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A THEORETICAL STUDY OF FLAME PROPERTIES AS A FUNCTION OF THE CHARACTERISTICS OF FLAME GASES

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Part I

General equations are presented for a method of calculating the net rate of production and the fractional mass-flow rate for each species without introducing the kinetic steady-state approximation. Mathematical problems of smoothness and stability which must be surmounted in any method which avoids the kinetic steady-state approximation are discussed in § 3. To facilitate applications, § 4 and Appendix C give the equations in a form and notation which singles out convenient calculational units and has been found to be adapted to the study of one-dimensional time-independent real flames. The checks used to test the validity of the results are summarized. Section 6 shows that the method's major disadvantage lies in the use of a more complex system of equations, while its major advantages are: (*a*) it reduces the number of differential equations and thereby simplifies the eigenvalue character of the problem; (*b*) in contrast to the conventional steady-state approximation, it is consistent in a sense which § 2 shows is required in problems of practical interest. Thus it avoids the most serious inadequacy of the conventional kinetic steady-state approximation: the failure to include the fractional mass flow for an intermediate species.

Part II

Various methods were applied to numerous numerical integrations of the hydrodynamic equations for a one-dimensional time-independent flame with idealized kinetics and transport properties. The method developed in part I proved to be very convenient for sets of parameters which do not lead to too great deviations from the kinetic steady state.

Part II is devoted to an analysis of these results to study: (*a*) how the kinetic model and the kinetic and transport parameters affect the properties of free-radical flames; (*b*) various assumptions and approximations which have been used in flame theories. The parameter variations were chosen to test the significance of the assumption of unit Lewis numbers and the use of the kinetic steady-state approximation.

To clarify the relation between these results and the behaviour of other systems, the significant aspects of the model are summarized and the equations are cast in suitable dimensionless forms which are used in interpreting numerical results. The total mass-flow rate appears in a dimensionless eigenvalue which is shown to be comparatively insensitive to the kinetic and transport parameters for intermediate species and to vary most from flame to flame, with changes in the thermal conductivity and the specific rates of reactions responsible for the major volume rate of heat release.

The analysis then considers the following points: (1) Relations are developed between the functional form of the curves for the mole fractions and fractional mass-flow rates of intermediate species and: (*a*) the processes of kinetics and diffusion; (*b*) the way typical intermediates enter the kinetic schema. (2) The shifts in the flame profiles with variations in parameters to increase the deviations from the kinetic steady state are interpreted. (3) Interpretations are given for shifts which parameter variations induce in curves for the relative importance of convection, diffusion, and thermal conduction in maintaining energy conservation. (4) For this flame, it appears that the approximation of constant specific enthalpy could be used to calculate the mole fraction of a major component with an error of at most a few per cent even when the Lewis numbers are not

unity. (5) The data show that the ignition temperature approximation would introduce two different serious errors. (6) The suggestion that radical recombination might serve as an important means of energy transport does not apply to this flame. (7) The explicit relation is given between the temperature gradient at the flame holder and the discontinuity in mole fractions in the Hirschfelder–Curtiss model. The discontinuity is not of a physically significant size.

PART I

1. Statement of the differential equations and the hot boundary conditions

This paper uses the Hirschfelder–Curtiss (1954) formulation of the flame equations, since their formulation has been shown to be adapted to the study of real systems such as hydrogen-bromine (Campbell 1957) and ozone-oxygen (Hirschfelder, Curtiss & Campbell 1953; Campbell 1965 *a*). The hydrodynamic equations for a one-dimensional steady-state flame can be written in the form

$$\mathrm{d}u_j(Z)/\mathrm{d}Z = F_j(\mathbf{u}), \tag{1·1}$$

where $\mathbf{u}$ is a vector whose components are T, the mole fractions and fractional mass-flow rates, and F_j are functions with continuous partial derivatives of all orders. Klein (1957) gives a particularly clear summary of several of the approximations required to derive the three following types of the $F_j(\mathbf{u})$:

An equation of continuity for each species, i:

$$F_{G_i}(\mathbf{u}) = m_i R_i^n/M, \tag{1·2}$$

$G_i = m_i n_i v_i/(\sum\limits_j m_j n_j v_j)$, the fractional mass-flow rate of species i,

m_j is the molecular weight of a molecule of j in g/mole,

n_j is the concentration of j in mole/cm^3,

v_j is the average velocity of particles of type j with respect to a fixed axis system in cm/s,

$M = \sum\limits_j m_j n_j v_j$, the total mass flow with respect to a fixed axis system, and

R_i^n is the net rate of production of a species i in mole/cm^3.

An equation of diffusion for each species i:

$$F_{x_i}(\mathbf{u}) = (M/n) \sum_{j \neq i} D_{ij}^{-1}[(x_i G_j)/m_j - (x_j G_i)/m_i], \tag{1·3}$$

where

D_{ij} is the binary diffusion coefficient for the pair i, j in cm^2/s,

$x_j = n_j/n$, the mole fraction of species j,

$n = \sum\limits_j n_j$, the total concentration in mole/cm^3.

The equation of energy balance

$$F_T(\mathbf{u}) = (M/\lambda) \sum_j [(H_j G_j)/m_j - \lim_{Z \to \infty} (H_j G_j)/m_j], \tag{1·4}$$

where

T is the absolute temperature,

H_j is the enthalpy of species j in cal/mole, and

λ is the thermal conductivity of the gaseous mixture in cal cm^{-1} s^{-1} deg^{-1}.

According to the discussion of § 15, the pressure variation can be ignored in most flames so that the total concentration can be obtained from the perfect gas equation

$$n = P/RT; \quad P \text{ a constant.} \tag{1·5}$$

The hot boundary conditions require an asymptotic approach to equilibrium as $Z \to +\infty$:

$$\lim_{Z\to\infty} F_j(\mathbf{u}) = 0. \tag{1·6}$$

Hirschfelder & Campbell (1953) have given reasons why T is a particularly appropriate independent variable whenever $T(Z)$ is an increasing function for all $Z > Z_{\text{cold}}$. In this case, since the $F_j(\mathbf{u})$ do not depend explicitly on Z, the new equations have the explicit form

$$T < T_{\text{max.}} \equiv \lim_{Z\to\infty} T(Z) : \mathrm{d}u_j(T)/\mathrm{d}T = F_j(\mathbf{u})/F_T(\mathbf{u}). \tag{1·7}$$

2. Need for the proposed method

The kinetic steady state for a chemical species j is defined by the equation

$$\left.\begin{array}{l} R_j^P, R_j^C \text{ rates of production and consumption of } j \text{, respectively,} \\ R_j^n = \text{the net rate} = R_j^P - R_j^C = 0. \end{array}\right\} \tag{2·1}$$

In many static chemical reactions and in most flames there is one or more chemical species whose mole fractions approximately obey the kinetic steady-state equation in the sense that the ratio

$$d_j^P = R_j^n/R_j^P \tag{2·2}$$

is of the order of $\frac{1}{10}$ or less.

Most flame studies have assumed that for an intermediate species s, x_s can be calculated from the kinetic steady-state equation (2·1) and the terms in G_s can be omitted. The approximation for G_s can in some cases be worse than that for x_s. Thus in the H_2–Br_2 system, when the approximation for x_{Br} is good to about 10 %, G_{Br} is the most important term in the temperature gradient (work reported in part by Campbell 1957). The ozone flame is a practical example where neither approximation is legitimate. Thus in the high temperature region x_{O_3} obeys a kinetic steady-state equation over a hundred-fold more closely than x_O does, so that the kinetic steady-state assumption for O sets the larger rate to zero! Furthermore, because of subtraction, the value of G_O must be known to three digits to obtain a single digit for $\mathrm{d}T/\mathrm{d}Z$ (Campbell 1965*a*). For these and other previously discussed reasons (Campbell 1965*b*), it is desirable to have a solution method which: (*a*) provides an estimate of G_s, a better estimate for x_s, and some check upon the error made; (*b*) does not depend upon initial approximations of unknown form; (*c*) is consistent in the sense that it gives solutions which approach the exact solutions as the chemical and physical parameters are varied to cause an approach to the kinetic steady state (in this case the method correctly assigns the relative importance of various terms and the solutions it generates can be used to understand the significance of different flame processes). Part I reports such a method to be used whenever the deviation from the kinetic steady state is not too large over a range $[T_2, T_1]$ which excludes the singularity at $T_{\text{max.}}$. This fills a gap left by (1) a published method which generates solutions in a neighbourhood of $T_{\text{max.}}$ (Campbell, Buehler, Hirschfelder & Hughes 1961); (2) a new technique which continues the solution when the deviations are sufficiently large (Campbell 1965*b*).

3. Two basic difficulties that the method must surmount

The numerical integration of the hydrodynamic equations of § 1 presents a problem of smoothness and an even more serious problem of stability when there is a species s whose mole fraction approximately follows the steady-state condition (2·1). In this case, F_{G_s} is numerically indeterminate in the sense that the calculation of R_s^n involves a loss in significant figures (and thus in accuracy) as a result of subtraction between R_s^P and R_s^C, i.e.

$$d_s^P \equiv R_s^n/R_s^P\text{: a ratio of the order of } 10^{-e} \quad (e \geqslant 1). \tag{3·1}$$

If a smooth numerical approximation is to be obtained, this subtraction sets an upper bound upon the size of the integration step for any of the standard methods which use some linear combination of first derivatives to integrate from T_n to T_{n+1}. Since $G_s(T_{n+1}) - G_s(T_n)$ is of the order of $(\mathrm{d}G_s/\mathrm{d}T)\,\Delta T$, it is clear that if

$$[(\mathrm{d}G_s/\mathrm{d}T)\,\Delta T]/G_s(T_n) = 10^{-f} \quad (f < e), \tag{3·2}$$

then the rounding error at T_{n+1} will be $(e-f)$ decimal digits to the left of the error at T_n. If smooth solutions are to be obtained, integrations have shown that the ratio of (3·2) should be at most of the order of 10^{-e}. In some cases, this demands such a small integration step (compared with the length of the interval to be covered) that the calculation requires an excessive time. Furthermore, such a great increase in the number of steps can lead to an undesirable increase in probable accumulation of round-off error.

The argument of appendix A supports the conclusion that the differential equation system suffers from instability of the sort discussed by Fox & Mitchell (1957) which Henrici (1961) terms mathematical instability: any alterations of the starting values, such as are inevitable in numerical integrations, define solutions which diverge drastically from the desired central solution. Therefore, it is desirable to have a numerical method which follows the desired solution and which is not so unstable mathematically. One such method, developed by Curtiss & Hirschfelder (1952), becomes more stable as the interval size increases. When applicable, it has the advantage of simplicity. However, the method proposed in this paper can be used when the interval required for stability of the former method is too large for the required accuracy.

4. Equations for the proposed method

(a) *Introduction*

Although the method can be extended readily to treat much more general functional forms, certain rather general characteristics of the flame equations of § 1 allow significant simplifications of the general formulae. Since the simplifications do not markedly obscure the essence of the general method, it is convenient to give an explicit application to the equations of § 1 in notation chosen to specify the computational elements of the calculation.

To simplify the exposition of the proposed method of successive approximations, the general principles are given in this section while appendix C justifies the statements and gives explicit equations in terms of the variables:

$$\left.\begin{array}{l} t \text{ a suitable reduced temperature [cf. equation (8·2)],} \\ \{x\}^N,\ \{G\}^L \text{ sets of } N(L) \text{ linearly independent mole fractions} \\ \quad \text{(fractional mass-flow rates).} \end{array}\right\} \tag{4·1}$$

Two intuitive phrases which will be used—'numerically determinate' and 'correction term'—are defined precisely in appendix B. For simplicity, suppose that a single mole fraction, x_s, approximately follows the kinetic steady-state equation (2·1) and let

$$\{x\}_s^{N-1},\ \{G\}_s^{L-1}\text{: the subsets of } \{x\}^N,\ \{G\}^L \text{ which exclude } x_s \text{ and } G_s. \tag{4·2}$$

(b) *Equations for the first approximation level*

The simultaneous solution of differential equations for the variables of $\{x\}_s^{N-1}$, $\{G\}_s^{L-1}$ and algebraic equations for (x_s, G_s, R_s^n) gives the first approximation. The first step in deriving the set of algebraic equations replaces the pair of differential equations in x_s and G_s with the single second order equation (C 7) in R_s^n. In this new system, x_s and G_s are obtained as follows: (1) (C 2) is a numerically determinate implicit algebraic equation for the function $x_s(\{x\}_s^{N-1}, R_s^n, t)$ in which R_s^n is a correction term; (2) (C 6) is a linear algebraic equation for the function $G_s(\{x\}^N, \{G\}_s^{L-1}, t, \mathrm{d}R_s^n/\mathrm{d}t)$ obtained by manipulating the derivative of (C 2). The algebraic equations can now be obtained as follows: arguments in appendix C support the assumption that in general the new system will have a property it possesses for the two flames to which this method has been applied: as d_s^P decreases, both $\mathrm{d}R_s^n/\mathrm{d}t$, $\mathrm{d}^2R_s^n/\mathrm{d}t^2$ enter the system as correction terms which can be dropped to obtain algebraic equations. Moreover, this suggests how alternative initial approximations of varying complexity and accuracy can be generated. The second order differential equation (C 7) can be differentiated g times to obtain a system of $(g+1)$ differential equations in R_s^n and its power series coefficients, $(R_s^n)_m$, $m \leqslant (g+2)$. The maximum g, $g_{\text{max.}}$, for which $(R_s^n)_{g_{\text{max.}}+1}$, $(R_s^n)_{g_{\text{max.}}+2}$ will be correction terms will of course depend upon the flame system and its parameters. If $g \leqslant g_{\text{max.}}$, then the system of $(g+1)$ differential equations can be converted to a set of $(g+1)$ simultaneous algebraic equations in the $(g+1)$ variables $[R_s^n, \ldots, (R_s^n)_g]$ by introducing the approximations

$$(R_s^n)_{g+1} \equiv 0, \quad (R_s^n)_{g+2} \equiv 0. \tag{4·3}$$

Thus the following system of equations is to be solved simultaneously:

$$\left.\begin{array}{ll} (a) & \text{one differential equation for each variable of } \{x\}_s^{N-1}, \{G\}_s^{L-1}, \\ (b) & (g+1) \text{ non-linear algebraic equations for } (R_s^n)_m\ (0 \leqslant m \leqslant g), \\ (c) & \text{algebraic equations (C 2) for } x_s \text{ and (C 6) for } G_s. \end{array}\right\} \tag{4·4}$$

(c) *The* $(k+1)$*st approximation*

The condition that the proposed method can be used only when $(R_s^n)_1$, $(R_s^n)_2$ enter equations (C 6, 7) as correction terms suggests the following successive approximation schema to reduce the error due to the neglect of $(R_s^n)_{g+1}$, $(R_s^n)_{g+2}$ at the level $k = 1$. *Stage* 1, $k = 1$: choose a g and integrate (4·4) over $[T_2, T_1]$, where $T_1 < T_{\text{max.}}$ and $[T_2, T_1]$ covers as much of the flame as possible for reasons discussed in appendix E and at the end of § 5. *Stage* 2: (*a*) numerically differentiate the kth approximation, $(R_s^n)^{(k)}$, to obtain $(R_s^n)_1^{(k)}$, $(R_s^n)_2^{(k)}$; (*b*) integrate (4·4) over $[T_2, T_1]$ using $(R_s^n)_1^{(k)}$, $(R_s^n)_2^{(k)}$. *Stage* 3: if necessary, repeat stage 2. Success in the iteration may depend upon the use of suitable techniques of numerical differentiation which are discussed in appendix E.

Stage 1 can be omitted if another technique can predict sufficiently accurate $(R^n_s)^{(1)}_1$, $(R^n_s)^{(1)}_2$ for use in stage 2 (*b*). For example, in studies of the flame of part II for different values of a parameter, ω, it was found that $(R^n_s)^{(1)}_1$, $(R^n_s)^{(1)}_2$ could be estimated for $\langle \omega_0, t\rangle$ using values for $\langle \omega_1, t\rangle$ and $\langle \omega_2, t\rangle$ provided ω_1, ω_2 and ω_0 were sufficiently close (Heinen 1962).

5. Validation of results; applicability of the method; choice of g

The tests discussed here were applied to results of integrations for the flame of part II and to various O_3 flames. The first check compared values of R^n_s computed by the proposed method with those computed by a series solution about $T_{\max.}$, constructed by the technique of Campbell *et al.* (1961). For sufficiently small d^p_s, the values computed from a first approximation level with $g = 4$ agreed with series values at a junction point to within rounding error in an eight digit calculation. For somewhat larger d^p_s, the successive approximations (which were used only for the flame of part II) did correct the initial values to agree with the series. The second check compared values of the flame variables computed by this method with values computed by other techniques of numerical integration. As d^p_s increases, a recently published method, $\mathscr{m}$, becomes more suitable (Campbell 1965 *b*), while the successive approximation schema must ultimately fail. This failure has two causes: (1) It is no longer possible to obtain sufficiently accurate initial approximations for use in numerical differentiation; (2) The derivatives affect the solution to an increasing extent. From a fundamental viewpoint, this is to be expected since the general solution to the equations for an asymptotic approach to equilibrium at the hot boundary involves two or more eigenvalues (Campbell, Heinen & Schalit 1963) which are available to satisfy the conditions on the G_j at the cold boundary which is not a singularity of the differential equation system in the Hirschfelder–Curtiss formulation (cf. § 18). Nevertheless, there is an intermediate range to which both methods have been applied. In one test case, (A), the sixth iteration (using a slight variant of the proposed method) gave values of R^n_s which agreed with an error in the fifth or sixth decimal with values obtained by $\mathscr{m}$. In a second test case, (B), the fourth iteration gave values which agreed within 2 % (and generally within 1 %) over most of the common range.†

Finally, results have shown that even when the proposed method cannot be applied over the entire flame, sometimes it may work satisfactorily over an interval in the neighbourhood of (but excluding) the hot boundary and possibly for a lower temperature interval. The failure over part of the flame has been caused by either (*a*) the failure of simple methods to solve the non-linear algebraic equations at the $k = 1$ level for a sufficiently high g to give the required accuracy; (*b*) the failure of successive k levels to converge (cf. appendix E). There is no simple relation between d^p_s and convergence in k. Errors in R^n_s are much more difficult to correct by successive approximation in the temperature range where R^n_s has its maxima and minima. Thus, in one case studied, it would have been necessary to use all of the special techniques of smoothing and numerical differentiation discussed in appendix E for the

† This was for the hypothetical flame discussed in part II. Case (A) used the parameter $\omega = 50$ with all Lewis numbers of unity. Method $\mathscr{m}$ was conducted with equations in which G_B and x_B were replaced as variables by $d\bar{R}/dt$ and $\bar{R}$, $(\bar{R} \equiv R^n_B/(1+2f))$. Case (B) used $\omega = 10$ and Lewis numbers for 'light' free radicals (see below).

hotter region where $|d_s^P| < ca.\ 0{\cdot}04$ while not all were essential in the colder region where $|d_s^P|$ was 0·15 to 0·20 and more.

In practice, values of g between 1 and 4 have been used at level $k = 1$. The choice depended upon balancing three factors: (1) *Desired accuracy.* A value of g which is too low to give sufficiently accurate values of R_s^n to be differentiated to obtain input for level $k = 2$ may still provide values of R_s^n good to within an error of several per cent, and values of the flame variables better by at least an order of magnitude than the values of R_s^n. If greater accuracy is required, provided d_s^P is not too great, it may be possible to increase g to obtain that accuracy and avoid the programming for $k \geqslant 2$. (2) *Character of the equation system.* For some systems, as g increases, there can be a prohibitive increase in calculation time, or simple methods of solving the non-linear equations can even fail to converge. (3) *Asymptotic convergence in k* (cf. the preceding paragraph and appendix E).

6. ADVANTAGES AND DISADVANTAGES OF THE METHOD

The major disadvantage of the proposed method—an increase in complexity of the set of equations—must be balanced against the advantage of avoiding the problem of mathematical instability for each flame system. For example, for O_3 the proposed method took between 6 and 7 times as much calculation to cover one interval using $g = 1$ as a Runge–Kutta fifth order method required. Nevertheless, for that part of the flame to which it could be applied, it required less time than the procedure $\mathscr{m}$, which could be used for the entire range, since the mathematical instability of the O_3 equations makes them so sensitive to the exact starting values, that $\mathscr{m}$ has to use repeated numerical integrations (Campbell 1965*a*, *b*).

According to § 2, practical cases of interest require a method which is consistent in the sense that it gives solutions which asymptotically approach the solutions for the complete equation system as the physical and chemical parameters are varied to cause $d_s^P \rightarrow 0$. The proposed method has been adjudged consistent on the following grounds: (*a*) For the flame of part II, successive approximations were generated for a fixed g at $k = 1$ for flames with different parameters and, therefore, different d_s^P. The difference between the levels $k = 1$ and 2 decreased with d_s^P. For the flame with the smallest d_s^P, use of $g = 4$ gave first and second approximations which agreed almost everywhere within the rounding error of the calculation even for R_s^n (i.e. $\mathrm{d}G_s/\mathrm{d}t$). According to the definition of the level $k = 2$, this means that the first approximation satisfied the differential equations at almost all points within the rounding error of the calculation. (There was, of course, slightly greater error in the immediate neighbourhood of extreme values.) (*b*) The argument of appendix C suggests that it is plausible to expect that this will be true for other flame systems.

Finally, the proposed method has the advantage that it ensures that G_s will satisfy the boundary condition for an intermediate, $G_s(Z_{\mathrm{cold}}) = 0$, to a sufficiently high approximation and thereby avoid the use of an additional eigenvalue (cf. § 10). This is a consequence of the following argument: (1) The use of (C 2) makes $x_s \rightarrow 0$ since in general R_s^P decreases much more rapidly with T than does the coefficient of x_s in R_s^C and the method only applies when $d_s^P = R_s^n/R_s^P \rightarrow 0$. (2) The use of the derivative of (C 2) also makes $(\mathrm{d}x_s/\mathrm{d}t) \rightarrow 0$ because: (*a*) under the conditions of § 12, x_s has a single internal maximum; (*b*) by (1), $x_s \rightarrow 0$. (3) The use of (C 6) is equivalent to solving for $\mathrm{d}x_s/\mathrm{d}t$ and using $F_t(\mathrm{d}x_s/\mathrm{d}t) = F_{x_s}$ to solve for G_s. (4) $F_t \rightarrow 0$

as $Z \to Z_{\text{cold}}$. (5) According to (1·3), the terms of F_{x_s} can be divided into one set which have x_s as a factor and a second which have G_s as a factor. By (1), $x_s \to 0$ and inspection shows that the coefficient of $G_s \nrightarrow 0$.

PART II

7. Introduction

Part II of this paper reports extensive calculations on one idealized flame. The method of part I was very convenient whenever deviations from the kinetic steady state were not too large. For larger deviations, another technique, which has been developed further and published (Campbell 1965*b*) was used. The purpose of part II is the analysis of these results in the following terms: (*a*) how the kinetic model and kinetic and transport parameters affect the properties of free-radical flames; (*b*) the significance of various assumptions and approximations which have been used in flame theories. To provide a basis for this discussion, the following section casts the general flame equations in a form and notation designed to clarify the relation between these results and experimental flame systems.

8. Dimensionless forms for the general flame equations

To facilitate the study of flame properties as a function of fuel properties by selecting a useful set of independently variable parameters, the general equations of § 1 are rewritten in terms of dimensionless variables as follows. A reduced distance, which is a constant multiple of Z is defined using C_j and m_j for species $j = j_0$:

$$\zeta = \{[MC_{j_0}]/[m_{j_0}\lambda(T_{\text{max.}})]\}\,Z, \tag{8·1}$$

where C_j is the heat capacity of j averaged over $[T_{\text{cold}}, T_{\text{max.}}]$. The reduced temperature,

$$t = [T - T_{\text{max.}}]/T_{\text{max.}}, \tag{8·2}$$

has two advantages in numerical integrations: (1) it scales the successive derivatives in series construction at T_{max}; (2) any power series coefficient of T^{κ} with respect to t is independent of $T_{\text{max.}}$ at $t = 0$. However, in a comparison of different flames it is more useful to have a reduced temperature having a fixed range of values:

$$\tau = [T - T_{\text{cold}}]/[T_{\text{max.}} - T_{\text{cold}}] = [t_{\text{cold}} - t]/t_{\text{cold}} \quad (0 \leqslant \tau \leqslant 1). \tag{8·3}$$

The terms of the energy balance equation are regrouped to give

$$\frac{\mathrm{d}T}{\mathrm{d}Z} = T_{\text{max.}}\left\{\frac{MC_{j_0}}{m_{j_0}\lambda(T_{\text{max.}})}\right\}\left\{\frac{\lambda(T_{\text{max.}})}{\lambda}\right\}F_t, \tag{8·4}$$

$$F_t = \mathscr{H} - \lim_{Z\to\infty}\mathscr{H}, \quad \mathscr{H} = \sum_j \{H_j/(C_{j_0}T_{\text{max.}})\}\{(m_{j_0}/m_j)\,G_j\}. \tag{8·5}$$

Then the derivatives for the reduced temperature, t, are

$$\mathrm{d}t/\mathrm{d}Z = T^{-1}_{\text{max.}}(\mathrm{d}T/\mathrm{d}Z) = \{MC_{j_0}/[m_{j_0}\lambda(T_{\text{max.}})]\}\,\mathrm{d}t/\mathrm{d}\zeta, \tag{8·6}$$

$$\mathrm{d}t/\mathrm{d}\zeta = [\lambda(T_{\text{max.}})/\lambda]\,F_t. \tag{8·7}$$

R^n_j, the net rate of production of species j, is assumed to be a linear combination of rates for reversible reactions:

$$\left.\begin{aligned} R_i &= R^f_i - R^r_i, \\ R^f_i(R^r_i)&: \text{the rate of the forward (reverse) } i\text{th reaction.}\end{aligned}\right\} \tag{8·8}$$

To determine the effect of varying the forward and reverse specific rates for a given reaction i_0 by a constant factor, γ_{i_0}, it is convenient to introduce reduced reaction rates:

$$r_i = R_i/\gamma_{i_0}; \quad r_j^n = R_j^n/\gamma_{i_0}. \tag{8·9}$$

Since § 11 will show that the mass-flow rate, M, is most sensitive to the dominant reactions in the net rate of consumption of one of the fuel molecules, and since such reactions should contribute heavily to the rate of heat release per unit volume, it is convenient to choose one of these reactions as i_0 and to combine M and γ_{i_0} into a dimensionless group of parameters. Then the equations of continuity become

$$\mathrm{d}G_j/\mathrm{d}\zeta = \mu^*(m_j/m_{j_0})\, r_j^n; \quad \mu^* = [m_{j_0}^2\lambda(T_{\text{max.}})\,\gamma_{i_0}]/[M^2C_{j_0}]. \tag{8·10}$$

The equations of diffusion assume the form

$$\mathrm{d}x_j/\mathrm{d}\zeta = [\lambda(T_{\text{max.}})/\lambda] \sum_{j\neq i} \delta_{ji}^{-1}[x_j\,G_i(m_{j_0}/m_i) - G_j\,x_i(m_{j_0}/m_j)], \tag{8·11 a}$$

$$\delta_{ji} = (C_{j_0}nD_{ji})/\lambda \quad \text{has the form of a Lewis number.} \tag{8·11 b}$$

9. SIGNIFICANT ASPECTS OF THE IDEALIZED MODEL; SPECIALIZATION OF THE GENERAL REDUCED EQUATIONS

This section summarizes the significance of various aspects of the idealized model and specializes the general reduced equations of § 8. The ABC schema, suggested by Hirschfelder & Curtiss [cf. Giddings & Hirschfelder (1957)], has two reactions:

$$\left.\begin{array}{ll}(1) & \text{free radical reaction: heat} + X + A \rightleftharpoons B + X \quad (X\text{, any molecule}),\\ (2) & \text{main combustion reaction: } B + A \rightleftharpoons C + B + \text{heat.}\end{array}\right\} \tag{9·1}$$

For suitable parameters, this schema mimics what appear to be the essential aspects of a free radical mechanism for flame kinetics with B as a free radical:

> The formation of a free radical by R_1^f requires a comparatively high activation energy while radical 'recombination' by R_1^r requires a comparatively low activation energy. (9·2 a)
>
> The main combustion reaction, R_2^f, uses a free radical, B, and requires a comparatively low activation energy. (9·2 b)

To obtain the simplest possible equations consistent with these requirements the following assumptions were introduced (although they are not quantitatively realistic, they were not expected to affect the results qualitatively):

(*a*) In the functional forms which Campbell & Fristrom (1958) suggested for use in specific rates in flame studies,

$$\left.\begin{array}{l}k = AT^b\exp(-\Delta E/RT) = A(T_{\text{max.}})^b\,(1+t)^b\exp[-\eta/(1+t)],\\ \eta = \Delta E/RT_{\text{max.}},\end{array}\right\} \tag{9·3}$$

the 'comparatively low' activation energies are zero and the comparatively high activation energies are the same:

$$\Delta E_1^r = \Delta E_2^f = 0; \quad \Delta E_1^f = \Delta E_2^r \equiv Q = \text{heat released.} \tag{9·4}$$

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Moreover, the collision characteristics are the same for the forward and reverse reactions, and

$$A_1^f = A_1^r \equiv A_1; \quad A_2^f = A_2^r \equiv A_2; \quad b_1^f = b_1^r = b_2^f = b_2^r \equiv b. \tag{9·5}$$

(*b*) The approximation of constant equal heat capacities gives the enthalpies:

$$\left.\begin{aligned} H_A = Q + C(T - T_{\text{max.}}), \quad H_B = 2Q + C(T - T_{\text{max.}}), \quad H_C = C(T - T_{\text{max.}}). \\ C \equiv C_A = C_B = C_C; \quad H_C(T_{\text{max.}}) \equiv 0. \end{aligned}\right\} \tag{9·6}$$

(*c*) The assumption that the δ_{ij} are independent of temperature is suggested, but by no means justified, by the fact that this would be true for hard spheres:

$$\delta_{ij}\text{: constant function of } T. \tag{9·7}$$

(*d*) The differences between the thermal conductivities of the species are ignored in order to make the thermal conductivity of the mixture be a function of T alone. Furthermore, so that the reduced conductivity would enter only the ζ and not the t equations, it is assumed to satisfy the equation

$$[\lambda/\lambda(T_{\text{max.}})]\,[T/T_{\text{max.}}]^b = [\lambda/\lambda(T_{\text{max.}})]\,(1+t)^b = 1. \tag{9·8}$$

According to the discussion of (8·9), i_0 should be chosen as 2. Then, because of assumptions (9·5, 8) it is convenient to define

$$\gamma_2 = A_2[T_{\text{max.}}]^b. \tag{9·9}$$

Then the eigenvalue μ^* of (8·10) is just the μ_2 of a previous paper (Campbell *et al.* 1963):

$$\left.\begin{aligned} \mu_2 = \mu^* \equiv \{m^2\lambda(T_{\text{max.}})\,A_2[T_{\text{max.}}]^b\}/\{M^2C\}, \\ m \equiv m_A = m_B = m_C \text{ (as required by the kinetic schema).} \end{aligned}\right\} \tag{9·10}$$

The general dimensionless equations are

$$\mathrm{d}u/\mathrm{d}t = \mathscr{F}_u/\mathscr{F}_t, \quad \mathscr{F}_u = [\lambda/\lambda(T_{\text{max.}})]\,\mathrm{d}u/\mathrm{d}\zeta, \quad \mathscr{F}_t = F_t; \tag{9·11}$$

$$F_t = t + h[\Delta G_A + 2\Delta G_B], \quad h = Q/(CT_{\text{max.}}), \quad \Delta u = u(t) - u(t=0); \tag{9·12}$$

$$\mathscr{F}_{xi} = \sum_{j \neq i} \delta_{ij}^{-1}(x_i G_j - x_j G_i); \tag{9·13}$$

$$\mathscr{F}_{GA} = \mu_2[-\mathscr{R}_1\omega^{-1} - \mathscr{R}_2']\dagger, \quad \mathscr{F}_{GB} = \mu_2\mathscr{R}_1\omega^{-1}; \tag{9·14a}$$

$$\mathscr{R}_1 \equiv [\lambda/\lambda(T_{\text{max.}})]\,\omega r_1 = x_A f - x_B \equiv \mathscr{R}_1^f - \mathscr{R}_1^r; \tag{9·14b}$$

$$\mathscr{R}_2' \equiv [\lambda/\lambda(T_{\text{max.}})]\,r_2 = x_B x_A - x_B x_C f \equiv \mathscr{R}_2'^f - \mathscr{R}_2'^r; \tag{9·14c}$$

$$\omega \equiv \gamma_2/(A_1[T_{\text{max.}}]^b) = A_2/A_1, \quad f = \exp[-\eta/(1+t)], \quad \eta = \Delta E/(RT_{\text{max.}}) = Q/(RT_{\text{max.}}). \tag{9·14d}$$

The numerical values for the parameters are summarized in appendix F.

10. Significance of conventional approximations

The significance of conventional approximations has three different aspects: (1) the simplifications they impart to flame theory; (2) how they depend upon the parameters

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† Note that in the notation of some previous reports, $\mathscr{R}_2' = \mathscr{R}_2/\omega$ and $\mu_2 = \mu\omega$. The switch to the notation of this paper emphasizes that the eigenvalue M depends primarily upon the parameters for the specific rates for the main combustion reactions and is much less strongly affected by those for the free-radical specific rates (see § 11).

describing the flame; (3) the error they introduce into μ^* (i.e. M), $t(Z)$, the $x_j(t)$, $G_j(t)$, and $R_j^n(t)$. This section is devoted to the first aspect. Two common idealizations are to assume that all Lewis numbers are unity,

$$\delta_{ij} = 1, \tag{10·1}$$

and that the mole fraction of any intermediate species, s, can be obtained from the kinetic steady-state equation,

$$\left.\begin{array}{c} R_s^n = R_s^P - R_s^C = 0, \\ R_s^P(R_s^C) \text{ being the rate of production of } s \text{ by chemical reactions.} \end{array}\right\} \tag{10·2}$$

Each of these approximations reduces the number of linearly independent x_j as follows. Hirschfelder (1960) has shown that (subject to the approximations required to derive the equations of § 1), the specific enthalpy remains constant ↔ (10·1) holds:†

$$\left.\begin{array}{c} \sum\limits_j H_j x_j = m \lim\limits_{Z\to\infty} m^{-1} \sum\limits_j H_j x_j, \\ m \equiv \sum\limits_j m_j x_j \neq \text{constant (in general).} \end{array}\right\} \tag{10·3}$$

Thus if (10·1) is applied to a flame with w different chemical species which include I different intermediates for which (10·2) is assumed, then there are only

$$w - 1 - (I+1) \tag{10·4}$$

linearly independent x_j.

A third common idealization omits the terms in G_s for any intermediate, s. However, § 2 shows that it may be necessary to obtain G_s from the consistent method of part I (cf. § 6). In either case, if there are I such intermediates and u linear relations between the net rates, R_j^n, then the form of equation (1·2) for F_{G_j} shows that there will be

$$(w-1) - (u+I) \tag{10·5}$$

linearly independent G_j. Because of its special simplicity, a favourite type of system for theoretical study is one in which $u = 0$ and $w = 1 + (I+1)$ so that the x_j are determined by the solution of the algebraic equations (10·2, 3) and there is only one differential equation in some $G_j(t)$.

An even greater advantage of obtaining G_s from an algebraic equation is that it simplifies the eigenvalue character of the problem. In all cases which have been studied, the general solution for the equations at the hot boundary defined by the asymptotic conditions (1·6) has had one eigenvalue for each of the linearly independent G_j. These eigenvalues can be adjusted to obtain the prescribed values at the cold boundary which is an ordinary point of the differential equation system (cf. § 18 and Campbell *et al.* 1963). The reduction to a single eigenvalue, μ^*, enormously simplifies the calculation.

The subsequent sections provide information about the second and third aspects of the significance of conventional approximations by analysing solutions for the idealized flame of § 9 for wide ranges of the Lewis numbers and of $\omega = A_2/A_1$.

11. Significance of the parameter μ^* and its dependence upon properties of flame gases

Table 1 summarizes some results (Campbell *et al.* 1963) to show that μ^* varies rather slowly with wide variations in the D_{ij} and the kinetic parameter, ω. Since $\omega = A_2/A_1$ and $\mu^* \sim A_2$, it follows that μ^* is rather insensitive to variations in the kinetic parameters for the

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† The symbol '↔' is used in the mathematical sense 'if and only if'.

TABLE 1. VARIATION IN $\mu^* \sim A_2/M^2$

For specific values of the Lewis numbers, see appendix F. The relative deviation, d_B^P, is defined by equation (2·2). $|d_B^P|^{\max.}$ is the maximum value for the temperature region over which $G_A \leqslant 0{\cdot}95G_A[T(Z_{\text{cold}})]$.

Lewis numbers	$\omega = A_2/A_1$	μ^*	$\lvert d_B^P\rvert^{\max.}$
‘heavy’ free radicals	1	4587·6	$1{\cdot}3\times10^{-3}$
	600	4557·0	$6{\cdot}7\times10^{-1}$
all unity	1	4578·3	$3{\cdot}2\times10^{-3}$
	1000	3880·0	$6{\cdot}7\times10^{0}$
‘light’ free radicals	1	4510·0	$3{\cdot}0\times10^{-2}$
	300	2583·0	$3{\cdot}7\times10^{+1}$

free-radical reaction. Furthermore, since these variations produce order of magnitude changes in the deviation from the kinetic steady state, μ^* is comparatively insensitive to such deviations. Thus the form of equation (8·10) for μ^* suggests that M will be most strongly affected by variations from one flame to another in thermal conductivity and in the specific rates for the dominant terms in the main combustion reactions responsible for the major heat release per unit volume. The qualitative form of the functional dependence should be the same as the one given by the defining equation for μ^*:

$$M = m_{j0}\{[\lambda(T_{\max.})\,\gamma_{i0}]/[\mu^* C_{j0}]\}^{\frac{1}{2}}. \tag{11·1}$$

These observations show that μ^* functions as a parameter which can be adjusted to match $G_j(Z_{\text{cold}})$ for a major component. According to the argument at the end of §6, when the method of part I is used for an intermediate s, then the condition $G_s(Z_{\text{cold}}) = 0$ is satisfied to a high approximation. In general, if $(w-1)-(u+I) > 1$, the following procedure should be used in numerical integrations: (1) For a fixed μ^*, vary certain other eigenvalues (Campbell *et al.* 1963) to satisfy the $G_j(Z_{\text{cold}})$ for all but one of the major components and any intermediates for which the method of part I is inapplicable; (2) Adjust μ^* to fit the condition on the remaining major component and repeat step (1).

12. QUALITATIVE CHARACTER OF CURVES FOR FREE-RADICAL INTERMEDIATES; RELATION TO PROCESSES OF KINETICS AND DIFFUSION

In contrast to diffusion theories of flame propagation (Tanford & Pease 1947) which predict a monotonic decrease of the mole fraction of an active intermediate, s, with temperature, every numerical integration of equations (1·1–6) has given: (*a*) an internal maximum in x_s; (*b*) a qualitative character for $G_s(T)$ and $R_s^n(T)$ which is the same for all s. The object of this section is to show that both (*a*) and (*b*) can be plausibly inferred from conditions which commonly occur in flames.

Appendix G gives a detailed argument which demonstrates that x_s can be expected to have a single internal maximum whenever the dominant reactions which produce s involve at least one fuel molecule (e.g. $X+Br_2 \rightarrow 2Br+X$ in the H_2–Br_2 flame) or an intermediate which has a single internal maximum in x_s and for which R_s^C is of the order of R_s^P at higher temperatures (e.g. $Br+H_2 \rightarrow H+Br$ in the H_2–Br_2 flame). Then the concentration gradients will be accompanied by diffusion away from the maximum so that the net rate will have a positive internal maximum flanked at both higher and lower temperatures by a negative minimum. This is the qualitative character of figure 1 of $\mathscr{R}_1/\omega$. According to equation (1·2),

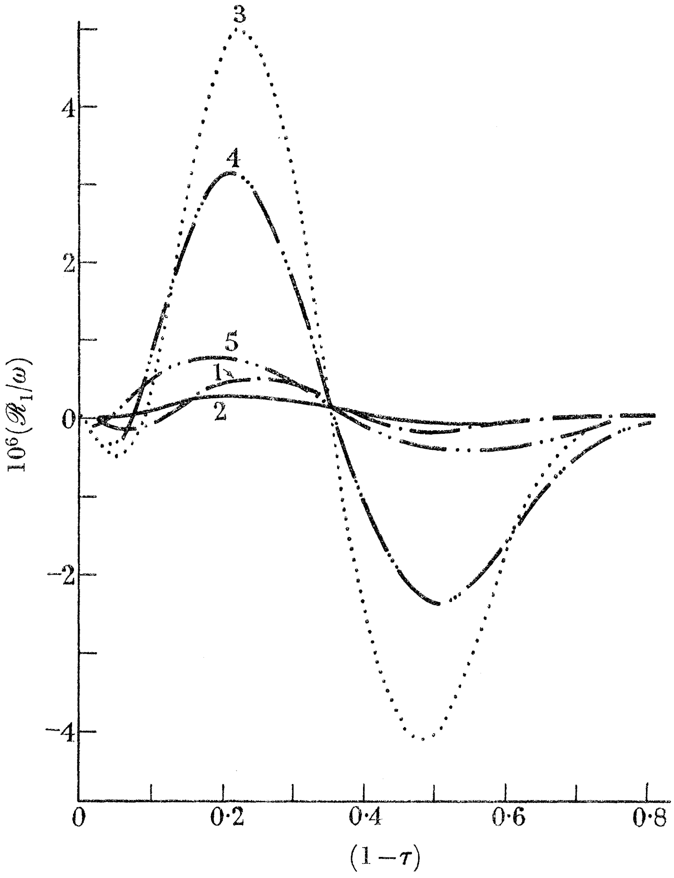

FIGURE 1. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 1$, set II; 4, $\omega = 20$, set II; 5, $\omega = 300$, set II.

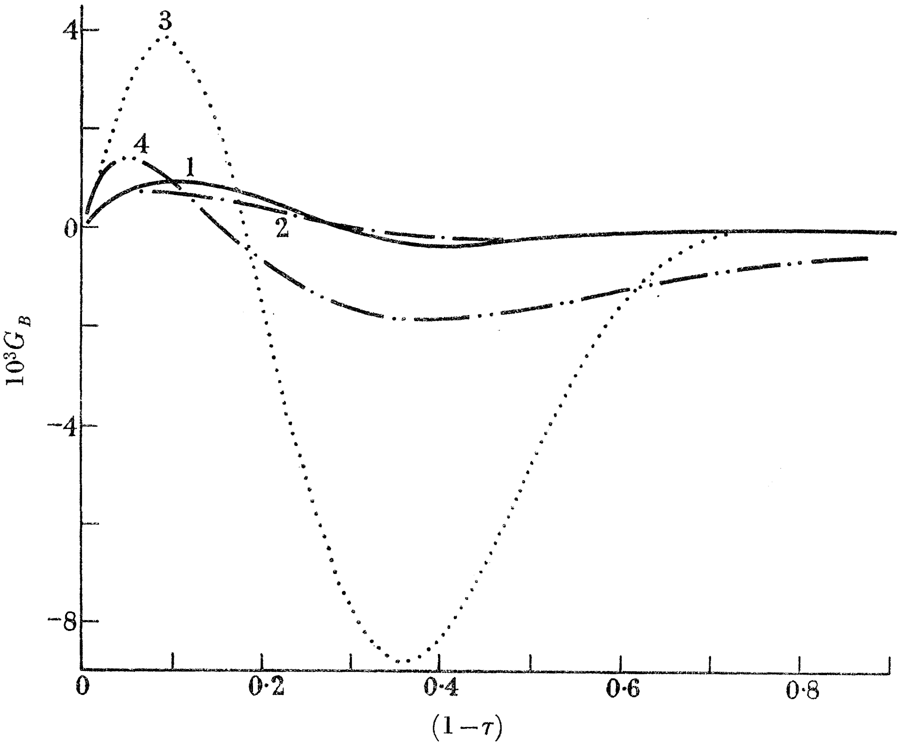

FIGURE 2. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 1$, set II; 4, $\omega = 300$, set II.

this sign variation in the net rate of free-radical production implies the type of fractional mass-flow curve shown by figure 2 in which G_B increases from its hot boundary value, passes successively through a positive maximum and a negative minimum and approaches zero asymptotically.

13. Relation between diffusion and kinetic parameters and deviation from the kinetic steady state

In general, an increase in $|d_s^P|$ can be expected for an intermediate, s, of § 12 under either of the following two conditions. First, an increase in the binary diffusion coefficients involving the intermediate compared with those involving only major components should increase the diffusion of s and thereby reduce the gradients accompanying the maximum in x_s and increase $|d_s^P|$.

Secondly, suppose the kinetic schema consists of one set of 'main combustion' reactions and a second set of reactions primarily responsible for the production and consumption of s. (For example, in the H_2–Br_2 flame the second set consists of the reaction $Br_2 + X \rightleftharpoons 2Br + X$, while for the *ABC* schema, the second set consists of reaction (1). Then the following steps show that $|d_s^P|$ should increase as the 'main combustion rates' are increased compared with the 'intermediate' rates. It will be convenient to consider the opposite variation, $d_s^P \rightarrow 0$. Then: (*a*) $\mathrm{d}G_s/\mathrm{d}t \nrightarrow 0$, since $0 = G_s(t_{\text{cold}}) \mp G_s(t = 0)$ and the form of equation (1·2) shows that G_s must be continuous in the absence of a catalytic surface; (*b*) $\mathrm{d}G_s/\mathrm{d}\zeta \nrightarrow 0$ since $\mathrm{d}G_s/\mathrm{d}t \nrightarrow 0$ and the form of equations (8·5, 7) shows that $\mathrm{d}t/\mathrm{d}\zeta \nrightarrow 0$; (*c*) $\mu^* r_s^n = \mu^* R_s^P\, d_s^P/\gamma_{i_0} \nrightarrow 0$ as a consequence of (*b*) and equation (8·10) for $\mathrm{d}G_s/\mathrm{d}\zeta$; (*d*) $R_s^P/\gamma_{i_0} \rightarrow \infty$ as $d_s^P \rightarrow 0$, since by § 11 μ^* is finite. This says that as $d_s^P \rightarrow 0$, the rates for the intermediate become increasingly rapid compared with those for the main combustion reactions.

For the *ABC* flame, table 1 shows the quantitative effects for the variation of the binary diffusion coefficients and of $\omega = A_2/A_1$.

14. Relations between (*a*) diffusion and kinetic parameters and (*b*) x_s, G_s and the diffusion velocity for an intermediate species

This section presents a table and graphs to show the quantitative relations for the *ABC* flame and singles out five qualitative aspects which are interpreted in terms of equations and physical processes to justify the conclusion that they will be common to any intermediate s, which satisfies the conditions of § 12.

According to §§ 11 and 13, $|d_s^P|$ for the *ABC* flame can be increased by increasing ω, i.e. by decreasing A_1 with comparatively little effect on M or by increasing A_2 which causes M to increase roughly as $\surd A_2$. Since the form of equations (1·3, 4) shows that $\mathrm{d}x_s/\mathrm{d}Z$ and $\mathrm{d}T/\mathrm{d}Z$ are approximately proportional to M, and since the diffusion velocity should also vary roughly as M, the appropriate quantities for discussion of $|d_s^P|$ should be the mass-average diffusion velocity compared with the total velocity, $\rho V_s/M$, and the reduced gradients

$$(\mathrm{d}x_s/\mathrm{d}\zeta \sim M^{-1}\,\mathrm{d}x_s/\mathrm{d}Z, \quad \mathrm{d}t/\mathrm{d}\zeta \sim M^{-1}\,\mathrm{d}t/\mathrm{d}Z).$$

Aspect 1. *As the kinetic parameters are varied to decrease* $|d_s^P|$, *both* $|\rho V_s/M|$ *and* $|\mathrm{d}x_s/\mathrm{d}\zeta|$ *decrease.* In the kinetic steady state, the reactions governing the net production of s are sufficiently rapid to maintain local equilibrium with respect to changes produced by total mass flow, diffusion, and other chemical reactions. Since if s satisfies the kinetic conditions of § 12, it will have a single internal maximum, and since the effect of diffusion must be to reduce gradients, it is plausible to conclude that in general the kinetic steady state corresponds to the greatest $|\mathrm{d}x_s/\mathrm{d}\zeta|$. Furthermore, (1·3) implies that $M^{-1}\,\mathrm{d}x_s/\mathrm{d}Z \sim$ the reduced diffusion velocity when all diffusion coefficients are equal:

$$\left.\begin{aligned} M^{-1}\,\mathrm{d}x_s/\mathrm{d}Z &= n^{-1}D^{-1}\sum_{j\neq s}(x_s\,G_j\,m_j^{-1}-x_j\,G_s\,m_s^{-1}) \\ &= M^{-1}D^{-1}\sum_j x_s\,x_j(v_j-v_s) = -(V_s^n/M)\,x_s\,D^{-1}, \end{aligned}\right\} \tag{14·1}$$

where $V_s^n \equiv v_s - \sum_j x_j\,v_j$, the number average velocity. It is plausible to surmise that $|\mathrm{d}x_s/\mathrm{d}\zeta|$ will be in general an increasing function of $|\rho V_s/M|$ even when the diffusion coefficients are not equal.

Table 2 shows the variations for $(\rho V_B/M)$.

TABLE 2. THE REDUCED DIFFUSION VELOCITY OF THE FREE RADICAL B AS A FUNCTION OF DIFFUSION AND KINETIC PARAMETERS

The symbols H, U, L designate solutions using the following Lewis numbers: set I ('heavy' free radicals); set II (all unity); set III ('light' free radicals) [cf. appendix F]. Since all masses are the same for the ABC system, (14·3) shows that $\rho V_B/M = (G_B/x_B)-1$.

	$\omega = 1$			$\omega = 100$			$\omega = 300$			$\omega = 1000$
τ	H	U	L	H	U	L	H	U	L	U
0·2436	−5·281	−10·018	—	−4·440	−6·673	−14·332	−3·212	−4·176	—	−2·540
0·3493	−4·337	−8·074	−59·528	−3·682	−5·767	−14·226	−2·863	−3·918	−10·524	−2·460
0·4550	−3·404	−6·234	−47·124	−2·882	−4·598	−13·245	−2·346	−3·353	−8·924	−2·232
0·4902	−3·077	−5·611	−42·731	−2·607	−4·180	−12·650	−2·251	−3·111	−8·477	−2·116
0·5431	−2·569	−4·661	−35·895	−2·198	−3·541	−11·501	−1·846	−2·713	−7·747	−1·906
0·6135	−1·871	−3·387	−26·472	−1·639	−2·679	−9·532	−1·423	−2·137	−6·576	−1·574
0·6488	−1·521	−2·761	−21·730	−1·363	−2·251	−8·385	−1·207	−1·837	−5·890	−1·390
0·7192	−0·845	−1·574	−12·486	−0·821	−1·409	−5·829	−0·775	−1·226	−4·315	−0·998
0·7545	−0·532	−1·033	−8·144	−0·558	−1·001	−4·442	−0·560	−0·919	−3·431	−0·793
0·8514	+0·163	+0·157	+1·762	+0·092	+0·017	−0·393	+0·008	−0·099	−0·712	−0·212
0·9505	+0·399	+0·585	+5·396	+0·401	—	+3·230	+0·391	+0·511	+2·240	+0·353

Aspect 2. *As $|d_s^P|$ increases, the maximum in x_s decreases.* The following quantitative argument supports the foregoing qualitative one. For a fixed t and a fixed set of x_j, $j \neq s$, consider the solution of the following equation for x_s:

$$R_s^C = R_s^P - R_s^n. \tag{14·2}$$

Since § 12 shows that $R_s^n > 0$ where x_s has its maximum, an argument similar to that of appendix G shows that x_s will be a monotone decreasing function of R_s^n and, therefore, of d_s^P. Furthermore, it is plausible to expect that the variation in the x_j for major components [and, therefore, the coefficients of the powers of x_s in (14·1)] will not be sufficient to alter the conclusion.

Aspect 3. $|\mathrm{d}x_s/\mathrm{d}\zeta|$ *is greater on the cold side of the maximum.* While the fact that the position of the maximum in x_s is much closer to $T_{\text{max.}}$ than to T_{cold} leads one to predict a larger t gradient on the hot side, the opposite is true for $\mathrm{d}x_s/\mathrm{d}\zeta$ [cf. figures 3 and 4]. The change in $\mathrm{d}x_s/\mathrm{d}\zeta$ follows from the facts that: (*a*) according to § 18, $\mathrm{d}t/\mathrm{d}\zeta$ is bounded away from zero at the flame holder; (*b*) there is a slow approach to thermal equilibrium about $T_{\text{max.}}$ in the sense that $\mathrm{d}t/\mathrm{d}\zeta$ is comparatively small over a significant range of t.

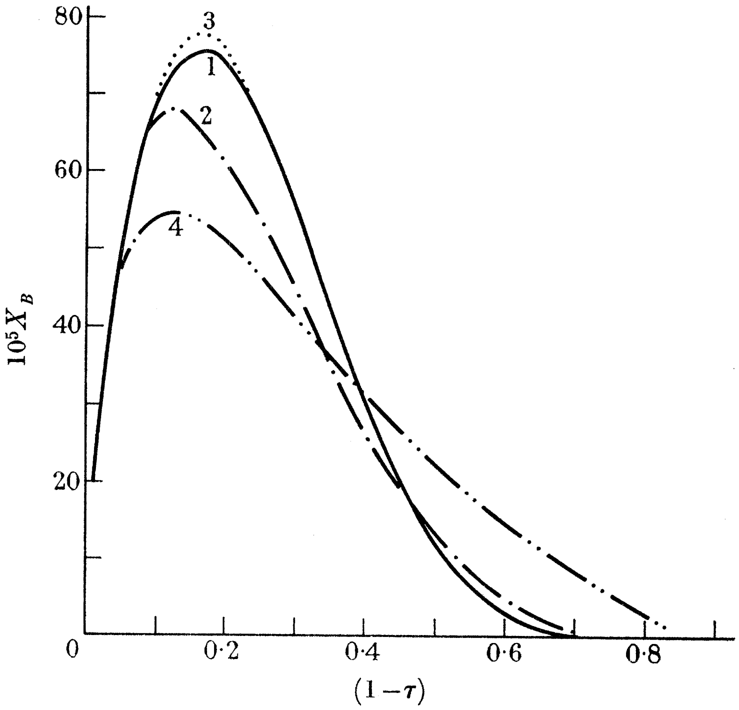

FIGURE 3. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 1$, set II; 4, $\omega = 300$, set II.

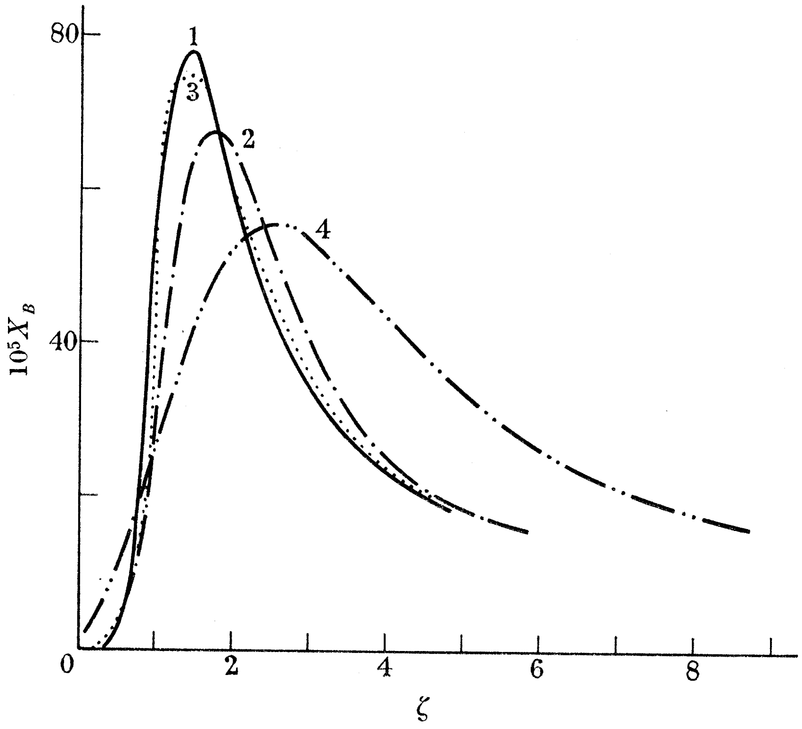

FIGURE 4. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 5$, set II; 4, $\omega = 300$, set II.

Aspect 4. *The maximum in x_s shifts toward the hot boundary as $|d_s^P|$ increases.* This follows from the fact that as the reactions governing the net production of s are no longer sufficiently rapid to maintain local equilibrium diffusion must cause a shift in the direction of the smaller $|V_s|$ which by Aspects (1, 3) are on the hot side.

Aspect 5. *The extreme values of* $|G_s|$ *decrease as the kinetic parameters are varied to increase* $|d_s^P|$.

Now
$$G_s = M^{-1} m_s n_s (V_s + v) = (\rho_s/\rho)\,[(\rho V_s/M) + 1]. \tag{14·3}$$

According to Aspect (1), the extreme values of $|\rho V_s/M|$ decrease. If, as is the case for the ABC flame, the maximum point shifts toward $t = 0$ and the minimum toward t_{cold} where ρ_s/ρ is smaller, the conclusion follows at once.

15. SIGNIFICANCE OF DIFFERENT PROCESSES IN MAINTAINING ENERGY CONSERVATION; CONSTANCY OF SPECIFIC ENTHALPY

This discussion of energy conservation is limited to flames for which the following four approximations can be introduced into the more general equation for a one-dimensional steady-state system which approaches equilibrium asymptotically as $Z \to \infty$ (Hirschfelder, Curtiss & Bird 1954, p. 750).

Approximation 1. The contribution of radiation to the energy-flux vector is ignored (cf. Hirschfelder *et al.* 1954, p. 761).

Approximation 2. The term in thermal diffusion in the energy-flux vector is ignored since it is believed to be important only for flames which have H_2 as a constituent (cf. Hirschfelder *et al.*; Waelbroeck, Lafleur & Prigogine 1955).

Substitution of this approximation for the energy-flux vector gives

$$0 = -\lambda \frac{\mathrm{d}T}{\mathrm{d}Z} + n \sum_i H_i x_i V_i + M\left(\frac{1}{m}\sum_i H_i x_i - \lim_{Z\to\infty} \frac{1}{m}\sum_i H_i x_i\right) + \tfrac{1}{2}M(v^2 - \lim_{Z\to\infty} v^2) - (\tfrac{4}{3}\eta + \kappa)\, v \frac{\mathrm{d}v}{\mathrm{d}Z} = 0. \tag{15·1}$$

$M = \rho v$, a constant in the one-dimensional steady state (Hirschfelder *et al.* 1954, p. 748) (15·2)

$$(\tfrac{4}{3}\eta + \kappa)\frac{\mathrm{d}v}{\mathrm{d}Z} = M(v - \lim_{Z\to\infty} v) + (P - \lim_{Z\to\infty} P), \tag{15·3}$$

η, κ being the coefficients of shear and bulk viscosity, respectively.

Approximation 3. The term in the kinetic energy of gas flow is dropped. In general, the relative importance of the kinetic energy of overall gas flow should be measured by comparison with the diffusion term in equation (15·1):

$$n \sum_i H_i x_i V_i = \frac{M}{m} \sum_i H_i[(m/m_i)\, G_i - x_i]. \tag{15·4}$$

The comparison should not be drawn with the terms in specific enthalpy since Hirschfelder (1960) has proven that the specific enthalpy is constant under special conditions (see below in this section). Since $[H_i - H_i(T = 0)]/m_i$ is of the order of the square of the mean peculiar speed for i, it is usually assumed that the velocity term is unimportant until the over-all flow velocity becomes of the order of the peculiar speed. However, it has been shown in the ozone flame, that, due to subtraction of the leading digits, the coefficient of H_i in equation (15·4) is sufficiently small that the term $(M/2)\,(v^2 - \lim_{Z\to\infty} v^2)$ cannot be ignored over an important range of high temperatures for richer fuel mixtures. Solutions including the kinetic energy term even have a different eigenvalue character (Campbell 1965*a*).

Approximation 4. The viscosity term is omitted. Even if (after multiplication by v) the two terms of equation (15·3) were not separately negligible, subtraction in their leading terms could make the viscosity term itself insignificant. Therefore, appendix H gives an argument which is not based on considering separate terms to show that the viscosity term can be expected to be negligible in common cases.

After the terms in kinetic energy and viscosity have been dropped, it is useful to regroup the terms of (15·1) to separate the contributions due to convection, thermal conduction, and diffusion, respectively:

$$\left.\begin{aligned} M\hat{H}-\lambda(\mathrm{d}T/\mathrm{d}Z)+n\sum_j H_j x_j V_j &= M\lim_{Z\to\infty}\hat{H} \\ \hat{H} = m^{-1}\sum_j H_j x_j &= \text{enthalpy/g.} \end{aligned}\right\} \tag{15·5}$$

The following ratios have been computed to determine the relative importance of the three processes using only dimensionless parameters:

$$\left.\begin{aligned} r_c &\equiv \frac{\text{convection term}}{\text{conduction term}} = \frac{M\hat{H}}{\lambda(\mathrm{d}T/\mathrm{d}Z)} = [t+h(x_A+2x_B)]/F_t,\dagger \\ r_D &\equiv \frac{\text{diffusion term}}{\text{conduction term}} = \frac{n\sum_j H_j x_j V_j}{\lambda(\mathrm{d}T/\mathrm{d}Z)} = \frac{h[G_A+2G_B-(x_A+2x_B)]}{F_t}.\dagger \end{aligned}\right\} \tag{15·6}$$

(Although the enthalpy is defined only up to an arbitrary constant,

$$n\sum_j H_j x_j V_j = \sum_j n_j m_j \hat{H}_j V_j$$

is well defined since the V_j are diffusion velocities with respect to the mass average velocity. Thus $\sum_j n_j m_j V_j = 0$ [cf. Hirschfelder *et al.* 1954, p. 454].)

Consider first the comparative importance of convection and thermal conduction. Because of the assumed approach to thermal equilibrium, $\lim_{Z\to\infty} r_c = \infty$. For the *ABC* flame convection is more important than conduction for $(T-T_{\text{max.}}) \geqslant ca. -0{\cdot}014T_{\text{max.}}$. As figure 5 shows, the importance of convection decreases rapidly with decreasing T until the ratio has a value of a few per cent. Since the conduction term has a maximum, the ratio has a minimum. For 'heavy free radicals', a 600-fold change in the kinetic parameter ω never introduces more than 20 % variation in r_c. A minimum of about 0·022 occurs in all cases at $(T-T_{\text{max.}}) \simeq -0{\cdot}4T_{\text{max.}}$. For 'light free radicals', $(r_c)_{\omega=300}/(r_c)_{\omega=1}$ reaches values as large as $\simeq 2{\cdot}5$. In this case the minima shift drastically:

ω	minimum value	$(T-T_{\text{max.}})$
1	0·026	$-0{\cdot}22\,T_{\text{max.}}$
300	0·045	$-0{\cdot}46\,T_{\text{max.}}$

The shift can be interpreted in terms of the change in temperature gradient produced by free-radical diffusion as follows. Figures 3 and 4 show how the greater diffusion of light free radicals decreases the maximum in x_B and increases the values at lower temperatures. Figure 6 shows how for a fixed A_2 this is accompanied by a decrease in the maximum reduced

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† Cf. equations (8·4), (9·6) and (9·12). To obtain the equation for r_D, note that since all masses are the same, it follows from (14·3) that $nmV_j = M\{(G_j/x_j)-1\}$.

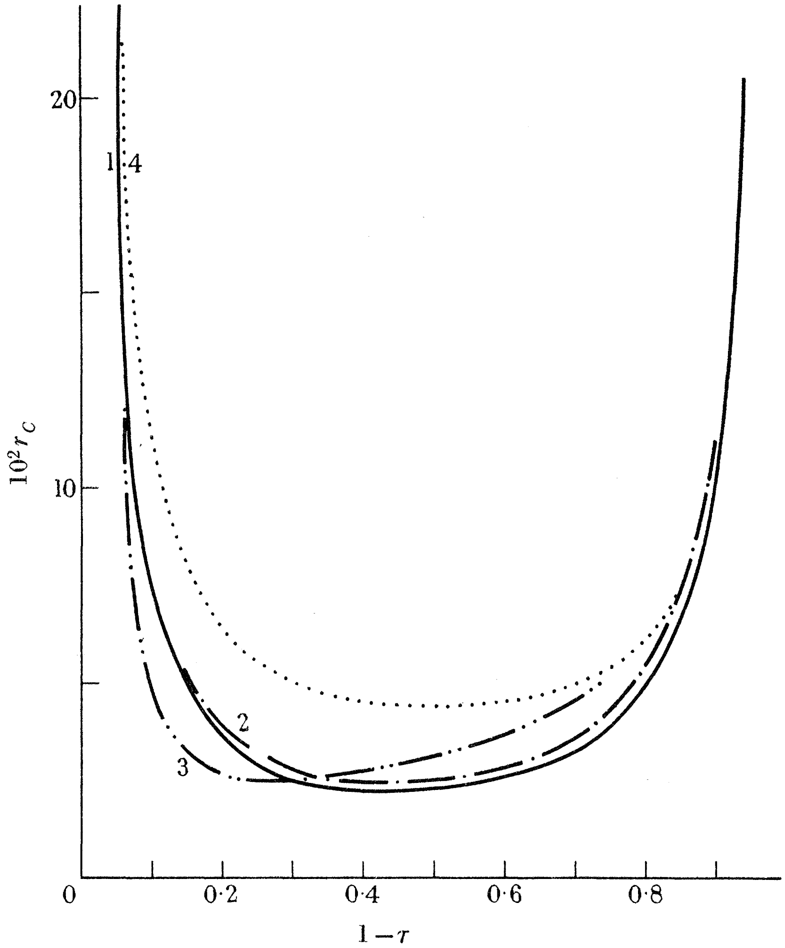

FIGURE 5. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 1$, set II; 4, $\omega = 300$, set II.

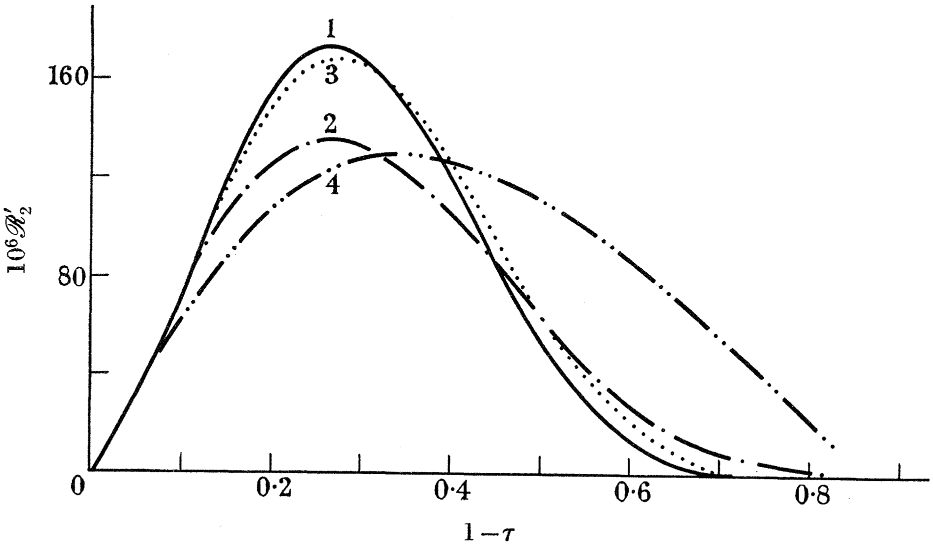

FIGURE 6. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 5$, set II; 4, $\omega = 300$, set II.

rate for the main combustion reaction. Figure 7 shows how this is reflected in a decrease in the maximum for the reduced temperature gradient and a shift in the maximum to lower temperatures. Since $M = \rho v$ is a constant (Hirschfelder *et al.* 1954, p. 454) and $\hat{H}$ varies much more slowly (cf. the discussion of Figure 9), the minimum or r_c increases and shifts to a lower temperature.

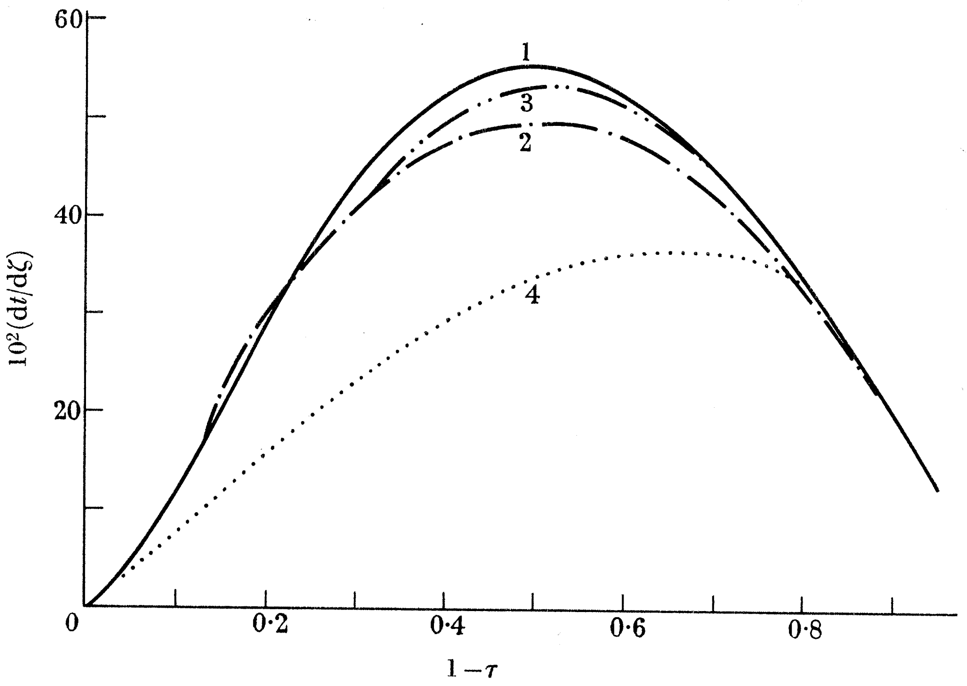

FIGURE 7. For a hard sphere model for which $\lambda(T_{\max.})/\lambda(T) = (1+t)^{-\frac{1}{2}}$. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 5$, set II; 4, $\omega = 300$, set II.

Next consider the relative importance of diffusion and thermal conduction. Hirschfelder (1960) has shown that when the approximations of equations (1·2–5) are used, the enthalpy per gram is constant ↔ all Lewis numbers are unity. Thus the processes of diffusion and thermal conduction are of equal importance $\leftrightarrow r_D = 1 \leftrightarrow$ the specific enthalpy is constant ↔ all Lewis numbers are unity. Thermal conduction will be the more important process $\leftrightarrow r_D < 1 \leftrightarrow \hat{H} > \lim_{Z\to\infty} \hat{H}$. Figure 8 of $(r_D - 1)$ shows the quantitative effect of non-unit Lewis numbers upon the relative importance of the two processes. With Lewis numbers for 'heavy free radicals', thermal conduction is the slightly more important process in the hot region for $\tau > ca.\, 0{\cdot}7$, and the less important process in the colder region. In any case, $|r_D - 1| < 0{\cdot}005$. Conversely, with Lewis numbers for 'light free radicals', diffusion is the more important process for $\tau > ca.\, 0{\cdot}7$, and thermal conduction dominates in the colder region. The approximate range for r_D is $0{\cdot}989 < r_D < 1{\cdot}16$. (Larger values which have been reported for a neighbourhood of $T_{\max.}$ are wrong because of errors in numerical integration in that region (Heinen 1962).)

Next consider whether a constant specific enthalpy approximation could be used to determine one mole fraction as a function of the others. In a theoretical study using a point-by-point numerical integration, this possibility depends upon how the error will grow. Since there has been no test of this growth, at the present it is only possible to calculate the relative error at a fixed point when the approximation is used to calculate the largest term in the enthalpy sum. The relative error for the *ABC* system is shown in figure 9 which gives

$$r_H = [\lim_{Z\to\infty} \hat{H} - \hat{H}]/\Delta H_+ = [x(t) - x_A - 2x_B]/x(t), \tag{15·7}$$

where $x(t) = [x_A(t=0) + 2x_B(t=0)] - h^{-1}t$ and $\Delta H_+ =$ sum of the positive terms in the enthalpy difference.

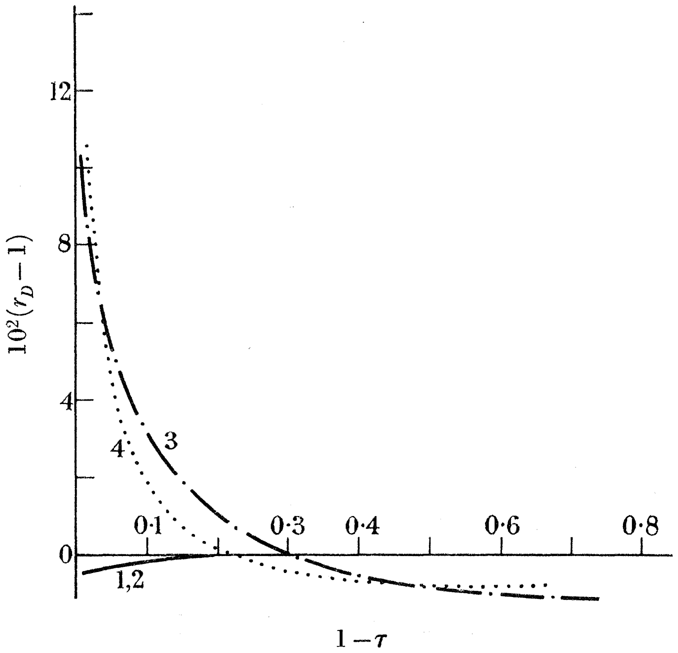

FIGURE 8. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 1$, set II; 4, $\omega = 300$, set II.

Figure 9 can be interpreted in terms of physical processes as follows. Let x_A^N, x_B^N be mole fractions in a 'normal' *ABC* flame with all unit Lewis numbers so that $r_H = 0$. (15·8)

Inspection of the steps in the calculation showed that the leading digit of r_H is determined wholly (primarily) by the difference $(x_A - x_A^N)$ in that case where diffusion coefficients have values for 'light' ('heavy') free radicals. Thus for 'light' ('heavy') free radicals

$$x_A < x_A^N \, (x_A > x_A^N)$$

in the neighbourhood of the hot boundary. This is correlated with the fact that a shift to 'light' free radicals spreads the main combustion reaction to lower temperatures (cf. figure 6) and decreases the eigenvalue μ^*. This, in turn, is associated with a lower G_A, and therefore a lower $|\mathrm{d}x_A/\mathrm{d}t|$ in the neighbourhood of $T_{\text{max.}}$ for 'light' free radicals. At lower temperatures, the decrease in $\mathrm{d}t/\mathrm{d}\zeta$ due to lower $G_A(t)$ causes a shift so that

$$|\mathrm{d}x_A/\mathrm{d}t| > |\mathrm{d}x_A^N/\mathrm{d}t|,$$

and, ultimately, $x_A > x_A^N$.

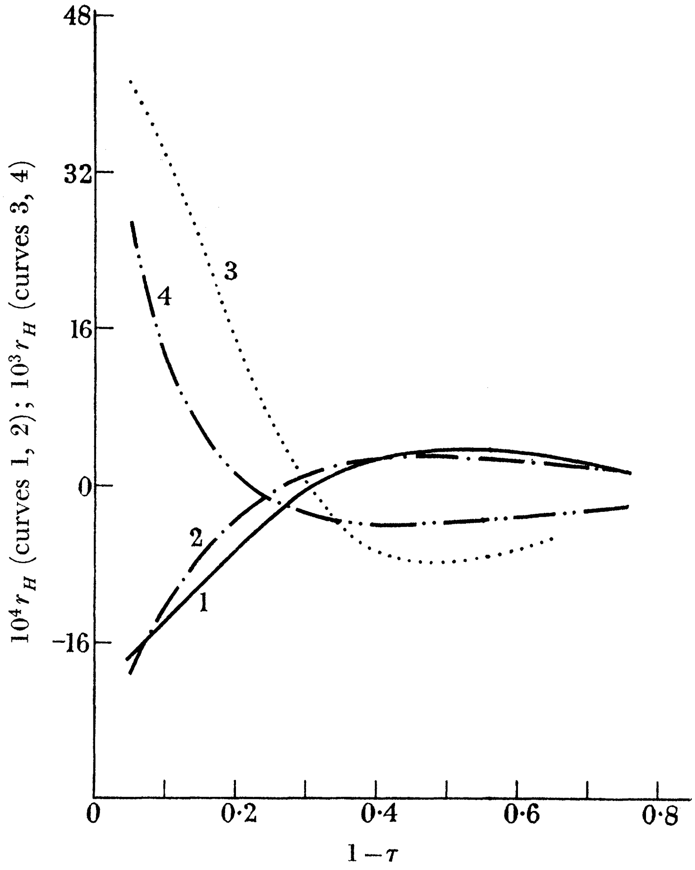

FIGURE 9. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 1$, set II; 4, $\omega = 300$, set II.

16. THE IGNITION TEMPERATURE CONCEPT

Data from the *ABC* flame show that the assumption of an ignition temperature, T_i, introduces two serious errors. Two common suggestions for T_i are: (*a*) $T_i \simeq 0{\cdot}6T_{\mathrm{max.}}$ or $t_i = -0{\cdot}4$; (*b*) $t_i = t(Z_0)$, $Z_0 \equiv$ inflexion point. Thus, use of table 3 shows that $-0{\cdot}55 \leqslant t_i \leqslant -0{\cdot}4$ for these choices. The first error—the assumption that no significant chemical reaction occurs below t_i—is shown by $1-G_A(t_i)$ since $\mathrm{d}G_A/\mathrm{d}Z = m_a R_A^n/M$. $G_A(-0{\cdot}4) = 0{\cdot}90\,(0{\cdot}75)$ for 'heavy' ('light') free radicals and table 3 gives $G_A[t(Z_0)]$. The second error—the inadequacy of an average reaction rate—is shown as follows. The ratio of the exponential factor in a specific rate at $T_{\mathrm{max.}}$ to that at T_i is

$$\exp\left[(-\Delta E/RT_{\mathrm{max.}})\,(t_i/[1+t_i])\right].$$

TABLE 3. INFLEXION POINT FOR $t(Z)$

For definition of 'light' and 'heavy' free radicals see appendix F.

	'light' free radicals		all unit Lewis numbers		'heavy' free radicals	
ω	$-t$	G_A	$-t$	G_A	$-t$	G_A
1	0·455	0·958	0·447	0·951	0·447	0·951
50	0·511	0·902	0·463	0·948	0·455	0·950
100	0·527	0·873	0·463	0·936	0·455	0·944
300	—	—	0·479	0·916	0·463	0·931
600	—	—	0·495	0·901	0·471	0·915
1000	—	—	0·511	0·892	—	—

Thus for $-0{\cdot}4 \geqslant t_i \geqslant -0{\cdot}55$, $\exp(0{\cdot}67\Delta E/RT_{\text{max.}}) \leqslant \text{ratio} \leqslant \exp(1{\cdot}2\Delta E/RT_{\text{max.}})$ so that for the reasonable value $\Delta E/RT_{\text{max.}} \simeq 5$, $27 \leqslant \text{ratio} \leqslant 400$.

17. ENERGY TRANSPORT BY FREE RADICALS

Since free radicals are highly energetic species, Bartholomé (1950) suggested that they might play an important role in energy transport from the hot gases to incoming fuel by carrying energy to be released upon recombination. Figure 10 gives the ratio of the heat released by the free-radical reaction (1) for the ABC flame to the total release:

$$-(\mathscr{R}_1\,\omega^{-1})/(\mathscr{R}_2' - \mathscr{R}_1\,\omega^{-1}).$$

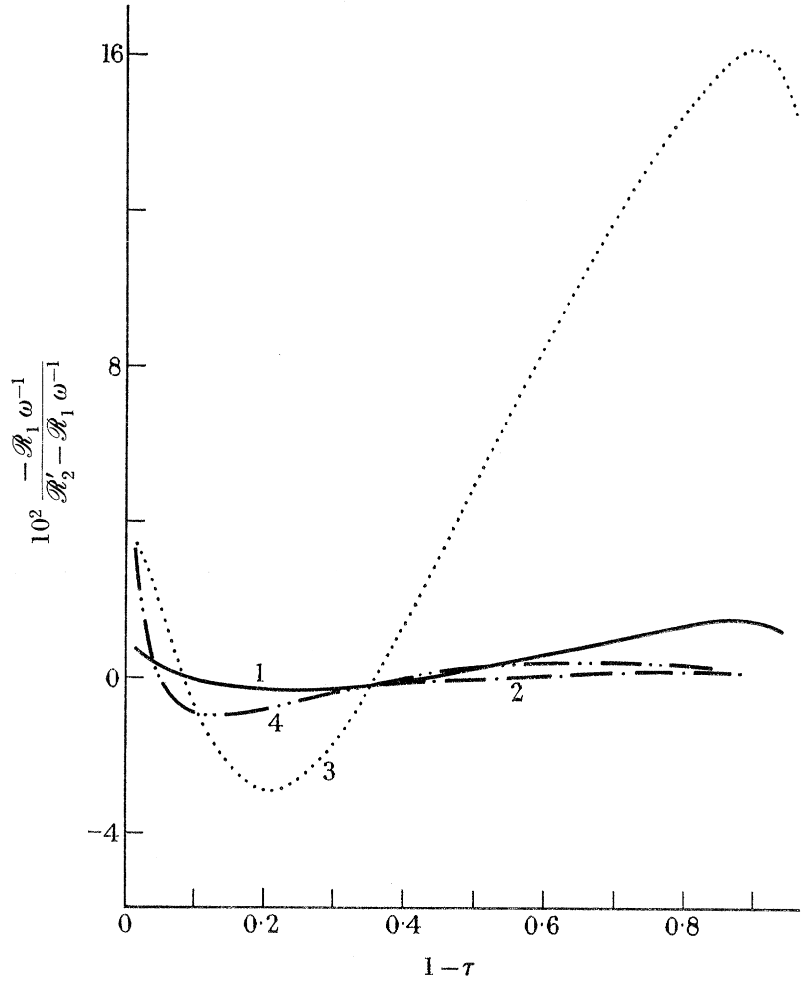

FIGURE 10. Curve 1, $\omega = 1$, set I; 2, $\omega = 600$, set I; 3, $\omega = 5$, set II; 4, $\omega = 300$, set II.

Comparison with figure 6 for $\mathscr{R}_2'$ shows that the increase in free-radical concentration in the colder region (with an increase in ω or a shift to Lewis numbers for 'light' free radicals) increases the volume rate of heat release for both reactions. Whereas the relative contribution of the free-radical reaction increases with a shift to Lewis numbers for 'light' free radicals, it decreases with an increase in ω. Nevertheless, the relative contribution of the free-radical reaction is at most *ca.* 1·5 % for 'heavy' free radicals and for 'light' free radicals it only reaches as much as 16·5 % near the cold boundary when $\omega = 5$. It is still necessary to examine other flames with more energetic free radicals to determine whether in such cases energy transport by free radicals might be significant.

18. Cold boundary conditions: the Hirschfelder–Curtiss model for the flame holder

This section has three purposes: (*a*) to show why the Hirschfelder–Curtiss model requires a non-vanishing temperature gradient; (*b*) to give a rigorous equation which proves that a constant enthalpy flame must have a discontinuity in the x_i; (*c*) to point out that other possible idealizations have features which are at least as artificial.

Consider, therefore, possible idealizations for a physical flame which is finite and not perfectly pre-mixed, in which some product does diffuse into the fuel gas. One way to obtain a definite mathematical problem including back diffusion would be to idealize the finite flame to an infinite flame with an asymptotic approach to pure fuel as $Z \to -\infty$. However, such an idealization would require replacing the actual specific rates by zeros for some temperature greater than $T(Z_{\text{cold}})$. Otherwise the reaction would all vanish to minus infinity. Thus it was at least as realistic for Hirschfelder and Curtiss to ignore back diffusion and to assume a perfectly pre-mixed fuel. Then the equation $\mathrm{d}G_\alpha/\mathrm{d}Z = m_\alpha R^n_\alpha/M$ led to two types of boundary conditions:

(*a*) Since $R^n_\alpha \neq 0$ for any fuel molecules and $\mathrm{d}T/\mathrm{d}Z$ is in general positive, the flame variables cannot be well-behaved functions of T unless

$$\lim_{Z \to Z^+_{\text{cold}}} (\mathrm{d}T/\mathrm{d}Z) > 0. \tag{18·1}$$

(Note that despite the fact that $T(Z_{\text{cold}})$ is an ordinary point, some arguments about the character of the mathematical problem have incorrectly treated it as a singular point.)

(*b*) In lieu of a catalytic surface, $G_\alpha(Z)$ must be continuous:

$$G_\alpha(Z_{\text{cold}}) = \lim_{Z \to Z^-_{\text{cold}}} m_\alpha x_\alpha/m. \tag{18·2}$$

The existence of the discontinuity can now be established. Substitution of equation (18·2) and of the similar equation for the approach to diffusion equilibrium at the hot boundary into equation (1·4) gives

$$\begin{aligned}\lim_{Z \to Z^+_{\text{cold}}} \lambda M^{-1}(\mathrm{d}T/\mathrm{d}Z) &= \lim_{Z \to Z_{\text{cold}}} \sum_\alpha [H_\alpha G_\alpha/m_\alpha - \lim_{Z\to\infty} H_\alpha G_\alpha/m_\alpha] \\ &= \sum_\alpha H_\alpha(Z_{\text{cold}}) \lim_{Z \to Z^-_{\text{cold}}} (m_\alpha x_\alpha/m) - \lim_{Z\to\infty} m^{-1} \sum_\alpha H_\alpha x_\alpha).\end{aligned} \tag{18·3}$$

Now, according to § 15, the specific enthalpy is constant when all Lewis numbers are unity:

$$\lim_{Z\to\infty} \sum_\alpha H_\alpha x_\alpha/m = \sum_\alpha H_\alpha(Z_{\text{cold}}) \lim_{Z \to Z^+_{\text{cold}}} (x_\alpha/m). \tag{18·4}$$

Substitution of equations (18·1, 4) into (18·3) gives

$$0 < \lim_{Z \to Z^+_{\text{cold}}} \lambda M^{-1}(\mathrm{d}T/\mathrm{d}Z) = \sum_\alpha H_\alpha(Z_{\text{cold}}) [\lim_{Z \to Z^-_{\text{cold}}} (x_\alpha/m) - \lim_{Z \to Z^+_{\text{cold}}} (x_\alpha/m)]. \tag{18·5}$$

This proves that the Hirschfelder-Curtiss model requires a discontinuity in the mole fractions whose magnitude is determined by the temperature gradient assumed. However, because the rates are so many orders of magnitude smaller at the lower temperature of the flame holder, it has been possible to choose $(\mathrm{d}T/\mathrm{d}Z)$ to satisfy two criteria:

(*a*) $\mathrm{d}T/\mathrm{d}Z$ is sufficiently large that for a fixed interval

$$[t_{\text{cold}}, t'] \quad \text{about} \quad t_{\text{cold}}, \quad \int_{t_{\text{cold}}}^{t'} (\mathrm{d}G_\alpha/\mathrm{d}t)\,\mathrm{d}t$$

makes no significant contribution to the total integral. Thus the solutions are comparatively insensitive to variations of $(\mathrm{d}T/\mathrm{d}Z)_{Z_{\text{cold}}}$ over an interval which excludes a neighbourhood of zero.

(*b*) The fractional discontinuity of the x_α is less than a part per hundred thousand (and therefore, less than the usual probable integration error in G_α).

Appendix A. Mathematical instability of the flame equations

First it will be shown that the linear equations derived from (1·1–4) by including only the first order terms in the Taylor series of the $F_j(\mathbf{u})$ at $Z = Z_0$ are mathematically unstable in Henrici's (1961) sense. Then evidence will be presented for the conclusion that the non-linear equations have the same instability. Let

$$\left.\begin{array}{l} [\mathrm{d}y/\mathrm{d}Z] = A[y]+[F^0] \\ \text{where} \\ \quad [y] \text{ is the } n\text{-rowed one-column matrix whose } j\text{th element is } y_j(Z); \\ \quad A \text{ is the matrix such that } A_i^j = (\partial F_j(\mathbf{u})/\partial u_i)_{\mathbf{u}(Z_0)}; \\ \quad [F^0] \text{ is the one-column matrix whose } j\text{th element is the constant, } F_j[\mathbf{u}(Z_0)]; \\ \text{and} \\ \quad y_j(Z_0) = 0. \end{array}\right\} \qquad (\text{A } 1)$$

If the set of flame variables has been chosen to be functionally independent, A will be non-singular. In this case the translation

$$[y] = [Y] - A^{-1}[F^0] \qquad (\text{A } 2)$$

gives the form

$$[\mathrm{d}Y/\mathrm{d}Z] = [\mathrm{d}y/\mathrm{d}Z] = A[Y]. \qquad (\text{A } 3)$$

For simplicity consider the case in which the nth order characteristic equation

$$|A_i^j - \alpha\delta_i^j| = 0 \qquad (\text{A } 4)$$

has n simple non-vanishing roots. In this case any $(n-1)\times(n-1)$ submatrix of $(A-\alpha I)$ will be non-singular and the general solution of equation (A 3) with n arbitrary constants can be written in the form

$$\left.\begin{array}{l} [Y(Z)] = U(Z)\,[\mathbf{N}] \\ \text{where} \\ \quad U(Z) \text{ is the matrix whose } j\text{th column } [\mathbf{U}_j(Z)] = [\mathbf{U}_j \exp\{\alpha_j(Z-Z_0)\}], \text{ where} \\ \quad\quad [\mathbf{U}_j] \text{ is the unit eigen vector for the root, } \alpha_j; \\ \quad [\mathbf{N}] \text{ is an arbitrary } n\text{-rowed one-column matrix.} \end{array}\right\} \qquad (\text{A } 5)$$

Since a standard theorem (Smirnov 1961) states that $U(Z_0)$ is non-singular whenever all the roots of equation (A 4) are distinct, $[\mathbf{N}]$ is determined uniquely by the boundary conditions

$$A^{-1}[F^0] = [Y(Z_0)] = U(Z_0)\,[\mathbf{N}]. \qquad (\text{A } 6)$$

In the cases which have been examined, the characteristic equation for the linearization (A 3) has had L negative roots:

$$\alpha_L < \alpha_{L-1} < \ldots < \alpha_1 < 0, \; L \text{ being the number of linearly independent } G_j. \qquad \text{(A 7)}$$

Whenever there is a species whose mole fraction approximately follows the kinetic steady state far more closely than the mole fractions of other species do, $|\alpha_L|$ has been orders of magnitude greater than $|\alpha_1|$. The argument is now parallel to that for examples considered by Fox & Mitchell (1957). Suppose that initial conditions (A 6) define a solution corresponding to $\exp[\alpha_1(Z-Z_0)]$. Then any arbitrarily small alteration in these initial conditions which introduces a component corresponding to $\exp[\alpha_L(Z-Z_0)]$ will give a solution which diverges drastically from the first as Z decreases from Z_0. For this reason, Henrici (1961) calls such systems mathematically unstable. Since the characteristic equation (A 4) in general also has positive roots of very different magnitude, the system is also mathematically unstable for integration as Z increases from $Z_0 = 0$. Since any numerical solution must introduce alterations in values, the desired solution to the linear system (A 3) can be dominated by the other components.

The following arguments, based on numerical studies, support the conclusion that the original non-linear system (1·1–4) has the same sort of mathematical instability as its linearization (A 3). First, in the cases which have been studied, it has been found that after all negative roots except α_1 have been removed by applying the kinetic steady-state approximation to one or two x_s, then the resulting equations have been integrated without difficulty in the direction of decreasing Z. Secondly, integrations of the complete equation system have been performed using the Runge–Kutta method which has been shown to be stable for sufficiently small interval sizes (Rutishauser, 1952). When the interval was sufficiently small to satisfy the restriction due to subtraction [cf. equation (3·1)], solutions which satisfy the central difference approximations to the derivatives at each point to 5 or 6 digits (or more) could be constructed. Nevertheless, alteration of the last of the eight digits carried caused positive (negative) divergence to switch to negative (positive) divergence and loss of the solution which fits the cold boundary conditions. Moreover, a switch from the Runge–Kutta to a second method of integration altered the starting values required to follow the central solution.

Appendix B. Concepts of ‘numerical determinancy’ and ‘correction terms’

Consider a compound function $H[\mathbf{w}(T)]$ subject to the equation

$$H[\mathbf{w}(T), T] = 0; \quad \mathbf{w} = \langle w_1, \ldots, w_m \rangle. \qquad \text{(B 1)}$$

By the implicit function theorem, if H has continuous first order partial derivatives at $\mathbf{w}^0$, and if $(\partial H/\partial w_m)_{\mathbf{w}^0} \neq 0$, then equation (B 1) defines a compound function $w_m(\mathbf{u})$ such that

$$\partial w_m/\partial u_j = -(\partial H/\partial w_j)/(\partial H/\partial w_m), \qquad \text{(B 2)}$$

$$u_j = w_j, \quad 1 \leqslant j \leqslant (m-1).$$

In this case, the limiting absolute value for the relative change in w_m induced by a change in w_j, for all other w_k fixed, is

$$\lim_{\Delta w_j \to 0} \left| \frac{(\Delta w_m/w_m)}{(\Delta w_j/w_j)} \right|_{\mathbf{w}^0} = \left| \frac{(\partial w_m/\partial u_j)\, w_j}{w_m} \right|_{\mathbf{w}^0} = \left| \frac{(\partial H/\partial w_j)\, w_j}{(\partial H/\partial w_m)\, w_m} \right|_{\mathbf{w}^0} \equiv d^0_{j,m}. \qquad \text{(B 3)}$$

The implicit equation (B 1) will be said to be a numerically determinate equation for $w_m \leftrightarrow s$ or fewer digits for each w_j, $1 \leqslant j \leqslant (m-1)$, determine an s digit value for w_m. Thus

$$\text{equation (B 1) is a numerically determinate implicit equation for } w_m \leftrightarrow \text{for each } j,\ d^0_{j,m} \leqslant c \tag{B 4}$$

c: a constant of the order of unity.

Furthermore, a variable $w_{j'}$ will be said to enter as a correction term $\leftrightarrow$ the limit as $\Delta w_{j'} \to 0$ of the relative change in w_m to the relative change in $w_{j'}$ is less than unity. Thus:

$$w_{j'} \text{ enters (B 1) as a correction term} \leftrightarrow d^0_{j',m} < 1. \tag{B 5}$$

APPENDIX C. EQUATIONS FOR THE FIRST APPROXIMATION, $k = 1$

This discussion will use symbols defined in § 4. It is convenient to use power series coefficients rather than derivatives since the formulae for products are simpler. Let

$$F \text{ be any differentiable variable or expression;} \tag{C 1}$$

$(F)_m \equiv (m!)^{-1}\,(\mathrm{d}^mF/\mathrm{d}t^m)$, the mth order power series coefficient;

$C[F]$: a symbol used to designate a convenient computational unit which occurs as a coefficient of F. $C[F; y, w]$ will be used when an explicit statement that $C[F]$ is a function of y and w is desired.

The equation for R^n_s is used as an implicit equation for x_s which is numerically determinate since x_s occurs as a factor of R^C_s and R^P_s depends only weakly on x_s through the relation, $\sum\limits_j x_j = 1$. R^n_s enters as a correction term since by hypothesis the method is to be applied for sufficiently small deviations from the kinetic steady state. In computational units, the equation for $x_s(\{x\}^{N-1}_s, R^n_s, t)$ is

$$\sum_\nu C[X_\nu; t]\, X_\nu - R^n_s = 0; \quad X_\nu = \prod_{j=1}^{N} x_j^{\nu_j},$$

where

$C[X_\nu; t]$ is the linear combination of specific rates which multiplies X_ν when R^C_s, R^P_s are rewritten in terms of the linearly independent mole fractions in $\{x\}^N$. (C 2)

The linear equation (C 6) for $G_s(\{x\}^N, \{G\}^{L-1}_s, (R^n_s)_1, t)$ is derived by the following steps: (a) differentiate (C 2) and multiply by $M^{-1}(\mathrm{d}t/\mathrm{d}Z)$ to obtain (C 3); (b) rewrite $M^{-1}F_{x_j}$ and $M^{-1}\,(\mathrm{d}t/\mathrm{d}Z)$ as functions of the elements of $\{x\}^N$, $\{G\}^L$ in equations (C 4, 5); (c) regroup the terms:

$$\sum_{j=1}^{N} C[M^{-1}F_{x_j}]\, M^{-1}F_{x_j} + C[M^{-1}(\mathrm{d}t/\mathrm{d}Z); \{x\}^N, t, (R^n_s)_1]\, M^{-1}(\mathrm{d}t/\mathrm{d}Z) = 0, \tag{C 3a}$$

$$C[M^{-1}F_{x_j}] = \sum_\nu C[X_\nu]\, \nu_j \prod_{k=1}^{N} x_k^{(\nu_k - \delta^j_k)}, \tag{C 3b}$$

$$C[M^{-1}(\mathrm{d}t/\mathrm{d}Z)] = -(R^n_s)_1 + \sum_\nu (C[X_\nu])_1\, X_\nu. \tag{C 3c}$$

$$M^{-1}F_{x_j} = \sum_{p=0}^{L} \sum_{q=0}^{N} C^j[G_p x_q; t]\, G_p x_q, \tag{C 4a}$$

$C^j[G_p x_q]$: the linear combinations of the $(nD_{ij})^{-1}$ which occur as coefficients of $(G_p x_q)$ when F_{x_j} is written as a function of the elements of $\{x\}^N, \{G\}^L$ (C 4*b*)

$$G_0 \equiv x_0 \equiv 1 \quad \text{(for symmetry)}. \tag{C 4c}$$

$$M^{-1}F_T = \lambda^{-1} \sum_{p=0}^{L} \mathscr{L}_p(t)\, G_p \tag{C 5a}$$

where

$\mathscr{L}_p(t)$ is the linear combination of the H_j which arises when $M^{-1}\lambda(\mathrm{d}t/\mathrm{d}Z)$ is written as a function of the elements of $\{G\}^L$, (C 5*b*)

$$\sum_{p=0}^{L} C[G_p]\, G_p = 0, \tag{C 6a}$$

$$C[G_p] = \sum_{j=1}^{N} C[M^{-1}F_{xj}] \sum_{q=0}^{N} C^j[G_p x_q]\, x_q + C[M^{-1}(\mathrm{d}t/\mathrm{d}Z); \{x\}^N, t, (R_s^n)_1]\, \lambda^{-1} \mathscr{L}_p(t). \tag{C 6b}$$

Equation (C 6) has been found to be numerically determinate for G_s and it is reasonable to expect this to be generally true since: (1) (C 2) can be expected to be numerically determinate for F_{x_s} as x_s is a factor of R_s^C; (2) it follows from the form of the diffusion equations (1·3) that F_{x_s} is numerically determinate for G_s.

Differentiation of (C 6) and multiplication by $M^{-1}F_t$ gives the second order differential equation in R_s^n:

$$[M^{-1}F_t] \sum_{p=0}^{L} (C[G_p])_1\, G_p + M^{-2} \sum_{q=0}^{L} C[G_p]\, m_p R_p^n = 0. \tag{C 7}$$

To minimize subtraction in (C 7), each R_P^n should be written as a combination of R_s^n plus net rates for elementary reactions. For example, three reactions have been used for an O_3 flame: (1) $O_3 + M \rightleftharpoons O_2 + O + M$; (2) $O_3 + O \rightleftharpoons 2O_2$; (4) $2O + M \rightleftharpoons O_2 + M$. In the neighbourhood of $T_{\text{max.}}$ where $R_{O_3}^n \ll R_O^n$, it is desirable to write $R_O^n = -R_{O_3}^n - 2(R_2 + R_4)$.

On the basis of the following argument it is plausible to expect that in general $(R_s^n)_1$, $(R_s^n)_2$ will enter (C 6, 7) as correction terms: (1) the shape of $R_s^n(t)$ can be expected to be invariant with d_s^P (as it is for the flame of part II); (2) since $(d_s^P \to 0) \to (R_s^n \to 0)$, step (1) implies that $(R_s^n)_1$, $(R_s^n)_2 \to 0$.

Appendix D1. Solution of the differential equations

No method which uses higher derivatives (as the Taylor series does) should be used since the relative error due to the approximation (4·3) in general increases with the order of the derivative. In most cases, a stable explicit method of numerical integration such as one of the Runge–Kutta methods has the following advantages: (1) it is self-starting; (2) the interval size can be readily increased and then decreased again as T decreases; (3) all of the G_j and x_j, $j \neq s$, which occur in equation (4·4) are known. The major disadvantage of the Runge–Kutta procedure is that the necessity of solving equations (4·4*b*, *c*) at each substitution level can require tenfold or more computing time than is needed for a stable implicit method. The latter methods have, however, the following disadvantages: (1) they require a separate program to start the integration; (2) it is difficult to decrease the interval size when required; (3) as d_s^p increases, these methods can require even more time than a Runge–Kutta. Studies have shown that the increase in time is due to: (*a*) the necessity for simultaneously solving for all x_j, G_j which are all unknown; (*b*) the increased coupling between the algebraic and differential equations. A method developed by Nordsieck (1962) should be tried in future studies since it appears to possess advantages of both methods: (1) it is self-starting; (2) it allows for automatic change of interval size; (3) it is stable; (4) although it is an implicit method it can be used with only two substitutions per step.

Appendix D2. Solution of the algebraic equations

If the set (4·4*b*, *c*) is quasilinear (as it was for the flame of part II), it can be solved iteratively by solving the linearized approximation, substituting the result in the non-linear terms and repeating the process until no further change occurs. When this is not the case, a procedure similar to the one used for the O_3 flame can be applied as follows: (*a*) use a numerical integration or other suitable extrapolation formula to predict the values for x_s, G_s, $(R_s^n)_j, j \leqslant g$; (*b*) to start a cycle, set a counter $p = 0$ and compute in order of increasing j, $(R_s^n)_j, j \leqslant p$. Repeat the cycle over j until a consistent set of values is obtained; (*c*) if $p < g$, replace p by $(p+1)$, calculate $(R_s^n)_{p+1}$ and then repeat (*b*) until all change is within pre-assigned error bounds.

Appendix E. Techniques for numerical differentiation

Extensive calculations by Schalit (1961) and Heinen (1962) have led to the following conclusions about the methods which should be used in differentiating R_s^n over $[T', T'']$, where $T_{\text{max.}} > T'' > T' > T_{\text{cold}}$.

(1) *Construction of second derivatives.* Numerical approximations for second derivatives can be constructed in the two following ways: (1) form a finite difference approximation beginning with the second difference at the point; (2) first form finite difference approximations to first derivatives at an equally spaced sequence of points and then form the finite difference approximation to the derivative of these first derivatives. The second procedure is preferable since it will use function values at points spaced over a wider interval and will, in general, involve less of a loss in accuracy due to subtraction of significant digits.

(2) *Use of forward and backward difference formulae.* These formulae introduce such a serious error growth when they are used at successive k levels that they should be used for as few points as possible at the beginning and end of the range of integration.

(3) *Use of central difference formulae.* The error growth with repeated use at successive k levels is less rapid than for forward or backward difference formulae. However, as k is increased, the increasing error in higher differences works down to second differences. The maximum k before this occurs depends upon d_s^p. In one case, it occurred at $k = 4$. This error build-up limits the number of k levels which can be run. Nevertheless, the central-difference formulae must be used to obtain data for points not covered by (2) or (4).

(4) *Use of least squares polynomials.* In any finite difference method, the derivative at each T is calculated using a different set of data points. This results in a lack of smoothness in

higher differences in the input for the second of the sequence of levels of successive approximation. This initial error and the error growth can be reduced by using a least squares polynomial of higher order for a wider range of data points and computing the derivatives for several points from the same polynomial. A least squares fit with polynomials of higher order (orders up to 11 were used) can be successful only if the polynomials are orthogonal with respect to the set of input points (Forsythe, 1957). Successful use requires attention to the following points:

(4*a*) *Use of a scaling function.* Let

$$\left.\begin{aligned} &P(Z) \text{ be a least squares polynomial;}\\ &E_j \equiv |f(Z_j)-P(Z_j)|/|f(Z_j)|, \text{ the relative error at } Z_j.\end{aligned}\right\} \tag{E 1}$$

If E_j and E_k are to make the same contribution to a least squares sum which depends upon absolute error, then

$$|f(Z_j)\,E_j|^2 = |f(Z_k)\,E_k|^2 \rightarrow E_j/E_k = |f(Z_k)/f(Z_j)|. \tag{E 2}$$

Since relative rather than absolute errors are of interest, it is desirable to reduce the exponent range of the input function values. It has been found that the variation in exponent of R^n_s can be reduced satisfactorily by using an idealized relative deviation, $d^P_{s,0} \equiv R^n_s/R^P_{s,0}$, where $R^P_{s,0}$ is an idealized rate of production which can be computed using the results from the kinetic steady-state hypothesis and unit Lewis numbers. For a three-component flame, this is particularly advantageous since this makes all mole fractions explicit functions of temperature (cf. §§ 10, 15). Since $d^P_{s,0}$ can be fitted by a least squares polynomial, P_r, which can be differentiated numerically and since $\mathrm{d}R^P_{s,0}/\mathrm{d}t$ can be calculated from its analytic formula, $\mathrm{d}R^n_s/\mathrm{d}t$ can be computed as

$$\mathrm{d}R^n_s/\mathrm{d}t = P_r(\mathrm{d}R^P_{s,0}/\mathrm{d}t) + R^P_{s,0}(\mathrm{d}P_r/\mathrm{d}t). \tag{E 3}$$

Note that it is desirable to scale the independent variable by using a reduced temperature such as t or τ of (8·2, 3).

(4*b*) *Use of overlapping intervals.* Suppose that the input function values have been scaled so that they are all of the same magnitude and that they are distributed with an approximately constant density. Then the error in the derivative can be an order of magnitude greater for a point near either end of the input data range than for a point near the centre. Heuristically, this is clear from the observation that: (*a*) the data points do not specify the behaviour of the function outside the range of input points; (*b*) the least squares criterion will minimize the error in fitting those points near the centre of the range. Thus, if a separate polynomial were determined for each of a sequence of intervals

$$([T_1, T_2],\ [T_2, T_3],\ [T_3, T_4], \ldots),$$

there could be much greater error and lack of smoothness at the junction points, $T_2, T_3, \ldots$. This can be reduced by fitting polynomials to data on overlapping intervals as follows. Let the jth polynomial be fitted to data points covering an interval $[T^i_j, T^f_j]$ where $T^i_{j+1} < T^f_j$. Then the jth polynomial should be used to compute over an interval, $[\tilde{T}^i_j, \tilde{T}^f_j]$, where

$$T^i_j < \tilde{T}^i_j < T^i_{j+1} < \tilde{T}^f_j < T^f_j; \quad \tilde{T}^f_j = \tilde{T}^i_{j+1}. \tag{E 4}$$

(4*c*) *Assembly of the polynomial.* The standard theorem that the error is a non-increasing function of the order of the least squares polynomial will not hold if non-orthogonal polynomials are used on computing machines which operate with truncated numbers. Moreover, if orthogonal polynomials are used, they must not be reassembled for economy in evaluating function values or derivatives. Otherwise, the subtraction involved in calculating the coefficients of the single reassembled polynomial can lead to an increase in numerical error as the order of the least squares approximation is increased.

Appendix F. Numerical values of the parameters

The following values have been selected:

$a = \Delta E/(RT_{\text{max.}}) = Q/(RT_{\text{max.}}) = 4{\cdot}5882\,98828$. (This is based on a related value used in previous studies of this system. There is no particular reason for choosing exactly this number. However, it is in a reasonable range, since if $T_{\text{max.}} = 3000\,°\text{K}$, $\Delta E/R \simeq 1{\cdot}4 \times 10^4$ degrees.)

$h = Q/(CT_{\text{max.}}) = 0{\cdot}91765\,97656$. (This is the value $h = a(R/C)$, for $C = 5R$.)

$t_{\text{cold}} \simeq -0{\cdot}90823\,4038$. (This corresponds to $\mathrm{d}T/\mathrm{d}Z = 0$ [cf. § 18].)

Lewis numbers for 'heavy' free radicals: $\delta_{AC} = 1$, $\delta_{BA} = \frac{1}{2}$, $\delta_{BC} = \frac{2}{3}$.

Lewis numbers for 'light' free radicals: $\delta_{AC} = 1$, $\delta_{BA} = 20/3$, $\delta_{BC} = 10$.

Although the foregoing Lewis numbers would not be expected for species of the same mass, it seemed desirable to ignore this inconsistency in order to test the significance of binary diffusion coefficients using this simple equation system.

Appendix G. Existence of a single internal maximum in x_s for an intermediate species, s

In general, the rate of production of s will be a sum of bimolecular rates:

$$R_s^P = \sum_{\{\langle j,k\rangle\}} R^P_{\langle j,k\rangle}; \quad R^P_{\langle j,k\rangle} = f^P_{\langle j,k\rangle}\, x_j\, x_k \quad (j \neq s, k \neq s). \tag{G 1}$$

Therefore, the derivative of R_s^P can be written as a sum

$$\left.\begin{aligned} \mathrm{d}R_s^P/\mathrm{d}t &= \sum_{\{\langle j,k\rangle\}} R^P_{\langle j,k\rangle} C_{\langle j,k\rangle}; \quad C_{\langle j,k\rangle} = C^t_{\langle j,k\rangle} + C_j + C_k; \\ C^t_{\langle j,k\rangle} &= (\mathrm{d}f^P_{\langle j,k\rangle}/\mathrm{d}t)/f^P_{\langle j,k\rangle}; \quad C_j = (\mathrm{d}x_j/dt)/x_j; \quad C_k = (\mathrm{d}x_k/\mathrm{d}t)/x_k. \end{aligned}\right\} \tag{G 2}$$

Since each $R^P_{\langle j,k\rangle} > 0$, $\mathrm{d}R_s^P/\mathrm{d}t$ can be negative only if some $C_{\langle j,k\rangle}$ is.

The following steps show that while $C_{\langle j,k\rangle}$ can be expected to be everywhere positive if both j and k are product molecules, it should be positive at lower and negative at higher temperatures whenever at least one of the species is a fuel molecule or an intermediate which has a single internal maximum in x_s and for which R_s^P is of the same order as R_s^C at higher temperatures.

(a) Typical free-radical production reactions have a sufficiently large positive activation energy that $C^t_{\langle j,k\rangle}$ is everywhere positive and decreases with increasing t approximately as T^{-2}:

$$C^t_{\langle j,k\rangle} = (\mathrm{d}f^P_{\langle j,k\rangle}/\mathrm{d}t)/f^P_{\langle j,k\rangle} \simeq (\Delta E_{\langle j,k\rangle}/RT)\,(T_{\text{max.}}/T). \tag{G 3}$$

(b) In those cases which have been studied, $x_j(t)$ for either a product or a fuel molecule is slowly varying and over most of the flame is of the order of the average value

$$\begin{aligned} [x_j(t_{\text{cold}}) - x_j(t=0)]/t_{\text{cold}} &\simeq [x_j(t=0) - x_j(t_{\text{cold}})] \\ &\simeq \{j = \text{product: } +x_j(t=0);\, j = \text{fuel: } -x_j(t_{\text{cold}})\}. \end{aligned} \tag{G 4}$$

(*c*) Consider the relative magnitudes. If $\Delta E \simeq 15$ Kcal., $T_{\text{cold}} \simeq 300^0$, and $T_{\text{max.}}$ had a very low value of 1000 °K, then $C^t_{\langle j,k\rangle}$ would decrease from $+25$ at T_{cold} to $+8$ at $T_{\text{max.}}$. For any fuel molecule, $x_j(T_{\text{max.}})$ should be at most of the order of 0·01 so that C_j would decrease from about -1 at T_{cold} to -100 at $T_{\text{max.}}$.

(*d*) Consider an intermediate with a single internal maximum for which R^P_s and R^C_s are of the same order in the high temperature region (e.g. Br for the reaction

$$H_2 + Br \rightleftharpoons HBr + H).$$

Then the following steps show that C_s can be expected to be $O(C_j)$ for the fuel molecule(s) involved in the dominant reaction(s) forming s: (*a*) $\mathrm{d}R^C_s/\mathrm{d}t$ is $O(\mathrm{d}R^P_s/\mathrm{d}t)$; (*b*) use an expression for $\mathrm{d}R^C_s/\mathrm{d}t$ analogous to (G 2); (*c*) observe that the specific rates for consumption reactions vary rather slowly with t and that the important high temperature reactions will involve s and product molecules.

Therefore, R^P_s can be expected to have a single internal maximum provided the dominant reactions involve either a fuel molecule *or* such an intermediate s. Furthermore, even when the Br_2 molecule in the H_2–Br_2 flame had a maximum in x_{Br_2} at about 600 °A due to the more rapid diffusion of the very light molecule, H_2 (Campbell 1957), C_{Br_2} and C_{H_2} were not large enough in this low temperature region to alter the conclusions. It is plausible to expect this to be true in general.

Whenever R^P_s has a single internal maximum, then in the limit as the kinetic parameters are varied to cause an approach to the kinetic steady state, the following steps show that x_s can also be expected to have a single internal maximum. (*a*) In general, any terms in R^C_s with x^3_s as a factor will be dominated by other terms so that the steady-state equation (2·1) is essentially a linear or quadratic equation in x_s in which the constant term, R^P_s, has a single internal maximum. (*b*) The root of a linear or quadratic equation is a monotone function of the constant. (*c*) The coefficients of x_s and of x^2_s can be expected to vary with temperature much more slowly than the constant.

The conclusion can be extended as the kinetic parameters are varied to cause increasing deviations from the kinetic steady state since: (*a*) any net rate of production due to chemical reactions in a time independent flame must be exactly balanced by a net rate due to diffusion and overall gas-flow; (*b*) § 11 shows that overall gas-flow appears to be rather insensitive to specific rates of reactions for intermediates; (*c*) diffusion reduces, but does not eliminate gradients.

APPENDIX H. THE IMPORTANCE OF THE VISCOSITY TERM IN THE ENERGY BALANCE EQUATION

In order to estimate the size of the viscosity term, it is convenient to use equation (15·2) to obtain

$$\frac{\mathrm{d}v}{\mathrm{d}Z} = -\frac{v}{\rho}\left(\frac{\mathrm{d}\rho}{\mathrm{d}Z}\right) = -\frac{v}{\rho}\left[m\left(\frac{1}{RT}\left(\frac{\mathrm{d}P}{\mathrm{d}Z}\right) - \frac{P}{RT^2}\left(\frac{\mathrm{d}T}{\mathrm{d}Z}\right)\right) + n\left(\frac{\mathrm{d}m}{\mathrm{d}Z}\right)\right]$$

$$= -v\left[\frac{\mathrm{d}\ln P}{\mathrm{d}Z} - \frac{\mathrm{d}\ln T}{\mathrm{d}Z} + \frac{\mathrm{d}\ln m}{\mathrm{d}Z}\right]. \qquad \text{(H 1)}$$

Now the following argument suggests that $(\mathrm{d}\ln P/\mathrm{d}Z)$ will be small compared with

$(\mathrm{d}\ln T/\mathrm{d}Z)$. The pressure difference across the flame front can be estimated from the fact that $\mathrm{d}v/\mathrm{d}Z \simeq 0$ at the flame holder. Thus, it follows from equation (15·3) that

$$P(Z_c) - \lim_{Z\to\infty} P \simeq -M^2[\rho^{-1}(Z_c) - \lim_{Z\to\infty} \rho^{-1}]. \tag{H 2}$$

If, for example, $P(Z_c) \simeq 1$ atm, $T(Z_c) \simeq 300\,°\mathrm{A}$, $T_{\mathrm{max.}} \simeq 2500\,°\mathrm{A}$; $M \simeq 1\,\mathrm{g\,cm^{-2}\,s^{-1}}$, $m \simeq 30$ g/mole, then $P(Z_c) - \lim_{Z\to\infty} P \simeq 6\times 10^3\,\mathrm{dynes/cm^2}$. Moreover, experimental measurements on some hydrocarbon flames at one atmosphere pressure (Lewis & von Elbe, 1951, p. 342) have given a similar pressure variation of the order of 0·1–1 mmHg. (See also Hirschfelder & Curtiss 1949, Appendix B.)

Furthermore, since

$$\frac{\mathrm{d}\ln m/\mathrm{d}Z}{\mathrm{d}\ln T/\mathrm{d}Z} = \frac{T}{m}\,\frac{\sum_i m_i\,\mathrm{d}x_i/\mathrm{d}Z}{\mathrm{d}T/\mathrm{d}Z} = \left(\frac{T}{T_{\mathrm{max.}}}\right)\sum_i \frac{m_i}{m}\,\frac{\mathrm{d}x_i}{\mathrm{d}t}, \tag{H 3}$$

it follows that $\mathrm{d}\ln m/\mathrm{d}Z$ should be at most of the order of $\mathrm{d}\ln T/\mathrm{d}Z$. Therefore the absolute value of the viscosity term should be at most of the order of

$$\left|(\tfrac{4}{3}\eta+\kappa)\,v\,\frac{\mathrm{d}v}{\mathrm{d}Z}\right| \simeq \left|(\tfrac{4}{3}\eta+\kappa)\,\frac{v^2}{T}\,\frac{\mathrm{d}T}{\mathrm{d}Z}\right| = \left(\frac{M^2}{4{\cdot}18\times 10^7\rho^2 T}\right)\frac{\mathrm{cal}}{\mathrm{deg\,C\,g}}\,(\tfrac{4}{3}\eta+\kappa)\,\frac{\mathrm{d}T}{\mathrm{d}Z}. \tag{H 4}$$

For dilute gases κ can be ignored. For an order of magnitude comparison with $\lambda\,\mathrm{d}T/\mathrm{d}Z$ it should be sufficient to use the relation for pure monatomic gases (Hirschfelder *et al.* 1954, p. 534):

$$\lambda \simeq \{(15/4)\;1{\cdot}98m^{-1}\,\mathrm{cal\;deg\,C^{-1}\,g^{-1}}\}\,\eta. \tag{H 5}$$

Even for $M \simeq 1\,\mathrm{g\,cm^{-2}\,s^{-1}}$, the viscosity term is only of the order of at most a fraction of a per cent of $\lambda\,\mathrm{d}T/\mathrm{d}Z$ for typical temperatures and densities.

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References

Bartholomé, E. 1950 *Z. Elektrochem.* **54**, 169.

Campbell, E. S. 1957 *Sixth International Symposium on Combustion*, p. 213. New York: Reinhold Publ. Corp.

Campbell, E. S. 1965*a* *Chem. Engng Sci.* **20**, 311–29.

Campbell, E. S. 1965*b* *Flame Combust.* **9**, 43–52.

Campbell, E. S. & Fristrom, R. M. 1958 *Chem. Rev.* **58**, 173.

Campbell, E. S., Heinen, F. J. & Schalit, L. M. 1963 *Ninth Int. Symp. Combustion*, p. 72. New York: Academic Press.

Campbell, E. S., Buehler, R., Hirschfelder, J. O. & Hughes, D. 1961 *J. Ass. Compt. Mach.* **8**, 374.

Campbell, E. S., Hirschfelder, J. O. & Schalit, L. M. 1959 *Seventh Int. Symp. Combustion*, p. 332. London: Butterworths.

Curtiss, C. F. & Hirschfelder, J. O. 1952 *Proc. Natn Acad. Sci. U.S.A.* **38**, 235.

Forsythe, G. E. 1957 *J. Soc. Ind. Appl. Math.* **5**, 2.

Fox, L. & Mitchell, A. R. 1957 *Quart. J. Mech. Appl. Math.* **10**, 232.

Giddings, J. C. & Hirschfelder, J. O. 1957 *Sixth Int. Symp. Combustion*, p. 199. New York: Reinhold Publ. Corp.

Heinen, F. J. 1962 Ph.D. Thesis, New York University.

Henrici, P. 1961 *Discrete variable methods in Ordinary Differential Equations.* New York: John Wiley and Sons.

Hirschfelder, J. O. 1960 *Phys. Fluids*, **3**, 109.

Hirschfelder, J. O. & Campbell, E. S. 1953 *Analytical solutions to the equations of flame propagation*, p. 48. University of Wisconsin, CM-784.

Hirschfelder, J. O. & Curtiss, C. F. 1949 *J. Chem. Phys.* **17**, 1076.

Hirschfelder, J. O., Curtiss, C. F. & Bird, R. B. 1954 *Molecular theory of gases and liquids.* New York: John Wiley and Sons.

Hirschfelder, J. O., Curtiss, C. F. & Campbell, D. E. 1953 *J. Phys. Chem.* **57**, 403.

Klein, G. 1957 *Phil. Trans.* A, **249**, 389.

Lewis, B. & von Elbe, G. 1951 *Combustion, flames and explosions*, p. 342. New York: Academic Press.

Nordsieck, A. 1962 *Math. Compt.* **16**, 22.

Rutishauser, H. 1952 *Z. Angew. Math. Phys.* **3**, 65.

Schalit, L. M. 1961 Ph.D. Thesis, New York University.

Smirnov, V. I. 1961 *Linear algebra and group theory*, pp. 127–8. New York: McGraw Hill.

Tanford, C. & Pease, R. N. 1947 *J. Chem. Phys.* **15**, 861.

Waelbroeck, F., Lafleur, S. & Prigogine, J. 1955 *Physica*, **21**, 667.