

$$\begin{pmatrix} \frac{\partial f_1}{\partial x} & \frac{\partial f_1}{\partial y} \\ \frac{\partial f_2}{\partial x} & \frac{\partial f_2}{\partial y} \end{pmatrix} \begin{pmatrix} \alpha - x \\ \beta - y \end{pmatrix} = \begin{pmatrix} -f_1(x, y) \\ -f_2(x, y) \end{pmatrix} \quad (50)$$

if γ equals zero for a particular set of conditions.

If the purpose of steam-methane reforming is to produce a mixture of carbon monoxide and hydrogen to be used in the direct reduction of iron ore, then the exit gases from the reformer are used directly. However, if the purpose is to produce hydrogen, e.g., for ammonia synthesis, then the exit gases from the reformer are passed through a heat exchanger and cooled to about 750°F. The gaseous mixture then passes into a shift converter where only reactions (2) and (3) may occur (reaction (1) is favored only at high temperatures). Thus, in the shift converter additional hydrogen is produced through reaction (2). The equations to be solved are

Let the initial number of moles of gaseous H_2O , CO , H_2 and CO_2 be a, b, c, d, and e, respectively, and the final yields of CO_2 and $\text{C}_{(s)}$ be y and z. From the equilibrium relationships of Eqs. (1) and (2), the final number of moles of H_2O , CH_4 , CO , and H_2 may be expressed in terms of a, b, c, d, e, y, and z as

$$\text{H}_2\text{O} = a - y + e + z \quad (51)$$

$$\text{CH}_4 = b \quad (52)$$

$$CO = c - y + e - z \quad (53)$$

$$H_2 = d + y - e - z. \quad (54)$$

The total number of moles of gas is then $\underline{a} + \underline{b} + \underline{c} + \underline{d} + \underline{e} - \underline{z}$, designated TMG. Thus, the equilibrium constants of Eqs. (2) and (3) may be written as

$$\begin{aligned} K_{p,2} &= \frac{p_{CO_2} \cdot p_{H_2}}{p_{CO} \cdot p_{H_2O}} \\ &= \frac{\frac{y}{TMG} p \cdot \frac{d + y - e - z}{TMG} p}{\frac{c - y + e - z}{TMG} p \cdot \frac{a - y + e + z}{TMG} p} \\ &= \frac{y(d + y - e - z)}{(c - y + e - z)(a - y + e + z)} \end{aligned} \quad (55)$$

$$\begin{aligned} K_{p,3} &= \frac{p_{CO_2}^2}{p_{CO}^2} \\ &= \frac{\frac{y}{TMG} p}{\frac{(c - y + e - z)^2}{(TMG)^2} p^2} \\ &= \frac{y \cdot TMG}{(c - y + e - z)^2 p} = \frac{y(a + b + c + d + e - z)}{(c - y + e - z)^2 p}, \end{aligned} \quad (56)$$

where p_i is the partial pressure of the component $\underline{i}$, and p is the total pressure of the system. Temperature dependence of the equilibrium constants is given by Eqs. (11) and (12).

For each temperature and pressure there are thus two equations, Eqs. (55) and (56), and two unknowns, $\underline{y}$ and $\underline{z}$. These are again solved

by the first-order Newton-Raphson method. We define two functions $f_2(y, z)$ and $f_3(y, z)$ as

$$f_2(y, z) = K_{p,2}(c - y + e - z)(a - y + e + z) - y(d + y - e - z) \quad (57)$$

$$f_3(y, z) = K_{p,3}(c - y + e - z)^2 p - y(a + b + c + d + e - z). \quad (58)$$

The derivatives of these functions with respect to y and z are

$$\begin{aligned} \frac{\partial f_2}{\partial y} &= -K_{p,2}(a - y + e + z) - K_{p,2}(c - y + e - z) \\ &\quad - (d + y - e - z) - y \end{aligned} \quad (59)$$

$$\frac{\partial f_2}{\partial z} = -K_{p,2}(a - y + e + z) + K_{p,2}(c - y + e - z) + y \quad (60)$$

$$\frac{\partial f_3}{\partial y} = -2K_{p,3}(c - y + e - z)p - (a + b + c + d + e - z) \quad (61)$$

$$\frac{\partial f_3}{\partial z} = -2K_{p,3}(c - y + e - z)p + y. \quad (62)$$

Let the initial value of y be $\underline{e}$, and z be the same as the initial guess $\underline{z}$ in the reforming calculation. We can get another set of values β and γ by using the equations:

$$f_{\underline{i}}(\beta, \gamma) = f_{\underline{i}}(y, z) + (\beta - y) \frac{\partial f_{\underline{i}}}{\partial y} + (\gamma - z) \frac{\partial f_{\underline{i}}}{\partial z} \quad (63)$$

where $\underline{i} = 2, 3$. Equation (63) may be written in matrix form as

$$\begin{pmatrix} \frac{\partial f_2}{\partial y} & \frac{\partial f_2}{\partial z} \\ \frac{\partial f_3}{\partial y} & \frac{\partial f_3}{\partial z} \end{pmatrix} \begin{pmatrix} \beta - y \\ \gamma - z \end{pmatrix} = \begin{pmatrix} -f_2(y, z) \\ -f_3(y, z) \end{pmatrix}, \quad (64)$$

and solved by pre-multiplying both sides of Eq. (64) by the inverse of the 2×2 matrix. β and γ are then equated with $\underline{y}$ and $\underline{z}$ and the procedure is repeated until the differences between two successive sets of values are smaller than 10^{-5} .

If γ happens to be zero, we can neglect Eq. (3) and consider Eq. (2) only. In this case let $\underline{x}$ be the number of moles of CO and H_2O reacted and rewrite the number of moles of CO, H_2O , CO_2 , and H_2 as $\underline{c} - \underline{x}$, $\underline{a} - \underline{x}$, $\underline{e} + \underline{x}$, and $\underline{d} + \underline{x}$, respectively. $K_{p,2}$ then becomes

$$K_{p,2} = \frac{(e + x)(d + x)}{(c - x)(a - x)}. \quad (65)$$

Equation (65) can be rearranged as

$$\begin{aligned} (K_{p,2} - 1)x^2 - (K_{p,2} a + K_{p,2} c + d + e) x \\ + (K_{p,2} ac - de) = 0. \end{aligned} \quad (66)$$

To solve equation (66) by the quadratic formula let $A = (K_{p,2} - 1)$, $B = (K_{p,2} a + K_{p,2} c + d + e)$, and $C = (K_{p,2} ac - de)$. Then

$$Ax^2 - Bx + C = 0 \quad (66')$$

Hence

$$x = \frac{B \pm \sqrt{B^2 - 4AC}}{2A} \quad (67)$$

In addition to calculating for a given set of conditions the equilibrium amounts of products formed in methane synthesis and steam-methane reforming it is of interest to calculate the heat effects involved in both processes. These include the sensible heats involved in heating the reactants to the temperature of operation and cooling the products to ambient temperature, as well as the enthalpies of reaction. The calculation of these quantities is described in the next two sections.

C. Sensible Heats

The sensible heat of a substance i over a temperature range t_1 to t_2 ($^{\circ}\text{F}$) is defined as

$$SH_i = \int_{t_1}^{t_2} C_{p_i} dt, \quad (68)$$

where C_{p_i} is the heat capacity of the substance i at constant pressure. Values of C_p as a function of temperature were taken from JANAF⁵ for each of the substances involved in the methane-steam equilibrium and fitted by the method of least squares to equations of the form

$$C_{p_i} = a_i + b_i t + c_i t^{-2} \quad (69)$$

Expressions for the SH_i were then obtained by substituting equation (69) into equation (68) and integrating. Hence,

$$SH_i = a_i(t_2 - t_1) + \frac{b_i}{2}(t_2^2 - t_1^2) - c_i\left(\frac{1}{t_2} - \frac{1}{t_1}\right) \quad (70)$$

In Table I are listed the parameters for equation (70) for the substances involved in the methane-steam equilibrium. The units of the SH_i are B.t.u./lb-mole.

TABLE I
PARAMETERS OF EQUATION (70) FOR THE SENSIBLE HEATS

Substances	a_i	b_i	c_i
CH ₄	9.03446	5.82421×10^{-3}	-6.16646×10^3
H ₂ O	7.66867	1.63605×10^{-3}	1.39796×10^3
CO	6.81334	7.95847×10^{-4}	5.17239×10^2
H ₂	6.76470	3.65184×10^{-4}	6.47006×10^2
CO ₂	1.00888×10	2.03493×10^{-3}	-8.45673×10^3

D. Enthalpy Changes

1. Methane Synthesis

Let $\underline{a}$ and $1 - \underline{a}$ be the initial mole fractions of H₂ and CO input to the reactor, and let the final yields of CH₄, H₂O, CO and CO₂ be CH₄, H₂O, CO, and CO₂ moles per mole input, respectively. Then, the enthalpy change ΔH per lb-mole input, in units of B.t.u., may be expressed as

$$\begin{aligned} \Delta H = & \text{CH}_4 \cdot \Delta H_{f, \text{CH}_4} + \text{H}_2\text{O} \cdot \Delta H_{f, \text{H}_2\text{O}} + [\text{CO} - (1 - a)] \\ & \cdot \Delta H_{f, \text{CO}} + \text{CO}_2 \cdot \Delta H_{f, \text{CO}_2}, \end{aligned} \quad (71)$$

where $\Delta H_{f, i}$, in units of B.t.u./lb-mole, is the heat of formation of the substance $\underline{i}$ which has been calculated using a temperature (°F) dependent third-order least-square-fitted equation⁵ as

$$\Delta H_{f, i} = a_{o, i} + a_{1, i}t + a_{2, i}t^2 + a_{3, i}t^3. \quad (72)$$

The parameters $\underline{a}_0$, $\underline{a}_1$, $\underline{a}_2$, and $\underline{a}_3$ for Eq. (72) are tabulated in Table II.

2. Steam-Methane Reforming

Let $\underline{a}$ and $1 - \underline{a}$ be the initial mole fractions of H_2O and CH_4 input to the reformer, and let the final yields of CH_4 , H_2O , CO , and CO_2 be CH_4 , H_2O , CO , and CO_2 moles per mole input, respectively. Then, the enthalpy change ΔH per lb-mole input, in units of B.t.u., may be expressed as

$$\begin{aligned} \Delta H = & [CH_4 - (1 - a)] \cdot \Delta H_{f,CH_4} + (H_2O - a) \cdot \Delta H_{f,H_2O} \\ & + CO \cdot \Delta H_{f,CO} + CO_2 \cdot \Delta H_{f,CO_2} \end{aligned} \quad (73)$$

3. Shift Converter

Let IH_2O , ICO , and ICO_2 be the initial numbers of moles of H_2O , CO , and CO_2 input to the shift converter, and the final yields of H_2O , CO , and CO_2 be H_2O , CO , and CO_2 , respectively. Then, the enthalpy change ΔH per lb-mole input, in units of B.t.u., may be expressed as

$$\begin{aligned} \Delta H = & (H_2O - IH_2O) \cdot \Delta H_{f,H_2O} + (CO - ICO) \cdot \Delta H_{f,CO} \\ & + (CO_2 - ICO_2) \cdot \Delta H_{f,CO_2} \end{aligned} \quad (74)$$

RESULTS AND DISCUSSION

A. Methane Synthesis

In studying methane synthesis, calculations were carried out at temperatures of 600°K, 700°K, 800°K, and 900°K, at pressures of 1, 10,

TABLE II
PARAMETERS OF EQUATION (72) FOR THE HEATS OF FORMATION

Substances	a_0	a_1	a_2	a_3
CH ₄	-3.14291×10^4	-8.96644	3.16520×10^{-3}	-3.67713×10^{-7}
H ₂ O	-1.03814×10^5	-2.61524	3.25639×10^{-4}	3.68627×10^{-8}
CO	-4.73377×10^4	5.13685×10^{-1}	-1.11742×10^{-3}	2.00704×10^{-7}
CO ₂	-1.69105×10^5	5.0×10^{-1}	-1.03398×10^{-25}	2.52435×10^{-29}

25, and 100 atmospheres. Hydrogen/carbon monoxide ratios of 0.5 to 4.5 were used at all temperatures and pressures except at one atmosphere, where the calculations were extended to a ratio of 5.5.

For a given set of initial conditions, the sensible heats involved in raising the temperature of the reactants to the temperature of operation were first calculated. At this latter temperature the equilibrium yields of CH_4 , H_2O , CO , H_2 , CO_2 , and $\text{C}_{(\text{s})}$ were computed, as well as the enthalpy change in the reactor. Finally, the sensible heats involved in cooling the equilibrium mixture of gases back to room temperature were calculated. In carrying out the calculations, the possible precipitation of carbon either as β -graphite or as "Dent" carbon were considered.

Figures 1 to 4 show plots of the mole fraction of ingoing carbon deposited vs. the initial H_2/CO ratio as a function of pressure and temperature. In all cases, when "Dent" carbon is precipitated, both the mole fraction of ingoing carbon deposited and the minimum H_2/CO ratio above which carbon no longer precipitates are lower. Plots of the minimum ratio of H_2/CO above which carbon is no longer deposited are shown as a function of temperature and pressure in Figure 5. When β -graphite is the form of carbon deposited, the effects of pressure and temperature on the minimum ratio are slight except at one atmosphere pressure, where the ratio increases markedly at higher temperatures. When "Dent" carbon is deposited the minimum ratios all increase as the temperature increases, with the greatest effect again at one atmosphere pressure. In all cases, at constant temperature, as the pressure increases the minimum ratio decreases.

Fig. 1. Plots of Mole Fraction of Ingoing Carbon Deposited vs. Initial H_2/CO Ratio for Methane Synthesis at a Total Pressure of One Atmosphere.

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Fig. 2. Plots of Mole Fraction of Ingoing Carbon Deposited vs. Initial H_2/CO Ratio for Methane Synthesis at a Total Pressure of 10 Atmospheres.

Fig. 3. Plots of Mole Fraction of Ingoing Carbon Deposited vs. Initial H_2/CO Ratio for Methane Synthesis at a Total Pressure of 25 atmospheres.

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Fig. 4. Plots of Mole Fraction of Ingoing Carbon Deposited vs. Initial H_2/CO Ratio for Methane Synthesis at a Total Pressure of 100 Atmospheres.

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Fig. 5. Temperature Dependence of the Minimum H_2/CO Ratio Above Which Carbon No Longer Precipitates ($^{\circ}K$).

Plots of the theoretical equilibrium yields of methane in moles per mole input gas vs. the initial H_2/CO ratio are shown as a function of pressure and temperature in Figures 6 through 9. As the initial H_2/CO ratio increases, the methane yield increases and the amount of carbon precipitated decreases. At the point where carbon no longer precipitates, either as "Dent" carbon or β -graphite, the methane yield reaches its maximum. As the H_2/CO ratio is increased beyond this point, the methane yield falls off.

In Table III are listed values of the equilibrium amounts of CH_4 , H_2O , CO , H_2 , and CO_2 (moles per mole input ($H_2 + CO$)) at the minimum H_2/CO ratio where β -graphite no longer precipitates, while corresponding values for the minimum ratio where "Dent" carbon no longer precipitates are shown in Table IV. Under these conditions the yield of methane is a maximum. At 600°K the effect of pressure on the amount of methane produced is very slight, and essentially the same amount of CH_4 is produced whether β -graphite or "Dent" carbon is precipitated. The minimum H_2/CO ratios are all lower for "Dent" carbon but becomes closer to those for β -graphite as the temperature increases. At one atmosphere pressure the yield of methane decreases markedly as the temperature increases, but as the pressure is increased the yields at the higher temperatures approach those obtained at 600°K. The equilibrium amounts of H_2O , CO , H_2 , and CO_2 are also shown in Tables III and IV.

The minimum ratios obtained in this work are lower than those obtained by M. Greyson and co-workers² at 600°K, but higher at 700, 800, and 900°K. Moreover, the methane yields obtained in this work are higher than those obtained by M. Greyson and co-workers at 600°K, but lower at

Fig. 6. Methane Yield vs. Initial H_2/CO Ratio at One Atmospheres Total Pressure.

Fig. 7. Methane Yield vs. Initial H_2/CO Ratio at 10 Atmospheres Total Pressure.

Fig. 8. Methane Yield vs. Initial H_2/CO Ratio at 25 Atmospheres Total Pressure.

Fig. 9. Methane Yield vs. Initial H_2/CO Ratio at 100 Atmospheres Total Pressure.

TABLE III

THEORETICAL EQUILIBRIUM YIELDS, MOLES PER MOLE INPUT ($H_2 + CO$), FOR METHANE SYNTHESIS.
 VALUES ARE AT THE MINIMUM RATIO WHERE β -GRAPHITE NO LONGER PRECIPITATES

P (atm)	T°K	minimum ratio	CH ₄	H ₂ O	CO	H ₂	CO ₂
1	600	2.710	0.241495	0.213612	0.000164	0.033855	0.027883
	700	3.015	.219636	.192060	.001855	.119603	.027576
	800	3.830	.170465	.146334	.012443	.305697	.024131
	900	5.025	.100470	.084153	.049188	.548932	.016317
10	600	2.625	.247308	.218805	.000052	.010718	.028503
	700	2.690	.240325	.210237	.000589	.038110	.030088
	800	2.855	.223619	.191962	.004128	.101397	.031657
	900	3.120	.192570	.161306	.018884	.210836	.031264
25	600	2.610	.248298	.219621	.000033	.006774	.028677
	700	2.640	.243875	.213397	.000372	.024128	.030478
	800	2.720	.233249	.200296	.002615	.064388	.032953
	900	2.850	.213076	.178533	.012122	.135575	.034542
100	600	2.600	.249148	.220534	.000016	.003393	.028614
	700	2.595	.246942	.215907	.000187	.012045	.031035
	800	2.610	.241608	.207515	.001308	.032261	.034092
	900	2.635	.231394	.193807	.006122	.068302	.037587

TABLE IV

THEORETICAL EQUILIBRIUM YIELDS, MOLES PER MOLE INPUT ($H_2 + CO$), FOR METHANE SYNTHESIS.

VALUES ARE AT THE MINIMUM RATIO WHERE "DENT" CARBON NO LONGER PRECIPITATES

P (atm)	T°K	minimum ratio	CH ₄	H ₂ O	CO	H ₂	CO ₂
1	600	1.025	0.247972	0.006742	0.004625	0.003486	0.241230
	700	1.310	.236645	.054547	.014156	.039262	.182099
	800	2.065	.194320	.102623	.040247	.182473	.091697
	900	3.045	.115885	.079185	.094633	.441826	.036700
10	600	1.025	.249356	.006392	.001508	.001070	.242964
	700	1.275	.245774	.056481	.004492	.012410	.189294
	800	1.825	.231962	.122906	.012964	.059187	.109056
	900	2.345	.200721	.137217	.034730	.162388	.063503
25	600	1.025	.249952	.006317	.000960	.000672	.243275
	700	1.270	.247326	.056960	.002837	.007859	.190366
	800	1.785	.238578	.126310	.008221	.037468	.112268
	900	2.230	.218449	.149480	.022180	.104025	.068969
100	600	1.025	.249796	.006247	.000483	.000334	.243548
	700	1.265	.248663	.057244	.001419	.003929	.191419
	800	1.750	.244289	.129067	.004125	.018719	.115222
	900	2.135	.234120	.160391	.011129	.052389	.073730

700, 800, and 900°K. The differences between these two studies are larger at higher temperatures and lower pressures.

Table V shows the total heat balance in the synthesis of methane with β -graphite the form of carbon precipitated, while Table VI shows the same quantities when "Dent" carbon precipitates. All values were computed at the minimum H_2/CO ratio where carbon no longer precipitates and where the yield of methane is a maximum. The net amount of heat evolved correlates strongly with the minimum ratio value: the higher the minimum ratio the less heat evolved. The effect of temperature is the greatest at one atmosphere pressure, becoming almost negligible at 100 atmospheres. Under the same conditions of temperature and pressure, more heat is evolved when "Dent" carbon is the form precipitated. The effect is most pronounced at 600°K and becomes increasingly less as the temperature increases.

B. Steam-Methane Reforming

Calculations for the steam-methane reforming process have been carried out at various temperatures (1200°F, 1400°F, 1600°F, 1800°F, and 2000°F), pressures (5 atm, 10 atm, 20 atm, 30 atm, and 40 atm), and initial steam-methane ratios (from 0.7 to 3.0).

For a given set of initial conditions, the sensible heats involved in raising the temperature of steam and methane from room temperature to the temperature at the bottom end of the reformer and from the latter temperature to the temperature at the top end were calculated. The temperature differential in the reformer has been taken in all cases as 600°F. Then the equilibrium yields of CH_4 , H_2O , CO , H_2 , CO_2 , and $C_{(s)}$

TABLE V

TOTAL HEAT BALANCES IN THE SYNTHESIS OF METHANE WITH GRAPHITE THE FORM OF CARBON
PRECIPITATED

p (atm)	T (°K)	Minimum Ratio	$SH_{293.15^{\circ}K \rightarrow T}$ $\times 10^{-3}$ B.t.u./lb-mole input	$\Delta H_{\text{reactor}}$ $\times 10^{-3}$ B.t.u./lb-mole input	$SH_{T \rightarrow 293.15^{\circ}K}$ $\times 10^{-3}$ B.t.u./lb-mole input	ΔH_{total} $\times 10^{-3}$ B.t.u./lb-mole input
1	600	2.710	3.843	-23.109	-2.721	-21.987
1	700	3.015	5.121	-21.294	-3.859	-20.032
1	800	3.830	6.407	-16.719	-5.274	-15.586
1	900	5.025	7.700	-9.953	-6.963	-9.216
10	600	2.625	3.844	-23.664	-2.695	-22.515
10	700	2.690	5.125	-23.298	-3.744	-21.917
10	800	2.855	6.420	-21.932	-4.934	-20.446
10	900	3.120	7.726	-19.077	-6.314	-17.665
25	600	2.610	3.844	-23.760	-2.690	-22.606
25	700	2.640	5.126	-23.642	-3.724	-22.240
25	800	2.720	6.422	-22.876	-4.872	-21.326
25	900	2.850	7.732	-21.108	-6.169	-19.545
100	600	2.600	3.844	-23.839	-2.686	-22.681
100	700	2.595	5.126	-23.942	-3.707	-22.523
100	800	2.610	6.424	-23.695	-4.819	-22.090
100	900	2.635	7.737	-22.924	-6.040	-21.227

TABLE VI

TOTAL HEAT BALANCES IN THE SYNTHESIS OF METHANE WITH "DENT" CARBON THE FORM OF CARBON PRECIPITATED

p (atm)	T (°K)	Minimum Ratio	$SH_{293.15^{\circ}K \rightarrow T}$ $\times 10^{-3}$ B.t.u./lb-mole input	$\Delta H_{\text{reactor}}$ $\times 10^{-3}$ B.t.u./lb-mole input	$SH_{T \rightarrow 293.15^{\circ}K}$ $\times 10^{-3}$ B.t.u./lb-mole input	ΔH_{total} $\times 10^{-3}$ B.t.u./lb-mole input
1	600	1.025	3.867	-27.282	-2.965	-26.380
1	700	1.310	5.153	-25.425	-4.036	-24.308
1	800	2.065	6.436	-20.076	-5.275	-18.915
1	900	3.045	7.727	-11.756	-6.921	-10.950
10	600	1.025	3.867	-27.440	-2.960	-26.533
10	700	1.275	5.154	-26.408	-3.995	-25.249
10	800	1.825	6.443	-23.958	-5.056	-22.571
10	900	2.345	7.745	-20.361	-6.348	-18.964
25	600	1.025	3.867	-27.468	-2.960	-26.561
25	700	1.270	5.154	-26.573	-3.987	-25.406
25	800	1.785	6.444	-24.643	-5.018	-23.217
25	900	2.230	7.749	-22.157	-6.228	-20.636
100	600	1.025	3.867	-27.492	-2.959	-26.584
100	700	1.265	5.154	-26.717	-3.981	-25.544
100	800	1.750	6.446	-25.237	-4.985	-23.776
100	900	2.135	7.752	-23.744	-6.122	-22.114

were computed at the temperature at the top end of the reformer, as well as the enthalpy of reaction. Next the sensible heats involved in cooling the equilibrium gas mixture to the temperature of the shift converter were calculated. The temperature of operation of the shift converter was taken in all cases as 750°F. At this temperature the equilibrium yields of H_2O , CO , H_2 , CO_2 , and $\text{C}_{(\text{s})}$ were recalculated as well as the enthalpy change in the shift converter. Finally, the sensible heats involved in cooling the equilibrium gas mixture to room temperature were calculated.

Figure 10 shows the effect of temperature and pressure on the minimum $\text{H}_2\text{O}/\text{CH}_4$ ratio above which carbon no longer precipitates in the reformer. The effect of pressure is greatest at the lowest temperature and at any given temperature the minimum ratio decreases as the pressure increases.

In Figure 11 are shown plots of the hydrogen yield in methane steam reforming as a function of temperature, pressure, and the $\text{H}_2\text{O}/\text{CH}_4$ ratio R . Except at 1200°F, pressure has little influence on the hydrogen yield at various ratios of $\text{H}_2\text{O}/\text{CH}_4$. At 1200°F the hydrogen yield steadily decreases as the pressure increases. At any given pressure the amount of hydrogen produced at 1200°F for any $\text{H}_2\text{O}/\text{CH}_4$ ratio from 1.5 to 3.0 is nearly the same. At higher temperatures much more hydrogen is produced at the lower ratio of $\text{H}_2\text{O}/\text{CH}_4$.

In Figure 12 are shown the equilibrium yields of H_2O , CO_2 , CO , and CH_4 in steam-methane reforming as a function of pressure, temperature, and the initial $\text{H}_2\text{O}/\text{CH}_4$ ratio. The amount of CO_2 present at equilibrium is practically unaffected by these variables. At any given $\text{H}_2\text{O}/\text{CH}_4$ ratio the amount of H_2O at equilibrium increases at constant temperature as the

Fig. 10. The Effect of Temperature and Pressure on the Minimum H_2O/CH_4 Ratio Above Which Carbon No Longer Precipitates in the Reformer.

Fig. 11. Hydrogen Yields in Methane-Steam Reforming as a Function of Temperature, Pressure, and Initial $\text{H}_2\text{O}/\text{CH}_4$ Ratio.

Fig. 12. Equilibrium Yields of H_2O , CO_2 , CO , and CH_4 in Steam-Methane Reforming as a Function of Pressure, Temperature, and Initial $\text{H}_2\text{O}/\text{CH}_4$ Ratio.

pressure increases, while at constant pressure and temperature the amount of H_2O increases as the $\text{H}_2\text{O}/\text{CH}_4$ ratio increases. At constant initial $\text{H}_2\text{O}/\text{CH}_4$ ratio the amount of CO at equilibrium decreases at constant temperature as the pressure increases; this effect becomes less at higher initial $\text{H}_2\text{O}/\text{CH}_4$ ratios. At constant pressure the amount of CO at equilibrium is practically independent of temperature at 1200°F ; at the higher temperatures the amount decreases as the initial $\text{H}_2\text{O}/\text{CH}_4$ ratio increases. Finally, the amount of CH_4 remaining at equilibrium increases at constant temperature and initial $\text{H}_2\text{O}/\text{CH}_4$ ratio as the pressure increases, while if pressure and temperature are held constant the amount of CH_4 remaining decreases as the initial $\text{H}_2\text{O}/\text{CH}_4$ ratio increases.

In Table VII are shown total heat balances for steam-methane reforming at total pressures of 5 and 40 atmospheres, upper reformer temperatures of 1200° , 1600° , and 1800°F , shift converter temperature of 750°F , and a steam/methane ratio of 1.5. At constant temperature, increasing the pressure decreases the heat needed, the effect being greater at lower temperatures.

TABLE VII

TOTAL HEAT BALANCES UNDER SPECIFIED CONDITIONS FOR METHANE-STEAM REFORMING AT AN INITIAL
 $\text{H}_2\text{O}/\text{CH}_4$ RATIO OF 1.5

p (atm)	t (°F)	B.t.u/lb-mole input $\times 10^{-3}$					
		$\text{SH}_{68^\circ\text{F} \rightarrow t}$	$\Delta\text{H}_{\text{reformer}}$	$\text{SH}_{t \rightarrow 750^\circ\text{F}}$	$\Delta\text{H}_{\text{shift converter}}$	$\text{SH}_{750^\circ\text{F} \rightarrow 68^\circ\text{F}}$	$\Delta\text{H}_{\text{total}}$
5	1200	11.653	15.084	- 5.623	-0.890	-7.675	12.549
5	1600	16.793	35.565	-11.593	-1.824	-8.823	30.118
5	1800	22.463	38.772	-17.404	-1.904	-8.965	32.962
40	1200	11.653	6.338	- 5.376	-0.228	-7.029	5.358
40	1600	16.793	20.444	-11.123	-1.752	-7.980	16.382
40	1800	22.463	36.031	-17.318	-2.076	-8.829	30.271

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APPENDIX

A listing of the FORTRAN program written to carry out the calculations for either methane synthesis or steam-methane reforming follows. Definitions of the variables which comprise the input to the program are given in the comment statements at the beginning of the program. For either methane synthesis or steam-methane reforming these variables are input on two cards per case according to the format shown in Table VIII. A blank card following the last case terminates the calculations

The temperatures on card 2 for either steam-methane reforming or methane synthesis may be in degrees Fahrenheit, degrees Centigrade, or degrees Kelvin.

TABLE VIII. INPUT DATA

Card No.	Field	Variable	Format
1	1 - 10	P	E10.0
	11 - 20	R	E10.0
	21 - 30	XI	E10.0
	31 - 40	YI	E10.0
	41 - 50	ZI	E10.0
	51 - 60	EPS	E10.0
	61 - 65	NIT	I5
	66 - 70	NSC	I5
	71 - 75	NMETH	I5
	76	NDC	I1
	77 - 80	NTC	I4
2	(for steam methane reforming)		
	1 - 10	T1	E10.0
	11 - 20	T2	E10.0
	21 - 30	T3	E10.0
	31 - 40	T4	E10.0
	41 - 50	T5	E10.0
2	(for methane synthesis)		
	1 - 10	T1	E10.0
	11 - 20	T2	E10.0
	21 - 30	T3	E10.0

C
C
C
C

C
C
C
C
CONSTANTS FOR LOG (KP2) ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) AS FUNCTION OF T (DEG. F)

DATA QP2/4.09775D0,-5.89713D-3,2.90724D-6,-5.3392D-10/

C
C
C
C
CONSTANTS FOR LOG (KP3) ($2\text{CO} = \text{C} + \text{CO}_2$) AS FUNCTION OF T (DEG. F) GRAPHITE

DATA QP3/1.72556D+1,-2.51018D-2,1.18293D-5,-2.12805D-9/

C
C
C
C
CONSTANTS FOR LOG (KP3) ($2\text{CO} = \text{C} + \text{CO}_2$) AS FUNCTION OF T (DEG. F) DENT CARBON

DATA QP4/3.35280D0,8.36512D-3,-1.63599D-5,6.05889D-9/

C
C
C
C
CONSTANTS FOR CP (HEAT CAPACITY) OF CH_4 AS FUNCTION OF T (DEG. F)

DATA CPCH4/9.03446D0,5.82421D-3,-6.16646D+3/

C
C
C
C
CONSTANTS FOR CP OF H_2O AS FUNCTION OF T (DEG. F)

DATA CPH20/7.66867D0,1.63605D-3,1.39796D+3/

C
C
C
C
CONSTANTS FOR CP OF CO AS FUNCTION OF T (DEG. F)

DATA CPCO/6.81334D0,7.95847D-4,5.17239D+2/

C
C
C
C
CONSTANTS FOR CP OF H_2 AS FUNCTION OF T (DEG. F)

DATA CPH2/6.76470D0,3.65183D-4,6.47006D+2/

C
C
C
C
CONSTANTS FOR CP OF CO_2 AS FUNCTION OF T (DEG. F)

DATA CPCO2/1.00888D+1,2.03493D-3,-8.45673D+3/

C
C
C
C
CONSTANTS FOR DELTA H (FORMATION) OF CH_4 AS FUNCTION OF T (DEG. F)

DATA H1/-3.14291D+4,-8.96644D0,3.16520D-3,-3.67713D-7/

C
C
C
C
CONSTANTS FOR DELTA H (FORMATION) OF H_2O AS FUNCTION OF T (DEG. F)

DATA H5/-1.03814D+5,-2.61524D0,3.25639D-4,3.68627D-8/

C
C
C
C
CONSTANTS FOR DELTA H (FORMATION) OF CO AS FUNCTION OF T (DEG. F)

DATA H3/-4.73377D+4,5.13685D-1,-1.11742D-3,2.00704D-7/

C
C
C
C
CONSTANTS FOR DELTA H (FORMATION) OF CO_2 AS FUNCTION OF T (DEG. F)

```

C
DATA H4/-1.69105D+5,-5.0D-1,-1.03398D-25,2.52435D-29/
C
C
C
C
FUNCTIONS AND DERIVATIVES FOR STEAM-METHANE REFORMING WITH C-PPT
C
F1C(Q1,P,A,X,Y,Z)=Q1*(1.-A-X)*(A-X-Y+Z)*(1.+2.*X-Z)**2-(X-Y-Z)*(3.
1*X+Y-Z)**3*P**2
F2C(Q2,A,X,Y,Z)=Q2*(X-Y-Z)*(A-X-Y+Z)-Y*(3.*X+Y-Z)
F3C(Q3,P,X,Y,Z)=Q3*(X-Y-Z)**2*P-Y*(1.+2.*X-Z)
C
DF1CX(Q1,P,A,X,Y,Z)=-Q1*(A-X-Y+Z)*(1.+2.*X-Z)**2-Q1*(1.-A-X)*(1.+2
1.*X-Z)**2+4.*Q1*(1.-A-X)*(A-X-Y+Z)*(1.+2.*X-Z)-(3.*X+Y-Z)**3*P**2-
29.*(X-Y-Z)*(3.*X+Y-Z)**2*P**2
DF1CY(Q1,P,A,X,Y,Z)=-Q1*(1.-A-X)*(1.+2.*X-Z)**2+(3.*X+Y-Z)**3*P**2
1-3.*(X-Y-Z)*(3.*X+Y-Z)**2*P**2
DF1CZ(Q1,P,A,X,Y,Z)=Q1*(1.-A-X)*(1.+2.*X-Z)**2-2.*Q1*(1.-A-X)*(A-X
1-Y+Z)*(1.+2.*X-Z)+(3.*X+Y-Z)**3*P**2+3.*(X-Y-Z)*(3.*X+Y-Z)**2*P**2
DF2CX(Q2,A,X,Y,Z)=Q2*(A-X-Y+Z)-Q2*(X-Y-Z)-3.*Y
DF2CY(Q2,A,X,Y,Z)=-Q2*(A-X-Y+Z)-Q2*(X-Y-Z)-(3.*X+Y-Z)-Y
DF2CZ(Q2,A,X,Y,Z)=-Q2*(A-X-Y+Z)+Q2*(X-Y-Z)+Y
DF3CX(Q3,P,X,Y,Z)=2.*Q3*(X-Y-Z)*P-2.*Y
DF3CY(Q3,P,X,Y,Z)=-2.*Q3*(X-Y-Z)*P-(1.+2.*X-Z)
DF3CZ(Q3,P,X,Y,Z)=-2.*Q3*(X-Y-Z)*P+Y
C
C
C
C
FUNCTIONS AND DERIVATIVES FOR STEAM-METHANE REFORMING WITHOUT
C-PPT
C
F1(Q1,P,A,X,Y)=Q1*(1.-A-X)*(A-X-Y)*(1.+2.*X)**2-(X-Y)*(3.*X+Y)**3*
1P**2
F2(Q2,A,X,Y)=Q2*(X-Y)*(A-X-Y)-Y*(3.*X+Y)
C
DF1X(Q1,P,A,X,Y)=-Q1*(A-X-Y)*(1.+2.*X)**2-Q1*(1.-A-X)*(1.+2.*X)**2
1+4.*Q1*(1.-A-X)*(A-X-Y)*(1.+2.*X)-(3.*X+Y)**3*P**2-9.*(X-Y)*(3.*X+
2Y)**2*P**2
DF1Y(Q1,P,A,X,Y)=-Q1*(1.-A-X)*(1.+2.*X)**2+(3.*X+Y)**3*P**2-3.*(X-
1Y)*(3.*X+Y)**2*P**2
DF2X(Q2,A,X,Y)=Q2*(A-X-Y)-Q2*(X-Y)-3.*Y
DF2Y(Q2,A,X,Y)=-Q2*(A-X-Y)-Q2*(X-Y)-(3.*X+Y)-Y
C
C
C
C
FUNCTIONS AND DERIVATIVES OF REACTIONS IN SHIFT CONVERTER WITH C-PPT
C
F2CSC(Q2,A,Y,Z,CO,H2,CO2)=Q2*(CO-Y-Z+CO2)*(A-Y+CO2+Z)-Y*(H2+Y-CO2-
1Z)
F3CSC(Q3,A,P,Y,Z,CO,H2,CO2)=Q3*(CO-Y-Z+CO2)**2*P-Y*(A+CO2+CO+H2-Z)
C
DF2CSY(Q2,A,Y,Z,CO,H2,CO2)=-Q2*(A-Y+CO2+Z)-Q2*(CO-Y-Z+CO2)-(H2+Y-
1CO2-Z)-Y
DF2CSZ(Q2,A,Y,Z,CO,CO2)=-Q2*(A-Y+CO2+Z)+Q2*(CO-Y-Z+CO2)+Y
DF3CSY(Q3,A,P,Y,Z,CO,H2,CO2)=-2.*Q3*(CO-Y-Z-CO2)*P-(A+CO2+CO+H2-Z)
DF3CSZ(Q3,P,Y,Z,CO,CO2)=-2.*Q3*(CO-Y-Z-CO2)*P+Y
C
C
C
C
ALL SENSIBLE HEATS IN BTU/(LB-MOLE)

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```

C      SENSIBLE HEAT FOR METHANE OVER TEMPERATURE RANGE T1 TO T2 (DEG. F)
C
C      SHCH4 (T2,T1)=CPCH4 (1) * (T2-T1) +CPCH4 (2) /2. * (T2**2-T1**2)-CPCH4 (3) *
1 (1./T2-1./T1)
C
C
C      SENSIBLE HEAT FOR STEAM OVER TEMPERATURE RANGE T1 TO T2 (DEG. F)
C
C      SHH2O (T2,T1)=CPH2O (1) * (T2-T1) +CPH2O (2) /2. * (T2**2-T1**2)-CPH2O (3) *
1 (1./T2-1./T1)
C
C
C      SENSIBLE HEAT FOR CARBON MONOXIDE OVER TEMPERATURE RANGE T1 TO T2 (DEG. F)
C
C      SHCO (T2,T1)=CPCO (1) * (T2-T1) +CPCO (2) /2. * (T2**2-T1**2)-CPCO (3) *
1 (1./T2-1./T1)
C
C
C      SENSIBLE HEAT FOR HYDROGEN OVER TEMPERATURE RANGE T1 TO T2 (DEG. F)
C
C      SHH2 (T2,T1)=CPH2 (1) * (T2-T1) +CPH2 (2) /2. * (T2**2-T1**2)-CPH2 (3) *
1 (1./T2-1./T1)
C
C
C      SENSIBLE HEAT FOR CARBON DIOXIDE OVER TEMPERATURE RANGE T1 TO T2 (DEG. F)
C
C      SHCO2 (T2,T1)=CPCO2 (1) * (T2-T1) +CPCO2 (2) /2. * (T2**2-T1**2)-CPCO2 (3) *
1 (1./T2-1./T1)
C
C
C      LOG (EQUILIBRIUM CONSTANT) FOR REACTION 1 (CH4+H2O=CO+3H2) AT T (DEG. F)
C
C      QPI1 (T)=QP1 (1) +QP1 (2) *T+QP1 (3) *T**2+QP1 (4) *T**3
C
C
C      LOG (EQUILIBRIUM CONSTANT) FOR REACTION 2 (CO+H2O=CO2+H2) AT T (DEG. F)
C
C      QPI2 (T)=QP2 (1) +QP2 (2) *T+QP2 (3) *T**2+QP2 (4) *T**3
C
C
C      LOG (EQUILIBRIUM CONSTANT) FOR REACTION 3 (2CO=C+CO2) AT T (DEG. F) GRAPHITE
C
C      QPI3 (T)=QP3 (1) +QP3 (2) *T+QP3 (3) *T**2+QP3 (4) *T**3
C
C
C      LOG (EQUILIBRIUM CONSTANT) FOR REACTION 3 (2CO=C+CO2) AT T (DEG. F) DENT C
C
C      QPI4 (T)=QP4 (1) +QP4 (2) *T+QP4 (3) *T**2+QP4 (4) *T**3
C
C
C      ALL HEATS OF FORMATION IN BTU/(LB-MOLE)
C
C      HEAT OF FORMATION OF CH4 AT T (DEG. F)
C
C      HCH4 (T)=H1 (1) +H1 (2) *T+H1 (3) *T**2+H1 (4) *T**3
C
C
C      HEAT OF FORMATION OF H2O AT T (DEG. F)

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```

C
HH2O(T)=H5(1)+H5(2)*T+H5(3)*T**2+H5(4)*T**3
C
C
HEAT OF FORMATION OF CO AT T(DEG. F)
C
HCO(T)=H3(1)+H3(2)*T+H3(3)*T**2+H3(4)*T**3
C
C
HEAT OF FORMATION OF CO2 AT T(DEG. F)
C
HCO2(T)=H4(1)+H4(2)*T+H4(3)*T**2+H4(4)*T**3
C
C
FUNCTIONS AND DERIVATIVES OF METHANE SYNTHESIS WITH C-PPT
C
FI(Q1,P,A,X,Y,Z)=Q1*(A-3.*X+Y-Z)**3*(1.-A-X-Y-Z)*P**2-X*(X-Y+Z)*
1(1.-2.*X-Z)**2
FJ(Q2,A,X,Y,Z)=Q2*(1.-A-X-Y-Z)*(X-Y+Z)-Y*(A-3.*X+Y-Z)
FK(Q3,P,A,X,Y,Z)=Q3*(1.-A-X-Y-Z)**2*P-Y*(1.-2.*X-Z)
C
DFIX(Q1,P,A,X,Y,Z)=-9.*Q1*(A-3.*X+Y-Z)**2*(1.-A-X-Y-Z)*P**2-Q1*
1(A-3.*X+Y-Z)**3*P**2-(X-Y+Z)*(1.-2.*X-Z)**2-X*(1.-2.*X-Z)**2+4.*X*
2(X-Y+Z)*(1.-2.*X-Z)
DFIY(Q1,P,A,X,Y,Z)=3.*Q1*(A-3.*X+Y-Z)**2*(1.-A-X-Y-Z)*P**2-Q1*
1(A-3.*X+Y-Z)**3*P**2+X*(1.-2.*X-Z)**2
DFIZ(Q1,P,A,X,Y,Z)=-3.*Q1*(A-3.*X+Y-Z)**2*(1.-A-X-Y-Z)*P**2-Q1*
1(A-3.*X+Y-Z)**3*P**2-X*(1.-2.*X-Z)**2+2.*X*(X-Y+Z)*(1.-2.*X-Z)
DFJX(Q2,A,X,Y,Z)=-Q2*(X-Y+Z)+Q2*(1.-A-X-Y-Z)+3.*Y
DFJY(Q2,A,X,Y,Z)=-Q2*(X-Y+Z)-Q2*(1.-A-X-Y-Z)-(A-3.*X+Y-Z)-Y
DFJZ(Q2,A,X,Y,Z)=-Q2*(X-Y+Z)+Q2*(1.-A-X-Y-Z)+Y
DFKX(Q3,P,A,X,Y,Z)=-2.*Q3*(1.-A-X-Y-Z)*P+2.*Y
DFKY(Q3,P,A,X,Y,Z)=-2.*Q3*(1.-A-X-Y-Z)*P-(1.-2.*X-Z)
DFKZ(Q3,P,A,X,Y,Z)=-2.*Q3*(1.-A-X-Y-Z)*P+Y
C
C
FUNCTIONS AND DERIVATIVES OF METHANE SYNTHESIS WITHOUT C-PPT
C
C
F11(Q1,P,A,X,Y)=Q1*(A-3.*X+Y)**3*(1.-A-X-Y)*P**2-X*(X-Y)*(1.-2.*X)
1**2
F22(Q2,A,X,Y)=Q2*(1.-A-X-Y)*(X-Y)-Y*(A-3.*X+Y)
C
DF11X(Q1,P,A,X,Y)=-9.*Q1*(A-3.*X+Y)**2*(1.-A-X-Y)*P**2-Q1*(A-3.*X+
1Y)**3*P**2-(X-Y)*(1.-2.*X)**2-X*(1.-2.*X)**2+4.*X*(X-Y)*(1.-2.*X)
DF11Y(Q1,P,A,X,Y)=3.*Q1*(A-3.*X+Y)**2*(1.-A-X-Y)*P**2-Q1*(A-3.*X+Y
1)**3*P**2+X*(1.-2.*X)**2
DF22X(Q2,A,X,Y)=-Q2*(X-Y)+Q2*(1.-A-X-Y)+3.*Y
DF22Y(Q2,A,X,Y)=-Q2*(X-Y)-Q2*(1.-A-X-Y)-(A-3.*X+Y)-Y
C
C
50 READ 2,P,P,XI,YI,ZI,EP,S,NIT,NSC,NMETH,NDC,NTC
C
2 FORMAT(6E10.0,3I5,I1,I4)
IF(NIT.EQ.0) CALL EXIT
A=R/(1.+R)
IF(NTC.EQ.1) GO TO 20

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      IF (NTC .EQ. 2) GO TO 22
C
      READ 1, T1, T2, T3, T4, T5
C
      1 FORMAT (8E10.0)
      T1C= (T1-32.) *5./9.
      T2C= (T2-32.) *5./9.
      T3C= (T3-32.) *5./9.
      T4C= (T4-32.) *5./9.
      T5C= (T5-32.) *5./9.
      T1K=T1C+273.15
      T2K=T2C+273.15
      T3K=T3C+273.15
      T4K=T4C+273.15
      T5K=T5C+273.15
      GO TO 21
C
      20 READ 1, T1C, T2C, T3C, T4C, T5C
C
      T1=T1C*9./5.+32.
      T2=T2C*9./5.+32.
      T3=T3C*9./5.+32.
      T4=T4C*9./5.+32.
      T5=T5C*9./5.+32.
      T1K=T1C+273.15
      T2K=T2C+273.15
      T3K=T3C+273.15
      T4K=T4C+273.15
      T5K=T5C+273.15
      GO TO 21
C
      22 READ 1, T1K, T2K, T3K, T4K, T5K
C
      T1C=T1K-273.15
      T2C=T2K-273.15
      T3C=T3K-273.15
      T4C=T4K-273.15
      T5C=T5K-273.15
      T1=T1C*9./5.+32.
      T2=T2C*9./5.+32.
      T3=T3C*9./5.+32.
      T4=T4C*9./5.+32.
      T5=T5C*9./5.+32.
      21 IF (NMETH .EQ. 1) GO TO 1000
C
C
C
C
C
      STEAM-METHANE REFORMING
C
      X=XI
      Y=YI
      Z=ZI
      V(1)=X
      V(2)=Y
      V(3)=Z
      SH1CH4=SHCH4(T2,T1)*(1.-A)
      SHCCH4=SH1CH4*0.251996D0
      SH1H2O=SHH2O(T2,T1)*A

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SHCH20=SH1H20*0.251996D0
H2OI=A
CH4I=1.-A
PRINT 5,T1,T2,T1C,T2C,T1K,T2K
5 FORMAT(1H1,22X,14HSENSIBLE HEATS/1H0,10X,17HTEMPERATURE RANGE,
1F8.2,1X,2HTO,F8.2,1X,9HDEGREES F,2X,1H(,F8.2,1X,2HTO,F8.2,1X,12HDE
2GREES C OR,F8.2,1X,2HTO,F8.2,1X,10HDEGREES K)/1H0,13X,9HSUBSTANCE,
310X,7HINITIAL,9X,19HSENSIBLE HEATS (BTU),6X,20HSENSIBLE HEATS (KCAL)
4/1H,28X,14HMOLE FRACTIONS,7X,17HPER LB-MOLE INPUT,8X,17HPER LB-MO
5LE INPUT)
PRINT 3,NA1,CH4I,SH1CH4,SHCCH4
PRINT 3,NA2,H2OI,SH1H20,SHCH20
3 FORMAT(1H0,14X,A8,8X,F9.6,11X,1PE13.5,12X,1PE13.5)
PRINT 30
30 FORMAT(1H0,/)
IF(T2+.01 .GT. T3) GO TO 500
C
C
C
SENSIBLE HEATS IN REFORMER
SH2CH4=SHCH4(T3,T2)*(1.-A)
SHCCH4=SH2CH4*0.251996D0
SH2H2O=SHH2O(T3,T2)*A
SHCH20=SH2H20*0.251996D0
PRINT 7,T2,T3,T2C,T3C,T2K,T3K
7 FORMAT(1H0,22X,14HSENSIBLE HEATS/1H0,10X,17HTEMPERATURE RANGE,
1F8.2,1X,2HTO,F8.2,1X,9HDEGREES F,2X,1H(,F8.2,1X,2HTO,F8.2,1X,12HDE
2GREES C OR,F8.2,1X,2HTO,F8.2,1X,10HDEGREES K)/1H0,13X,9HSUBSTANCE,
37X,19HSENSIBLE HEAT (BTU),7X,20HSENSIBLE HEAT (KCAL)/1H,30X,17HPE
4R LB-MOLE INPUT,9X,17HPER LB-MOLE INPUT)
PRINT 6,NA1,SH2CH4,SHCCH4
PRINT 6,NA2,SH2H2O,SHCH20
6 FORMAT(1H0,14X,A8,9X,1PE13.5,13X,1PE13.5)
C
500 T=T3
TC=T3C
TK=T3K
NN=1
CO=0.
CO2=0.
CH4=1.-A
Q1=QPI1(T3)
Q2=QPI2(T3)
IF(NDC .EQ. 1) GO TO 23
Q3=QPI3(T3)
GO TO 24
23 Q3=QPI4(T3)
24 Q1=DEXP(2.30259*Q1)
Q2=DEXP(2.30259*Q2)
Q3=DEXP(2.30259*Q3)
DHCH4=HCH4(T3)
DHH2O=HH2O(T3)
DHCO=HCO(T3)
DHCO2=HCO2(T3)
DELH1=DHCH4*CH4+DHH2O*A+DHCO*CO+DHCO2*CO2
C
DO 200 J=1,NIT
M=J
B(1,1)=DF1CX(Q1,P,A,X,Y,Z)

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      B(1,2)=DF1CY(Q1,P,A,X,Y,Z)
      B(1,3)=DF1CZ(Q1,P,A,X,Y,Z)
      B(2,1)=DF2CX(Q2,A,X,Y,Z)
      B(2,2)=DF2CY(Q2,A,X,Y,Z)
      B(2,3)=DF2CZ(Q2,A,X,Y,Z)
      B(3,1)=DF3CX(Q3,P,X,Y,Z)
      B(3,2)=DF3CY(Q3,P,X,Y,Z)
      B(3,3)=DF3CZ(Q3,P,X,Y,Z)
      G(1)=-F1C(Q1,P,A,X,Y,Z)
      G(2)=-F2C(Q2,A,X,Y,Z)
      G(3)=-F3C(Q3,P,X,Y,Z)
      CALL INVERT(B,3,1.0D-70,NEROR,DELTA)
      IF (NEROR) 252,252,251
251 PRINT 113
113 FORMAT(1H0,10X,15HSINGULAR MATRIX)
      GO TO 50
252 DO 253 K=1,3
      C(K)=0.0D0
      DO 253 L=1,3
253 C(K)=C(K)+B(K,L)*G(L)
      DO 254 K=1,3
254 V1(K)=V(K)+C(K)
      IF (V1(1) .LE. 0.) GO TO 505
      IF (V1(2) .LE. 0.) GO TO 505
      IF (V1(3) .LE. 0.) GO TO 100
      DO 256 K=1,3
      CONV(K)=DABS(V(K)/V1(K)-1.0D0)
      IF (CONV(K)-EPS) 256,256,257
256 CONTINUE
      GO TO 270
257 DO 258 K=1,3
258 V(K)=V1(K)
      X=V(1)
      Y=V(2)
      Z=V(3)
200 CONTINUE
C
270 PRINT 10
10 FORMAT(1H1,10X,20HOUTPUT FROM REFORMER,/)
      X=V1(1)
      Y=V1(2)
      Z=V1(3)
      CH4=1.-A-X
      H2O=A-X-Y+Z
      CO=X-Y-Z
      H2=3.*X+Y-Z
      CO2=Y
      CAR=Z
      TOTAL=1.+2.*X
      YCH4=CH4/TOTAL
      YH2O=H2O/TOTAL
      YCO=CO/TOTAL
      YH2=H2/TOTAL
      YCO2=CO2/TOTAL
      YCAR=CAR/TOTAL
      TMG=1.+2.*X-Z
      XCH4=CH4/TMG
      XH2O=H2O/TMG

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XCO=CO/TMG
XH2=H2/TMG
XCO2=CO2/TMG
XCAR=0.
ZCAR=CAR/CH4I
EK1=(X-Y-Z)*(3.*X+Y-Z)**3*P**2/((1.-A-X)*(A-X-Y+Z)*(1.+2.*X-Z)**2)
EK2=Y*(3.*X+Y-Z)/((X-Y-Z)*(A-X-Y+Z))
EK3=Y*(1.+2.*X-Z)/((X-Y-Z)**2*P)
PRINT 11
11 FORMAT(1H0,13X,6HP(ATM),5X,8HT(DEG F),5X,8HT(DEG C),5X,8HT(DEG K),
15X,21HINITIAL H2O/CH4 RATIO)
PRINT 12,P,T,TC,TK,R
12 FORMAT(1H0,F18.0,3F13.2,F20.3)
PRINT 9000
9000 FORMAT(/1H0,11X,9HCOMPONENT,5X,20HMOLES PER MOLE INPUT,11X,14HMOL
1E FRACTIONS,5X,21HMOLE FRACTIONS IN GAS)
IF(NDC.EQ.1) GO TO 218
PRINT 215,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR,ZCAR
215 FORMAT(1H0,13X,3HCH4,3F25.6/1H0,13X,3HH2O,3F25.6/1H0,14X,2HCO,3F25
1.6/1H0,14X,2HH2,3F25.6/1H0,13X,3HCO2,3F25.6/1H0,15X,1HC,3F25.6/1H0
2/1H0,11X,41HMOLE FRACTION INGOING CARBON DEPOSITED = ,F8.6)
GO TO 219
218 PRINT 217,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR,ZCAR
217 FORMAT(1H0,13X,3HCH4,3F25.6/1H0,13X,3HH2O,3F25.6/1H0,14X,2HCO,3F25
1.6/1H0,14X,2HH2,3F25.6/1H0,13X,3HCO2,3F25.6/1H0,10X,6HDENT C.3F25.
26/1H0,11X,41HMOLE FRACTION INGOING CARBON DEPOSITED = ,F8.6)
219 PRINT 15
15 FORMAT(1H0,10X,34HRECALCULATED EQUILIBRIUM CONSTANTS)
PRINT 16,EK1,EK2,EK3
16 FORMAT(1H0,17X,2HK1,1PE16.4/1H0,17X,2HK2,E16.4/1H0,17X,2HK3,E16.4)
PRINT 17,M
17 FORMAT(1H0,10X,12HCONVERGED IN,I5,11H ITERATIONS//)
A=A-X-Y+Z
DELTAH=DHCH4*CH4+DHH2O*H2O+DHCO*CO+DHCO2*CO2-DELH1
DELHC=DELTAH*0.251996D0
PRINT 510
510 FORMAT(1H0,10X,21HENTHALPY CHANGE (BTU),5X,22HENTHALPY CHANGE (KCA
1L)/1H,12X,17HPER LB-MOLE INPUT,9X,17HPER LB-MOLE INPUT)
PRINT 511,DELTAH,DELHC
511 FORMAT(1H0,2(10X,1PE16.4))
GO TO 300

C
C STEAM-METHANE REFORMING WITHOUT C-PPT
C
100 CONTINUE
C
DO 60 J=1,NIT
M=J
B(1,1)=DF1X(Q1,P,A,X,Y)
B(1,2)=DF1Y(Q1,P,A,X,Y)
B(2,1)=DF2X(Q2,A,X,Y)
B(2,2)=DF2Y(Q2,A,X,Y)
G(1)=-F1(Q1,P,A,X,Y)
G(2)=-F2(Q2,A,X,Y)
CALL INVERT(B,2,1.0D-70,NEROR,DELTA)
IF(NEROR) 52,52,51

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51 PRINT 113
   GO TO 50
52 DO 53 K=1,2
   C(K)=0.0D0
   DO 53 L=1,2
53 C(K)=C(K)+B(K,L)*G(L)
   DO 54 K=1,2
54 V1(K)=V(K)+C(K)
   DO 55 K=1,2
   IF (V1(K) .GT. 0.) GO TO 55
   PRINT 4, V1(1),V1(2)
4  FORMAT(1H0,10X,6HCO2 = ,0PF7.4,10X,6HCH4 = ,F7.4)
   GO TO 50
55 CONTINUE
   DO 56 K=1,2
   CONV(K)=DABS(V(K)/V1(K)-1.0D0)
   IF(CONV(K)-EPS) 56,56,57
56 CONTINUE
   GO TO 70
57 DO 58 K=1,2
58 V(K)=V1(K)
   X=V(1)
   Y=V(2)
60 CONTINUE
C
70 PRINT 10
   X=V1(1)
   Y=V1(2)
   CH4=1.-A-X
   H2O=A-X-Y
   CO=X-Y
   H2=3.*X+Y
   CO2=Y
   CAR=0.
   TOTAL=1.+2.*X
   YCH4=CH4/TOTAL
   YH2O=H2O/TOTAL
   YCO=CO/TOTAL
   YH2=H2/TOTAL
   YCO2=CO2/TOTAL
   YCAR=CAR/TOTAL
   TMG=1.+2.*X
   XCH4=CH4/TMG
   XH2O=H2O/TMG
   XCO=CO/TMG
   XH2=H2/TMG
   XCO2=CO2/TMG
   XCAR=0.
   EK1=(X-Y)*(3.*X+Y)**3*P**2/((1.-A-X)*(A-X-Y)*(1.+2.*X)**2)
   EK2=Y*(3.*X+Y)/((X-Y)*(A-X-Y))
   PRINT 11
   PRINT 12,P,T,TC,TK,R
   PRINT 9000
   IF(NDC .EQ. 1) GO TO 220
   PRINT 214,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR
214 FORMAT(1H0,13X,3HCH4,3F25.6/1H0,13X,3HH2O,3F25.6/1H0,14X,2HCO,3F25
1.6/1H0,14X,2HH2,3F25.6/1H0,13X,3HCO2,3F25.6/1H0,15X,1HC,3F25.6)

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      GO TO 221
220 PRINT 216, CH4, YCH4, XCH4, H2O, YH2O, XH2O, CO, YCO, XCO, H2, YH2, XH2, CO2,
      1YCO2, XCO2, CAR, YCAR, XCAR
216 FORMAT (1H0, 13X, 3HCH4, 3F25.6/1H0, 13X, 3HH2O, 3F25.6/1H0, 14X, 2HCO, 3F25.
      1.6/1H0, 14X, 2HH2, 3F25.6/1H0, 13X, 3HCO2, 3F25.6/1H0, 10X, 6HDENT C, 3F25.
      26)
221 PRINT 15
      PRINT 16, EK1, EK2
      PRINT 17, M
      V(1)=X
      V(2)=Y
      A=A-X-Y
      DELTAH=DHCH4*CH4+DHH2O*H2O+DHCO*CO+DHCO2*CO2-DELH1
      DELHC=DELTAH*0.251996D0
      PRINT 510
      PRINT 511, DELTAH, DELHC
C
C      SHIFT CONVERTER
C
300 CONTINUE
      SH3CH4=SHCH4(T4,T)*CH4
      SHCCH4=SH3CH4*0.251996D0
      SH3H2O=SHH2O(T4,T)*H2O
      SHCH2O=SH3H2O*0.251996D0
      SH3CO2=SHCO2(T4,T)*CO2
      SHCCO2=SH3CO2*0.251996D0
      SH3CO=SHCO(T4,T)*CO
      SHCCO=SH3CO*0.251996D0
      SH3H2=SHH2(T4,T)*H2
      SHCH2=SH3H2*0.251996D0
      PRINT 8, T, T4, TC, T4C, TK, T4K
8  FORMAT (1H1, 22X, 14HSENSIBLE HEATS/1H0, 10X, 17HTEMPERATURE RANGE,
      1F8.2, 1X, 2HTO, F8.2, 1X, 9HDEGREES F, 2X, 1H(, F8.2, 1X, 2HTO, F8.2, 1X, 12HDE
      2GREES C OR, F8.2, 1X, 2HTO, F8.2, 1X, 10HDEGREES K)/1H0, 13X, 9HSUBSTANCE,
      37X, 19HSENSIBLE HEAT (BTU), 7X, 20HSENSIBLE HEAT (KCAL)/1H , 30X, 17HPE
      4R LB-MOLE INPUT, 9X, 17HPER LB-MOLE INPUT)
      PRINT 6, NA1, SH3CH4, SHCCH4
      PRINT 6, NA2, SH3H2O, SHCH2O
      PRINT 6, NA3, SH3H2, SHCH2
      PRINT 6, NA4, SH3CO, SHCCO
      PRINT 6, NA5, SH3CO2, SHCCO2
      IF(NSC) 800, 800, 613
800 DHH2O=HH2O(T4)
      DHCO=HCO(T4)
      DHCO2=HCO2(T4)
      DELH1=DHH2O*A+DHCO*CO+DHCO2*CO2
      Q2=QPI2(T4)
      IF(NDC .EQ. 1) GO TO 25
      Q3=QPI3(T4)
      GO TO 26
25 Q3=QPI4(T4)
26 Q2=DEXP(2.30259*Q2)
      Q3=DEXP(2.30259*Q3)
      Y=CO2
      Z=ZI
      V(1)=Y
      V(2)=0.0D0
C

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DO 750 J= 1, NIT
M=J
B(1,1)=DF2CSY(Q2,A,Y,Z,CO,H2,CO2)
B(1,2)=DF2CSZ(Q2,A,Y,Z,CO,CO2)
B(2,1)=DF3CSY(Q3,A,P,Y,Z,CO,H2,CO2)
B(2,2)=DF3CSZ(Q3,P,Y,Z,CO,CO2)
G(1)=-F2CSC(Q2,A,Y,Z,CO,H2,CO2)
G(2)=-F3CSC(Q3,A,P,Y,Z,CO,H2,CO2)
CALL INVERT(B,2,1.0D-70,NEROR,DELTA)
IF (NEROR) 710,710,51
710 DO 720 K=1,2
C(K)=0.0D0
DO 720 L=1,2
720 C(K)=C(K)+B(K,L)*G(L)
DO 730 K=1,2
730 V1(K)=V(K)+C(K)
IF(V1(1).LE.0.) GO TO 507
IF(V1(2).LE.0.) GO TO 598
DO 735 K=1,2
CONV(K)=DABS(V(K)/V1(K)-1.0D0)
IF(CONV(K)-EPS) 735,735,736
735 CONTINUE
GO TO 760
736 DO 737 K=1,2
737 V(K)=V1(K)
Y=V(1)
Z=V(2)
750 CONTINUE
C
760 PRINT 610
Y=V1(1)
Z=V1(2)
TOTAL=A+CO2+CO+H2+CH4
TMG=A+CO2+CO+H2-Z+CH4
H2O=A-Y+CO2+Z
CO=CO-Y-Z+CO2
H2=H2+Y-CO2-Z
CO2=Y
CAR=Z
YCH4=CH4/TOTAL
YH2O=H2O/TOTAL
YCO=CO/TOTAL
YH2=H2/TOTAL
YCO2=CO2/TOTAL
YCAR=CAR/TOTAL
XCH4=CH4/TMG
XH2O=H2O/TMG
XCO=CO/TMG
XH2=H2/TMG
XCO2=CO2/TMG
XCAR=0.
EK2=CO2*H2/(CO*H2O)
EK3=Y*TMG/(CO**2*P)
DELTAH=DH2O*H2O+DHCO*CO+DHCO2*CO2-DELH1
DELHC=DELTAH*0.251996D0
PRINT 11
PRINT 12,P,T4,T4C,T4K,R
PRINT 9000

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      IF(NDC .EQ. 1) GO TO 222
      PRINT 214,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR
      GO TO 223
222 PRINT 216,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCC,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR
223 PRINT 15
      PRINT 18,EK2,EK3
18  FORMAT(1H0,17X,2HK2,1PE16.4/1H0,17X,2HK3,E16.4,/)
      PRINT 510
      PRINT 511,DELTAH,DELHC
      GO TO 613
C
C      SHIFT CONVERTER WITHOUT C-PPT
C
598 XB=Q2*CO+Q2*H2O+CO2+H2
      ARG=(XB**2-4.*(Q2-1.)*(Q2*CO*H2O-CO2*H2))
      X=(XB+DSQRT(ARG))/(2.*(Q2-1.))
      H2O=H2O-X
      CO=CO-X
      IF(CO .LT. 0. .OR. H2O .LT. 0.) GO TO 599
      CO2=CO2+X
      H2=H2+X
      GO TO 600
599 H2O=H2O+X
      CO=CO+X
      X=(XB-DSQRT(ARG))/(2.*(Q2-1.))
      H2O=H2O-X
      CO=CO-X
      H2=H2+X
      CO2=CO2+X
600 CONTINUE
      CAR=0.
      TOTAL=A+CO2+CO+H2+CH4
      YCH4=CH4/TOTAL
      YH2O=H2O/TOTAL
      YCO=CO/TOTAL
      YH2=H2/TOTAL
      YCO2=CO2/TOTAL
      YCAR=CAR/TOTAL
      TMG=A+CO2+CO+H2+CH4
      XCH4=CH4/TMG
      XH2O=H2O/TMG
      XCO=CO/TMG
      XH2=H2/TMG
      XCO2=CO2/TMG
      XCAR=0.
      EK2=CO2*H2/(CO*H2O)
      DELTAH=DHH2O*H2O+DHCO*CO+DHCO2*CO2-DELH1
      DELHC=DELTAH*0.251996D0
      PRINT 610
610  FORMAT(1H1,10X,27HOUTPUT FROM SHIFT CONVERTER)
      PRINT 11
      PRINT 12,P,T4,T4C,T4K,R
      PRINT 9000
      IF(NDC .EQ. 1) GO TO 224
      PRINT 214,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR

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      GO TO 225
224 PRINT 216,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
      1YCO2,XCO2,CAR,YCAR,XCAR
225 PRINT 611
611 FORMAT(1H0,10X,33HRECALCULATED EQUILIBRIUM CONSTANT)
      PRINT 612,EK2
612 FORMAT(1H0,17X,2HK2,1PE16.4,/)
      PRINT 510
      PRINT 511,DELTAH,DELHC
C
C      SENSIBLE HEATS IN HEAT EXCHANGER
C
613 CONTINUE
      SH4CH4=SHCH4(T5,T4)*CH4
      SHCCH4=SH4CH4*0.251996D0
      SH4H2O=SHH2O(T5,T4)*H2O
      SHCH2O=SH4H2O*0.251996D0
      SH4CO2=SHCO2(T5,T4)*CO2
      SHCCO2=SH4CO2*0.251996D0
      SH4CO=SHCO(T5,T4)*CO
      SHCCO=SH4CO*0.251996D0
      SH4H2=SHH2(T5,T4)*H2
      SHCH2=SH4H2*0.251996D0
      PRINT 8,T4,T5,T4C,T5C,T4K,T5K
      PRINT 6,NA1,SH4CH4,SHCCH4
      PRINT 6,NA2,SH4H2O,SHCH2O
      PRINT 6,NA3,SH4H2,SHCH2
      PRINT 6,NA4,SH4CO,SHCCO
      PRINT 6,NA5,SH4CO2,SHCCO2
      GO TO 50
505 PRINT 506,V1(1),V1(2),V1(3)
506 FORMAT(1H0,10X,1PE17.4)
      V(1)=XI
      V(2)=YI
      X=XI
      Y=YI
      GO TO 100
507 PRINT 508,V1(1),V1(2)
508 FORMAT(1H0,10X,1PE17.4)
      GO TO 598
C
C
C      METHANE SYNTHESIS
C
1000 X=XI
      Y=YI
      Z=ZI
      V(1)=X
      V(2)=Y
      V(3)=Z
      Q1=-QPI1(T2)
      Q2=QPI2(T2)
      IF (NDC.EQ. 1) GO TO 27
      Q3=QPI3(T2)
      GO TO 28
27 Q3=QPI4(T2)
28 Q1=DEXP(2.30259*Q1)

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```

Q2=DEXP (2.30259*Q2)
Q3=DEXP (2.30259*Q3)
SH1H2=SHH2 (T2,T1) *A
SHCH2=SH1H2*0.251996D0
SH1CO=SHCO (T2,T1) *(1-A)
SHCCO=SH1CO*0.251996D0
H2I=A
COI=1.-A
PRINT 5,T1,T2,T1C,T2C,T1K,T2K
PRINT 3,NA3,H2I,SH1H2,SHCH2
PRINT 3,NA4,COI,SH1CO,SHCCO
DHCH4=HCH4 (T2)
DHH2O=HH2O (T2)
DHCO=HCO (T2)
DHCO2=HCO2 (T2)
T=T2
TC=T2C
TK=T2K

```

C

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DO 1020 I=1,NIT
M=I
B (1,1)=DFIX (Q1,P,A,X,Y,Z)
B (1,2)=DFIY (Q1,P,A,X,Y,Z)
B (1,3)=DFIZ (Q1,P,A,X,Y,Z)
B (2,1)=DFJX (Q2,A,X,Y,Z)
B (2,2)=DFJY (Q2,A,X,Y,Z)
B (2,3)=DFJZ (Q2,A,X,Y,Z)
B (3,1)=DFKX (Q3,P,A,X,Y,Z)
B (3,2)=DFKY (Q3,P,A,X,Y,Z)
B (3,3)=DFKZ (Q3,P,A,X,Y,Z)
G (1)=-FI (Q1,P,A,X,Y,Z)
G (2)=-FJ (Q2,A,X,Y,Z)
G (3)=-FK (Q3,P,A,X,Y,Z)
CALL INVERT (B,3,1.0D-70,NEROR,DELTA)
IF (NEROR) 75,75,76
76 PRINT 113
GO TO 50
75 DO 80 J=1,3
C (J)=0.0D0
DO 80 K=1,3
80 C (J)=C (J)+B (J,K)*G (K)
DO 81 J=1,3
81 V1 (J)=V (J)+C (J)
IF (V1 (1) .LE. 0.) GO TO 50
IF (V1 (2) .LE. 0.) GO TO 50
IF (V1 (3) .LE. 0.) GO TO 2001
DO 1051 J=1,3
CONV (J)=DABS (V (J)/V1 (J)-1.0D0)
IF (CONV (J)-EPS) 1051,1051,1052
1051 CONTINUE
GO TO 1053
1052 DO 1101 J=1,3
1101 V (J)=V1 (J)
X=V (1)
Y=V (2)
Z=V (3)
1020 CONTINUE

```

C

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1053 PRINT 2000
2000 FORMAT(1H1,13X,6HP(ATM),5X,8HT(DEG F),5X,8HT(DEG C),5X,8HT(DEG K),
15X,19HINITIAL H2/CO RATIO)
PRINT 12,P,T,TC,TK,R
X=V1(1)
Y=V1(2)
Z=V1(3)
CH4=X
H2O=X-Y+Z
CO=1.-A-X-Y-Z
H2=A-3.*X+Y-Z
CO2=Y
CAR=Z
TOTAL=1.-2.*X
YCH4=CH4/TOTAL
YH2O=H2O/TOTAL
YCO=CO/TOTAL
YH2=H2/TOTAL
YCO2=CO2/TOTAL
YCAR=CAR/TOTAL
TMG=1.-2.*X-Z
XCH4=CH4/TMG
XH2O=H2O/TMG
XCO=CO/TMG
XH2=H2/TMG
XCO2=CO2/TMG
XCAR=0.
ZCAR=CAR/COI
FK1=X*(X-Y+Z)*(1.-2.*X-Z)**2/((A-3.*X+Y-Z)**3*(1.-A-X-Y-Z)*P**2)
EK2=Y*(A-3.*X+Y-Z)/((1.-A-X-Y-Z)*(X-Y+Z))
EK3=Y*(1.-2.*X-Z)/((1.-A-X-Y-Z)**2*P)
COI=1.-A
DELTAH=(CO-COI)*DHCO+CH4*DHCH4+H2O*DHH2O+CO2*DHC02
DELHC=DELTAH*0.251996D0
PRINT 9000
IF(NDC.EQ.1)GO TO 226
PRINT 215,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR,ZCAR
PRINT 30
GO TO 227
226 PRINT 217,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR,ZCAR
PRINT 30
227 PRINT 15
PRINT 16,EK1,EK2,EK3
PRINT 17,M
PRINT 510
PRINT 511,DELTAH,DELHC
GO TO 3000

```

C
C
C

METHANE SYNTHESIS WITHOUT C-PPT

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2001 X=V(1)
Y=V(2)
DO 900 I=1,NIT
M=I
B(1,1)=DF11X(Q1,P,A,X,Y)
B(1,2)=DF11Y(Q1,P,A,X,Y)

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      B(2,1)=DF22X(Q2,A,X,Y)
      B(2,2)=DF22Y(Q2,A,X,Y)
      G(1)=-F11(Q1,P,A,X,Y)
      G(2)=-F22(Q2,A,X,Y)
      CALL INVERT(B,2,1.0D-70,NEROR,DELTA)
      IF(NEROR) 901,901,76
901 DO 902 J=1,2
      C(J)=0.0D0
      DO 902 K=1,2
902 C(J)=C(J)+B(J,K)*G(K)
      DO 903 J=1,2
903 V1(J)=V(J)+C(J)
      DO 904 J=1,2
      IF(V1(J).LE.0.) GO TO 50
904 CONTINUE
      DO 905 J=1,2
      CONV(J)=DABS(V(J)/V1(J)-1.0D0)
      IF(CONV(J)-EPS) 905,905,906
905 CONTINUE
      GO TO 400
906 DO 907 J=1,2
907 V(J)=V1(J)
      X=V(1)
      Y=V(2)
900 CONTINUE
400 PRINT 2000
      PRINT 12,P,T,TC,TK,R
      X=V1(1)
      Y=V1(2)
      CH4=X
      H2O=X-Y
      CO=1.-A-X-Y
      H2=A-3.*X+Y
      CO2=Y
      CAR=0.
      TOTAL=1.-2.*X
      YCH4=CH4/TOTAL
      YH2O=H2O/TOTAL
      YCO=CO/TOTAL
      YH2=H2/TOTAL
      YCO2=CO2/TOTAL
      YCAR=CAR/TOTAL
      TMG=1.-2.*X
      XCH4=CH4/TMG
      XH2O=H2O/TMG
      XCO=CO/TMG
      XH2=H2/TMG
      XCO2=CO2/TMG
      XCAR=0.
      EK1=X*(X-Y)*(1.-2.*X)**2/((A-3.*X+Y)**3*(1-A-X-Y)*P**2)
      EK2=Y*(A-3.*X+Y)/((1.-A-X-Y)*(X-Y))
      EK3=0.
      COI = 1.-A
      DELTAH = (CO - COI)*DHCO + CH4*DHCH4 + H2O*DHH2O + CO2*DHCO2
      DELHC=DELTAH*0.251996D0
      PRINT 9000
      IF(NDC.EQ.1) GO TO 228
      PRINT 214,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,

```

```

1YCO2,XCO2,CAR,YCAR,XCAR
GO TO 229
228 PRINT 216,CH4,YCH4,XCH4,H2O,YH2O,XH2O,CO,YCO,XCO,H2,YH2,XH2,CO2,
1YCO2,XCO2,CAR,YCAR,XCAR
229 PRINT 15
PRINT 16,EK1,EK2,EK3
PRINT 17,M
PRINT 510
PRINT 511,DELTAH,DELHC
C
C      SENSIBLE HEATS IN HEAT EXCHANGER
C
3000 SH2H2=SHH2(T3,T2)*H2
SHCH2=SH2H2*0.251996D0
SH2CO=SHCO(T3,T2)*CO
SHCCO=SH2CO*0.251996D0
SH2CH4=SHCH4(T3,T2)*CH4
SHCCH4=SH2CH4*0.251996D0
SH2H2O=SHH2O(T3,T2)*H2O
SHCH2O=SH2H2O*0.251996D0
SH2CO2=SHCO2(T3,T2)*CO2
SHCCO2=SH2CO2*0.251996D0
PRINT 31
31 FORMAT(1H1)
PRINT 7,T2,T3,T2C,T3C,T2K,T3K
PRINT 6,NA1,SH2CH4,SHCCH4
PRINT 6,NA2,SH2H2O,SHCH2O
PRINT 6,NA3,SH2H2,SHCH2
PRINT 6,NA4,SH2CO,SHCCO
PRINT 6,NA5,SH2CO2,SHCCO2
GO TO 50
END

```

```

SUBROUTINE INVERT(A,N,EPS,NEROR,DELTA)
DOUBLE PRECISION A,Y,W,DELTA,C,B,EPS
DIMENSION A(3,3),B(3),C(3),LZ(3)
DELTA=1.0D0
NEROR=0
DO 10 J=1,N                                0050
10 LZ(J)=J                                    0060
DO 20 I=1,N                                    0070
K=I                                            0080
Y=A(I,I)
L=I-1                                         0100
LP=I+1                                         0110
IF(N-LP) 14,11,11                            0120
11 DO 13 J=LP,N                                0130
W=A(I,J)                                      0140
IF(DABS(W)-DABS(Y)) 13,13,12
12 K=J                                         0160
Y=W                                           0170
13 CONTINUE                                   0180
14 DELTA=DELTA*Y
DO 15 J=1,N
C(J)=A(J,K)                                0200
A(J,K)=A(J,I)                                0210
A(J,I)=-C(J)/Y                                0220
A(I,J)=A(I,I)/Y                                0230
15 B(J)=A(I,J)                                0240
A(I,I)=1.0D0/Y
J=LZ(I)                                       0260
LZ(I)=LZ(K)                                   0270
LZ(K)=J                                       0280
DO 19 K=1,N                                   0290
IF(I-K) 16,19,16                             0300
16 DO 18 J=1,N                                0310
IF(I-J) 17,18,17                             0320
17 A(K,J)=A(K,J)-B(J)*C(K)                   0330
18 CONTINUE                                   0340
19 CONTINUE                                   0350
20 CONTINUE                                   0360
IF(DABS(DELTA)-EPS) 80,80,81
80 NEROR=1
GO TO 82
81 DO 200 I=1,N                                0370
IF(I-LZ(I)) 100,200,100                       0380
100 K=I+1                                       0390
IF(I-N) 800,200,200
800 DO 500 J=K,N                                0400
IF(I-LZ(J)) 500,600,500                       0410
600 M=LZ(I)                                    0420
LZ(I)=LZ(J)                                    0430
LZ(J)=M                                        0440
DELTA=-DELTA
DO 700 L=1,N                                0450
C(L)=A(I,L)                                    0460
A(I,L)=A(J,L)                                    0470
700 A(J,L)=C(L)                                0480
500 CONTINUE                                   0490
200 CONTINUE                                   0500
82 RETURN                                       0510

```

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