Installation of a heater unit with feedback on-off switches made it possible to control the temperatures in the heat-pipe ovens separately to a fraction of a degree Celsius. Holding the temperature in one oven constant and raising or lowering the temperature in the other gave measurable fringe shifts which could then be related to the recorded pressure and density change. Typical fringe-shift studies were carried out in the regime between 440° and 480°C for sodium number density changes of the order of 5×10^{21} m^{-3} corresponding to temperature changes of approximately 10°C.

The fringes were focused on a plate with a pinhole in front of a high-gain photomultiplier tube (RCA C31000F) which was cooled down to −30°C to lower the dark current and increase the signal-to-noise ratio. The output of the PMT was then recorded with an X-Y plotter, monitoring the intensity changes in a typical periodic fashion as the fringes marched across the pinhole.

Results and Discussion

Investigation of the computed absorption and refractivity profiles showed some noteworthy features which were confirmed by the experimental results. The shape of the refractivity curves are highly insensitive to the Voigt parameter a and temperature T, allowing us to write Eq. (1) in the following form

$$n_r(\lambda,T)-1=K_r(\lambda)\rho(T) \tag{1a}$$

where subscript r means near the resonance regime.

Figure 2 shows the graph of the calculated values for $K_r(\lambda)$ which are valid to a high degree of accuracy for a broad temperature range and for λ smaller than 5890 Å. The experimental results in the investigated wavelength range are in good accordance with the theory. As mentioned above, the fringe shifts were measured and then related to the known change of density and effective length of sodium column according to

$$S\cdot\lambda_0=K_r(\lambda)(\rho_1\ell_1-\rho_2\ell_2) \tag{8}$$

where S denotes the fringe shift, λ_0 the wavelength of the dye laser, and $\rho_{1,2}$ and $\ell_{1,2}$ the mass density and length of the sodium column before and after the temperature change, respectively.

The maximum refractivity enhancement was limited by the resonance absorption of the approximately 0.5-m-long sodium column. At about 7 Å away from resonance and $T=465$°C the absorption coefficient of $\mu\approx7$ m^{-1} makes it virtually impossible to measure fringe shifts even closer to resonance. Nevertheless, the relatively gentle slope of the dispersion curve enables us to achieve enhancements in the wings which are of the order of 200 to 300 compared to the zero-frequency Dale-Gladstone constant $K_{0_{Na}}=4.051\times10^{-3}$ m^3/kg of sodium. If compared with the nonresonant value of air $K_{0_{air}}\approx2.3\times10^{-4}$ m^3/kg the resonance refractivity enhancement reaches a value of 5.0×10^3.

Furthermore, the relative magnitude of the absorption line shape in the wings is proportional to the Lorentzian line width, whereas (as mentioned above) the refractivity line shape is quite insensitive to a [see Eq. (6b)] and any change of γ_L. Therefore, any decrease of γ_L would make it possible to go closer to the resonance line and to utilize a larger index of refraction.

In this respect the resonant refractivity technique for seeded flow-field visualization looks quite promising. The collision linewidth for sodium in the presence of an inert buffer gas like argon, which behaves quite similarly to nitrogen and air, is over 25 times smaller than in the present case with sodium-sodium collisions. Assuming the same maximum tolerable absorption and the same length of sodium column it should be possible to make use of an enhanced specific refractivity significantly larger than in the case of sodium self-broadening.

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Chemical Equilibrium Compositions of Hydrogen-Oxygen-Nitrogen Systems

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Chemical Equilibrium Formulation

THE prediction of hydrogen-air diffusion flames (see, e.g., Ref. 1) has focused interest in solution techniques for the calculation of chemical equilibrium compositions. The technique presented here is based on the method of equilibrium constants, which is stated below.

Because of low pressures and high temperatures in flames, the theory of thermally perfect gases can be applied. Thus we consider the perfect gas mixture of nine species (H_2, O_2, H, O, OH, H_2O, N_2, N, NO; $i=1,\ldots,N$). These species consist of three elements (H, O, N; $j=1,\ldots,E$). The element fractions $\tilde{Y}_j$ can be written as

$$\text{H:}\quad \tilde{Y}_1=\tilde{W}_1(2Z_1+Z_3+Z_5+2Z_6) \tag{1}$$

$$\text{O:}\quad \tilde{Y}_2=\tilde{W}_2(2Z_2+Z_4+Z_5+Z_6+Z_9) \tag{2}$$

$$\text{N:}\quad \tilde{Y}_3=\tilde{W}_3(2Z_7+Z_8+Z_9) \tag{3}$$

where the abbreviation $Z_i=Y_i/W_i$ has been used. Y_i and W_i are the mass fraction and the molecular weight of the ith species, respectively, and $\tilde{W}_j$ is the atomic weight of the jth element.

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Table 1 Equilibrium reactions and parameters for equilibrium constants[2]

r	Reaction	DC_r	EC_r	FC_r
1	$2H \rightarrow H_2$	3.22455E−04	−2.20776E−02	5.23901E+04
2	$2O \rightarrow O_2$	1.68444E−06	3.93683E−01	6.01219E+04
3	$H_2+O_2 \rightarrow 2OH$	7.94191E+02	−3.86732E−01	−9.59870E+03
4	$2H_2+O_2 \rightarrow 2H_2O$	3.19678E−04	3.93851E−02	5.84710E+04
5	$2NO \rightarrow N_2+O_2$	3.07175E−02	5.39651E−02	2.18089E+04
6	$N+NO \rightarrow N_2+O$	5.07105E−01	−9.66399E−02	3.77342E+04

The condition of chemical equilibrium is expressed by six ($L=N-E$) reactions which are listed in Table 1. The equilibrium constant in terms of concentrations for the rth reaction is given by

$$K_{c,r}=\rho^{\Delta\nu}\prod_{i=1}^{N}(Z_i)^{\nu_{r,i}}[\text{kmol/m}^3]^{\Delta\nu}, \quad (r=1,\ldots,L) \tag{4}$$

where

$$\Delta\nu=\sum_{i=1}^{N}\nu_{r,i}$$

and ρ is the density of the gas mixture. The coefficient $\nu_{r,i}$ concerns the ith species in the rth reaction. Table 1 includes the parameters DC_r, EC_r, and FC_r for the equilibrium constants

$$K_{c,r}(t)=DC_r T^{EC_r}\exp(FC_r/T), \quad (r=1,\ldots,L) \tag{5}$$

which have been approximated by Cremer[2] using the JANAF data.

In order to calculate the equilibrium compositions we have to make use of the equation of state

$$\rho=PW/\Re T \tag{6}$$

$$W^{-1}=\sum_{i=1}^{N}Z_i \tag{7}$$

where $\Re$ and W are the universal gas constant and the molecular weight of the gas mixture, respectively. Thus, for specified values of the pressure P, the temperature T, and the element fractions $\tilde{Y}_j$, the equilibrium calculation is reduced to the solution of Eqs. (1-3, 4, and 6).

In conjunction with the prediction of diffusion flames using finite-difference methods the equilibrum compositions have to be determined at all grid points for known values of T, P, and $\tilde{Y}_j$. The efficiency of the prediction procedure depends on the equilibrium calculation. Thus, extremely fast methods are desirable for calculating the equilibrium concentrations. On the other hand, a wide variation of temperature and element fraction occurs in diffusion flames. Therefore, the solution technique should rapidly converge for all specified values T and $\tilde{Y}_j$. Although general procedures[3] for the calculation of chemical equilibrium are available, it is more advisable to pay attention to the special aspects of the system considered.

In this study we develop an efficient technique for the equilibrium calculation of hydrogen-oxygen-nitrogen systems. The procedure has been successfully applied to the calculation of turbulent jet diffusion flames.[4] Based upon the numerical results presented, some useful simplifications are obtained.

Numerical Method

The basis of the numerical method is that the equilibrium calculation will be reduced to the solution of only one nonlinear algebraic equation. By rewriting the equilibrium Eq. (4) such that Z_1, Z_2, and Z_7 are taken to be unknown, we get from Eqs. (1-3) with $\tilde{Z}_j=\tilde{Y}_j/\tilde{W}_j$

$$2Z_1+K_1\sqrt{Z_1}+K_3\sqrt{Z_2Z_1}+2K_4\sqrt{Z_2}Z_1-\tilde{Z}_1=0 \tag{8}$$

$$2Z_2+K_2\sqrt{Z_2}+K_3\sqrt{Z_2Z_1}+K_4\sqrt{Z_2}Z_1+K_5\sqrt{Z_7Z_2}-\tilde{Z}_2=0 \tag{9}$$

$$2Z_7+K_6\sqrt{Z_7}+K_5\sqrt{Z_7Z_2}-\tilde{Z}_3=0 \tag{10}$$

where the abbreviations are:

$$K_1=1/\sqrt{\rho K_{c,1}}, \quad K_2=1/\sqrt{\rho K_{c,2}}, \quad K_3=\sqrt{\rho K_{c,3}}$$

$$K_4=\sqrt{\rho K_{c,4}}, \quad K_5=1/\sqrt{K_{c,5}}, \quad K_6=K_2\sqrt{K_{c,5}}/K_{c,6}$$

Equation (10), which is quadratic in Z_7, has the unique solution

$$Z_7=-\tfrac{1}{4}(K_6+K_5\sqrt{Z_2})+\tfrac{1}{4}\sqrt{(K_6+K_5\sqrt{Z_2})^2+8\tilde{Z}_3} \tag{11}$$

since negative concentrations do not occur from the chemical viewpoint.

It is worthwhile to consider combustion processes under the aspect of oxygen-fuel ratio. Dropping the species, H, O, N, OH, and NO, Eqs. (1-3) yield for rich mixtures which have a deficiency of oxygen ($Z_2=0$), where $0.5\,\tilde{Z}_1>\tilde{Z}_2$:

$$Z_6=\tilde{Z}_2 \tag{12}$$

$$Z_1=0.5\tilde{Z}_1-\tilde{Z}_2 \tag{13}$$

and for lean mixtures which have an excess of oxygen ($Z_1=0$), $0.5\,\tilde{Z}_1<\tilde{Z}_2$:

$$Z_6=0.5\tilde{Z}_1 \tag{14}$$

$$Z_2=0.5\tilde{Z}_1-0.25\tilde{Z}_1 \tag{15}$$

where $Z_7=0.5\,\tilde{Z}_3$. For the same reason the solution of Eqs. (8) and (9) will be performed by considering two cases. For rich mixtures Z_1 is chosen to be unknown. Using the solution of Eq. (8), $\sqrt{Z_2}=A_1/B_1$, together with Eq. (11) we can write Eq. (9) after some rearrangement as

$$f_1(Z_1)=2A_1^2+(C_1+D_1)A_1B_1-\tilde{Z}_2B_1^2=0 \tag{16}$$

Here, the abbreviations are:

$$A_1=\tilde{Z}_1-2Z_1-K_1\sqrt{Z_1}, \quad B_1=K_3\sqrt{Z_1}+2K_4Z_1,$$

$$C_1=K_2+0.25K_5(H_1-G_1), \quad D_1=K_3\sqrt{Z_1}+K_4Z_1,$$

$$G_1=K_6+K_5A_1/B_1, \quad H_1=\sqrt{G_1^2+8\tilde{Z}_3}$$

Similarly, for lean mixtures with the unknown Z_2, Eq. (8) yields $\sqrt{Z_1}=D_2/4B_2$. By inserting this result and Eq. (11) into Eq. (9) we get

$$f_2(Z_2)=16B_2^2C_2+4K_3\sqrt{Z_2}B_2D_2+K_4\sqrt{Z_2}D_2^2$$

$$+4K_5\sqrt{Z_2}B_2^2(H_2-G_2)=0 \tag{17}$$

Table 2 Equilibrium compositions for hydrogen-air combustion

$\tilde{Y}_H = 0.4$, $\tilde{Y}_O = 0.1392$, $\tilde{Y}_N = 0.4608$

Temp. K	Y_{H_2}	Y_{O_2}	Y_H	Y_O	Y_{OH}	Y_{H_2O}	Y_{N_2}	Y_N	Y_{NO}	PW	$\bar{n}^a$	m
200	0.382461	0.0	0.0	0.0	0.0	0.156739	0.460800	0.0	0.0	0.4654	1	1
700	0.382461	0.0	0.0	0.0	0.0	0.156739	0.460800	0.0	0.0	0.4654	1	1
1700	0.382368	0.0	0.000093	0.0	0.000004	0.156735	0.460800	0.0	0.0	0.4653	2	1
2700	0.347715	0.000034	0.035326	0.000884	0.007478	0.147592	0.460646	0.000004	0.000320	0.4298	9	3
3700	0.069466	0.000645	0.328696	0.111281	0.022289	0.004624	0.456997	0.001876	0.004128	0.2593	14	4
4700	0.003553	0.000024	0.396373	0.137256	0.001235	0.000007	0.406139	0.054003	0.001409	0.2369	15	3
				$\tilde{Y}_H = 0.02$, $\tilde{Y}_O = 0.22736$, $\tilde{Y}_N = 0.75264$								
200	0.0	0.068630	0.0	0.0	0.0	0.178730	0.752640	0.0	0.0	2.569	1	1
700	0.0	0.068630	0.0	0.0	0.0	0.178730	0.752640	0.0	0.0	2.569	2	1
1700	0.000005	0.067496	0.0	0.000020	0.000501	0.178416	0.751834	0.0	0.001726	2.568	3	1
2700	0.002882	0.062862	0.001360	0.016182	0.029468	0.125217	0.744416	0.000002	0.017612	2.404	9	3
3700	0.001334	0.012277	0.017756	0.189292	0.013478	0.000994	0.741002	0.000931	0.022936	1.706	12	3
4700	0.000061	0.000437	0.019898	0.222039	0.000686	0.000001	0.721416	0.027515	0.007946	1.621	17	3

[a] $\bar{n}_\ell = \sum_{\ell=1}^{m} n_\ell$; n_ℓ is the number of iterations n for solution of either Eq. (16) or Eq. (17) at the ℓth iteration for the density ρ.

where the following abbreviations have been used:

$$A_2 = K_1 + K_3\sqrt{Z_2},\quad B_2 = 1 + K_4\sqrt{Z_2},\quad C_2 = 2Z_2 + K\sqrt{Z_2} - \tilde{Z}_2$$

$$D_2 = -A_2 + \sqrt{A_2^2 + 8B_2\tilde{Z}_1},\quad G_2 = K_6 + K_5\sqrt{Z_2},$$

$$H_2 = \sqrt{G_2^2 + 8\tilde{Z}_3}$$

For the solution of either of the two nonlinear equations, Eqs. (16) or (17), we apply Newton's method. To start the iteration procedure we use either Eq. (13), $Z_1^0 = 0.5\ \tilde{Z}_1 - \tilde{Z}_2$, or Eq. (15), $Z_2^0 = 0.5\ \tilde{Z}_2 - 0.25\ \tilde{Z}_1$. For stoichiometric mixtures ($0.5\ \tilde{Z}_1 = \tilde{Z}_2$) we choose $Z_2^0 = 10^{-5}$ and solve Eq. (17). The iteration procedure is repeated until the convergence criterion $|Z^{n+1} - Z^n| < \epsilon_1 Z^n$ is satisfied.

Here, it should be noted that the derivation of the described method has been made under the assumption of constant molecular weight W. For specified values of P, $\tilde{Y}_j$, and T the molecular weight W and, hence, the density ρ are determined by the equilibrium concentrations through Eqs. (7) and (6), respectively. Thus, a second iteration cycle is necessary in most cases. We start the iteration where ρ^0 is calculated from Eq. (6) using Eq. (7) with the help of Eqs. (12) and (13) and (14) and (15), respectively. By applying ρ^0, new values for the species concentrations are obtained by the solution of either Eq. (16) or Eq. (17). Then, an improved guess ρ^1 is determined by Eqs. (6) and (7) and the iteration is continued. The convergence criterion used is $|\rho^{m+1} - \rho^m| < \epsilon_2 \rho^m$. The numerical calculations have shown that the criteria $\epsilon_1 = 10^{-6}$ and $\epsilon_2 = 10^{-3}$ provide great precision for all cases considered.

Results and Conclusions

By using the method described, equilibrium calculations have been performed for a wide variation in temperature, pressure, and element fraction. In order to present the features of the procedure, the equilibrium calculation of hydrogen-air combustion is discussed for a given pressure ($P = 1/10$ atm).

The calculations have been carried out for variations in the element fraction $\tilde{Y}_H$ from zero to one. Some of the results are shown in Table 2. The equilibrium concentrations at various temperatures are presented for a rich mixture ($Y_H = 0.4$) and a lean mixture ($Y_H = 0.02$). For one iteration ($n = 1$) solving either Eq. (16) or Eq. (17) the computer time required is about $5 \cdot 10^{-4}$ s on a CDC 6500. The total number of iterations $\bar{n}$ increases with the temperature as element fractions are employed in order to start the iteration procedure. The maximum number of iterations concerning the density ρ is $m = 4$.

The virtue of the solution procedure proposed is that the calculation of chemical equilibrium compositions is reduced to the solution of one algebraic equation. By applying Newton's method only a few iterations are necessary. As initial approximations for the equilibrium compositions and, hence, the molecular weight and the density are provided, the method is "self-starting." Other, "non-self-starting" methods (see e.g., Ref. 5) require an initial guess. An additional advantage of the method presented is that for given pressure, temperature, and element fractions the molecular weight of the gas mixture does not have to be assumed but results from the species concentrations by Eq. (7).

Some useful conclusions for the equilibrium calculation can be derived from the results. At temperatures less than 1700 K the equilibrium compositions can be determined by solely employing the element fractions, either Eqs. (12) and (13) or Eqs. (14) and (15). Hence, iterations are not necessary. The species N and NO must only be considered at temperatures higher than about 2400 K. For practical calculations it is sufficient to use less strict convergence criteria $\epsilon_1 = 10^{-4}$, $\epsilon_2 = 10^{-2}$. Then the maximum number of iterations reduces to $\bar{n} = 9$ and $m = 2$, respectively. Thus, the method presented offers an efficient technique for calculating the equilibrium compositions of hydrogen-nitrogen systems.

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