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A Contribution to Flame Theory

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A CONTRIBUTION TO FLAME THEORY

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CONTENTS

Part I

The equations of a reacting gas mixture and their application to flames are briefly reviewed; ordinary diffusion is fully taken into account in terms of binary diffusion coefficients, but the diffusion thermo-effect and radiation are neglected. A one-dimensional flame model is considered whose equations are written concisely by means of suitable dimensionless quantities and temperature is chosen as independent variable. It is assumed that the flame velocity is not given, so that a related unknown constant, determined by the boundary conditions, occurs in non-linear differential equations. These are to be solved simultaneously with the complicated diffusion equations, and a general method of solution is aimed at. With a view to later generalization, the equations of the simplest ideal flame of reaction $A \rightleftharpoons B$ are discussed in detail. It is found that they

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are most conveniently solved in two stages: (i) by successive approximations to the solution of an integral equation, corresponding to the case of zero energy flux, and (ii) by a perturbation method, based on this 'unperturbed' case, which may be applied directly or, in general, in terms of parameter expansions.

Part II

Results of some physical and mathematical interest are given of computations relating to special ideal flames which separately bear some of the features of real ones. For example, in the case of an ideal flame in which there are two simultaneous reactions, the problem is solved by first assuming one of these reactions to be in equilibrium and then attacking the complete problem by considering the reaction rate previously neglected as a perturbation.

The treatment of the general one-dimensional flame problem, proposed in part I, is then continued, and it is shown that the methods used there for the solution of the simple $A \rightleftharpoons B$ flame can be readily generalized as follows: (i) The complexity due to diffusion can be separated from that due to the eigenvalue character of the problem; the equations should first be solved with a set of certain well-defined 'ideal' binary diffusion coefficients—corresponding to a vanishing energy flux—and it will then generally be possible to arrive at the solution of the complete problem, with the actually given set of diffusion coefficients, by a perturbation method involving only linear equations, based on the 'ideal' or 'unperturbed' case. (ii) This 'ideal' problem can be made to depend on the solution of a single non-linear 'eigenvalue' differential equation (which is treated as an integral equation) by successive approximations, all other equations serving as mere definitions for better approximations to terms occurring in this fundamental equation.

PART I

1. INTRODUCTION

In describing flames mathematically, as with many other phenomena, the task falls roughly into three difficult parts: the setting up of certain differential equations, the stipulation of boundary conditions, and the solution of the equations. In formulating the problem not much is known, for instance, concerning the transfer between translational and vibrational energies. Nevertheless, ordinary hydrodynamic continuity equations will be applicable, even if there is some uncertainty about some of the quantities which enter into them, such as reaction rate constants. Similarly, the diffusion equations for a multi-component gas, as derived from kinetic theory (Hirschfelder, Curtiss & Bird 1954), may be used.

One describes, in any case, only a model. Suppose one is primarily interested in the chemical reactions taking place. The general character of the flame will then not be violated, except through geometrical distortion, if only a one-dimensional model is considered. (Such a model will, in fact, correspond to the 'flat' flames produced experimentally.) Again, since all the significant processes take place in the hot region, no crucial importance need be attached to the cold boundary, apart from the initial composition of the gas; one finds, on inspection of the relevant functions, that a relatively simple model answers the purpose, in which the boundary conditions are symmetrical.

Once a consistent mathematical model has been adopted, it is desirable and necessary to study the structure of the very complex flame equations: in order to bring out their mathematical peculiarities and as much physical information as possible, even at this stage, and in order to find some guidance towards an appropriate method of solution. These are the objects of the following treatment.

Though the numerical data to be used have to be constantly borne in mind, and some computations are indispensable for the elucidation of the problem, such an algebraical approach is instructive and promising. The equations and individual terms in them carry very unequal weights: one will try to distinguish and group together those which are essential for giving a mathematically consistent flame-profile. Once this has been established, the neglected 'perturbations', not necessarily small, are to be determined by a method of successive approximations.

In §§ 2 and 3 the equations of a reacting gas mixture are taken as a starting point and, by suitable transformations, are made manageable for the problem in hand. In § 4 they are applied to the simplest possible flame of the type $A \rightleftharpoons B$, previously solved by another method by Hirschfelder and Curtiss (cf. Hirschfelder *et al.* 1954). This problem depends on the solution of an eigenvalue differential equation which is here treated as an integral equation. In part II other ideal flames will be considered which separately bear at least some of the characteristics of real flames, and a natural extension of the description and method of solution proved possible. This suggests that the model of a real flame, too, can ultimately be based on the $A \rightleftharpoons B$ problem, and in part II a scheme will be proposed showing in what manner this may be done.

2. Equations of a gas mixture

(a) *Conservation equations of the gas as a whole*

The equations expressing the over-all conservation of mass, momentum and energy in a gas, when there are no external forces, may be written in the form

$$\frac{\partial}{\partial t}\rho + \frac{\partial}{\partial \boldsymbol{r}}.\boldsymbol{M} = 0, \tag{2·1}$$

$$\frac{\partial}{\partial t}\boldsymbol{M} + \frac{\partial}{\partial \boldsymbol{r}}.\mathbf{B} = 0, \tag{2·2}$$

$$\frac{\partial}{\partial t}e + \frac{\partial}{\partial \boldsymbol{r}}.\boldsymbol{L} = 0, \tag{2·3}$$

where

$$\boldsymbol{M} = \rho\boldsymbol{v}, \tag{2·4}$$

$$\mathbf{B} = \boldsymbol{M}\boldsymbol{v} + \mathbf{P}, \tag{2·5}$$

$$e = \rho u + \tfrac{1}{2}\rho\boldsymbol{v}^2, \tag{2·6}$$

$$\boldsymbol{L} = e\boldsymbol{v} + \boldsymbol{q} + \mathbf{P}\,.\,\boldsymbol{v}, \tag{2·7}$$

in which ρ is the mass density of the gas mixture, $\boldsymbol{v}$ the mean mass velocity, u the internal energy per unit mass, $\boldsymbol{q}$ the energy flux vector. The pressure tensor $\mathbf{P}$ consists of two parts, the hydrostatic pressure p and components due to viscosity,

$$\mathbf{P} = \mathbf{U}p + \mathbf{P}^{(\text{visc.})}, \tag{2·8}$$

where $\mathbf{U}$ is the unit tensor. Instead of the internal energy per unit mass u, the enthalpy or heat content per unit mass h will be employed; the two are related by the definition

$$\rho h = \rho u + p. \tag{2·9}$$

Thus the vector (2·7) may be expressed as

$$\boldsymbol{L} = \boldsymbol{q} + \boldsymbol{v}\rho h + \boldsymbol{v}\tfrac{1}{2}\rho\boldsymbol{v}^2 + \boldsymbol{v}\,.\,\mathbf{P}^{(\text{visc.})}. \tag{2·10}$$

(*b*) *Equations relating to the components*

The composition of the gas mixture may be described by the mole fractions $\ldots, x_S, \ldots$ referring to the components $\ldots, S, \ldots$. Let component S have mass density ρ_S and mean mass velocity $\boldsymbol{v}_S$ and let m_S be its mass per mole. Let n be the total number of moles per unit volume and $\overline{m}$ be the mean mass per mole in the mixture. Then, by definitions,

$$\Sigma x_S = 1, \tag{2·11}$$

$$\Sigma m_S x_S = \overline{m}, \tag{2·12}$$

$$\rho_S = n x_S m_S, \tag{2·13}$$

$$\rho = \Sigma \rho_S = n\overline{m}, \tag{2·14}$$

$$\rho \boldsymbol{v} = \Sigma \rho_S \boldsymbol{v}_S = \boldsymbol{M} \tag{2·15}$$

(cf. (2·4)). For a chemically reacting gas mixture the detailed continuity equations for the densities of the various components are required and these are

$$\frac{\partial}{\partial t}\rho_S + \frac{\partial}{\partial \boldsymbol{r}} \cdot \rho_S \boldsymbol{v}_S = m_S R_S, \tag{2·16}$$

where R_S is the rate of production of component S in moles per unit volume per unit time. In order that mass should be conserved,

$$\Sigma m_S R_S = 0, \tag{2·17}$$

so that (2·1) is a consequence of (2·16) and (2·17). For particular reactions there will be further relations similar to (2·17) expressing the conservation of atomic species. The set of equations (2·16) contains two sets of variables, the x_S and the $\boldsymbol{v}_S$, so that another set of equations is needed; these are the diffusion equations

$$\frac{\partial}{\partial \boldsymbol{r}} x_S = -x_S \Sigma \frac{1}{D_{SS'}} x_{S'} (\boldsymbol{v}_S - \boldsymbol{v}_{S'}) - x_S (1 - m_S/\overline{m}) \frac{\partial}{\partial \boldsymbol{r}} \ln p, \tag{2·18}$$

where thermo-diffusion has been neglected and the $D_{SS'}$ are binary diffusion coefficients (cf. Hirschfelder, Curtiss & Bird 1954).

(*c*) *Equations of state. Energy flux*

It remains to express the dependence of pressure and internal energy on the temperature. It will be assumed that the gas is sufficiently rarefied so that the perfect gas law applies,

$$p = nRT, \tag{2·19}$$

and the so-called caloric equation of state may be considered as contained in the relations

$$h_S = h_S^\infty - \int_T^{T_\infty} c_S \, \mathrm{d}T, \tag{2·20}$$

$$\rho h = \Sigma \rho_S h_S, \tag{2·21}$$

where h_S is the enthalpy per unit mass of component S at temperature T, and c_S is its specific heat at constant pressure per unit mass; h_S^∞ is the value of the former at a definite temperature

T_∞ (cf. § 3). For simplicity it will be assumed that for any one component the specific heat is constant over the temperature range to be considered—one adopts a mean value—so that

$$h_S = h_S^\infty - c_S(T_\infty - T) \tag{2·22}$$

and

$$m_S c_S = R\gamma_S/(\gamma_S - 1), \tag{2·23}$$

in which γ_S is the ratio of specific heats of component S.

It can be shown that when radiation and the thermo-diffusion effect are neglected, the energy flux vector has the form

$$\boldsymbol{q} = -\lambda \frac{\partial}{\partial \boldsymbol{r}} T + \Sigma(\boldsymbol{v}_S - \boldsymbol{v})\, \rho_S h_S, \tag{2·24}$$

where λ is the heat conductivity of the mixture. Thus, with (2·21) and (2·22), the vector (2·10) becomes

$$\boldsymbol{L} = -\lambda \frac{\partial}{\partial \boldsymbol{r}} T + \Sigma h_S^\infty \rho_S \boldsymbol{v}_S - (\Sigma c_S \rho_S \boldsymbol{v}_S)\,(T_\infty - T) + \boldsymbol{v}\tfrac{1}{2}\rho \boldsymbol{v}^2 + \boldsymbol{v}\,.\,\mathbf{P}^{(\mathrm{visc.})}. \tag{2·25}$$

Also

$$\mathbf{P}^{(\mathrm{visc.})} = -\mu\left\{\frac{\partial}{\partial \boldsymbol{r}}\boldsymbol{v} + \left(\frac{\partial}{\partial \boldsymbol{r}}\boldsymbol{v}\right)^{(\mathrm{transpose})}\right\} + (\tfrac{2}{3}\mu - \kappa)\,\frac{\partial}{\partial \boldsymbol{r}}\,.\,\boldsymbol{v}\mathbf{U}, \tag{2·26}$$

where μ and κ are the coefficients of shear and bulk viscosity, respectively.

(*d*) *One-dimensional variation under stationary conditions*

Under stationary conditions and when all quantities may be assumed to vary in one dimension only, the conservation equations (2·1) to (2·3) can be immediately integrated. In particular,

$$M = \rho v = \text{constant}, \tag{2·27}$$

and it has become usual to adopt fractional momenta variables

$$G_S = \frac{\rho_S v_S}{\rho v} = \frac{\rho_S v_S}{M} = \frac{m_S}{\overline{m}} x_S \frac{v_S}{v} \tag{2·28}$$

instead of the component velocities (cf. Hirschfelder *et al.* 1954), so that

$$\Sigma G_S = 1. \tag{2·29}$$

Integration of (2·2) and (2·3) gives (cf. (2·5), (2·25) and (2·26))

$$B = \rho v^2 + p - \mu' \frac{\mathrm{d}v}{\mathrm{d}z} = \text{constant}, \tag{2·30}$$

$$L = -\lambda \frac{\mathrm{d}T}{\mathrm{d}z} + M\Sigma h_S^\infty G_S - M(\Sigma c_S G_S)\,(T_\infty - T) + v\left(\tfrac{1}{2}\rho v^2 - \mu' \frac{\mathrm{d}v}{\mathrm{d}z}\right) = \text{constant}, \tag{2·31}$$

where z is the distance variable and the factor

$$\mu' = \tfrac{4}{3}\mu + \kappa \tag{2·32}$$

takes into account the effect of viscosity. With (2·14) and (2·27) the equation of state (2·19) may be written

$$pv = (M/\overline{m})\,RT, \tag{2·33}$$

and in terms of (2·28) the reaction and diffusion equations (2·16) and (2·18) become

$$M\frac{\mathrm{d}G_S}{\mathrm{d}z} = m_S R_S, \tag{2·34}$$

$$\frac{\mathrm{d}x_S}{\mathrm{d}z} = -M\Sigma\frac{1}{nD_{SS'}}\left(x_{S'}G_S/m_S - x_S G_{S'}/m_{S'}\right) - x_S(1-m_S/\overline{m})\frac{\mathrm{d}}{\mathrm{d}z}\ln p. \tag{2·35}$$

3. One-dimensional flame equations

(a) *Further assumptions*

It will be assumed that the flame velocity is always small compared with the velocity of sound, that is, small compared with the root-mean-square velocity in the gas. The pressure may then be taken as approximately constant throughout the flame (cf. the definition of the pressure tensor and (2·4), (2·5) and (2·30)). Similarly, heat-energy transport will be much larger than the macroscopic translational energy transport and the term $\frac{1}{2}\rho v^3$ in (2·31) is negligible.

Further, the viscosity terms will at first be neglected. The assumption is that the effect of viscosity will no more than distort the flame profile obtained by ignoring it. In the appendix to part II it will be shown how viscosity may be taken into account without vitiating the method.

Let Z be a particular component, the 'last' component or (one of) the main combustion product(s); more definitely, the component for which h_S^∞ is least, though this is not essential. Let T_∞ be the temperature at which the temperature gradient vanishes (cf. § 3 (*d*)), and let $\ldots, G_S^\infty, \ldots$ be the values of $\ldots, G_S, \ldots$ at this temperature. Then, with the use of (2·29) the integrated energy transport equation (2·31) becomes

$$\frac{\lambda}{M}\frac{\mathrm{d}T}{\mathrm{d}z} = \Sigma(h_S^\infty - h_Z^\infty)\,G_S - \{\Sigma(h_S^\infty - h_Z^\infty)\,G_S^\infty + (\Sigma c_S G_S)(T_\infty - T)\}. \tag{3·1}$$

In this equation, in view of the normalization (2·29), the quantity

$$\Sigma c_S G_S \tag{3·2}$$

is a kind of dynamic mean specific heat per unit mass of the gas which may be expected not to vary very violently. On a first approximation it may even be permissible to take it as constant, but in the following it will be assumed only that the curved bracket expression in (3·1) does not deviate abnormally from a linear function in the temperature.

(b) *Reduced quantities*

It will be convenient to introduce certain constants and to change some of the variables. The standard constants and their dimensions are: E (energy per mole), m (mass per mole) and c (specific heat per unit mass); their magnitudes will be defined later (cf. (3·37), (3·31), (3·32) and (3·13)). The specific heats and the enthalpies at the temperature T_∞ are to enter through new constants

$$b_S = m_S c_S/R = \gamma_S/(\gamma_S - 1), \tag{3·3}$$

$$l_S = m_S(h_S^\infty - h_Z^\infty)/E. \tag{3·4}$$

The new variables are the reduced temperature

$$\tau = RT/E, \tag{3·5}$$

and the flow variables

$$y_S = \frac{m}{m_S} G_S = \frac{m}{\overline{m}} x_S \frac{v_S}{v}, \tag{3·6}$$

which have an advantage over the fractional momenta owing to the form of the diffusion equations; in place of (2·29),

$$\Sigma \frac{m_S}{m} y_S = 1. \tag{3·7}$$

On division by E/m the energy equation (3·1) becomes

$$\frac{\lambda m}{RM} \frac{\mathrm{d}\tau}{\mathrm{d}z} = \Sigma l_S y_S - \{\Sigma l_S y_S^\infty + (\Sigma b_S y_S)(\tau_\infty - \tau)\}, \tag{3·8}$$

and the reaction and diffusion equations (2·34) and (2·25) are now

$$\frac{\mathrm{d}y_S}{\mathrm{d}z} = \frac{m}{M} R_S, \tag{3·9}$$

$$\frac{\mathrm{d}x_S}{\mathrm{d}z} = M \Sigma \frac{1}{nmD_{SS'}} (x_S y_{S'} - x_{S'} y_S). \tag{3·10}$$

The quantity

$$D = \lambda/(nmc) \tag{3·11}$$

has the dimensions of a diffusion coefficient (thermal diffusivity) and it may be used to define reduced binary diffusion coefficients

$$\delta_{SS'} = D_{SS'}/D. \tag{3·12}$$

(For a single-component gas, this quantity, with the self-diffusivity in the numerator, would be the ratio of the Prandtl to the Schmidt number, of order unity.) In analogy with (3·3) we also define the constant

$$b = mc/R. \tag{3·13}$$

(*c*) *Temperature as independent variable*

On substitution of (3·12), (3·11) into (3·10) one is naturally led to adopt a reduced distance variable ζ, instead of z, defined by

$$\frac{\mathrm{d}\zeta}{\mathrm{d}z} = \frac{Mc}{\lambda} = b \frac{MR}{m\lambda}. \tag{3·14}$$

The distance does not occur explicitly but only in differentials; one can take the reduced temperature τ as independent variable, and write the equations in terms of the reduced temperature gradient

$$g = \frac{\mathrm{d}\tau}{\mathrm{d}\zeta}, \tag{3·15}$$

which will be considered as the principal dependent variable, while the x_S, y_S may be considered as 'intermediate' dependent variables. Thus, with (3·11) to (3·15), the flame equations (3·8) to (3·10) become

$$g \frac{\mathrm{d}y_S}{\mathrm{d}\tau} = \left(\frac{1}{b} \frac{m^2}{M^2} \frac{\lambda}{R}\right) R_S(\ldots, x_{S'}, \ldots; \tau), \tag{3·16}$$

$$g\frac{\mathrm{d}x_S}{\mathrm{d}\tau} = \Sigma\frac{1}{\delta_{SS'}}(x_S y_{S'} - x_{S'} y_S), \tag{3·17}$$

$$bg = \Sigma l_S y_S - \{\Sigma l_S y_S^\infty + (\Sigma b_S y_S)(\tau_\infty - \tau)\}. \tag{3·18}$$

(It is assumed that the heat conductivity λ and the binary diffusion coefficients $D_{SS'}$ are given explicitly as functions of the temperature—their values are in any case not accurately known at high temperatures and can only be estimated. With the use of (3·11) and (2·19) the reduced binary diffusion coefficients, $\delta_{SS'}$, are then known as functions of τ.) After (3·16) to (3·18) have been solved, one can easily calculate

$$\zeta = \int^\tau \frac{1}{g}\,\mathrm{d}\tau, \tag{3·19}$$

$$z = \frac{1}{b}\frac{m}{MR}\int^\tau \frac{\lambda}{g}\,\mathrm{d}\tau. \tag{3·20}$$

Combustion is supposed to take place between the reduced temperatures τ_0 and τ_∞; values of variables at these 'boundary' temperatures will be indicated by suffixes or superscripts 0 and ∞, respectively.

For conciseness, the factor λ in (3·16) may be absorbed into the rates of production R_S, so that the reaction equations (3·16) may be written

$$g\frac{\mathrm{d}y_S}{\mathrm{d}\tau} = b\alpha K_S(\ldots, x_{S'}, \ldots; \tau), \tag{3·21}$$

where
$$K_S(\ldots, x_{S'}, \ldots; \tau) = \frac{\lambda(\tau)}{\lambda(\tau_0)} R_S(\ldots, x_{S'}, \ldots; \tau), \tag{3·22}$$

and the constant
$$\alpha = \frac{1}{b^2}\frac{m^2}{M^2}\frac{\lambda(\tau_0)}{R} \tag{3·23}$$

will play an important role in the following treatment. Its dimensions are the reciprocal of (moles per unit volume per unit time).

(d) *Boundary conditions. Standard constants*

At the hot boundary, $\tau = \tau_\infty$, chemical activity, diffusion and heat conduction (that is, the temperature gradient) must all vanish. The last condition has already been taken care of by the choice of the integration constant in (2·31) (cf. (3·1) and (3·18)), so that

$$g^\infty = g(\tau_\infty) = 0. \tag{3·24}$$

Reactions will cease when for all components

$$K_S^\infty = K_S(\ldots, x_{S'}^\infty, \ldots; \tau_\infty) = 0, \tag{3·25}$$

and there will be no diffusion, that is, all drift velocities v_S are identical with the mean mass velocity v when (cf. (3·6))

$$y_S^\infty = (m/\overline{m}^\infty)\, x_S^\infty. \tag{3·26}$$

It will be seen from the flame equations (3·17), (3·18) and (3·21) that these conditions are consistent.

At the cold boundary, $\tau = \tau_0$, it will be assumed that analogous conditions obtain, viz.

$$g^0 = g(\tau_0) = 0, \tag{3·27}$$

$$K_S^0 = K_S(\dots, x_{S'}^0, \dots; \tau_0) = 0, \tag{3·28}$$

$$y_S^0 = (m/\overline{m}^0)\, x_S^0. \tag{3·29}$$

One could stipulate a fictitious flame-holder ensuring the conditions (3·27) to (3·29). Nevertheless, condition (3·28) may at first sight appear unacceptable. Reaction rates, and hence rates of production, contain functions of the temperature with mole fractions as factors: in order that (3·28) shall be satisfied, it is therefore required either that certain of these functions shall be zero at the cold-boundary temperature, or that certain components, usually free radicals, shall be absent at the cold boundary. Now, although the analytic functions generally assumed are never accurately zero, in practice, where one confines oneself to a limited number of decimal places, the relevant functions as entries in a numerical table are zero, or can be taken as such for computational purposes.

The boundary condition (3·27) and the energy equation (3·18) entail the necessary relation

$$(\Sigma b_S y_S^0)\,(\tau_\infty - \tau_0) = \Sigma l_S (y_S^0 - y_S^\infty). \tag{3·30}$$

The standard constants m, c (or b, cf. (3·13)), and E (cf. (3·37)), introduced at the beginning of this section will now be defined by the equations

$$m = \overline{m}^0 \quad = \Sigma m_S x_S^0, \tag{3·31}$$

$$b = \Sigma b_S y_S^0 = \Sigma b_S x_S^0, \tag{3·32}$$

$$1 = \Sigma l_S y_S^0 \ = \Sigma l_S x_S^0, \tag{3·33}$$

where the last members of the last two follow from (3·31) and (3·29), viz.

$$y_S^0 = x_S^0. \tag{3·34}$$

The second sum in the energy equation (3·18) represents an integration constant which will be denoted by

$$a = \Sigma l_S y_S^\infty = (\overline{m}^0/\overline{m}^\infty)\, \Sigma l_S x_S^\infty. \tag{3·35}$$

It will generally be a small fraction of unity, as will be seen on comparison with the sum (3·33), since the main combustion product Z does not enter into either of these sums; cf. (3·4) which gives $l_Z = 0$. With (3·32) to (3·35) the necessary relation (3·30) becomes

$$b(\tau_\infty - \tau_0) = 1 - a. \tag{3·36}$$

Now $b > \frac{5}{2}$ (cf. (3·32) and (3·3)), so that the reduced temperature range $(\tau_\infty - \tau_0) < \frac{2}{5}$. Usually, $b \sim 4$, so that $(\tau_\infty - \tau_0) \sim 0{\cdot}25$, while, of course, $\tau_\infty/\tau_0 = T_\infty/T_0$.

(*e*) *Standard energy. Energy flux. Flame velocity*

Explicitly, the standard energy E is defined by (3·33) and (3·4) as

$$E = \Sigma m_S (h_S^\infty - h_Z^\infty)\, x_S^0. \tag{3·37}$$

It is necessarily positive and has some physical significance: the quantity E/m is easily seen to be the heat content per unit mass which the gas would have at the hot-boundary temperature if no reaction had taken place, less the heat content per unit mass at that temperature if it were wholly composed of the main combustion product, component Z.

The actual heat content per unit mass at the hot boundary is equal to that at the cold boundary; this follows immediately from (2·10) and (2·4), since with the assumed boundary conditions the energy flux (2·24) will be zero at the boundaries. Elsewhere the energy flux will not, in general, vanish, and it is of interest to consider its functional form. Let

$$q = (ME/m)\,\phi, \tag{3·38}$$

where ϕ may be called the reduced energy flux. Writing (2·24) in terms of reduced quantities, one finds

$$\phi = -bg + \Sigma\{y_S - (m/\overline{m})\,x_S\}\{l_S - b_S(\tau_\infty - \tau)\}. \tag{3·39}$$

The first term is due to ordinary heat conduction and the second to diffusion (cf. (3·15) and (3·6)). On elimination of the temperature gradient by means of the energy equation (3·18), it may alternatively be expressed in terms of the mole fractions only:

$$\phi = a - (m/\overline{m})\,\Sigma x_S\{l_S - b_S(\tau_\infty - \tau)\}. \tag{3·40}$$

An important property of a flame is its initial velocity. With (2·33) and (3·31) it is found to be related to the constant α (3·23) by

$$v_0^2 = \left\{\frac{1}{b^2}\frac{\lambda_0}{R}\left(\frac{RT_0}{p}\right)^2\right\}\frac{1}{\alpha}. \tag{3·41}$$

This flame velocity can usually be determined experimentally. Its agreement with a theoretically derived value may therefore be made one of the criteria of a satisfactory flame theory.

(*f*) *The flame problem*

The flame problem may be posed in different ways, depending on which quantities are given. In the present treatment it is conceived as follows: the hot-boundary *temperature* is given, so that the hot-boundary composition ..., x_S^∞, ... can be calculated by simultaneous solution of (3·25); the h_S^∞ are known; the cold-boundary *composition* is given, and since the specific heats are known, the cold-boundary temperature is then calculated from (3·30) (in irreduced quantities). The cold-boundary temperature so found must be sufficiently low for (3·28) to hold under the reservation mentioned earlier. The standard constants are now calculated from (3·31), (3·32) and (3·37), and the problem consists in the simultaneous solution of (3·17), (3·18) and (3·21) under the boundary conditions (3·24) and (3·27), the other boundary conditions being already ensured. One requires the flame profile, that is, g and all the x_S and y_S, as functions of the temperature.

The difficulty of the flame problem, in this form, arises from the fact that the constant α is not known. Its character is that of an eigenvalue (though the equations are not linear), whose magnitude has to be determined along with the unknown functions. It depends partly on the given boundary conditions but also on what happens between the boundaries at all temperatures. Again, since this single constant depends on what happens over the temperature range *as a whole* (cf. (4·29)), one is led to describe flames in terms of integral equations rather than differential equations. Once this is done, various methods of solution by successive approximations suggest themselves.

On this approach, a very simple ideal flame will be considered first of all, which will then be used as a basis for a more general treatment in part II.

4. THE $A \rightleftharpoons B$ FLAME

(*a*) *Equations of the* $A \rightleftharpoons B$ *flame*

An ideal conversion of fuel into combustion product may be represented by the reaction

$$A \rightleftharpoons B \tag{4·1}$$

(which is an abbreviation for $O+A \rightleftharpoons B+O$, where O is A or B). Here

$$m = m_A = m_B = \overline{m} \quad \text{for all } \tau, \tag{4·2}$$

and in anticipation of later generalization the following notation will be used:

$$X = x_A = 1 - x_B \qquad \text{(cf. (2·11))}, \tag{4·3}$$

$$Y = y_A = 1 - y_B \qquad \text{(cf. (3·7))}, \tag{4·4}$$

$$K = -K_A(x_A, x_B; \tau) = K_B(x_A, x_B; \tau) = K(X; \tau) \qquad \text{(cf. (2·17))}, \tag{4·5}$$

$$\delta = \delta_{AB} = \delta(\tau). \tag{4·6}$$

For the forward reaction to predominate, $h_A^\infty > h_B^\infty$, so that with the special initial composition

$$x_A^0 = 1, \quad x_B^0 = 0, \tag{4·7}$$

it follows that (cf. (3·32))

$$l_A = 1, \quad l_B = 0. \tag{4·8}$$

(Note that here $E = m(h_A^\infty - h_B^\infty)$ (cf. (3·37)), while for *any* initial composition $l_B = 0$; B is here the 'last' component Z!) It will at first be assumed that the specific heats of the two components are equal so that (cf. (3·3) and (3·32))

$$b = b_A = b_B. \tag{4·9}$$

The flame equations, (3·17), (3·18) and (3·21) now reduce to the following three:

$$g\frac{\mathrm{d}Y}{\mathrm{d}\tau} = -b\alpha K(X; \tau), \tag{4·10}$$

$$g\frac{\mathrm{d}X}{\mathrm{d}\tau} = \frac{1}{\delta}(X - Y), \tag{4·11}$$

$$bg = Y - X^*, \tag{4·12}$$

where

$$X^* = a + b(\tau_\infty - \tau) \tag{4·13}$$

is a known linear function of the temperature with

$$a = x_A^\infty. \tag{4·14}$$

The equations are thus written in terms of the fuel variables, X and Y, and of the rate of consumption of fuel K. Next, Y can be eliminated and the resulting absorption of the energy equation (4·12) into the reaction and diffusion equations makes the $A \rightleftharpoons B$ problem depend on the simultaneous solution of the equations

$$g\left(1 - \frac{\mathrm{d}g}{\mathrm{d}\tau}\right) = \alpha K(X; \tau), \tag{4·15}$$

$$\delta g \frac{\mathrm{d}(X - X^*)}{\mathrm{d}\tau} - (X - X^*) = -b(1-\delta)\, g. \tag{4·16}$$

It will be noted that if in the second equation g were known, it would be a simple linear differential equation in $X-X^*$ or X.

In passing, it is instructive to consider the energy flux in this simple case. In the form (3·39) it becomes

$$\phi = -bg + Y - X, \tag{4·17}$$

while (3·40) reduces to

$$\phi = -(X - X^*). \tag{4·18}$$

Thus it appears that (4·16) is, in effect, an equation in the energy flux, relating it to the temperature gradient. Again, (4·17) and the diffusion equation (4·11) lead to the following suggestive relations:

$$\phi = -bg - \delta g \frac{\mathrm{d}X}{\mathrm{d}\tau} = -g\left(b + \delta \frac{\mathrm{d}X}{\mathrm{d}\tau}\right) = -b\frac{\mathrm{d}\tau}{\mathrm{d}\zeta} - \delta \frac{\mathrm{d}X}{\mathrm{d}\zeta}. \tag{4·19}$$

Returning to (4·15) and (4·16), one finds that in two special cases the problem reduces to a single differential equation. (i) When diffusion is neglected, $\delta = 0$, it follows that

$$X = X^* + bg, \tag{4·20}$$

and the equation to be solved is

$$g\left(1 - \frac{\mathrm{d}g}{\mathrm{d}\tau}\right) = \alpha K(X^* + bg; \tau). \tag{4·21}$$

But an even simpler and more realistic case is the one (ii) when the energy flux vanishes everywhere, which results only if the reduced binary diffusion coefficient has the constant value $\delta = 1$ (cf. the remark after (3·12)), and which implies constant enthalpy per unit mass everywhere. Here (cf. (4·18) and (4·16))

$$X = X^*, \tag{4·22}$$

so that the fuel decreases linearly with temperature (cf. (4·13)), and the equation to be solved is now

$$g\left(1 - \frac{\mathrm{d}g}{\mathrm{d}\tau}\right) = \alpha K(X^*; \tau), \tag{4·23}$$

where the function on the right is known but the constant α is not and depends on the boundary conditions $g_0 = g_\infty = 0$. One may consider an equation of this type as the core of the flame problem which deserves close examination. (Equations of the form (4·21) and (4·23) are named after Abel (1881), who was, however, not concerned with the eigenvalue problem.)

(b) *The fundamental differential equation*

It is required to solve the first-order, non-linear, ordinary differential equation

$$g\left(1 - \frac{\mathrm{d}g}{\mathrm{d}\tau}\right) = \alpha K(\tau), \tag{4·24}$$

where α is an unknown constant, under the boundary conditions

$$g(\tau_0) = 0, \quad g(\tau_\infty) = 0. \tag{4·25}$$

The solution in the range $\tau_0 < \tau < \tau_\infty$ only is of physical interest. The function $K(\tau)$ is assumed to have the following properties. In the range $\tau_0 < \tau < \tau_\infty$ it is never negative (rate of consumption of fuel!). It is vanishingly small near $\tau = \tau_0$; more precisely, it will be assumed that

$$K(\tau) = 0, \quad \tau \leqslant \tau_0; \qquad [\mathrm{d}K(\tau)/\mathrm{d}\tau]_{\tau_0} = 0 \tag{4·26}$$

(cf. (3·28) and the remarks there following). The function then reaches a maximum and vanishes again at $\tau = \tau_\infty$ (cf. (3·25))

$$K(\tau_\infty) = 0, \tag{4·27}$$

where, in general, it actually crosses the τ axis.

The eigenvalue problem involved can be interpreted geometrically by mere inspection of equation (4·24) in which $K(\tau)$ has the properties stated. The integral curves of the equation for $\tau < \tau_0$ and near $\tau = \tau_0$ are parallel straight lines inclined at 45° to the axes. Those which later cross the curve $\alpha K(\tau)$ before its maximum have their maxima at the points of intersection. Some of these turn upwards again, having had their minima likewise on $\alpha K(\tau)$, while others turn sharply down and cross the τ axis at right angles: the two sets are separated by the particular curve which passes through $(\tau_\infty, 0)$ where the integral curves thus form, in general, a saddle-point. The required solution is therefore a singular one, and the constant α must be such that it ensures its passing through $(\tau_0, 0)$ also. (Cf. figure 4, p. 407.)

There is an obvious advantage in considering the solution of (4·24) and (4·25) as an integral equation problem, since then the boundary conditions will be contained in the equation itself. Now, a differential equation may be turned into an integral equation in an infinite number of ways; the most immediate form in which (4·24) and (4·25) may be written as an integral equation is

$$\tfrac{1}{2}g^2 = \alpha\int_\tau^{\tau_\infty} K(\tau)\,\mathrm{d}\tau - \int_\tau^{\tau_\infty} g\,\mathrm{d}\tau, \tag{4·28}$$

where, in order that the boundary conditions (4·25) shall be satisfied,

$$\alpha = \int_{\tau_0}^{\tau_\infty} g\,\mathrm{d}\tau \Big/ \int_{\tau_0}^{\tau_\infty} K(\tau)\,\mathrm{d}\tau \tag{4·29}$$

is in this connexion only an abbreviation to be used in (4·28), but once (4·28) has been solved it represents the desired eigenvalue.

Since the required variable g occurs in equation (4·28) twice in integrals, and it may be supposed that the integrals are not much affected if slightly incorrect values for g are substituted into them, the following scheme for a solution by successive approximations suggests itself:

$$g^{(\nu+1)} = \left[2\left\{\alpha^{(\nu+1)}\int_\tau^{\tau_\infty} K(\tau)\,\mathrm{d}\tau - \int_\tau^{\tau_\infty} g^{(\nu)}\mathrm{d}\tau\right\}\right]^{\frac{1}{2}}, \tag{4·30}$$

where

$$\alpha^{(\nu+1)} = \int_{\tau_0}^{\tau_\infty} g^{(\nu)}\,\mathrm{d}\tau \Big/ \int_{\tau_0}^{\tau_\infty} K(\tau)\,\mathrm{d}\tau. \tag{4·31}$$

One guesses a lowest 'approximation' $g^{(0)}(\tau)$ which has the general character of g, viz. starting from $\tau = \tau_0$ with derivative unity, rising to a maximum, and vanishing again at $\tau = \tau_\infty$. The method will clearly be justified if on application of (4·30) and (4·31) the successive values of $g^{(0)}(\tau)$, $g^{(1)}(\tau)$, $g^{(2)}(\tau)$, ..., for all τ, and the constants $\alpha^{(1)}$, $\alpha^{(2)}$, $\alpha^{(3)}$, ... form convergent sequences.

(c) *Solution of the $A \rightleftharpoons B$ problem*

The case of negligible diffusion, contained in equation (4·21), can be solved by the same method; in the argument of K on the right of (4·21) a lower approximation, $g^{(\nu)}$, is used when successive approximations are calculated by equations analogous to (4·30) and (4·31).

The general problem, for *any* diffusion coefficient δ, constant or variable, can be similarly dealt with. On solving (4·16) formally as a linear equation, the problem depends on the solution of

$$g\left(1-\frac{\mathrm{d}g}{\mathrm{d}\tau}\right)=\alpha K(X;\tau), \tag{4·32}$$

$$X=X^{*}+b\left[\exp\left\{\int^{\tau}(1/g\delta)\,\mathrm{d}\tau\right\}\right]\int_{\tau}^{\tau_{\infty}}\exp\left\{-\int^{\tau}(1/g\delta)\,\mathrm{d}\tau\right\}\frac{1-\delta}{\delta}\,\mathrm{d}\tau. \tag{4·33}$$

One finds an approximation $X^{(\nu)}$ corresponding to a lower approximation $g^{(\nu)}$ by (4·33). This is substituted on the right of (4·32), and a better approximation $g^{(\nu+1)}$ can then be found by the method of the preceding subsection. The process is then repeated until successive $g^{(\nu)}$ and $X^{(\nu)}$ become indistinguishable to the degree of accuracy desired or warranted by the method of numerical or graphical integration employed.

In numerical applications successive $\alpha^{(\nu)}$ were always found to converge excellently. Similarly, successive values of the $g^{(\nu)}(\tau)$, except, in some cases, over a very small fraction of the temperature range near τ_{∞}, where they showed oscillatory divergence (about mean values which were the solutions) leading ultimately to a breakdown of the method. In such cases the method need only be slightly modified, e.g. by using as 'input' $\frac{1}{2}\{g^{(\nu)}+g^{(\nu+1)}(\tau)\}$. The criterion is always that the final output should be as close as desired to the input from which it has been obtained; one can then be sure of having reached a numerical solution as close to the actual one as required.

(*d*) *Perturbation method*

The simultaneous solution of (4·32) and (4·33), as outlined, proves very tedious. The relatively simple case of zero energy flux, $\delta=1$, by whose solution the general chemical aspect of the flame will have been brought out already, is now complicated solely by the particular value of the diffusion coefficient, $\delta\neq 1$. This suggests using a perturbation method for the general problem, based on the 'unperturbed' case $\delta=1$. Writing

$$\alpha=\alpha^{*}(1+\Delta\alpha), \tag{4·34}$$

$$g=g^{*}(1+\Delta g), \tag{4·35}$$

$$\Delta X=X-X^{*}, \tag{4·36}$$

$$\Delta K=K(X^{*}+\Delta X;\tau)-K(X^{*};\tau), \tag{4·37}$$

where starred quantities refer to the solution of the case of vanishing energy flux, (4·23), one easily finds suitable *linear* equations for the evaluation of successively better ΔX, $\Delta\alpha$ and $\Delta g+\frac{1}{2}(\Delta g)^{2}$, and the problem can be rapidly solved.

It will be shown in part II that the method can be extended to cover one-dimensional flames in general. Moreover, the perturbations may, in general, with advantage be expressed as expansions in various parameters.

(*e*) *Parameter expansions*

In order to illustrate this approach, the $A\rightleftharpoons B$ problem with constant δ will be considered briefly. An appropriate parameter is here

$$\epsilon=1-\delta, \tag{4·38}$$

and the perturbation terms in (4·34) to (4·37) are expanded thus:

$$\Delta X = \epsilon\Delta_1 X + \epsilon^2\Delta_2 X + \ldots, \tag{4·39}$$

$$\Delta g = \epsilon\Delta_1 g + \epsilon^2\Delta_2 g + \ldots, \tag{4·40}$$

$$\Delta\alpha = \epsilon\Delta_1 \alpha + \epsilon^2\Delta_2 \alpha + \ldots, \tag{4·41}$$

etc.; only after solution is ϵ replaced by its numerical value. On substituting into (4·16) and (4·15) and equating coefficients of powers of ϵ, one obtains *linear* equations with simple integrating factors which can be solved successively. Thus the first coefficients in (4·39) and (4·40) are

$$\Delta_1 X = b\,\mathrm{e}^{\zeta^*}\int_{\tau}^{\tau_\infty} \mathrm{e}^{-\zeta^*}\,\mathrm{d}\tau, \tag{4·42}$$

$$\Delta_1 g = \alpha^*(g^*)^{-2}\,\mathrm{e}^{\zeta^*}\left\{\int_{\tau}^{\tau_\infty} \mathrm{e}^{-\zeta^*}\Delta_1 K\,\mathrm{d}\tau + \Delta_1\alpha\int_{\tau}^{\tau_\infty} \mathrm{e}^{-\zeta^*} K^*\,\mathrm{d}\tau\right\}, \tag{4·43}$$

where (4·42) is used in the first integral of (4·43), ζ^* is the function (3·19) of g^*, and, in order that the boundary conditions shall be satisfied,

$$\Delta_1\alpha = -\int_{\tau_0}^{\tau_\infty} \mathrm{e}^{-\zeta^*}\Delta_1 K\,\mathrm{d}\tau \bigg/ \int_{\tau_0}^{\tau_\infty} \mathrm{e}^{-\zeta^*} K^*\,\mathrm{d}\tau. \tag{4·44}$$

The method can be generalized for a temperature-dependent δ (cf. part II).

Further, when the specific heats of the components are not equal, it will usually be reasonable to regard an appropriate correction term, vanishing at both boundaries, as a perturbation which can be dealt with by the methods of this or the previous subsection. Likewise, the effect of viscosity, expressed by the last term in (2·31) which vanishes at the boundaries, may be included in the solution.

Examples to which these methods were applied will be summarized in part II, and further details will be found in the author's original laboratory reports (Klein 1954/5), obtainable on request.

PART II

5. The general one-dimensional flame problem

(a) *Introduction*

In part I the equations of a reacting gas mixture were adapted to the description of one-dimensional flames and then used for the solution of an ideal flame of the simplest possible type. The path has been from a very complicated situation to an ideally simple one, and the task is now to return to the general problem without getting lost in its complexity.

The equations to be solved will be reviewed presently. Such analogy of the general problem with the $A \rightleftharpoons B$ problem as persists will be pointed out, and it will be seen that two of the main difficulties are of familiar character. A program for the solution will be outlined briefly, but before embarking on the detailed method, a summary will be given of the successful numerical treatment of certain ideal flames which will make the present approach more intelligible.

It has been shown (cf. (3·17), (3·18) and (3·21)) that the problem of a one-dimensional flame in which the effects of radiation, thermo-diffusion, viscosity and variation of pressure may be neglected is contained in the equations

$$g\frac{\mathrm{d}y_S}{\mathrm{d}\tau} = \alpha b K_S, \tag{5·1}$$

$$g\frac{\mathrm{d}x_S}{\mathrm{d}\tau} = \Sigma\frac{1}{\delta_{SS'}}(x_S y_{S'} - x_{S'} y_S), \tag{5·2}$$

$$bg = \Sigma l_S y_S - \{a + (\Sigma b_S y_S)(\tau_\infty - \tau)\}, \tag{5·3}$$

where the reduced temperature τ is the independent variable, the reduced temperature gradient g is the principal dependent variable, the x_S, y_S are intermediate dependent variables describing the composition and flow in the gas, and α is the unknown constant related to the initial flame velocity. The b_S are reduced specific heats and $b = \Sigma b_S x_S^0 = \Sigma b_S y_S^0$. Suffixes or superscripts 0 and ∞ refer to boundary values, and the boundary conditions are $g^\infty = g^0 = 0$ (cf. (3·28)).

(b) *Analogy with the $A \rightleftharpoons B$ flame*

The energy equation (5·3) may be written

$$bg = \Sigma l_S y_S - \{a + b(\tau_\infty - \tau)\} - b\sigma_1, \tag{5·4}$$

where

$$\sigma_1 = (\tau_\infty - \tau)\{\Sigma(b_S - b)\, y_S\}/b \tag{5·5}$$

may be considered as a function of secondary importance. It represents a perturbation for which only the inequality of the specific heats of the components is responsible (cf. (3·2), (3·3) and (3·7)). As it vanishes at both boundaries (cf. (3·32)), the boundary conditions will not be affected by neglecting it altogether on a first computation, and in a method of successive approximations it will always be permissible to express it in terms of lower approximations to the y_S.

In order to appreciate the problem, it will be convenient to imagine a flame in which there is one main combustion product Z, but the formulation is independent of this assumption and demands only that the enthalpy constants l_S of the principal final components shall be small, with one of them identically zero (cf. (3·4)), $l_Z = 0$. Hence the sum

$$Y = \Sigma l_S y_S \tag{5·6}$$

will, in general, decrease from unity to a small fraction a (cf. (3·33) and (3·35)). It may be considered as the flow variable of a fictitious over-all fuel-like component, corresponding to A in the $A \rightleftharpoons B$ problem, whose rate of consumption is

$$K = -\Sigma l_S K_S = K(\ldots, x_S, \ldots; \tau). \tag{5·7}$$

Thus the reaction and energy equations give relations analogous to those of the $A \rightleftharpoons B$ problem,

$$g\frac{\mathrm{d}Y}{\mathrm{d}\tau} = -\alpha b K, \tag{5·8}$$

$$bg = Y - \{a + b(\tau_\infty - \tau)\} - b\sigma_1, \tag{5·9}$$

and on elimination of Y follows an equation of familiar form (cf. (4·15)),

$$g\left(1 - \sigma_1' - \frac{\mathrm{d}g}{\mathrm{d}\tau}\right) = \alpha K(\ldots, x_S, \ldots; \tau). \tag{5·10}$$

where σ_1' is the derivative of (5·5) with respect to τ.

(*c*) *Program of solution*

This relation (5·10) expresses the eigenvalue problem very concisely, and it will be considered as the fundamental equation of the theory. A solution is to be built on it whose detailed structure depends on the individual reaction and diffusion equations. The plan is therefore to deal with (5·10) in the same manner as in the simple case of the $A \rightleftharpoons B$ flame, that is, by assigning lower approximations to the x_S on the right (and to σ_1 on the left), and thus to find by the method of § 4 (*b*) approximations to $g(\tau)$ and to the constant α. These are then to be used in the remaining equations which, treated judiciously, are to serve as mere definitions for better approximations to the x_S, and the process is then to be repeated until convergence results.

The complexity of the diffusion equations (5·2) might easily discourage such a program or reduce it to a meaningless manipulation of the symbols. But, here again, the $A \rightleftharpoons B$ flame points the way. It will be recalled that this problem became particularly simple when diffusion was such as to result in a vanishing energy flux, and that this special case could be taken as a base for the solution of the more general problem by perturbation methods, involving only linear equations. In § 7 it will be shown that for one-dimensional flames in general, similar considerations apply. The solution of the problem for the given binary diffusion coefficients may therefore be dismissed as trivial in principle, provided a solution of the special case of vanishing energy flux can be obtained. The solution of this key problem is discussed in § 8.

6. Examples of some ideal flames

(*a*) *First order, unimolecular reaction*

The method of § 4 was applied to the ideal flame

$$A \rightleftharpoons B \tag{6·1}$$

(cf. Hirschfelder, Curtiss & Bird 1954) with the reaction rate (4·5) of the form

$$K = x_A\,\mathrm{e}^{-1/\tau} - x_B\,\mathrm{e}^{-(1+\beta)/\tau}, \tag{6·2}$$

and for values of the diffusion constant $\delta = 0, \frac{3}{4}, 1$. Also, for constant δ, a parameter expansion method in powers of $(1-\delta)$ and based on the case $\delta = 1$ was found to be quickly converging. It is found that the g curve is rather insensitive to the value of δ; that the K curve has the sharpest maximum for $\delta = 0$, so that the reaction is confined to a smaller region and is there more intense when there is no diffusion; that the eigenvalue increases very approximately linearly with δ, $\alpha_{(\delta=1)} \sim 3\alpha_{(\delta=0)}$, i.e. (cf. (3·41)) $v_{0(\delta=0)} \sim \sqrt{3}\,v_{0(\delta=1)}$; but that the curves of x_A for varying δ crowd towards $(x_A)_{\delta=1} = X^*$ and thin towards $(x_A)_{\delta=0}$. (Cf. figures 1 to 3.)

(*b*) *Second order, unimolecular reaction*

Next, the method of § 4 (*b*), together with the parameter expansion method just mentioned, was applied to the simple flame

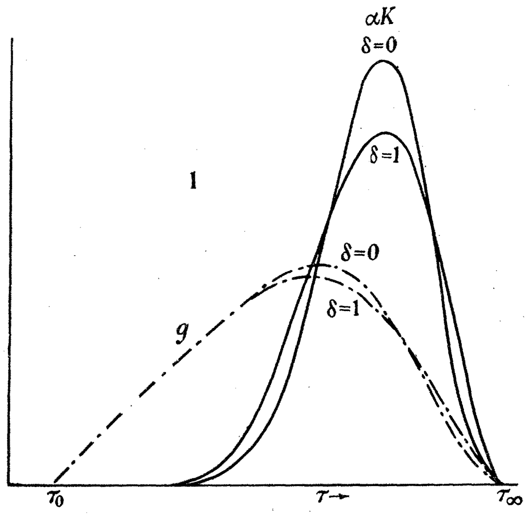
$$A \rightleftharpoons B, \tag{6·3}$$

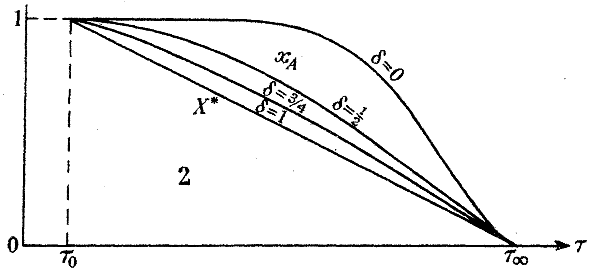
whose reaction rate was now assumed to be of the form (cf. (6·12) and (6·13)),

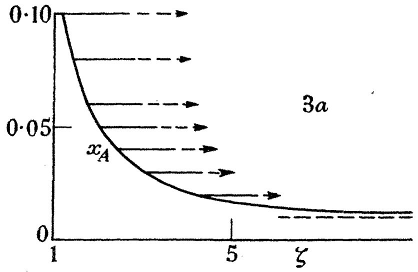
$$K = x_A\,\mathrm{e}^{-1/\tau}\,[x_A - \{1 - x_A(1-\mathrm{e}^{-1/\tau})\}\,\mathrm{e}^{-1/\tau}]. \tag{6·4}$$

The results are qualitatively very similar to those of the first-order reaction problem except that near the hot boundary all the curves g, K and x_A are now concave upwards. This is connected with a feature which deserves attention. For simplicity only the case $\delta = 1$ will be considered where the reaction rate (6·4) is immediately known, viz.

$$K = X^* \,\mathrm{e}^{-1/\tau}\,[X^* - \{1 - X^*(1-\mathrm{e}^{-1/\tau})\}\,\mathrm{e}^{-1/\tau}], \tag{6·5}$$







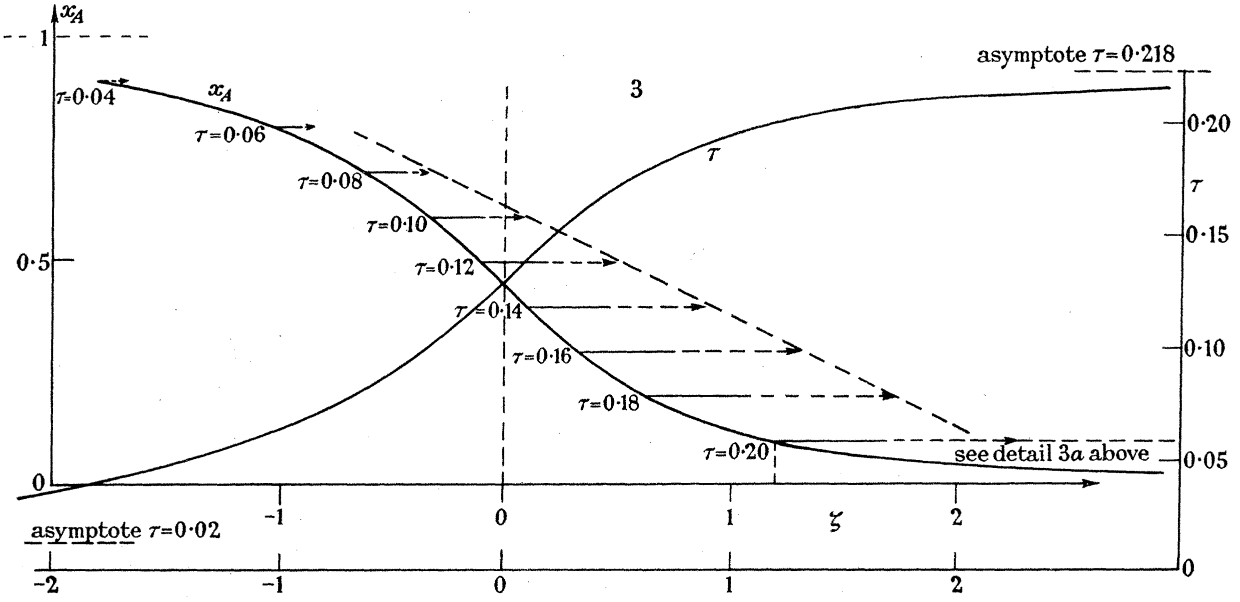


FIGURE 1. Reaction rates and solutions g for $\delta = 1$, $\delta = 0$ of the $A \rightleftharpoons B$, second-order reaction flame. (Curves for $A \rightleftharpoons B$, first-order reaction, are very similar except that they are concave downward near τ_∞.)

FIGURE 2. Decrease of mole fraction of fuel with temperature for various diffusion coefficients. $A \rightleftharpoons B$, second-order reaction.

FIGURE 3. $A \rightleftharpoons B$, second-order reaction, for $\delta = 1$. Increase of reduced temperature τ and decrease of fuel x_A with reduced distance ζ. The arrows represent velocities of the fuel on the scale (vel. at cold boundary) $\approx 1/10$ in. The end portions of the arrows represent the velocities over and above the mean mass velocity of the mixture x_A, x_B.

where
$$X^* = a+b(\tau_\infty-\tau) = x_A^\infty+\frac{x_A^0-x_A^\infty}{\tau_\infty-\tau_0}(\tau_\infty-\tau). \tag{6·6}$$

One may put
$$X^* = b(\tau_\infty^*-\tau) = \frac{x_A^0-x_A^\infty}{\tau_\infty-\tau_0}(\tau_\infty^*-\tau), \tag{6·7}$$

where
$$\tau_\infty^* = \tau_\infty+\frac{x_A^\infty}{x_A^0-x_A^\infty}(\tau_\infty-\tau_0). \tag{6·8}$$

The physically fictitious temperature τ_∞^* thus defined is very close to but just beyond the hot-boundary temperature, since there is very little unconsumed fuel left at the hot boundary $x_A^\infty \sim \frac{1}{100}$, and $x_A^0 = 1$. Now the relation between x_A^∞ and τ_∞ comes from $K^\infty = 0$ (cf. (3·25)), that is, here, from the square bracket in (6·5) vanishing. Hence the reaction rate (6·5) may be written
$$K = (\tau_\infty^*-\tau)(\tau_\infty-\tau)f(\tau), \tag{6·9}$$

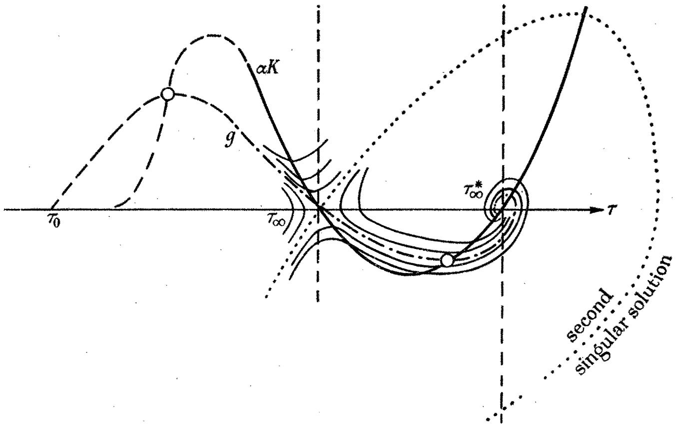


FIGURE 4. Singular points of the differential equation of the $A\rightleftharpoons B$, second-order reaction flame (not to scale: $\tau_\infty^*-\tau_\infty \approx \frac{1}{100}(\tau_\infty-\tau_0)$).

where $f(\tau)$ vanishes only at τ_0 and below. If one investigates the integral curves of (4·24), using (6·9), one finds that there are two singular points, the saddle-point at $\tau = \tau_\infty$ and, very close to it, a spiral point at $\tau = \tau_\infty^*$. The required singular solution passes through the former and coils around the latter, and though its final fate lies beyond the physically significant region, it warns against methods involving or implying power series in $(\tau_\infty-\tau)$; the spiral may make its influence felt even before $\tau = \tau_\infty$, and a spiral is unamenable to a polynomial approximation (see figure 4).

(*c*) *Simultaneous reactions*†

As a step towards chain reactions, a flame was considered whose underlying reactions are
$$A\rightleftharpoons B, \tag{6·10}$$
$$A+B\rightleftharpoons B+C, \tag{6·11}$$

where the reaction rates were taken as
$$K_1 = K_B = x_A\,\mathrm{e}^{-1/\tau}-x_B, \tag{6·12}$$
$$K_2 = K_C = \omega(x_A x_B - x_B x_C\,\mathrm{e}^{-1/\tau}). \tag{6·13}$$

---

† Cf. footnote to the following subsection.

It will be seen that the problem reduces very nearly to that of the second-order unimolecular reaction just treated if the first reaction (6·10) is assumed to be in equilibrium at all temperatures (cf. (6·12), (6·13) and (6·4)). This suggests at once a method of solution: one solves first the reduced problem ($K_1^{(0)} = 0$, giving $x_B^{(0)}$ in terms of $x_A^{(0)}$ and τ), and then, by a perturbation or parameter expansion method, one arrives at the solution of the complete problem. The constant ω in (6·13) is left undetermined in order that one may investigate the dependence of the solution on this 'intensity factor'. It is found that for a wide range, $\omega < 1000$, the dependence of g, x_A, x_B, and of K/ω (cf. (5·7), with $l_A = 1$, $l_B = 2$) is inappreciable, while the eigenvalue is practically inversely proportional to ω. One puts

$$\alpha' = \omega\alpha = \alpha_0'(1+\omega\alpha_1'+\omega^2\alpha_2'+\ldots) \tag{6·14}$$

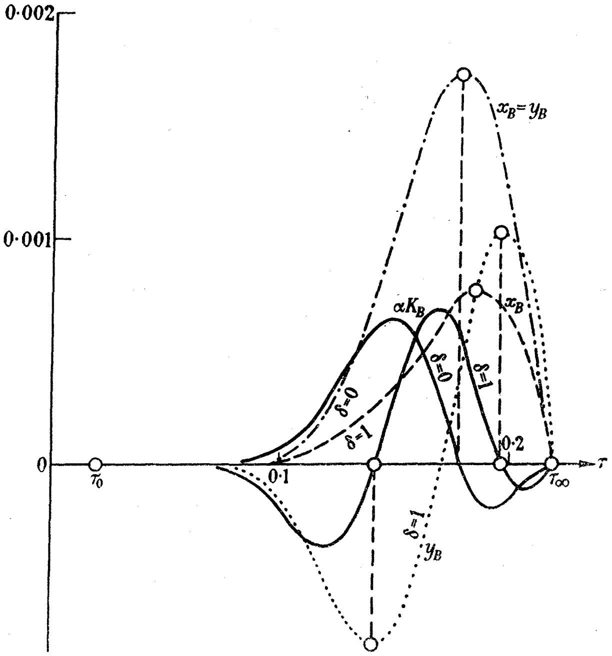


FIGURE 5. Catalyst concentration and catalyst production rate in the flame $A \rightleftharpoons B$, $A+B \rightleftharpoons B+C$, for negligible and standard diffusion. (The curve $(x_B)_{\delta=1}$ has been slightly distorted: the actual curve happens to pass through the intersection of the αK_B curves.)

and solves the equations by expanding all variables in powers of ω and equating coefficients. In particular, the reaction rate (6·12) is treated as an intermediate variable and expanded:

$$K_1 = K_B = \omega\{k_0(\tau)+\omega k_1(\tau)+\omega^2 k_2(\tau)+\ldots\}. \tag{6·15}$$

With ω left open, a parameter expansion is almost inevitable. There is, however, an interesting physical interpretation for the form of (6·15): ω is an intensity factor of (6·13), and any one reaction in a flame may be expected to entrain any other possible one; ω is therefore a factor of both K_1 and K_2. In more complicated flames, too, it will certainly be reasonable, and it may well be advantageous to introduce such a parameter artificially, and to equate it to unity after solution. In the present case, three terms for the expansions were found to be sufficient for $\omega < 1000$. The graphs for g, K and x_A are practically indistinguishable from those of figure 1 (read α' for α) and figure 2. The curves for x_B, y_B, and particularly K_B, for different diffusion constants, are very interesting (cf. figure 5). When $\delta = 1$, as against

$\delta = 0$, the rate of chemical production of the catalyst B is negative near the cold boundary; this shows that the component corresponding to a free radical in a real flame occurs in the cold-temperature region overwhelmingly by diffusion.

(*d*) *Simultaneous reactions: branching*†

A closer approach to real flames is furnished by the ideal flame

$$A \rightleftharpoons 2B, \tag{6·16}$$

$$A+B \rightleftharpoons B+C. \tag{6·17}$$

Though the results are qualitatively very similar to those of the previous problem, there is, mathematically, a significant difference and increase in complexity; the masses of the components are now not all equal, and the reaction rate of (6·16) is quadratic in x_B. The solution is again based on the $A \rightleftharpoons B$ flame and the perturbation terms are obtained by successive approximations. These perturbations are not always small; their squares have sometimes to be taken into account and quadratic equations have to be solved.

(*e*) *Simple associative reaction*

Lastly, an ideal flame with the reaction

$$A+B = 2C \tag{6·18}$$

was similarly solved. The reaction rate was roughly modelled on the HBr flame, but the aim here was solely to show that temperature-dependent and unequal binary diffusion coefficients, and unequal specific heats can be satisfactorily dealt with. The components A and B correspond to H_2 and Br_2, respectively. In figure 6, only near the cold boundary, where the doubtful reaction assumed hardly takes place, while diffusion is described rather well, will there be any resemblance to the real situation.

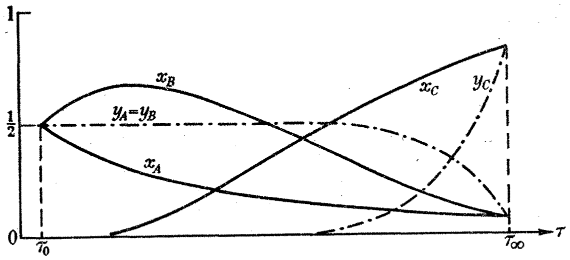


FIGURE 6. Change in composition with temperature in the $A+B \rightleftharpoons 2C$ flame. (The curves for g and αK are very similar to those of figure 1.)

Details of the methods employed for the solution of these examples, and the numerical data and results, will be found in the author's Naval Research Laboratory reports, available on request (Klein 1954/5).

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† Since the communication of this paper, further research along these lines has been carried out by J. O. Hirschfelder & J. Calvin Giddings which is in the course of publication. (Cf. *Sixth Symposium* (*International*) *on Combustion*, publ. Williams & Wilkins, (1956); *Journal of Physical Chemistry*; and original reports of the Naval Research Laboratory, University of Wisconsin.)

7. Solution of the general problem

(*a*) *Ideal diffusion coefficients*

The diffusion equations (5·2) are non-linear and thus greatly responsible for the complexity of the problem. That there is no intrinsic difficulty, however, can be seen by comparing them with the diffusion equation of the $A \rightleftharpoons B$ problem (4·11) which is linear. It is of interest, therefore, to inquire what particular sets of binary diffusion coefficients would make the equations linear. Bearing in mind the normalizations (cf. (3·7))

$$\Sigma x_S = 1, \quad \Sigma(m_S/m)\, y_S = 1, \tag{7·1}$$

one finds that coefficients of the form

$$\delta_{SS'} = \frac{m^2}{m_S m_{S'}}\,\delta, \tag{7·2}$$

where δ is a function independent of the pair of components, would produce the desired linearization, viz.

$$g\frac{\mathrm{d}x_S}{\mathrm{d}\tau} = \frac{1}{\delta}\frac{m_S}{m}\left(x_S - \frac{\overline{m}}{m}y_S\right). \tag{7·3}$$

It should be noted that the form (7·2) represents the diffusional behaviour of the molecules at least as far as may be expected on account of their unequal masses.

For such a set of diffusion coefficients the energy flux (3·39) becomes

$$\phi = -g\left[b + \delta\frac{m}{\overline{m}}\Sigma\frac{m}{m_S}\{l_S - b_S(\tau_\infty - \tau)\}\frac{\mathrm{d}x_S}{\mathrm{d}\tau}\right] \tag{7·4}$$

(cf. (4·19)), while its alternative expression (3·40)

$$\phi = a - (m/\overline{m})\,\Sigma\{l_S - b_S(\tau_\infty - \tau)\}\,x_S \tag{7·5}$$

remains, so that a linear relation between the x_S will result when the energy flux is zero, that is, when δ has the particular form given by

$$\frac{1}{\delta} = -\frac{1}{b}\frac{m}{\overline{m}}\Sigma\frac{m}{m_S}\{l_S - b_S(\tau_\infty - \tau)\}\frac{\mathrm{d}x_S}{\mathrm{d}\tau}. \tag{7·6}$$

It will be seen that if all the masses and the specific heats per unit mass of the components were the same, the over-all diffusion function δ would reduce to the constant value unity (cf. (7·6) and (7·5)).

(*b*) *Complete solution by parameter expansions*

It has been shown that the solution of the general $A \rightleftharpoons B$ problem can be based on the special case when the energy flux is zero (cf. § 4 (*d*)). The same may be done in the general one-dimensional flame problem. For, let α^*, g^*, x_S^*, y_S^* be the solution of the problem in which the energy flux is zero (cf. (8·1) to (8·5)), that is, where (7·2) and (7·6) hold, and let $1/\delta^*$ be the function (7·6) in terms of the x_S^*. Then in the complete problem (5·1) to (5·3), the diffusion coefficients are replaced by

$$\frac{1}{\delta_{SS'}} = \frac{m_S m_{S'}}{m^2}\frac{1}{\delta^*}(1 + \theta d_{SS'}), \tag{7·7}$$

where
$$d_{SS'} = \frac{m^2}{m_S m_{S'}} \frac{\delta^*}{\delta_{SS'}} - 1 \tag{7·8}$$

is a known function, and θ is a *parameter* whose value is left open; it is a device which enables us to pass from the set of ideal diffusion coefficients to that of the actually given ones. All dependent variables and their functions and α are formally expanded in powers of θ, e.g.

$$\alpha = \alpha^* + \theta\alpha_1 + \theta^2\alpha_2 + \dots, \tag{7·9}$$

$$g(\tau) = g^*(\tau) + \theta g_1(\tau) + \theta^2 g_2(\tau) + \dots, \tag{7·10}$$

and substituted into the equations (5·1) to (5·3). On equating coefficients of powers of θ, one obtains successively systems of *linear* ordinary differential equations with known variable but well-behaved coefficients (cf. § 4 (*d*); the coefficients in (7·9) follow from the boundary conditions, here without difficulty). These equations are then solved by standard numerical methods, and in the expansions (7·9), (7·10), etc., so derived one finally puts $\theta = 1$. The method will be laborious algebraically and computationally, but there is no difficulty in principle. There appears to be no reason to doubt the convergence of the expansions, since $\theta = 0 \to 1$ simply means a gradual distortion of the flame profile for fixed boundary values, and as the general character of the reaction rates remains the same, no singularities will be encountered in the process.

8. THE ZERO-ENERGY FLUX PROBLEM

(*a*) *The equations*

The refined treatment of diffusion has now been separated from the other main difficulty of the problem: the eigenvalue and the solution of non-linear differential equations. It remains in the ideal case in which the energy flux vanishes at all temperatures, and the equations to be solved are (cf. (5·1), (7·3), (7·6), (7·5) and (7·1))

$$g\frac{\mathrm{d}y_S}{\mathrm{d}\tau} = \alpha b K_S, \tag{8·1}$$

$$g\frac{\mathrm{d}x_S}{\mathrm{d}\tau} = \frac{1}{\delta}\frac{m_S}{m}\left(x_S - \frac{\overline{m}}{m}y_S\right), \tag{8·2}$$

where
$$\frac{1}{\delta} = -\frac{1}{b}\frac{m}{\overline{m}}\Sigma\frac{m}{m_S}\{l_S - b_S(\tau_\infty - \tau)\}\frac{\mathrm{d}x_S}{\mathrm{d}\tau} \tag{8·3}$$

and
$$\Sigma\{l_S - b_S(\tau_\infty - \tau)\}x_S = a\overline{m}/m, \tag{8·4}$$

together with
$$\Sigma x_S = 1, \quad \Sigma(m_S/m)\,y_S = 1. \tag{8·5}$$

The energy equation (8·4) and the diffusion function (8·3) may be written more suggestively if one introduces correction terms

$$\sigma_2 = (\tau_\infty - \tau)\,\{\Sigma(b_S - b\overline{m}/m)\,x_S\}/b, \tag{8·6}$$

$$\sigma_3 = (\tau_\infty - \tau)\frac{\mathrm{d}}{\mathrm{d}\tau}\left(\Sigma\frac{m}{m_S}b_S x_S\right)\Big/b, \tag{8·7}$$

which, like (5·5), will generally be only of secondary significance (cf. (8·13) and (8·15) below).

Suppose there are N components. Instead of using all $(N-1)$ relations (8·1), one of them may be left out and be replaced by a transformed combination of them all, viz. (5·10), so that the equations are

$$g\left(1-\sigma_1'-\frac{\mathrm{d}g}{\mathrm{d}\tau}\right)=\alpha K(\ldots,x_S,\ldots;\tau), \tag{8·8}$$

$$\left\{\begin{aligned} &y_S=\frac{m}{\overline{m}}x_S-\left(\frac{m}{\overline{m}}\delta\right)g\frac{m}{m_S}\frac{\mathrm{d}x_S}{\mathrm{d}\tau} \quad (N-1 \text{ relations}), && (8·9)\\ &\Sigma(m_S/m)\,y_S=1, && (8·10)\end{aligned}\right.$$

$$\left\{\begin{aligned} &K_S=\frac{1}{\alpha b}g\frac{\mathrm{d}y_S}{\mathrm{d}\tau} \quad (N-2 \text{ relations}), && (8·11)\\ &\Sigma x_S=1, && (8·12)\\ &\Sigma l_S x_S=\frac{\overline{m}}{m}\{a+b(\tau_\infty-\tau)\}+b\sigma_2, && (8·13)\end{aligned}\right.$$

$$K=-\Sigma l_S K_S, \tag{8·14}$$

$$\frac{\overline{m}}{m}\frac{1}{\delta}=-\frac{1}{b}\frac{\mathrm{d}}{\mathrm{d}\tau}\left(\Sigma\frac{m}{m_S}l_S x_S\right)+\sigma_3. \tag{8·15}$$

(*b*) *Method of successive approximations*

The program of solution proposed in § 5 (*c*) is immediately applicable to the equations (8·8) to (8·15), whose form and order partly embody it. The detailed method of successive approximations is as follows.

(i) Let $x_S^{(i)}$ be known approximations to the x_S, satisfying (8·12) and (8·13). Then approximations $K^{(i)}$, $(\delta m/\overline{m})^{(i)}$ and $(m/\overline{m})^{(i)}$ can be found from (8·14), (8·15) and (2·12), with $K_S^{(i)}=K_S(\ldots,x_{S'}^{(i)},\ldots;\tau)$.

(ii) Let $y_S^{(i-1)}$ be known approximations to the y_S, then an approximation $\sigma_1^{(i)}$ to σ_1 can be found from (5·5); for the lowest approximation this item is ignored and one puts $\sigma_1^{(0)}=0$.

(iii) One uses (8·8) with the approximations $K^{(i)}$ and $\sigma_1^{(i)}$ to find, by the method of § 4 (*b*), an approximate function $g^{(i)}$ and an approximate constant $\alpha^{(i)}$.

(iv) With the $g^{(i)}$ so obtained, and quantities of (i), one can now calculate from (8·9) and (8·10) better approximations $y_S^{(i)}$ to the y_S.

(v) From these, by (8·11), one finds, *as functions of the temperature*, better approximations than those used in (i) for $(N-2)$ production rates, $K_S^{(i+1)}$.

(vi) One calculates better approximations $x_S^{(i+1)}$ to the mole fractions by simultaneous solution of the $(N-2)$ simultaneous quadratic equations

$$K_{S'}(\ldots,x_S^{(i+1)},\ldots;\tau)=K_{S'}^{(i+1)}(\tau) \quad (N-2 \text{ relations}) \tag{8·16}$$

and of (8·12) and (8·13), where on the right of (8·13) one uses $(\overline{m}/m)^{(i)}$ and $\sigma_2^{(i)}$. This will be laborious but presents no difficulty in principle.

(vii) With the new $x_S^{(i+1)}$, or with modified values as indicated below, the process is then repeated.

The following points should be borne in mind for the successful application of this scheme:

(1) Relations expressing the conservation of atomic species simplify matters and, in effect, replace some of the equations (8·9) and (8·11).

(2) Which two of the rates of production should be left out in (8·11) or (8·16) will depend on the particular flame considered, that is, on how sensitive the profile proves to be to the various individual rates of production.

(3) On no account may more than $N-2$ relations (8·16) be used in the calculations; this is obvious from the derivation of the equations. A comparison of *all* successive $K_S^{(i)}$ will, however, throw light on the convergence and on (2).

(4) It is not implied that the scheme is genuinely convergent everywhere on the temperature range or for all possible forms of the rate constants; even if convergence could be proved for certain ranges $|x_S^{(0)}-x_S|$, it is unlikely that one will hit on a suitable lowest approximation. The scheme, as it stands, represents, therefore, on the one extreme, a perfect guide to the solution, involving genuinely converging approximations, on the other, a mere rule by which certain 'input' quantities $x_S^{(i)}$ may be made to produce certain 'output' quantities $x_S^{(i+1)}$.

(5) A numerical solution only, as close as desired to the actual solution, is required. It can generally be attained by putting, for example, $x_S^{(i)\prime} = \frac{1}{2}\{x_S^{(i)}+x_S^{(i-1)}\}$, or by more refined means. This procedure is not arbitrary; one adopts a definite rule for relating the latest 'input' values to previous 'output' values, and adheres to it. It is successful if eventually the last 'output' differs by as little as desired from the 'input' producing it.

(6) An excellent criterion for the over-all convergence of the scheme are the successive values of the $\alpha^{(i)}$. With reasonable lowest approximations $x_S^{(0)}$, it is surprising how quickly these will converge and thus stabilize the behaviour of the approximations to all the dependent variables.

(*c*) *The lowest approximation*

It will be seen that the method is sufficiently flexible to allow modifications appropriate to particular flames. While the actual calculation of successive approximations thus remains to some extent an art demanding skill of a mathematician, the choice of the lowest approximation calls for the intuition of a chemist. If there are N components, N values $x_S^{(0)}$ are required. *Two* relations for these subsist, viz. (8·12) and (8·13)—it is the great advantage of basing the complete problem on the special case of vanishing energy flux in that it provides the second relation (8·13). Where are the other $(N-2)$ relations to come from? This will have to depend on the particular flame under investigation: for the *lowest approximation only* one may be able to assume some reaction rate identically zero at all temperatures, some rate of production negligible, some reaction rate equal to or a simple multiple of another, etc.; only inspection of the rate constants and chemical experience can guide here.

At most, as a last resort, the theory suggests a *third* linear relation *for the lowest approximations only*, viz. since (8·15) will certainly be of order unity (cf. the remark after (7·6)), the relation contained in

$$\left(\frac{\overline{m}}{m}\frac{1}{\delta}\right)^{(0)} = 1, \tag{8·17}$$

where σ_3 can generally be ignored. It would mean that the reaction rates are assumed to be such as to give a value to the diffusion function which is at least not absurd, and this is all one can ask of a lowest approximation. Thus only $(N-3)$ more relations between the $x_S^{(0)}$ need be given on chemical grounds.

When the diffusion coefficients are of the 'ideal' form (7·2) (the energy flux not necessarily vanishing in addition), it is easy to write down a relation between the mean velocity

$$\bar{v} = \Sigma x_S v_S, \tag{8·18}$$

and the mean mass velocity, v. For, from (8·18), (3·6) and (8·9) it follows that

$$\frac{\bar{v}-v}{v} = -\delta g \frac{\mathrm{d}}{\mathrm{d}\tau}\left(\Sigma \frac{m}{m_S} x_S\right). \tag{8·19}$$

Thus, for some flames, particularly for those in which the predominating components are of similar molecular weights, it will be reasonable to start with a linear relation

$$\Sigma \frac{m}{m_S} x_S^{(0)} = \Sigma \frac{m}{m_S} x_S^{\infty} + \left\{\Sigma \frac{m}{m_S}\left(x_S^{0} - x_S^{\infty}\right)\right\} \frac{\tau_\infty - \tau}{\tau_\infty - \tau_0}, \tag{8·20}$$

but it will hardly have more justification than

$$\Sigma \frac{m_S}{m} x_S^{(0)} = \left(\frac{\overline{m}}{m}\right)^{(0)} = \frac{\overline{m}^{\infty}}{m} + \left(1 - \frac{\overline{m}^{\infty}}{m}\right) \frac{\tau_\infty - \tau}{\tau_\infty - \tau_0}. \tag{8·21}$$

It may be noted also that if estimates for $g^{(0)}(\tau)$ and $\alpha^{(0)}$ are available from experimental observations, the scheme of § 8 (*b*) may conveniently be started at the stage (iv).

(*d*) *Conclusion*

The underlying principle of the preceding treatment has been that any initial modification of the problem is permissible provided it does not crucially change the character of the flame and that it can serve as a stepping-stone towards the solution of the complete problem. Although the various transformations of the equations were made with a particular method of solution in mind, they are distinct from it; and since the special methods of successive approximations and perturbations, with or without parameter expansions, may well be improved upon, only the general approach is put forward as a contribution to the mathematical description of flames.

Finally, the solution of the reduced problem corresponding to vanishing energy flux appears to the author as more than a mathematical device. A rough estimate shows that the only reduced binary diffusion coefficients of any importance differ from the ideal ones by at most a factor of order 10. If one considers that in most flames not even all the reactions are known, and in those where they are, the rate constants are often uncertain to powers of 10, the transition to the complete problem, briefly indicated in § 7 (*b*), is not of immediate importance, and one should always concentrate first on solving the zero energy flux case. This gives a mathematically consistent flame profile, takes diffusion into account as far as the differences in mass of the components are concerned, and it may be expected to afford a tolerable picture of the consequences of the reactions assumed which can be compared with experimental evidence.

The author owes his introduction to the theory of flames and the opportunity of having been able to widen his experience through his association with the University of Wisconsin, to Professor Joseph O. Hirschfelder to whom he expresses his sincere gratitude.

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APPENDIX: VISCOSITY

The effect of viscosity can be taken into account as follows. Since the pressure is still assumed approximately constant, (2·30) is ignored as before, but now the viscosity term in (2·31) leads to additional terms

$$-\frac{1}{2}\frac{\mu'}{M}\frac{dv^2}{dz}, \quad -\frac{1}{2}\frac{\mu' m}{EM}\frac{dv^2}{dz}, \quad -\eta g\frac{d}{d\tau}\tfrac{1}{2}mv^2/E \tag{A 1}$$

on the right of (3·1), (3·8) and (3·18), respectively, where

$$\eta = \mu' c/\lambda \tag{A 2}$$

may be regarded as a reduced viscosity coefficient, known as function of τ; it will be of order unity, having the same form as a Prandtl number. Owing to the factor g the term (A 1) vanishes at both boundaries; the relations (3·30) to (3·39) remain unaltered. Now, by (2·33), (3·5) and (3·41),

$$v^2 = v_0^2\left(\frac{m}{\overline{m}}\frac{\tau}{\tau_0}\right)^2 = \frac{1}{b^2}\frac{\lambda_0}{R}\left(\frac{E}{p}\right)^2\frac{1}{\alpha}\left(\frac{m}{\overline{m}}\tau\right)^2, \tag{A 3}$$

so that (A 1) becomes

$$-b\sigma_1^{(\text{visc.})} = -\left(\frac{m\lambda_0 E}{2b^2Rp^2}\right)\frac{1}{\alpha}\eta g\frac{d}{d\tau}\left(\frac{m}{\overline{m}}\tau\right)^2, \tag{A 4}$$

where the first bracket is a constant. The equations (8·8) to (8·15) are found to remain unaffected if σ_1 of (5·5) is replaced by

$$\sigma_1 + \sigma_1^{(\text{visc.})} \tag{A 5}$$

and σ_2 of (8·6) by

$$\sigma_2 + \sigma_2^{(\text{visc.})}, \tag{A 6}$$

where

$$\sigma_2^{(\text{visc.})} = \frac{\overline{m}}{m}\sigma_1^{(\text{visc.})}. \tag{A 7}$$

The method of successive approximations remains unaffected; one expresses (A 4) always in terms of the best known approximations to α, g and $m/\overline{m}$, and ignores it in the first stage of the method.