where

$$I_1^*(\tau_y,\ \theta,\phi) = \int_0^\infty [1-\alpha(\nu)]\ I_{1\nu}(\tau_y,\ \theta,\phi)\mathrm{d}\nu$$

and

$$I_2^*(\tau_y,\ \theta,\phi) = \int_0^\infty [1-\alpha(\nu)]\ I_{2\nu}(\tau_y,\ \theta,\phi)\mathrm{d}\nu \tag{18}$$

The first term in Eq. (17) represents the net flux exchanged through the "windows." When the medium is gray, $\alpha(\nu)$ is unity and I_1^* and I_2^* are zero. The remaining terms are identical to those of the gray case.[4]

For the collimated boundary condition, the radiative flux becomes

$$q_z(\tau_y,\ \tau_z) = I_0^*(\tau_y)/\sigma_0$$

$$+ \int_{-\infty}^{\infty} g(\beta)\ \exp(i\beta\tau_y)\ Q_\beta(\tau_z,\ \sigma_0;\ \tau_0)\mathrm{d}\beta \tag{19}$$

where

$$I_0^*(\tau_y) = \int_0^\infty [1-\alpha(\nu)]I_{0\nu}(\tau_y)\mathrm{d}\nu$$

and

$$Q_\beta(\tau_z,\sigma;\tau_0) = \exp(-\sigma\tau_z)/\sigma + \frac{1}{2}\int_0^{\tau_0} J_\beta(\tau_z',\sigma;\tau_0)$$

$$\mathrm{sign}(\tau_z-\tau_z')\ \mathcal{E}_2(|\tau_z-\tau_z'|,\ \beta)\mathrm{d}\tau_z' \tag{20}$$

For the medium confined between black walls, the flux is

$$q_z(\tau_y,\tau_z) = q_0(\tau_y,\tau_z)\ +\ \int_{-\infty}^{\infty} g_1(\beta)\ \exp(i\beta\tau_y)F_\beta(\tau_z;\ \tau_0)\mathrm{d}\beta$$

$$-\int_{-\infty}^{\infty} g_2(\beta)\ \exp(i\beta\tau_y)F_\beta(\tau_0-\tau_z;\ \tau_0)\mathrm{d}\beta \tag{21}$$

where

$$F_\beta(\tau_z;\ \tau_0) = 2\mathcal{E}_3(\tau_z,\ \beta)\ +\ 2\int_0^{\tau_0} \phi_\beta(\tau_z';\ \tau_0)$$

$$\mathrm{sign}(\tau_z-\tau_z')\mathcal{E}_2(|\tau_z-\tau_z'|,\beta)\mathrm{d}\tau' z \tag{22}$$

with

$$\mathcal{E}_3(\tau,\ \beta) = \tau\int_1^\infty \mathcal{E}_2(\tau x,\ \beta)\mathrm{d}x/x \tag{23}$$

$q_0(\tau_y,\ \tau_z)$ represents the net flux exchanged through the "windows," i.e.,

$$q_0(\tau_y,\tau_z) = \int_0^{2\pi}\int_0^{\pi/2} [I_1^*(\tau_y^+) - I_2^*(\tau_y^-)]\ \cos\theta\sin\theta\ \mathrm{d}\theta\ \mathrm{d}\phi \tag{24}$$

The energy equation has been reduced to a form identical with that of the gray analysis, whereas the expression for the z component of the radiative flux is the same as the gray case, except for a term accounting for the "windows." The influence of the "bands" occurs in functions E, I_1, and I_2, whereas the effect of the "windows" is accounted for by I_1^* and I_2^*.

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Solution Technique for Equilibrium Chemistry of Hydrogen-Oxygen Systems

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Background

REFERENCES 1,2 describe an equilibrium chemistry model developed and used in conjunction with a computer program to predict the properties in a hydrogen-oxygen flame. The main features of the model are described.

For equilibrium reactions are assumed as follows

$$O+O\rightarrow O_2,\quad H+H\rightarrow H_2,\quad H+OH\rightarrow H_2O,\quad O+H\rightarrow OH \tag{1-4}$$

The six species involved in these reactions are considered to be present with nitrogen which is inert. In developing the equations to predict the equilibrium concentration of the species, two quantities are defined, namely

$$X = m_{O_2} + m_0 + \frac{W_O}{W_{H_2O}}\, m_{H_2O} + \frac{W_O}{W_{OH}}\, m_{OH} \tag{5}$$

$$F = m_{H_2} + m_H + \frac{W_{H_2}}{W_{H_2O}}\, m_{H_2O} + \frac{W_H}{W_{OH}}\, m_{OH} \tag{6}$$

where X is the total fraction of oxygen in any form, and F is the total fraction of hydrogen in any form. Since the molecular weight of the various oxygen species is approximately equal to that of nitrogen, it is assumed that the rate of diffusion of nitrogen is equal to that of the oxygen; and, therefore, nitrogen is present at any location in a fixed ratio to the fraction of oxygen compounds. This fraction, OFAC is assumed constant and equal to the fraction of oxygen in the air being used as the oxidizer. Thus,

$$X = (\mathrm{OFAC})\,(X + m_{N_2}) \tag{7}$$

The total mass fraction must be unity which gives

$$X + m_{N_2} + F = 1 \tag{8}$$

Substituting Eq. (7) into Eq. (8) and solving for X gives

$$X = (\mathrm{OFAC})(1\text{-}F) \tag{9}$$

Therefore, if F is known, X can be determined by Eq. (9).

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From thermodynamic considerations the equilibrium constant is defined for the reaction $aA + bB \rightarrow cC$ by

$$K_p = (X_C^c / X_A^a \; X_B^b) P^{c-a-b} \tag{10}$$

where P is in atmospheres. For each of the four reactions in the present model $c-a-b=-1$. It is convenient to express the concentrations in terms of mass fractions. Noting that

$$m_i = (W_i / W) X_i \tag{11}$$

and substituting Eq. (11) into Eq. (10) gives

$$K_p' \equiv K_p P W \frac{W_C^c}{W_A^a \; W_B^b} = \frac{m_C^c}{m_A^a \; m_B^b} \tag{12}$$

Thus the equilibrium equations for the reactions, Eqs. (1-4), can be written

$$K_1' = \frac{m_{H_2}}{m_H^2}, \quad K_2' = \frac{m_{O_2}}{m_O^2}, \quad K_3' = \frac{m_{H_2O}}{m_H \; m_{OH}}, \quad K_4' = \frac{m_{OH}}{m_O \; m_H} \tag{13-16}$$

The condition of equilibrium is expressed by using four equilibrium constants for the four chemical reactions. Once F and X are specified, the six species (m_{H_2}, m_H, m_{O_2}, m_O, m_{OH}, m_{H_2O}) can be determined from Eqs. (5), (6), and (13-16) in which these species are unknowns. The procedure adopted in Ref. 1 was to solve a differential equation for the distribution of F, and then to solve Eqs. (5), (6), and (13-16) by iteration for the concentration of individual species. The iteration technique used converged for only carefully selected initial approximations for species concentration. It is desirable to formulate a solution technique which converges rapidly for any initial distribution of individual species.

The continued use of the model and equations employed in Ref. 1 is recommended in this paper. However, a new solution procedure is proposed. The remaining discussion defines the proposed new solution procedure and gives some results and conclusions regarding its application.

Derivation of Solution

The present procedure is based on the reduction of the number of variables under consideration. Two equations are derived as follows. Equations (13-16) are solved to give the relationships

$$m_H = \sqrt{K_1'} \sqrt{m_{H_2}}, \quad m_O = \frac{1}{\sqrt{K_2'}} \sqrt{m_{O_2}} \tag{17,18}$$

$$m_{H_2O} = \frac{K_3' K_4'}{K_1' \sqrt{K_2'}} \; m_{H_2} \sqrt{m_{O_2}} \tag{19}$$

$$m_{OH} = \frac{K_3'}{\sqrt{K_1' K_2'}} \sqrt{m_{H_2}} \sqrt{m_{O_2}} \tag{20}$$

It is convenient to define the following parameters

$$\bar{A} = \frac{1}{\sqrt{K_1'}}, \quad \bar{B} = \frac{1}{\sqrt{K_2'}}, \quad \bar{C} = \frac{K_3' K_4'}{K_1' \sqrt{K_2'}}, \quad \bar{D} = \frac{K_3'}{\sqrt{K_1' K_2'}} \tag{21-24}$$

Using Eqs. (17-20) to eliminate m_O, m_{H_2O}, m_H, and m_{OH} from Eqs. (5) and (6) gives

$$X = m_{O_2} + \sqrt{m_{O_2}} \left[\bar{B} + \frac{8}{9} \bar{C} m_{H_2} + \frac{16}{17} \bar{D} \sqrt{m_{H_2}} \right] \tag{25}$$

$$F = m_{H_2} \left[1 + \frac{1}{9} \bar{C} m_{O_2} \right] + \sqrt{m_{H_2}} \left[\bar{A} + \frac{1}{17} \bar{D} m_{O_2} \right] \tag{26}$$

where the definitions given by Eqs. (21-24) have been used. These equations have the form of a quadratic equation. The solutions are, respectively

$$\sqrt{m_{O_2}} = X \Bigg/ \left[\frac{\bar{B} + \frac{8}{9} \bar{C} m_{H_2} + \frac{16}{17} \bar{D} \sqrt{m_{H_2}}}{2} + \left[\left(\frac{\bar{B} + \frac{8}{9} \bar{C} m_{H_2} + \frac{16}{17} \bar{D} \sqrt{m_{H_2}}}{2} \right)^2 + X \right]^{1/2} \right] \tag{27}$$

$$\sqrt{m_{H_2}} = F \Bigg/ \left[\frac{\bar{A} + \frac{1}{17} \bar{D} \sqrt{m_{O_2}}}{2} + \left[\left(\frac{\bar{A} + \frac{1}{17} \bar{D} \sqrt{m_{O_2}}}{2} \right)^2 + \left(1 + \frac{1}{9} \bar{C} \sqrt{m_{O_2}} \right) F \right]^{1/2} \right] \tag{28}$$

Table 1 Values of equilibrium parameters for various temperatures

Temp. K	K_1'	K_2'	K_3'	K_4'	$\bar{A}$	$\bar{B}$	$\bar{C}$	$\bar{D}$
200	5.0+100	3.1E+99	2.6+100	2.6+100	4.4E-51	1.7E-50	2.1E+00	2.5E+50
600	2.3E+33	4.3E+36	5.8E+32	9.0E+37	2.0E-17	4.7E-19	5.7E-03	1.0E+19
1000	9.7E+17	1.2E+19	4.5E+17	2.2E+20	1.0E-09	2.7E-10	1.2E-01	2.8E+10
1400	2.1E+11	3.5E+11	1.2E+11	5.4E+12	2.1E-06	1.6E-06	4.7E-01	5.5E+06
1800	3.9E+07	2.1E+07	2.7E+07	3.0E+08	1.5E-04	2.1E-04	9.5E-01	4.6E+04
2200	1.5E+05	4.3E+04	1.2E+05	5.8E+05	2.5E-03	4.8E-03	1.4E+00	2.2E+03
2600	3.4E+03	5.8E+02	2.8E+03	7.6E+03	1.7E-02	4.1E-02	2.0E+00	2.6E+02
3000	2.0E+02	2.4E+01	1.7E+02	3.1E+02	7.0E-02	2.0E-01	2.5E+00	5.5E+01
3400	2.3E+01	2.1E+00	2.1E+01	2.0E+01	2.0E-01	6.7E-01	2.9E+00	1.6E+01
3800	4.1E+00	3.2E-01	3.8E+00	3.9E+00	4.9E-01	1.7E+00	3.3E+00	6.5E+00
4200	1.0E+00	6.8E-02	9.8E-01	8.3E-01	9.8E-01	3.8E+00	3.7E+00	3.0E+00
4600	3.2E-01	1.8E-02	3.1E-01	2.2E-01	1.7E+00	7.2E+00	4.0E+00	1.6E+00
5000	1.2E-01	6.4E-03	1.2E-01	7.7E-02	2.8E+00	1.2E+01	4.2E+00	9.5E-01
5400	5.3E-02	2.5E-03	5.3E-02	3.1E-02	4.3E+00	1.9E+01	4.5E+00	6.0E-01
5800	2.6E-02	1.1E-03	2.6E-02	1.4E-02	6.1E+00	2.9E+01	4.7E+00	4.1E-01

Table 2 Typical equilibrium distributions of species for oxygen-hydrogen equilibrium model

TEMP.K	F	X	m_{H_2}	m_{O_2}	m_H	m_O	m_{OH}	m_{H_2O}	RES_1 [a]	RES_2 [b]
200	0	.23200	.00000	.23200	0	0	0	.00000	-.00000	0
200	.4	.13920	.38259	.00000	0	0	0	.15665	-.00005	0
200	1.0	.00000	1.00000	.00000	0	0	0	.00001	-.00000	0
700	0	.23200	.00000	.23200	0	0	0	.00000	-.00000	0
700	.4	.13920	.38239	.00000	0	0	0	.15665	-.00005	0
700	1.0	.00000	1.00000	.00000	0	0	0	.00001	-.00000	0
1700	0	.23200	.00000	.23196	.00000	.00004	0	.00000	-.00000	0
1700	.4	.13920	.38255	.00000	.00004	.00000	0	.15665	-.00005	0
1700	1.0	.00000	.99993	.00000	.00007	.00000	0	.00000	-.00000	0
2700	0	.23200	.00000	.20310	.00000	.02890	.00000	.00000	-.00000	0
2700	.4	.13920	.36746	.00001	.01534	.00016	.00317	.15311	-.00004	0
2700	1.0	.00000	.97501	.00000	.02499	.00000	.00000	.00000	-.00000	0
3700	0	.23200	.00000	.02210	.00000	.20990	.00000	.00000	-.00000	0
3700	.4	.13920	.20737	.00102	.18380	.04514	.04766	.05420	-.00000	0
3700	1.0	.00000	.66970	.00000	.33030	.00000	.00000	.00000	-.00000	0
4700	0	.23200	.00000	.00076	.00000	.23124	.00000	.00000	0	0
4700	.4	.13920	.03336	.00023	.36589	.12760	.01140	.00072	0	0
4700	1.0	.00000	.17119	.00000	.82881	.00000	.00000	.00000	0	0

[a] Residual in F Eq. (28).
[b] Residual in X Eq. (27).

Equations (27) and (28) contain the unknowns m_{O_2} and m_{H_2}. Before detailing the solution procedure, several properties of these equations will be discussed. Table 1 gives the values of $K_1', K_2', K_3', K_4', \bar{A}, \bar{B}, \bar{C}$, and $\bar{D}$ for the temperatures from 100 to 6000°K at a constant PW product of 2.5 (corresponding approximately to 1/10 atm). Note that while the individual constants vary from less than 1 to 10^{100}, the groups appearing in Eqs. (27) and (28) vary much less, and can be easily processed on a digital computer. Second, it is to be observed that the equations have been derived so that a "natural" relationship has been established between m_{O_2} and X, and m_{H_2} and F, i.e., as $X \rightarrow 0$, $m_{O_2} \rightarrow 0$, and as $F \rightarrow 0$, $m_{H_2O} \rightarrow 0$. It should also be observed that m_{O_2} and m_{H_2} can never be less than zero or greater than 1. Finally, neither equation becomes indefinite as m_{H_2} or m_{O_2} approach zero. Thus, the equations are well-behaved and can be readily solved for wide variations in temperature and pressure.

The solution procedure is described next. A value of m_{H_2} is guessed in the following way. If the value at the equivalent upstream station is known, then that value is used; otherwise, a value of zero will always lead to a converged solution. This assumed value of m_{H_2} is substituted into Eq. (27) which yields m_{O_2}. Then the computed value of m_{O_2} is substituted into Eq. (28) which allows calculation of a new value of m_{H_2}. The assumed and calculated values of m_{H_2} are compared. If their values differ by more than a specified convergence criteria, the calculated value of m_{H_2} is taken as the assumed value, and the process previously described is repeated until convergence is obtained. The behavior of this solution technqiue is shown in Fig. 1.

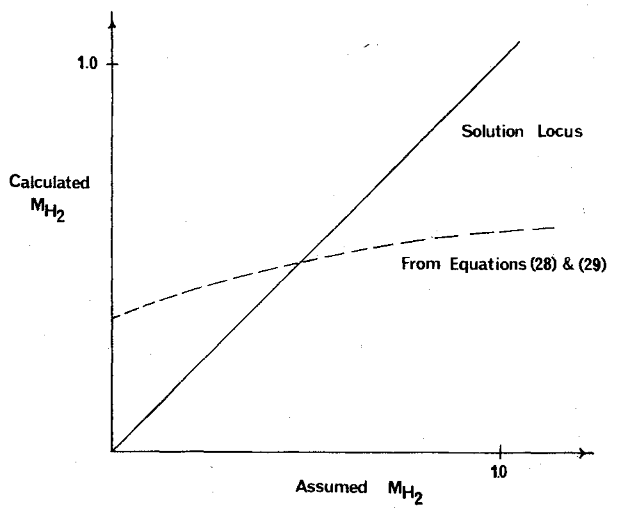

Fig. 1 Graphical plot of trial-and-error solution.

Figure 1 shows with the broken line a plot of m_{H_2} calculated vs m_{H_2} assumed. The correct value is achieved when the two values are equal. The locus of points for this situation is a straight line with a slope of unity. If m_{H_2} assumed is less than the correct value, the figure shows the calculated value will always be larger. Thus, when this calculated value of m_{H_2} is taken as the assumed value, the resulting newly calculated value will be closer to the correct one. The same argument can be made to shown that if the initial assumed value of m_{H_2} is too large, the iteration process will again cause convergence to the correct value.

Typical Results

The solution procedure previously described was programed on a digital computer and used to determine equilibrium concentrations for variation in F and X from zero to one for temperatures from 200 to 4700°K. The product PW was taken at 2.5 (approximately 1/10 atm pressure). Table 2 shows these calculated results. The residuals in F and X are shown in the last two columns. Their values indicate that great precision can be obtained with this method. The convergence criteria for these calculations was

$$|m_{H_2 \text{ calculated}} - m_{H_2 \text{ assumed}}| < .001 \; m_{H_2 \text{ calculated}}$$

Greater precision could easily be achieved by a stricter convergence criteria; however, the present one is sufficient for most practical calculations. It is concluded that the method offers a reliable, simple and extremely fast technqiue for solving the equilibrium equations arising from the chemical model considered in this work.

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