```
  222   IF(AA)11,11,12
   12   IF(BB)21,21,22
   22   IF(CC)31,31,32
   32   IF(DD)41,41,42
   11   DELA=DELA/2.
        AA=A+DELA
        GO TO 222
   21   DELB=DELB/2.
        BB=B+DELB
        GO TO 12
   31   DELC=DELC/2.
        CC=C+DELC
        GO TO 22
   41   DELD=DELD/2.
        DD=D+DELD
        GO TO 32
   42   A=AA
        B=BB
        C=CC
        D=DD
        GO TO 15
C         COMPUTE MOLAL ENTHALPIES
            OF THE PRODUCTS OF COM-
            BUSTION
  404   TR=298.15
        IF(T-2000.)215,215,225
  225   TR=2000.
  215   TD1= T-TR
        TD2=(T**2-TR**2)/2.
        TD3=(T**3-TR**3)/3.
        TD4=(T**4-TR**4)/4.
        TD5=(T**5-TR**5)/5.
        TD6=(T**6-TR**6)/6.
        TD7=(T**7-TR**7).7.
        IF(T-2000.)155,155,165
  155   DO 1200 I=1,18
        HT(I)=CF(I,1)+CF(I,2)*TD1+CF(I,3)-
            *TD2+CF(I,4)*TD3+CF(I,5)*TD4
        HT(I)=HT(I)+CF(I,6)*TD5+CF(I,7)*T-
            D6+CF(I,8)*TD7
 1200   CONTINUE
        GO TO 145
  165   DO 1300 I=1,18
        HT(I)=CF(I,9)+CF(I,10)*TD1+CF(I-
            ,11)*TD2+CF(I,12)*TD3+CF(I,13)-
            *TD4
        HT(I)=HT(I)+CF(I,14)*TD5+CF(I,15-
            )*TD6+CF(I,16)*TD7
 1300   CONTINUE
  145   HPRO=A*HT(1)+B*HT(2)+C*H-
            T(3)+D1*HT(4)+E*HT(5)+F*HT-
            (6)+G*HT(7)
        HPRO=H-
            PRO+H*HT(8)+P*HT(9)+Q*HT
            (10)+R*HT(11)+S*HT(12)+U*HT(13
        HPRO=H-
            PRO+V*HT(14)+W*HT(15)+X*
            HT(16)+Y*HT(17)+Z*HT(18)
        XD2=XD1
        IF(CVI-CVF)331,325,331
  331   SUME=ATS/SATS
        XSUM=SMF
C         COMPUTE TOTAL ENTHALPY
            OF THE PRODUCTS OF COM-
            BUSTION
        HPRO=SUME*HPRO
        XDX=HPRO-HREA
        GO TO 345
  325   SUME=SMF
C         COMPUTE TOTAL INTERNAL
            ENERGY OF THE PRODUCTS
            OF COMBUSTION
        RT=1.987*T
        UPRO=HPRO-SUME*RT
        XDX=UPRO-UREA
  345   XD1=ABSF(XDX)
        RETURN
        END
```

DISCUSSION

J. H. Lienesch[2]

This paper presents a computer program whose purpose and output appear similar to those of several other programs which have been previously published. The authors acknowledge that the computing methods they used are well-documented but they state that "complete computer programmes for such calculations are seldom published so that the reader has to develop his own programme." I would like to call the authors' attention to three publications which describe, in detail, such computer programs. The first, and probably the grandfather of all such efforts, is the U. S. government-funded NASA-Lewis CEC code. This program was first published in its entirety in 1967. The most recent publication, by Gordon and McBride, appeared in 1971 [9].[3]

The NASA code is extremely versatile, and can be used to calculate chemical equilibrium at assigned thermodynamic states, theoretical rocket performance, incident and reflected shock properties, and Chapman-Jouguet detonation properties. The program considers condensed as well as gaseous species. The solution technique minimizes the Gibbs free energy of all possible molecules that can be formed from given reactants. Included are thermodynamic data for hundreds of species making it possible to calculate the molecular composition and gas properties for products of combustion of practically any fuel and oxidant. The two particular cases considered by the authors in their paper today (constant-pressure, constant-volume combustion) are special cases of assigned thermodynamic states in the NASA-Lewis program (enthalpy-pressure and internal energy-volume).

The authors' results and the Purdue data shown in Table 1 in the paper were checked against the NASA-Lewis program for the case

[2] Engine Research Department, GM Research Laboratories, General Motors Corp., General Motors Technical Center, Warren, Mich.

[3] Numbers in brackets designate Additional References at end of discussion.

of constant pressure combustion of both CH_4 and C_8H_{18}. Agreement was within 1 K for all values of initial pressure and stoichiometry considered. Hence the accuracy of their program appears good, as it should, since it uses the same thermochemical data as does the NASA-Lewis program.

One problem with the NASA-Lewis procedure is that its great generality can be costly in computer time. For cases in which gas properties are required to be calculated many thousands of times, as in an engine simulation program for example, alternative techniques may be preferable.

The second analysis suggested for the authors' review was published in January 1975 by the University of Wisconsin [10]. This analysis is less general than the NASA code in that it, similar to the authors' program, is limited to combustion of a C-H-O-N fuel with air. Also similar to the authors' program, the Wisconsin program utilizes curve-fits of equilibrium constant data from the JANAF thermochemical tables. Because it is designed primarily for internal-combustion engine analysis, the Wisconsin program is limited to a maximum temperature of 4000 K and computes an equilibrium with 12 chemical species. However, the Wisconsin analysis computes not only the equilibrium mole fractions but also the gas constant, internal energy and enthalpy, and all partial derivatives of these with respect to temperature, pressure, and equivalence ratio.

The final program called to the authors' attention is an approximate technique developed recently at MIT [11]. It is based upon a fitting of data obtained from the NASA-Lewis program to a functional form obtained from a consideration of carbon-air combustion. MIT's interest was in a general division of the products into monatomic, diatomic, and triatomic molecules because this division completely determines mean molecular weight and is the principal factor in determining enthalpy. This code is useful for determining properties of combustion products but, of course, cannot be used to determine equilibrium species concentrations.

Selection of equilibrium programs should be based on the needs of the analyst. The authors' program includes species whose equilibrium concentrations will be essentially zero for all but the most unusual conditions. These species are O_3, NO_2, HNO_3, HCN, CH_4, and NH_3. It is interesting to note that the authors neglect argon in their equilibrium. Although nonreactive, argon composes about one percent of dry air and will certainly have a higher equilibrium mole fraction in hydrocarbon-air combustion products than the six species mentioned in the foregoing.

The 6000 K temperature limit is also questionable. A gas temperature of this magnitude is not reached in any practical air-burning device.

In summary, the authors' technical contribution does not appear to offer any obvious advantage over other published equilibrium programs.

Additional References

9 Gordon, S., and McBride, B. J., "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations," NASA Publication SP-273, 1971.

10 Olikara, C., and Borman, G. L., "A Computer Program for Calculating Properties of Equilibrium Combustion Products With Some Applications to I.C. Engines," SAE Paper No. 750468, Feb. 1975.

11 Martin, M. K., "Photographic Study of Stratified Combustion Using a Rapid Compression Machine," MS thesis, Department of Mechanical Engineering, MIT, Jan. 1975.

Authors' Closure

The authors thank Dr. Lienesch for drawing their attention to the publications of Gordon, et al., Olikara, et al., and Martin. The authors regret that they were not aware of these publications. It may be noted that the last two of the foregoing publications appeared at about the same time (February 1975) when the present paper was communicated to the Diesel and Gas Power Division of ASME.

The authors feel that since their program is not as generalized as the NASA-Lewis program it is perhaps more economical in computer time. Compared to the Olikara, et al., program, the present program has a higher maximum temperature limit and it considers a larger number of product species. It computes the internal energy and enthalpy of the products, which can also be printed if desired. The gas constant and various partial derivatives can be computed by a few simple additions in the program.

The authors, however, agree with Dr. Lienesch that their program is essentially similar to the Olikara, et al., program.