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GOVERNING EQUATIONS OF COMBUSTION

1 Approach

The development of the equations governing combustion involves derivation of the equations of motion of a chemically reacting gaseous mixture and judicious simplification to render them tractable while retaining their essential characteristics. A rigorous derivation requires a long apprenticeship in either kinetic theory or continuum mechanics. (Indeed, the general continuum theory of reacting mixtures is only now being perfected.) We choose instead a plausible, but potentially rigorous, derivation based on the continuum theory of a mixture of fluids, guided by experience with a single fluid. *Ad hoc* arguments, in particular the inconsistent assumption that the mixture itself is a fluid for the purpose of introducing certain constitutive relations, will not be used.

Treating the flow of a reacting mixture as an essentially isobaric process, the so-called combustion approximation, is a safe simplification under a wide range of circumstances if detonations are excluded. But the remaining simplifications, designed as they are solely to make the equations tractable, should be accepted tentatively. They are always revocable should faulty predictions result; for that reason they are explained carefully. Nevertheless, whosoever is primarily interested in solving nontrivial combustion problems, as we are, can have the same confidence in the final equations as is normally placed in the equations of a non-Newtonian fluid, for example.

These final equations retain most of the complexity of a compressible, heat-conducting, viscous fluid; but diffusion of the species, and source terms representing the chemical reaction, have been added. This complexity has usually been fought with irrational approximation and computers. Combustion processes, however, tend by their very nature to have large activation energies. It is, therefore, more appropriate to analyze the

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problem rationally by localizing the reaction in layers (or flames), which can be done through activation-energy asymptotics, as is shown in section 8. Such an approach was scarcely mentioned before publication of the review article of Williams (1971), which contains the first suggestion of so forming a mathematical theory of combustion. The classic paper of Bush & Fendell (1970) did come earlier and Frank-Kamenetskii (1969, p. 375) did introduce approximations based on large activation energy more than forty years ago, but Williams marked the start of a clear path through the complex and fascinating problems of combustion, as is shown by the wealth of papers that have appeared since.

Our immediate intention is to reach a convincing set of equations and a method of attack, so as to come to grips with the subject of laminar flames.

2 Continuum theory of a mixture of reacting species

The mixture has density ρ and is considered to be made up of N fluids whose separate densities are ρY_i ($i = 1, 2, \dots, N$). Here the Y_i are mass fractions (or concentrations), with

$$\sum_{i=1}^N Y_i = 1. \quad (1)$$

If \mathbf{v}_i is the velocity of the i th fluid, i.e. species, the balance of mass requires

$$\partial(\rho Y_i)/\partial t + \nabla \cdot (\rho Y_i \mathbf{v}_i) = \dot{\rho}_i, \quad (2)$$

where $\dot{\rho}_i$ is the rate of production of species i (mass per unit volume) by the chemical reactions so that

$$\sum_{i=1}^N \dot{\rho}_i = 0. \quad (3)$$

Summation of the equations over all species yields the familiar continuity equation

$$\partial \rho / \partial t + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (4)$$

where

$$\mathbf{v} = \sum_{i=1}^N Y_i \mathbf{v}_i \quad (5)$$

is the mass-average velocity of the mixture. Each balance equation (2) can now be recast by subtracting Y_i times the overall equation (4) and introducing the diffusion velocities

$$\mathbf{V}_i = \mathbf{v}_i - \mathbf{v}; \quad (6)$$

this gives

$$\rho(\partial Y_i / \partial t + \mathbf{v} \cdot \nabla Y_i) = \dot{\rho}_i - \nabla \cdot (\rho Y_i \mathbf{V}_i). \quad (7)$$

The momentum balances of the separate fluids will not be given since they play no role in the sequel. But Truesdell (1965) shows that if they are added the result is the single-fluid balance

$$\rho(\partial \mathbf{v} / \partial t + \mathbf{v} \cdot \nabla \mathbf{v}) = \nabla \cdot \Sigma + \rho \mathbf{g}, \quad (8)$$

provided no momentum is created by the chemical reactions. Here Σ is the sum of the stresses in the individual fluids plus stresses due to diffusion of the species and \mathbf{g} is the gravity force, assumed to be the only force external to the mixture. Interactions between the species (see also the discussion of Fick's law (19)), which give additional external forces on each individual fluid, sum to zero.

We shall also forego writing the energy balances for the separate fluids, but Truesdell shows their sum gives the single-fluid balance

$$\rho(\partial U / \partial t + \mathbf{v} \cdot \nabla U) = \Sigma : \nabla \mathbf{v} + \nabla \cdot \mathbf{q}. \quad (9)$$

provided no energy is created by the chemical reactions and the work of the interaction forces is negligible. (For the forces mentioned at the end of this section the work is nonlinear in the (small) V_i .) Here U is the sum of the separate internal energies plus kinetic energies of diffusion, while \mathbf{q} is the sum of the separate energy fluxes plus fluxes due to diffusion. Note that the work of the gravity force has not been neglected: it is $\sum_{i=1}^N (\rho Y_i) \mathbf{g} \cdot V_i = 0$ by virtue of the result

$$\sum_{i=1}^N Y_i V_i = 0, \quad (10)$$

which follows from the definition (6).

The new variables $\dot{\rho}_i$, V_i , Σ , U , and \mathbf{q} introduced by these balances have to be related to the primitive variables by constitutive equations. Continuum mechanics does not supply such relations, but rather judges them for consistency with certain general principles after they have been proposed. For reacting mixtures such judgements are still being made, but the linear equations we propose are acceptable (Bowen 1976). With the exception of those for $\dot{\rho}_i$ and V_i they result from experience with a single fluid. The coefficients (50) that will appear are, for the moment, to be considered functions of the primitive variables.

The primitive variables will be Y_i , v , ρ , and p ; but in formulating the constitutive equations it is convenient to introduce the temperature T , which is assumed to be the same for all fluids. If each species is a perfect gas its partial pressure is

$$p_i = R(\rho Y_i)T/m_i, \quad (11)$$

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and the consequence of Dalton’s law is

$$p = R\rho T \sum_{i=1}^N (Y_i/m_i), \tag{12}$$

which determines the common temperature. Here R is the gas constant and m_i is the mass of a molecule of species i . The separate internal energies of the fluids are then functions of T alone, which may be written

$$U_i = h_i - p_i/(\rho Y_i), \tag{13}$$

where the enthalpies are

$$h_i = h_i^0 + \int_{T^0}^T c_{pi}(T) dT. \tag{14}$$

Here h_i^0 is the heat of formation of the species i at some standard temperature T^0 and the c_{pi} are the specific heats at constant pressure. If we neglect the kinetic energies of diffusion because they are nonlinear in the V_i , the internal energy of the mixture is now

$$U = \sum_{i=1}^N Y_i h_i - p/\rho. \tag{15}$$

Next the energy flux \mathbf{q} is specified by requiring that the energy flux in each individual fluid is due entirely to heat conduction, so that

$$\mathbf{q} = \lambda \nabla T - \rho \sum_{i=1}^N Y_i h_i \mathbf{V}_i, \tag{16}$$

where λ , the coefficient of thermal conductivity of the mixture, is the sum of the species coefficients. Each of the diffusion fluxes is that of a single fluid moving relative to the mixture with velocity V_i when kinetic energy and deviation of the stress tensor (17) from $-p_i \mathbf{I}$ are neglected, the latter anticipating the combustion approximation (section 5) that makes v_i small. Such a \mathbf{q} neglects, in particular, radiative transfer and the Dufour effect (heat flux due to concentration gradients).

The separate stresses are assumed to be Newtonian, i.e.

$$\Sigma_i = -(p_i + \frac{2}{3}\kappa_i \nabla \cdot \mathbf{v}_i) \mathbf{I} + \kappa_i [\nabla \mathbf{v}_i + (\nabla \mathbf{v}_i)^T], \tag{17}$$

where \mathbf{I} is the unit tensor and bulk viscosity has been neglected (for simplicity only). We shall take the remaining coefficients $\kappa_i = Y_i \kappa$; this corresponds to assuming that the intrinsic viscosities of the fluids are all equal. (Otherwise gradients of V_i must be neglected in comparison with those of \mathbf{v} to arrive at the result (18).) Since stresses due to diffusion and terms $V_i \nabla Y_i$ are nonlinear, the separate stresses sum to give

$$\Sigma = -(p + \frac{2}{3}\kappa \nabla \cdot \mathbf{v}) \mathbf{I} + \kappa [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] \tag{18}$$

by virtue of the result (10).

3 The Arrhenius factor

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The thermomechanical constitution is completed by equations for the diffusion velocities V_i ; we adopt Onsager's (1945) generalization of Fick's (1855) law

$$\rho Y_i V_i = - \sum_{j=1}^N \mu_{ij} \nabla Y_j, \quad (19)$$

making each diffusive mass flux a linear combination of the concentration gradients. The result (10) now reads

$$\sum_{i=1}^N \sum_{j=1}^N \mu_{ij} \nabla Y_j = \sum_{j=1}^{N-1} \left[\sum_{i=1}^N (\mu_{ij} - \mu_{iN}) \right] \nabla Y_j = 0$$

when the relation (1) is used to eliminate ∇Y_N . Since the remaining gradients are independent of each other, it follows that the coefficients μ_{ij} must satisfy

$$\sum_{i=1}^N \mu_{ij} = \sum_{i=1}^N \mu_{iN} \quad \text{for } j=1, 2, \dots, N-1. \quad (20)$$

An equivalent of the law (19), in which the gradients are expressed as linear combinations of the diffusion velocities, can be derived from the separate momentum balances by making assumptions about the interaction forces between the species (Williams 1965, p. 416). An implicit new assumption in such arguments is that the accelerations $\partial V_i / \partial t$ are negligible. They only occur in unsteady problems and then produce a finite velocity of propagation of diffusion effects (Müller 1977): such an effect appears to be of no great importance in combustion. The generalized Fick's law (which neglects the Soret effect of a diffusive flux due to temperature gradients) is the only nonchemical constitutive equation not derived from experience with a single fluid.

Finally we come to the ρ_i , which require a discussion of chemical reactions.

3 The Arrhenius factor

For simplicity we shall first consider one-step combustion, where a single unopposed chemical reaction is involved. If N_i is the number of molecules of species i per unit volume, then by definition

$$\dot{\rho}_i = m_i \dot{N}_i. \quad (21)$$

The chemical reaction may be described in terms of the m_i as the mass balance

$$\sum_{i=1}^N v_i m_i = \sum_{i=1}^N \lambda_i m_i, \quad (22)$$

where v_i and λ_i are called the stoichiometric coefficients, each a non-

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negative integer; v_i is zero if the species i is not a reactant, while λ_i is zero if it is not a product. Both are zero for an inert. Since these coefficients represent the relative numbers of molecules consumed or produced by the reaction we may write

$$\dot{N}_i = (\lambda_i - v_i)\omega, \quad (23)$$

where $\omega (> 0)$ measures the rate at which the reaction is proceeding. Clearly the requirement (3) is now a consequence of the definition (21) and the mass balance (22).

For example, consider the exothermic reaction



by which nitrosyl chloride is formed from nitric oxide and chlorine. If the three species are numbered

$$1: \text{NO}; \quad 2: \text{Cl}_2; \quad 3: \text{NOCl};$$

then the stoichiometric integers are

$$v_1 = 2, \quad v_2 = 1, \quad v_3 = 0; \quad \lambda_1 = 0, \quad \lambda_2 = 0, \quad \lambda_3 = 2;$$

and

$$\dot{N}_1 = -2\omega, \quad \dot{N}_2 = -\omega, \quad \dot{N}_3 = 2\omega$$

are the rates of consumption (negative) and production (positive) of the molecules. Note that the reaction (24) is written



when single molecules are used.

It is, therefore, ω that must be related to the primitive variables; a common assumption is that it is proportional to the number density (concentration) $\rho Y_j/m_j$ of each reactant, where the species j is counted v_j times as a reactant (see the single-molecule form (25) of the reaction). Thus,

$$\omega = k \prod_{j=1}^N (\rho Y_j/m_j)^{\nu_j} = k\rho^\nu \prod_{j=1}^N (Y_j/m_j)^{\nu_j}, \quad \text{where } \nu = \sum_{j=1}^N v_j \quad (26)$$

and the factor k is assumed to depend only on the temperature. Since experimental determinations of k are often done under isothermal conditions, it is called the rate constant; but we shall avoid the term since the temperature dependence of k is an essential feature in our analysis. The Arrhenius (1889) law

$$k = BT^\alpha e^{-E/RT} \quad (27)$$

will be taken for its variation with temperature, where B , α (equals $\frac{1}{2}$ theoretically), and E are constants. The latter is known as the activation energy since E/R is roughly the temperature below which k is relatively small.

4 Differential mass diffusion; equalities 7

Thus we now have

$$\dot{\rho}_i = \mu_i \omega, \quad (28)$$

where

$$\mu_i = m_i(\lambda_i - \nu_i), \quad \omega = BT^\alpha e^{-E/RT} \rho^v \prod_{j=1}^N (Y_j/m_j)^{\nu_j}. \quad (29)$$

More complex reactions are first split up into elementary reaction steps that may contain reversals of each other (opposing reactions). For each elementary reaction a formula (28) holds and for the complete reaction $\dot{\rho}_i$ is the sum of all such terms. (A pair of opposing reactions may be in equilibrium, i.e. the corresponding terms cancel and thereby furnish an algebraic relation between mass fractions.) The central question of reaction kinetics is to determine these elementary steps and their parameters B , α , and E . This monograph will be restricted to a single elementary reaction. Equilibrium is then reached only when one of the reactants is exhausted, i.e.

$$Y_i = 0 \quad \text{for some } i. \quad (30)$$

In practice, a combustion reaction may be a complex network of elementary steps, so that attempts are made to model the overall reaction with a smaller number of terms of the form (28), preferably one. The exponents ν_i are then released from being the stoichiometric coefficients of the overall reaction and ν is not necessarily their sum. On the other hand, the μ_i retain their meaning since they still represent the proportions in which the species take part in the reaction. The free constants B , α , E , ν , and ν_i are determined experimentally; of course, the ν_i need no longer be integers.

4 Differential mass diffusion; equality of c_{p_i} and of m_i

Once the various parameters (constants and functions) that appear in the constitutive equations (12), (15), (16), (18), (19), and (28) are given, there are $N + 6$ equations (1), (4), (7), (8), and (9) for the $N + 5$ unknowns Y_i , \mathbf{v} , ρ , and p . Equation (1) is consistent with the remainder since they conserve $\sum_{i=1}^N Y_i$ whenever the relations (20) hold between the μ_{ij} ; initial or boundary conditions will then give it the value 1. The system is very complicated and must be simplified if it is to be analyzed in detail.

The law (19) leads to terms

$$\sum_{j=1}^N \nabla \cdot (\mu_{ij} \nabla Y_j) \quad (31)$$

in the mass balances (7). To simplify these terms while retaining different diffusion properties for the species, it is tempting to set

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$$\mu_{ij}=0 \quad \text{for } i \neq j \quad (32)$$

and allow the μ_{ii} to change with i (Emmons 1971). The conditions (20), however, would be violated: they require

$$\mu_{ii}=\mu_{NN}=\mu(\text{say}) \quad \text{for all } i. \quad (33)$$

Conclusions (32) and (33) are reached quite generally by Williams's theory when the so-called binary diffusion coefficients are equal, i.e. whenever the interactions between pairs of species are identical for momentum.

The same goal, however, can effectively be reached by taking the values (32) for all i except the last, and

$$\mu_{Nj}=\mu_{NN}-\mu_{jj} \quad \text{for } j \neq N \quad (34)$$

with the μ_{jj} different. The conditions (20) are now satisfied and the terms (31) simplify to

$$\nabla \cdot (\mu_{ii} \nabla Y_i) \quad \text{for } i \neq N. \quad (35)$$

Only the N th equation remains complicated but, since Y_N can be otherwise calculated from $1 - \sum_{i=1}^{N-1} Y_i$, that does not matter. Such a scheme can be justified from Williams's formulas when the first $N-1$ species are scarce compared to the last, a condition often roughly approximated in combustion where, for example, a stoichiometric air/propane mixture contains 76% by volume of the inerts nitrogen and argon.

In short, we shall generally employ the values (32) and (33) but, when differential diffusion cannot be ignored, the μ_{ii} for $i=1, 2, \dots, N-1$ will be given different values. The results will then apply to a mixture of reactants and products highly diluted in an inert. Note that a common value of the μ_{ii} can still depend on the Y_i and, hence, take different values in different locations. This can give the appearance of differential diffusion when, for example, there are two reactants ($i=1, 2$) that do not coexist. Where $Y_1=0$ its equation is irrelevant and μ_{22} there may differ from μ_{11} in the region where $Y_2=0$ with irrelevant equation. Such is the case in the burning of a fuel droplet treated by Kassoy & Williams (1968). They use different diffusion coefficients for the fuel and oxidant equations but do not apply the equations in the same place: the combustion field is divided into two parts, in each of which there is either no fuel or no oxidant. There is no question of an abundant inert.

We come now to the energy balance (9). First note that the individual c_{pi} disappear from U in favor of

$$c_p(T, Y_i) = \sum_{i=1}^N Y_i c_{pi}. \quad (36)$$

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Thus, we have immediately

$$U = \sum_{i=1}^N Y_i h_i^0 + I - p/\rho, \tag{37}$$

where

$$I(T, Y_i) = \sum_{i=1}^N Y_i \int_{T^0}^T c_{pi} dT = \int_{T^0}^T c_p dT, \tag{38}$$

the last integral being taken with the Y_i fixed, i.e. for constant composition. Adoption of $\mu_{ij} = \mu \delta_{ij}$ ensures that the same happens to \mathbf{q} : we have

$$\begin{aligned} \rho \sum_{i=1}^N Y_i h_i V_i &= \rho \sum_{i=1}^N Y_i h_i^0 V_i + \rho \sum_{i=1}^N \left(\int_{T^0}^T c_{pi} dT \right) Y_i V_i \\ &= \rho \sum_{i=1}^N Y_i h_i^0 V_i - \mu \sum_{i=1}^N \left(\int_{T^0}^T c_{pi} dT \right) \nabla Y_i \\ &= \rho \sum_{i=1}^N Y_i h_i^0 V_i - \mu \left(\nabla I - \sum_{i=1}^N Y_i c_{pi} \nabla T \right) \\ &= \rho \sum_{i=1}^N Y_i h_i^0 V_i + \mu (c_p \nabla T - \nabla I). \end{aligned} \tag{39}$$

Next note the form that the energy balance now takes. The total contribution to the equation from the heats of formation h_i^0 , when placed on the right side, is

$$- \sum_{i=1}^N h_i^0 [\rho(\partial Y_i/\partial t - \mathbf{v} \cdot \nabla Y_i) + \nabla \cdot (\rho Y_i V_i)] = - \sum_{i=1}^N h_i^0 \rho_i \tag{40}$$

according to the mass balances (7). Also, the total contribution from heat conduction and terms containing c_p , when placed on the left side, is

$$\rho(\partial I/\partial t + \mathbf{v} \cdot \nabla I) + \nabla \cdot [\mu(c_p \nabla T - \nabla I) - \lambda \nabla T]. \tag{41}$$

The remaining terms, when placed on the right side, contribute

$$\partial p/\partial t + \mathbf{v} \cdot \nabla p - \frac{2}{3} \kappa (\nabla \cdot \mathbf{v})^2 + \kappa [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] : \nabla \mathbf{v} \tag{42}$$

according to the continuity equation (4). In the combustion approximation discussed later the velocity is small, implying also that the pressure is effectively a spatial constant, so that these last terms are ignored, except for $\partial p/\partial t$, which is a function of t alone.

It is tempting to take the Lewis number

$$\mathcal{L} = \lambda/\mu c_p \tag{43}$$

equal to 1; then the terms (41) contain I only. If the c_{pi} , however, are not all equal, c_p is a linear function (36) of the Y_i that μ/λ can only equal for very special mixtures, if at all. Only when the c_{pi} are all equal does c_p lose

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its dependence on the composition of the mixture, and then it is unnecessary to make any assumption about the Lewis number, as we shall see next.

We are, therefore, faced with taking all the c_{pi} equal, when c_p becomes a function of T alone:

$$c_p(T) = c_{pi} \quad \text{for all } i. \quad (44)$$

Since ∇I is then $c_p \nabla T$ the energy equation reads

$$\rho(\partial I/\partial t + \mathbf{v} \cdot \nabla I) - \nabla \cdot [(\lambda/c_p)\nabla I] = - \left[\sum_{i=1}^N h_i^0 \mu_i \right] \omega + \partial p/\partial t, \quad (45)$$

where

$$I(T) = \int_{T^0}^T c_p dT \quad (46)$$

is a function of T only and we have used the rate result (28). When considering specific enthalpy the species are distinguished only by their heats of formation; thus, equation (45) is that of a single fluid in which differences in these heats are liberated as reactants change into products. The species equations (7) take a similar form

$$\rho(\partial Y_i/\partial t + \mathbf{v} \cdot \nabla Y_i) - \nabla \cdot (\mu \nabla Y_i) = \mu_i \omega. \quad (47)$$

Even differential diffusion leads to the energy equation (45) when the specific heats are equal; the sum in which the c_{pi} first appear in the calculation (39) is again zero, now by virtue of the identity (10). When all but the N th species are scarce, the specific heats need not be equal to obtain an equation of the form (45); then $Y_1, Y_2, \dots, Y_{N-1}, V_N$ are small and the same sum is negligible compared to the heat-conduction term in the resulting equation. A corresponding approximation of I then leads to equation (45) with c_p replaced by c_{pN} . On the other hand, the species equations (47) are changed by differential diffusion (the terms $\mu \nabla Y_i$ being replaced by $\sum_{j=1}^N \mu_{ij} \nabla Y_j$).

Another complication is the presence of the mass fractions in the equation of state (12). They effectively disappear if the first $N-1$ species are scarce compared to the last; but the same simplification can only be achieved, in general, when all the molecular masses are the same, i.e. $m_i = m$ for all i . Then the law (12) becomes

$$p = R\rho T/m \quad (48)$$

and the mixture behaves like a perfect gas. Such is the case when the reaction changes a single molecule into a single molecule, but in practice the condition is never met exactly.

We may certainly expect the assumptions of equal specific heats and