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# Atomic Recombination in Nozzles: Methods of Analysis for Flows with Complicated Chemistry

By

K.N.C. Bray and J.P. Appleton

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Atomic Recombination in Nozzles:  
 Methods of Analysis for Flows with Complicated Chemistry  
 - By -  
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SUMMARY

The object of this review is to study the feasibility of performing accurate calculations on the non-equilibrium flow of a complicated gas mixture through nozzles, with particular reference to the propulsive nozzle of the hypersonic ramjet.

Equations are given for the steady, quasi-one-dimensional, adiabatic flow of a general reacting gas mixture, consisting of  $\eta$  species related through  $N$  chemical reactions. A number of alternative methods of obtaining numerical solutions to these equations are described and evaluated.

The formulation of the system of chemical reactions is also discussed, together with the availability of the large amount of thermodynamic and chemical kinetic data which is required before a numerical solution can be attempted.

It is found that by far the most serious difficulty to be overcome, before accurate non-equilibrium nozzle calculations can be performed, is obtaining reliable data on the rates of the many chemical reactions which may be involved.

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LIST OF SYMBOLS

A	Nozzle cross-sectional area
$B^r$	Non-dimensional parameter defined in Section 4.2 for the r <sup>th</sup> reaction
$C_{p_j}$	Specific heat at constant pressure of the j <sup>th</sup> species
$G_j^r$	Defined in Section 3.5.4 for the j <sup>th</sup> species in the r <sup>th</sup> reaction
H	Specific enthalpy
$\Delta H_f^{\circ j}$	Standard heat of formation of the j <sup>th</sup> species
$K_c^r$	Equilibrium constant based on mole concentrations for the r <sup>th</sup> reaction
$K_p^r$	Equilibrium constant based on partial pressure for the r <sup>th</sup> reaction
$K_y^r$	Equilibrium constant based on mass fractions for the r <sup>th</sup> reaction
$M_j$	Chemical formula of j <sup>th</sup> species
N	Total number of reactions taking place in a reacting mixture
$Q^r$	Numerical constant of order unity defined in Section 4.2 for the r <sup>th</sup> reaction
R	Universal gas constant
$R_f^r$	Quantity defined in Section 4.2
$R_b^r$	Quantity defined in Section 4.2
T	Temperature
$W_j$	Molecular weight of the j <sup>th</sup> species

$X^r$	Defined in Section 3.3 for the $r^{\text{th}}$ reaction
$Y^r$	Defined in Section 3.5.4. for the $r^{\text{th}}$ reaction
$Z^r$	Characteristic reaction time for the $r^{\text{th}}$ reaction defined in Section 3.4.1
$k_f^r$	Reaction rate parameter for the $r^{\text{th}}$ reaction in the forward direction
$k_b^r$	Reaction rate parameter for the $r^{\text{th}}$ reaction in the backward direction
$m$	Mass flow rate
$n$	Total number of species present
$p$	pressure
$s_{jq}$	Number of atoms of the $j^{\text{th}}$ species in the $q^{\text{th}}$ molecular species
$t$	Time
$v$	Flow velocity in direction of nozzle axis
$x$	Co-ordinate along nozzle axis
$\gamma_j$	Mass fraction of the $j^{\text{th}}$ species
$\Gamma_j$	Total mass fraction of the $j^{\text{th}}$ atomic species in both atomic and molecular form
$\nu_j^{r'}$ , $\nu_j^{r''}$	Stoichiometric coefficients of the $j^{\text{th}}$ species for the $r^{\text{th}}$ reaction; reactants and products respectively
$\rho$	Density
$\tau^r$	Characteristic reaction time defined in Section 4.1 for the $r^{\text{th}}$ reaction

Superscripts

$q, r$  Refers to the  $q^{\text{th}}$  and  $r^{\text{th}}$  reactions respectively

Subscripts

$A$  Refers to atomic species

$e$  Refers to equilibrium conditions evaluated on the basis of infinite reaction rates

$m$  Refers to molecular species

$o$  Refers to stagnation conditions

$os$  Refers to equivalent stagnation conditions at station (3); see Section 2.

Other symbols are defined in the text.

## Chapter 1

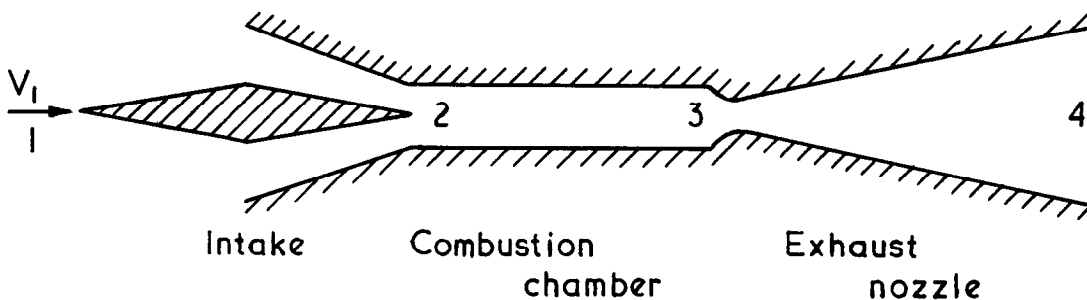
### 1. Introduction

There has been much interest recently in the ramjet as a means of propulsion for hypersonic vehicles (Refs.1 ~ 4). Calculations (Ref.4) have shown that the ramjet appears to offer an attractive and efficient means of propulsion at high Mach numbers. However, there are many severe problems to be solved before such an engine can be built, including the intake configuration, engine cooling, supersonic combustion of the fuel and recombination of the combustion products in the exhaust nozzle. The present note is concerned only with the last-named of these problems.

It is well known that if a fuel is burned in a heated gas stream, a large proportion of the chemical energy released may be used in breaking chemical bonds to produce simpler species. If the initial temperature before combustion is high, very little energy goes into raising the temperature of the gas mixture. It follows that if the combustion products are then expanded through a supersonic nozzle, very little of the chemical energy can be converted to kinetic energy unless it is first made available to the gas through reassociation of the dissociated combustion products.

The thrust produced by any propulsive system, in which combustion products are expanded through a nozzle, will be reduced if the recombination process cannot occur rapidly enough to remain in equilibrium. Unfortunately, the hypersonic ramjet engine is likely to be particularly sensitive to this effect. Two reasons may be given: firstly, the overall thrust of the engine is much less than the jet thrust of the exit nozzle, consequently a fall of a few percent in jet thrust has a drastic effect on performance. Secondly, the density in the exit nozzle will be low because the hypersonic ramjet is most attractive at great altitudes; the rate of recombination is proportional to a positive power of the density, thus recombination will be slow under these conditions. Olsen (Ref.5) quotes simple calculations illustrating the importance of recombination on hypersonic ramjet performance. These calculations indicate net thrusts per pound of air which are attractively high if equilibrium is maintained, but which approach zero between  $M = 10$  and  $M = 11$  if the combustion products are frozen with constant composition.

The sketch below defines the regions to be considered in ramjet performance calculations.



As the present note is not concerned with intake and combustion chamber performance, it is assumed that these have already been calculated, so that the thermodynamic state and velocity of the combustion products at station (3) are known. In general,  $v_3$  may be subsonic or supersonic. If it is subsonic, the exhaust nozzle will require a sonic throat whose area will determine the mass flow rate through the nozzle. If it is supersonic, no throat is required.

Calculations such as those outlined below are ultimately concerned with the thrust,  $F$ , which is conventionally defined as the exit jet thrust minus the momentum per second,  $m_1 v_1$ , of the air entering the ramjet. That is

$$F = m_4 v_4 + (p_4 A_4 - p_1 A_1) - m_1 v_1 .$$

It would appear, therefore, that not only the nozzle mass flow rate,  $m_4$ , and exit velocity,  $v_4$ , but also the exit pressure,  $p_4$ , are required.

The conditions to be expected at the entrance to the nozzle, station (3), vary widely with such parameters as the flight Mach number, the altitude and the Mach number in the combustion chamber. However, numerous performance calculations have been carried out, e.g., Refs.1, 2 and 4, and these give a good indication of conditions to be expected. For example, Dugger (Ref.2) presents results for hypersonic ramjets using kerosene as fuel and employing either subsonic or supersonic combustion. For an engine with subsonic combustion, he predicts values of total temperature and total pressure at station (3) lying within the ranges: 2 900 ~ 3 900°K and 53 ~ 280 p.s.i. at flight Mach numbers between 6 and 10, and typical altitudes, (for a constant dynamic pressure trajectory with  $q_1 = 2.43$  p.s.i.). Nozzle area ratios for complete expansion to atmospheric pressure are of the order of hundreds at the higher Mach numbers, but underexpanded nozzles may be employed in order to reduce the size of the exit area  $A_4$ . Corresponding typical static temperatures and pressures at station (3) for supersonic combustion are 2 300 ~ 3 100°K and 12 ~ 39 p.s.i. Maximum thrust and engine efficiency are obtained when sufficient heat is added to choke the flow at the combustor exit, i.e.,  $M_3 = 1$ .

It will be seen that supersonic combustion reduces both  $T_3$  and  $p_3$  below the corresponding values with subsonic combustion. A reduction in temperature favours equilibrium in the nozzle, whereas a reduction in pressure favours frozen flow, so it is not obvious which type of combustion will lead to a nozzle flow nearer to equilibrium.

Although this review is concerned specifically with the problem of recombination of combustion products in a ramjet exhaust nozzle, the methods of analysis and main conclusions will apply to other nozzle flow problems involving chemical reactions.

## Chapter 2

### 2. The Governing Equations for Non-Equilibrium Nozzle Flows

It is assumed that the working fluid is a mixture of ideal gases, that the flow is steady, adiabatic and quasi-one-dimensional, and the effects of diffusion, heat conduction and viscosity are negligible. The derivation of the following equations is outlined in Refs.6 and 7.

The conservation equations are:-

$$\rho v A = m_3 = \text{constant} \quad \dots (1)$$

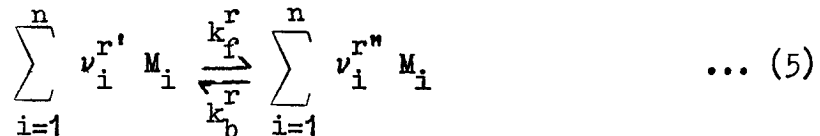
$$H + \frac{1}{2}v^2 = H_{03} = \text{constant} \quad \dots (2)$$

$$\frac{dv}{dx} + \frac{1}{\rho} \frac{dp}{dx} = 0 \quad \dots (3)$$

and  $A = A(x) \quad \dots (4)$

specifies the nozzle geometry.

Let the total number of chemical species such as  $M_i$  in the gas mixture be  $n$ , of which the first  $n_A$  are atomic species and the remaining  $(n - n_A)$  are molecular species. The  $r^{\text{th}}$  chemical reaction taking place in the mixture is formally written as,



where  $r = 1, 2, \dots, N$ , and  $N$  is the total number of reactions, and  $k_f^r$  and  $k_b^r$  are the reaction rate parameters of the forward and backward chemical changes in the  $r^{\text{th}}$  reaction.

It can be shown (Ref.7) that the total possible number of elementary, independent reactions is equal to the number of molecular species,  $(n - n_A)$ . At least this number of reactions must be postulated in order that the problem may be completely formulated.. In fact,  $N$  will be greater than  $(n - n_A)$  if, for example, a given chemical process brought about by more than one different catalyst is treated as several different reactions; the number of reactions being equal to the number of catalysts. This may be necessary when the reaction rate is greatly affected by the nature of the catalyst. The above general statements are not intended to imply that all of the  $N$  reactions will be of equal importance in a given flow system.

The equations of state are

$$p = \sum_{i=1}^n p_i = \rho^* R \sum_{i=1}^n \frac{y_i}{W_i} \quad \dots (6)$$

$$H = \sum_{i=1}^n y_i \left\{ \int_{T^0}^T C_{pi} dT + \Delta H_f^0 \right\} \quad \dots (7)$$

There are  $(n - n_A)$  differential continuity equations corresponding to the reactions (5), which will be written for the molecular species. The  $i$ th of these equations is

$$\rho \frac{D}{Dt} y_i = \sum_{r=1}^N W_i (\nu_i^{r''} - \nu_i^{r'}) \left\{ k_f^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r'}} - k_b^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r''}} \right\} \quad \dots (8)$$

where in the steady case  $\frac{D}{Dt} \equiv v \frac{d}{dx}$ . There are also  $n_A$  algebraic continuity equations for the atomic species

$$y_i + \sum_{q=n_A+1}^n \left\{ S_{iq} \frac{W_i}{W_q} y_q \right\} = \Gamma_i \quad \dots (9)$$

where  $\Gamma_i$  is the total mass fraction of the  $i$ th atomic species in the gas mixture in both atomic and molecular forms, and  $S_{iq}$  is the number of atoms of the  $i$ th species in the  $q$ th molecular species.

If the chemical kinetic data suggests that the  $r$ th reaction proceeds sufficiently fast to remain in chemical equilibrium, then the mass fractions of the species taking part in the reaction are related by the law of mass action, i.e.,

$$\frac{k_f^r}{k_b^r} = K_c^r = \prod_{i=1}^n \left( \frac{\rho y_i}{W_i} \right)^{\nu_i^{r''} - \nu_i^{r'}} \quad \dots (10)$$

where, 
$$K_c^r = K_p^r (RT)^{-\sum_{i=1}^n (\nu_i^{r''} - \nu_i^{r'})} = K_y^r \prod_{i=1}^n \left( \frac{\rho}{W_i} \right)^{\nu_i^{r''} - \nu_i^{r'}} \quad \dots (11)$$

Equation (10) then replaces one of the set of differential equations (8). If all the  $N$  reactions remain in equilibrium, then clearly,  $N$  laws of mass action may be written. However, it will be found that only  $(n - n_A)$  of these are independent and they will replace the  $(n - n_A)$  differential equations (8).

The general non-equilibrium nozzle flow problem is specified by the  $(n + 6)$  equations (1) - (4) and (6) - (9) above, of which  $(n - n_A + 1)$  are differential equations. The independent variable is  $x$  and the  $(n + 6)$  dependent variables are:  $p, \rho, T, H, v, A$  and  $y_i (i = 1, 2, \dots, n)$ . It is assumed that the area distribution  $A(x)$  is given. The initial conditions to be specified are the values of the dependent variables at the entrance to the nozzle where  $x = x_3$ . If the velocity is subsonic at  $x_3$ ,

then/



then one of these initial values ( $v_3$  say) must be determined from the condition that the velocity is sonic at the nozzle throat. In general, the value of  $v_3$  which satisfies this condition can only be found by trial and error. Alternatively, all the initial conditions, including  $v_3$ , may be specified and the throat area determined by trial and error. No such trial and error process is required if  $v_3$  is supersonic.

The choice of suitable thermodynamic and chemical data for substitution into the above set of equations is discussed in Chapter 5.

### Chapter 3

#### 3. Methods of Solution of the Governing Equations

In this chapter, methods of finding solutions for the set of equations listed in the previous chapter will be reviewed. Some of the methods are taken from the published literature and others are new. However, the authors are not aware of any published results in which more than one chemical reaction is considered

The methods given below, for the general case of  $N$  reactions are much more complicated algebraically than those previously published for a single reaction, and a high speed digital computer will be required in most cases. The review does not include all the methods of analysis that have been described in the literature. No numerical results are given, but recommendations are made regarding the most suitable techniques.

##### 3.1 Equilibrium or infinite rate flow

The solution of equations (1) - (4), (6) - (7) and (9) - (10), which describe the adiabatic, quasi-one-dimensional flow of a gas mixture in which all chemical reactions are sufficiently rapid to remain in equilibrium is by no means trivial. The problem reduces to the solution of the equations of state (6) - (7) and equilibrium composition (9) - (10) along an isentropic path. Once this is done, the flow velocity follows immediately from equation (2) and the nozzle area ratio from equation (1).

Brinkley has developed a general method for calculating the equilibrium composition of a complicated gas mixture at specified temperature and pressure. This and other computational techniques are described in detail in Ref.8. An extension of the Brinkley method to permit computation along an isentropic path was described in Ref.9.

##### 3.2 Step-by-step integration: non-equilibrium flow

The full set of differential and algebraic equations, (1) - (4) and (6) - (9), may be solved by conventional step-by-step techniques from the given initial conditions at  $x_3$ , to the nozzle exit at  $x_4$ . This technique has been used (Refs.9 - 13) successfully for flows with a single chemical reaction.

##### Comments

(i) A very long but algebraically straightforward computer programme will be required if both  $N$  and  $n$  are large.

(ii)/

\* Since this paper was written, results have been published from several numerical computations involving coupled chemical reactions. Examples are: Eschenroeder, A.Q., Boyer, D. W. and Hall, J. G., Physics of Fluids, 5, 5, 1962 and papers by I. N. Momtchiloff and E. D. Tabac, and by A. A. Westenberg and S. Favin in the Proceedings of the Ninth Symposium (International) on Combustion, Academic Press, 1963.

(ii) If the initial conditions at  $x_3$  are subsonic, then a lengthy iteration process is required to find the mass flow rate together with one of the initial conditions at  $x_3$ .

(iii) Comparison of equations (8) and (10) suggests that as the  $r$ th reaction approaches equilibrium, the term in the curly bracket in (8) approaches zero for the  $r$ th reaction. From this we deduce that in a real gas mixture in which  $k_f^r$  and  $k_b^r$  are finite, the flow can never be in a state of complete chemical equilibrium if the time derivatives of the flow variables are finite. However, the flow of a real gas may maintain a state very close to equilibrium provided that

$$k_f^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r'}}$$

and

$$k_b^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r''}}$$

are very large in comparison with the difference between them. In such circumstances, the term within the curly bracket is almost indeterminate, as shown by previous calculations (Ref.12), and then the interval size of the step-by-step integration process must be very small indeed. Consequently, if there are many reactions which are all initially close to equilibrium and which depart from equilibrium at different stages in the calculation, a prohibitively small interval size may be required everywhere within the nozzle.

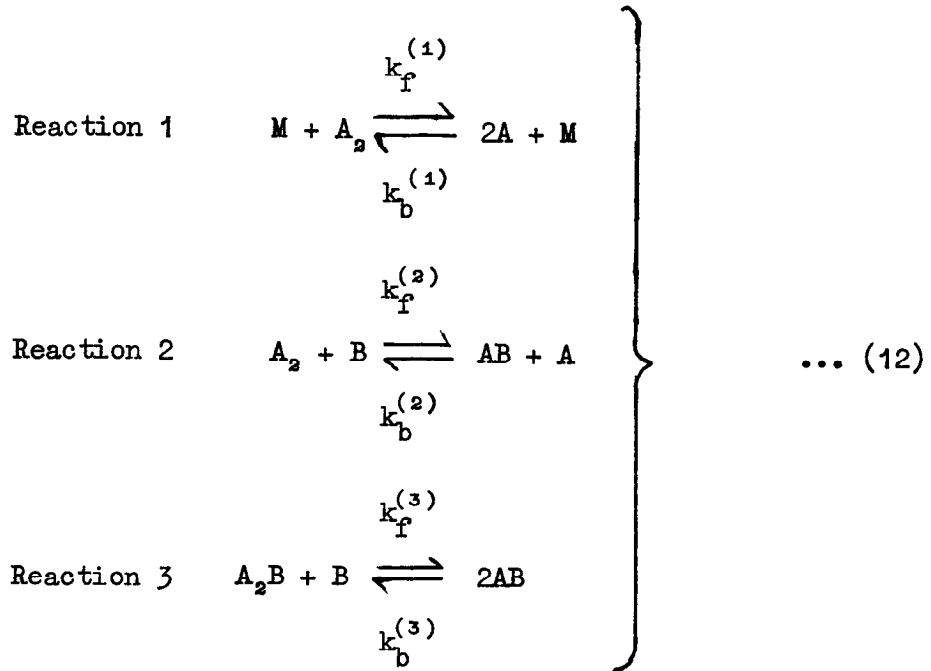
### 3.3 The partial equilibrium approximation

The last difficulty, (iii) above, may be overcome by an extension to a technique introduced in Ref.12. The differential equations (8) are replaced by the corresponding laws of mass action (10) whenever the reactions are sufficiently close to equilibrium. Criteria for the determination of whether a particular reaction is sufficiently close to equilibrium will be discussed in Chapter 4; it is sufficient here to assume that such a criterion, which gives a reliable indication of when a reaction starts to depart significantly from equilibrium in any given flow system, can be devised.

The procedure to be used is as follows. Step-by-step integration of the flow equations is begun at  $x_3$  with the  $(n - n_A)$  equations (8) replaced by the  $(n - n_A)$  laws of mass action (10). After every few steps, each reaction is tested by a suitable criterion to determine whether the reaction is still close to equilibrium. If at any stage the reaction fails the test, then the relevant law of mass action is discarded and replaced by a corresponding equation (8).

In order to clarify the above procedure, we will consider the following simple hypothetical system of reactions.

Reaction 1/



Reactions 1 - 3 involve three molecular species  $A_2$ ,  $AB$  and  $A_2B$ , and two atomic species  $A$  and  $B$ . Three differential continuity equations (8) are therefore required, and these will be written in the following form:-

$$\frac{d}{dx} y_{A_2} = a X^{(1)} + b X^{(2)} \quad \dots (13a)$$

$$\frac{d}{dx} y_{AB} = c X^{(2)} + d X^{(3)} \quad \dots (13b)$$

$$\frac{d}{dx} y_{A_2B} = e X^{(3)} \quad \dots (13c)$$

where  $a$ ,  $b$ , etc., are the relevant coefficients  $\frac{W_i(\nu_i^{r''} - \nu_i^{r'})}{\rho v}$ , and

$X^{(1)}$ ,  $X^{(2)}$  and  $X^{(3)}$  are the contents of the curly brackets of equation (8) for reaction 1, 2 and 3 respectively. These three latter quantities become numerically indeterminate in turn as each reaction approaches equilibrium. The algebraic continuity equations corresponding to (9) are

$$y_A + 2 \frac{W_A}{W_{A_2}} y_{A_2} + \frac{W_A}{W_{AB}} y_{AB} + 2 \frac{W_A}{W_{A_2B}} y_{A_2B} = \Gamma_A \quad \dots (14a)$$

$$y_B + \frac{W_B}{W_{AB}} y_{AB} + \frac{W_B}{W_{A_2B}} y_{A_2B} = \Gamma_B \quad \dots (14b)$$

Under/

Under conditions sufficiently close to equilibrium, equations (13a) - (13c) are replaced by the laws of mass action, equation (10), these are

$$K_c^{(1)} = \rho \frac{W_{A_2} y_A^2}{W_A y_{A_2}} \quad \dots (15a)$$

$$K_c^{(2)} = \frac{W_{A_2} W_B y_{AB} y_A}{W_{AB} W_A y_{A_2} y_B} \quad \dots (15b)$$

$$K_c^{(3)} = \frac{W_{A_2 B} W_B y_{AB}^2}{W_{AB} y_{A_2 B} y_B} \quad \dots (15c)$$

A step-by-step integration of equations corresponding to (1) - (4) and (6) - (7) together with (14) and (15) is begun at  $x_3$ . After every few steps each reaction 1 ~ 3 is tested to ensure that it is close to equilibrium, if the equilibrium test fails, then a procedure similar to that outlined in the following two cases is employed.

Case 1

Assume that the reactions depart from equilibrium in the order 3, 2, 1. When reaction 3 fails the equilibrium test, equation (15c) is discarded in favour of (13c) which should now be more amenable to the step-by-step integration process. However, equations (15a) and (15b) are retained. Later, reaction 2 fails the equilibrium test, and equation (13b) is used to replace (15b). Finally, when reaction 1 has failed the test, equation (13a) is used in place of (15a).

Case 2

Assume that the reactions depart from equilibrium in the order 1, 2, 3. When reaction 1 fails the equilibrium test, equation (15a) must be discarded since it no longer describes the first reaction accurately. Equation (13a) must be used in its place; however, we note that this equation contains a term  $X^{(2)}$  which is indeterminate in the sense that reaction 2 is still assumed to be in equilibrium. Now, although  $X^{(2)}$  and  $X^{(3)}$  in equations (13b) and (13c) are indeterminate, since reactions 2 and 3 are sufficiently close to equilibrium for the infinite rate solutions to be valid, these equations may still be used to replace  $X^{(2)}$  in

equation (13a) in terms of the derivatives  $\frac{d}{dx} y_{AB}$  and  $\frac{d}{dx} y_{A_2 B}$ . Then

equation (13a) becomes,

$$\frac{d}{dx} y_{A_2} = aX^{(1)} + \frac{b}{c} \left[ \frac{d}{dx} y_{AB} - \frac{d}{e} \frac{d}{dx} y_{A_2 B} \right] \quad \dots (16)$$

and/

and equation (16) is used together with (15b) and (15c). When reaction 2 fails the equilibrium test, equation (13a) can be used to replace (16) and the following equation:

$$\frac{d}{dx} \gamma_{AB} = c X^{(2)} + \frac{d}{e} \frac{d}{dx} \gamma_{A_2B} \quad \dots (17)$$

used to replace (15b), equation (15c) being retained. Finally, when reaction 3 fails the equilibrium test, equations (13a) - (13c) are used to replace the laws of mass action (15a) - (15c).

For the three hypothetical reactions chosen here, there are four other orders in which the reactions may depart from equilibrium. The techniques outlined above may again be used in order to formulate the problem before step-by-step integration.

Comments

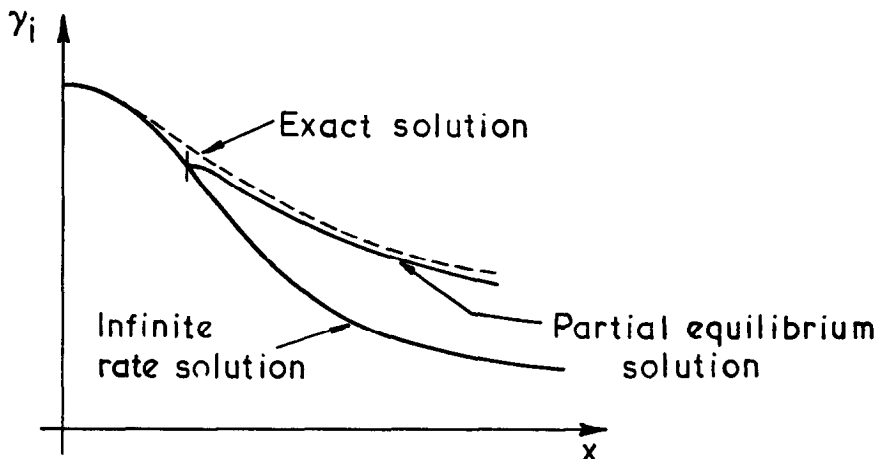
(i) The comments (i) and (ii) of Section 3.2 are still valid. However, provided that some of the reactions remain close to equilibrium over a reasonable nozzle length, the partial equilibrium approximation should give rise to a considerable saving in computation time, since the interval size for the integration will be longer than that used in the exact method described in Section 3.2. The process of swapping over from equation (10) to equations (8), as described in the example above, will complicate the programme.

(ii) It is clear that at the point in the nozzle where equation (10) is replaced by equation (8), the relevant

$\frac{d}{dx} \gamma_i$  will not be correctly predicted. For example, in case 1 above,

$\frac{d}{dx} \gamma_{A_2B}$  will be zero from equation (13c) at the point where reaction 3

fails the equilibrium test. Calculations quoted in Ref.13 suggest that errors from this source will be small, and that further downstream  $\gamma_{A_2B}$ , calculated by the partial equilibrium method, will be close to the true value if the equilibrium test is sufficiently stringent. (See sketch below).



### 3.4 Sudden freezing methods

For a simple flow with a single chemical reaction passing through a nozzle with a large area ratio, it has been shown (Ref.12) that three flow regions may be distinguished. These are:

- (i) A region of near equilibrium flow in which deviation from the infinite rate solution is small.
- (ii) A transition region.
- (iii) A region of nearly frozen flow in which the reaction has almost ceased.

If the area ratio is very large, a good approximation to the conditions at the exit of the nozzle may be obtained by reducing the transition region to a point, which will be called the sudden freezing point. Upstream of this point, the flow is assumed to remain in complete equilibrium, so that the infinite rate solution applies. Downstream of the sudden freezing point, the reaction ceases and the composition of the gas remains frozen. This approximation cannot give the exact values of all the flow properties a long way downstream however well the sudden freezing point is chosen, because it does not take account of the entropy rise which actually occurs due to the non-equilibrium phase of the reaction. However, the errors may be very small.

Various ways of extending this technique to flows with many reactions are discussed below. Empirical criteria, which may be used to define the sudden freezing points, are described in Chapter 4.

3.4.1 The most rigorous extension of the method is as follows. It is assumed that a sudden freezing criterion is defined for each of the  $N$  reactions (see Chapter 4). Step-by-step integration of the flow equations (1) - (4), the equations of state (6) - (7), equation (9) and the equilibrium laws of mass action equations (10), is begun at station  $x_3$ . After every few steps, the sudden freezing criterion is applied to each of the  $N$  reactions and each reaction is assumed to cease completely at the point where it first fails the test. In general, there may be up to  $N$  sudden freezing points in the flow. This procedure will be illustrated by a simple example in which we shall consider the hypothetical systems of reactions given by (12). At station  $x_3$ , all these reactions are assumed to be in equilibrium, so equations (15) are used to calculate the composition. Two cases will be considered as in Section 3.3.

#### Case 1

The reactions are assumed to freeze in the order 3, 2, 1. When reaction 3 passes the sudden freezing test, it is assumed to cease completely, so that equation (15c) is replaced by

$$y_{A_2B} = \text{constant} \quad \dots (18)$$

the constant being determined from the condition that no discontinuity in the value of  $y_{A_2B}$  occurs at the sudden freezing point. Equations (15a) and (15b) are retained. Further downstream when reaction 2 freezes, equation (15b) is replaced by

$$y_{AB} = \text{constant} \quad \dots (19)$$

but/

but, once again, (15a) is retained. Finally (15a) is replaced by

$$y_{A_2} = \text{constant} \quad \dots (20)$$

at the sudden freezing point for reaction 1. Downstream of the point the gas composition is completely frozen; it is given by equations (18), (19) and (20).

Case 2

The reactions are assumed to freeze in the order 1, 2, 3. Downstream of the freezing point for reaction 1, equation (15a) must be replaced by a stoichiometric condition which can be derived from (13a) with  $X^{(1)} = 0$  and  $X^{(2)}$  replaced using (13b) and (13c) in terms of

$$\frac{d}{dx} y_{AB} \quad \text{and} \quad \frac{d}{dx} y_{A_2B}$$

$$\frac{d}{dx} y_{A_2} = \frac{b}{c} \left[ \frac{d}{dx} y_{AB} - \frac{d}{e} \frac{d}{dx} y_{A_2B} \right].$$

This can be integrated to give:

$$y_{A_2} - \frac{b}{c} y_{AB} + \frac{bd}{ce} y_{A_2B} = \text{constant} . \quad \dots (21)$$

Equation (21) is then used together with equations (15b) and (15c) to give the gas composition. When reaction 2 also freezes, equation (21) is replaced by equation (20), because both reactions affecting  $y_{A_2}$  have now ceased. Equation (15b) must be replaced by another stoichiometric equation, and this is

$$y_{AB} - \frac{d}{e} y_{A_2B} = \text{constant} \quad \dots (22)$$

but (15c) is still retained. Finally, reaction 3 also freezes, and equations (15c) and (22) are replaced by equations (18) and (19) respectively.

The four other possible orders of freezing are dealt with in a similar manner.

Comments

(i) The number of differential equations to be solved is reduced from  $(n - n_A + 1)$  to only one, equation (3).

(ii) The method is empirical and needs to be checked against a more accurate solution.

(iii) The problem of determining the mass flow rate for initially subsonic flows still remains.



3.4.2 A simpler sudden freezing analysis has been used by Boyer, Eschenroeder and Russo (Ref.14), to study non-equilibrium flow of air in nozzles. One dominant reaction, the  $q^{\text{th}}$  say, is chosen involving the most important reacting species. Then a single sudden freezing point is chosen from a criterion which tests the  $q^{\text{th}}$  reaction only. Upstream of this point, all the  $N$  reactions are in equilibrium and downstream they are all frozen.

Comments

(i) This method is much simpler but also more approximate than 3.4.1. It is likely to give good results only if one reaction dominates the chemistry.

(ii) If the one sudden freezing point is situated downstream of the throat, the problem of determining the mass flow rate is greatly simplified.

(iii) The approximation of freezing all reactions together with the dominant  $q^{\text{th}}$  reaction may be justified to some extent. When the dominant reaction freezes, the rate of fall of temperature will be greatly increased due to the energy lost in freezing, and the reduced temperature downstream of this freezing point will tend to make the other reactions freeze more rapidly.

3.4.3 It has been shown by Bray (Ref.15) that the sudden freezing point, calculated by the method of Ref.12 for the case of a binary gas mixture with a single chemical reaction, or by the method of Ref.14 for a more complicated mixture dominated by a single reaction, is a function of upstream stagnation entropy only, to a very close approximation. A Mollier-type of diagram may therefore be drawn to represent all non-equilibrium flows of these types through a given nozzle. On this diagram, sudden freezing is represented by a line above which the flow is in equilibrium and below which it is frozen. Very simple graphical solutions may therefore be obtained. It seems likely that similar diagrams can be drawn from general calculations of the type suggested in Section 3.4.1 in which the sudden freezing of each specie is represented by a different freezing line.

In the same paper (Ref.15) mention is made of the fact that the upstream stagnation entropy is a useful correlating parameter for step-by-step integrations of the full set of flow equations. If such integrations are started from the same reservoir entropy but different reservoir temperatures and pressures, then the solutions pass through very similar thermodynamic states. These states occur at differing area ratios and velocities depending on the reservoir conditions.

Comments:

(i) Very simple graphical solutions may be obtained from the Mollier-type diagrams described above, and the accuracy obtained should be at least as good as that corresponding to some of the kinetic data referred to in Chapter 5.

(ii) A large reduction in the number of calculations required to cover a given range of operating conditions may be obtained by correlating results on the basis of upstream stagnation entropy.

(iii) Application of the method to systems with many chemical reactions requires further study.



### 3.5 Small perturbation methods

Under this heading are grouped several approximate techniques for solving the equations of Chapter 2. The methods have in common the assumption that some specified quantity is small. A rigorous linearisation of the full set of equations is not described here, but has in fact been used in recent numerical computations.

3.5.1 A near equilibrium solution for flow with only one chemical reaction ( $N = 1$ ) but an arbitrary number of species, has been developed by Penner (Ref.6). Equation (8) for the  $i^{\text{th}}$  species is first written in the form

$$\frac{d}{dT} \ln y_i = \left( \frac{DT}{Dt} \right)^{-1} (\nu_i'' - \nu_i') \frac{W_i}{y_i} k_r \left( 1 - \frac{K'_Y}{K_Y} \right) \rho^{m-1} \prod_{j=1}^n \left( \frac{y_j}{W_j} \right)^{\nu_j} \dots (23)$$

where

$$m = \sum_{j=1}^n \nu_j'$$

$$K_Y = \prod_{j=1}^n y_{je}^{\nu_j'' - \nu_j'}$$

$$K'_Y = \prod_{j=1}^n y_j^{\nu_j'' - \nu_j'}$$

$y_{je}$  = mass fraction of the  $j^{\text{th}}$  species under equilibrium conditions at true local  $T$  and  $p$ .

$y_j$  = true mass fraction of the  $j^{\text{th}}$  species.

The suffix  $r$  has been dropped as only one reaction is considered.  $K'_Y$  is treated as an equilibrium constant evaluated at a temperature  $T'$ . If  $T' - T \ll T$ , then

$$K'_Y = K_Y(T') \approx K_Y(T) + K_Y(T) \left[ \frac{d}{dT} \ln K_Y \right]_T (T' - T). \dots (24)$$

It follows that the quantity  $(1 - K'_Y/K_Y)$  in equation (23) is equal to

$$- \left[ \frac{d}{dT} \right]$$


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\*Eschenroeder et al, loc. cit., p.12.

$$-\left[ \frac{d}{dT} \ln K_Y \right]_T (T' - T) .$$

If equation (23) is multiplied by  $(\nu_i'' - \nu_i')$  and summed over  $i$ , the left-hand side reduces to  $\left[ \frac{d}{dT} \ln K_Y \right]_T$  to a first approximation, and this cancels out with the same quantity on the right-hand side. The equation then reduces to

$$T' - T = - \frac{DT}{Dt} Z \quad \dots (25)$$

where  $Z$  is a characteristic reaction time given by

$$Z = \left\{ k_f \rho^{m-1} \prod_{j=1}^n \left( \frac{y_j}{W_j} \right)^{\nu_j'} \sum_{j=1}^n (\nu_j'' - \nu_j')^2 \frac{W_j}{y_j} \right\}^{-1}$$

and  $\frac{DT}{Dt}$  is dependent on the nozzle shape.

Penner points out that equation (25) may be solved in a step-by-step manner, choosing a constant value of  $Z$  for each step. It also leads to a simple empirical criterion for near equilibrium flow, namely

$$\frac{Z_{\max}}{t_r} \leq 10^{-3}$$

where  $Z_{\max}$  is the maximum value of  $Z$  and  $t_r$  is the residence time of a typical particle in the nozzle.

Comments

(i) If the analysis is repeated for a case with several reactions ( $N > 1$ ), the simple result, equation (25), cannot be repeated because:

(a) There will be  $N$  different values of  $T'$  corresponding to the different reactions.

(b) The cancellation of the term  $\left[ \frac{d}{dT} \ln K_Y \right]_T$  from equation (25) can no longer occur because of the summation over  $r$ .

(ii) It might be possible to use this or a similar technique in a complicated gas mixture, to deal with a single reaction which is independent of all the other reactions, and which is known to be close to equilibrium.

3.5.2 Penner has also developed (Ref.6) a similar analysis for near frozen flow with a single chemical reaction, again beginning from equation (8). In this case the temperature  $T'$  at which  $K'_Y$  is evaluated is assumed to be very close to the initial temperature  $T_3$ , then

$$K'_Y = K_Y(T') = K_Y(T_3) - K_Y(T_3) \left[ \frac{d}{dT} \ln K_Y \right]_{T_3} (T_3 - T') \dots (26)$$

Substitution for  $K'_Y$  into equation (23) together with a number of simplifications leads to the result

$$\frac{T_3 - T'}{T_3 - T} = - \left( \frac{DT}{Dt} \right)^{-1} Z^{-1} \left[ \left( \frac{d}{dT} \ln K_Y \right)_{T_3} \right]^{-1} \left\{ \frac{K_Y(T_3)}{K_Y(T)} - 1 \right\} \\ \times \left[ 1 - (T_3 - T) \frac{K_Y(T_3)}{K_Y(T)} \left( \frac{DT}{Dt} \right)^{-1} Z^{-1} \right]^{-1}$$

Several criteria for near frozen flow may also be deduced.

Comments

As with the near equilibrium solution in Section 3.5.1, simple results cannot be obtained if  $N > 1$ , except for an isolated reaction which proceeds independently of all the others.

3.5.3 If a constituent,  $M_k$ , of the reacting gas mixture is present in such a low concentration that it is thermodynamically unimportant, i.e.,  $H_{O_3} \gg \gamma_k H_k$ , and also kinetically unimportant, i.e.,

the contributions to  $\frac{Dy_i}{Dt}$  from all reactions involving  $M_k$  must be negligible for all  $i$ : a condition for this is  $\gamma_k \ll 1$ , then the following simplification may be made.

The equations of Chapter 2 may be integrated with  $\gamma_k \equiv 0$  to give values of all the remaining dependent variables. These variables may then be substituted into equation (8) for  $\frac{Dy_k}{Dt}$ , which may then be integrated in a numerically straightforward manner to give  $\gamma_k(x)$ .

Comments

This technique together with other simplifications has been used by Eschenroeder and Daiber (Ref.16) in a study of non-equilibrium ionisation. It is only suitable for species which can have little overall effect on the flow.

3.5.4 Another approximate technique involving linearisation is that of Hall and Russo (Ref.9), which has been applied successfully to flows with a single chemical reaction. Extension of the method to a general system of reactions is straightforward and is outlined below. Hall and Russo first noted that for a critical mass flow very close to the equilibrium value, the specific enthalpy  $H$  is not greatly affected by small departures from equilibrium because of two opposing effects. The fall in temperature due to the departure from equilibrium tends to reduce  $H$ , but the relative increase of the atom mass fraction above the equilibrium value tends to increase  $H$ . Consequently the net change in  $H$  is small. The same trend is to be expected in a complicated gas mixture.

Thus, the assumption is made that for a gas flow close to equilibrium,

$$H = H_e(x)$$

where the suffix  $e$  denotes equilibrium and  $H_e(x)$  is determined from the infinite rate equilibrium solution. Equations (2) and (1) then yield the results:

$$v = v_e(x)$$

and

$$\rho = \rho_e(x).$$

Having specified one variable  $H$ , without reference to the governing equations, one of these equations must be discarded and this is chosen to be equation (3). Incorporation of equation (3) would lead to the inaccurate restriction:

$$p = p_e(x).$$

Since comparatively large departures from their equilibrium values are to be expected for  $T$  and  $\gamma_i$ , we write

$$T = T_e(x) + \Delta T \quad ; \quad \Delta T \ll T_e$$

$$\gamma_i = \gamma_{ie}(x) + \Delta \gamma_i \quad ; \quad \Delta \gamma_i \ll \gamma_{ie}.$$

Now equation (7) gives  $H$  as a function of  $T$  and  $\gamma_i$ , so it follows from the assumption,  $H = H_e$ , that

$$\Delta T = - \sum_{j=1}^n \frac{\frac{\partial H}{\partial \gamma_j}}{\frac{\partial H}{\partial T}} \Delta \gamma_j \quad \dots (27)$$

where, /

where, to a first order approximation, the partial derivatives may be evaluated from equation (7) and the known equilibrium solutions. Equation (8) may be rewritten in the following form:

$$\begin{aligned} \frac{D}{Dt} y_i &= \sum_{r=1}^N \frac{W_i}{\rho} (\nu_i^{r''} - \nu_i^{r'}) k_b^r \left\{ K_c^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r'}} - \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r''}} \right\} \\ &= \sum_{r=1}^N G_i^r Y^r \end{aligned} \quad \dots (28)$$

where,

$$G_i^r = \frac{W_i}{\rho} (\nu_i^{r''} - \nu_i^{r'}) k_b^r$$

and  $Y^r$  is the function within the curly brackets. Under conditions of complete equilibrium we note that  $Y^r = 0$ , thus it follows that for a flow which is close to equilibrium

$$\frac{D}{Dt} y_i = \frac{D}{Dt} y_{ie} + \frac{D}{Dt} (\Delta y_i) \approx \sum_{r=1}^N G_{ie}^r \Delta Y^r \quad \dots (29)$$

now

$$\Delta Y^r = \sum_{j=1}^n \frac{\partial Y^r}{\partial y_j} \Delta y_j + \frac{\partial Y^r}{\partial T} \Delta T \quad \dots (30)$$

thus, from equations (27), (29) and (30) we have:

$$\frac{D}{Dt} y_{ie} + \frac{D}{Dt} (\Delta y_i) = \sum_{r=1}^N G_{ie}^r \left[ \sum_{j=1}^n \frac{\partial Y^r}{\partial y_j} \Delta y_j - \frac{\frac{\partial Y^r}{\partial T}}{\frac{\partial H}{\partial T}} \sum_{j=1}^n \frac{\partial H}{\partial y_j} \Delta y_j \right] \quad \dots (31)$$

The derivative  $\frac{D}{Dt} y_{ie}$ , is a known function of  $x$ , so equation (31) is the  $i$ th member of a set of  $(n - n_A)$  linear first order differential equations in the  $\Delta y_j$ 's. The coefficients are given by the equilibrium solution. This set of equations may be solved together with equations (9) by standard numerical techniques.

Hall and Russo noted a further simplification to equations (31), namely, that in the cases they considered,  $\frac{D}{Dt} (\Delta y_i) < \frac{D}{Dt} y_{ie}$ . If the smaller terms are omitted, equations (31) reduce to the following algebraic set:

$$\frac{D}{Dt} y_{ie}$$

$$\frac{D}{Dt} y_{ie} = \sum_{r=1}^N G_{ie}^r \left[ \sum_{j=1}^n \frac{\partial Y^r}{\partial y_j} \Delta y_j - \frac{\partial Y^r}{\partial T} \sum_{j=1}^n \frac{\partial H}{\partial y_j} \Delta y_j \right] \dots, \quad (32)$$

which may be solved much more simply. It is also suggested that equations (32) may be used as the first step in an iterative solution of (31).

Comments

(i) The coefficients in equation (31) are algebraically complicated functions of the infinite rate equilibrium solution.

(ii) The assumption  $H = H_e$  requires further justification for the case with  $N > 1$ , similarly for the assumption

$$\frac{D}{Dt} (\Delta y_i) \ll \frac{D}{Dt} y_{ie} .$$

(iii) If numerical calculations justify these assumptions then the technique appears to be attractive since it only requires the solution of the algebraic equations (27) and (31).

(iv) The method as it is outlined above, is only valid for a region of near equilibrium flow; considerable caution is required in extending it too far downstream, although the results of Ref.9 suggest that this can be done under certain circumstances.

Chapter 4

4. Method of Choosing Important Species and Reactions

The various methods of analysis which were outlined in the previous chapter, cannot be applied to the solution of specific problems until the  $n$  chemical species and  $N$  reactions have been chosen.

We consider first the choice of species. From prior knowledge of the elements contained in the mixture, it is possible to choose the various species which are likely to be present. Then isentropic equilibrium calculations, over the range of temperature and pressure likely to be encountered, will give an indication as the concentrations of the various species present in the mixture, and as a consequence, will suggest which of them may be thermodynamically important. To illustrate this point, calculations (Ref.17) on the equilibrium flow of a stoichiometric hydrogen ~ air mixture with  $p_{O_3} = 0.2$  atmos.,  $T_{O_3} = 6000^\circ K$  and  $p_4$  corresponding to an altitude of  $1.2$  and  $10^5$  ft, show that only  $H$ ,  $N_2$ ,  $O$  and  $N$  will have equilibrium mole fractions greater than  $10^{-2}$  at any point in the nozzle. The other species considered in descending order of mole fractions are  $A$ ,  $NO$ ,  $CO$ ,  $H_2$ ,  $OH$ ,  $O_2$ ,  $Ne$ ,  $CO_2$  and  $H_2O$ . Thus, over the range of pressure and temperature covered by the calculations, the last nine species will be thermodynamically unimportant in equilibrium, since their contribution to the gross specific enthalpy will be small.

Even/

Even in a non-equilibrium flow, the species A, Ne, CO and CO<sub>2</sub> will still be thermodynamically unimportant, since the elements involved are known to be present in the mixture only in very small proportions. The rate of any reaction between CO and CO<sub>2</sub> cannot affect this conclusion because of the small amount of carbon available to form either of these species.

The position regarding the remaining species considered in Ref.17 which have a low equilibrium concentration, i.e., NO, H<sub>2</sub>, OH and O<sub>2</sub>, is not so straightforward. Consider O<sub>2</sub> as an example. If O<sub>2</sub> is formed in a reaction involving O and an inert third body, then it is clear that departure from equilibrium of this particular reaction within the nozzle will tend to reduce the O<sub>2</sub> concentration. However, departure from equilibrium of another reaction involving neither O<sub>2</sub> nor O, may reduce the gas temperature and so increase the O<sub>2</sub> concentration provided that the three-body oxygen recombination reaction still remains close to equilibrium. Also, if O<sub>2</sub> is consumed, for example in an exchange reaction involving NO, then departure of this reaction from equilibrium will tend to increase to O<sub>2</sub> concentration.

Departure from equilibrium may therefore either increase or decrease the O<sub>2</sub> concentration, and it cannot be concluded that O<sub>2</sub> is a negligible constituent simply because its equilibrium concentration is small. In the particular example cited above, the O<sub>2</sub> mole fraction in equilibrium is always less than  $5 \times 10^{-5}$ , and it seems likely that this species will still be thermodynamically unimportant if equilibrium is not maintained. However, it must be emphasised that this conclusion cannot be substantiated without detailed numerical computations. Similar arguments may be applied to the species NO, H<sub>2</sub> and OH.

Now, although a particular species may be thermodynamically unimportant, this fact does not necessarily preclude it from being kinetically important. For example, it may be a very efficient third body in promoting either dissociation or recombination in a particular reaction which does involve thermodynamically important species. Thus, having established all the species which may be present in the mixture, it is desirable to consider all the possible reactions which can take place, and then endeavour to decide which reactions are likely to be dominant.

An unimportant reaction must be one for which the rate of production of the species is slow in comparison with the gross rate of production of the same species due to the remaining reactions. Such reactions we shall call "slow" reactions; "fast" reactions are those which make substantial contributions to the gross rate of production of the various species, and for this reason they are important. So far, the terms "slow" and "fast" have only relative meanings, and thus any parameter which measures the speed of the various reactions requires to be related to the flow transit time through a particular nozzle configuration before one can say whether a particular reaction may be regarded as being in equilibrium or not. Such relationships have so far been empirical, and they require further verification from calculations on the flow of more complex mixtures before reliance can be placed on them.

A fundamental difficulty associated with all the empirical criteria used in dealing with non-equilibrium flow problems, is that as soon as one of the N reactions departs from equilibrium, the thermodynamic state of the gas is affected by the extent to which this reaction has departed from equilibrium. In other words, the rates of all other reactions are affected in a manner which cannot be accurately predicted without solving the whole flow problem. Thus it is only possible to give an approximate answer to the question, which reactions are "fast" in a given flow, prior to flow problem being solved.



Two criteria are considered below. The first is derived without reference to any particular flow configuration, and it results in the definition of a parameter for each of the  $N$  reactions called the "characteristic reaction time". These quantities, which are analogous to Penner's reaction time  $Z$  (Section 3.5.1), may be evaluated under typical conditions of density and temperature to give a measure of the relative speeds of the reactions under near-equilibrium conditions. The second criterion to be considered in this chapter is that which was introduced in Ref.12 as part of a sudden freezing analysis. It leads to definitions of near-equilibrium and near frozen flow for a particular nozzle configuration, and also to an empirical equation for the sudden freezing points referred to in Section 3.4.

#### 4.1 Criteria based on characteristic reaction time

According to the classical theory of chemical kinetics (Ref.6), the net rate of change of the mass of the  $i$ th species per unit volume of a reacting mixture of gases is

$$\frac{d}{dt} (\rho y_i) = \sum_{r=1}^N W_i (\nu_i^{r''} - \nu_i^{r'}) \left\{ k_f^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r'}} - k_b^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r''}} \right\} \dots (34)$$

We shall consider a given closed volume of such a mixture to be held at rest and at a constant temperature  $T$ . Since  $K_C^r$  is classically assumed to be function of temperature alone and also the volume of the sample considered remains constant, it follows that  $y_{je}$ , evaluated at local  $\rho$  and  $T$ , is constant. Equation (34) can thus be rewritten in the form

$$\frac{dy_i}{dt} = \sum_{r=1}^N \frac{W_i (\nu_i^{r''} - \nu_i^{r'}) k_b^r}{\rho \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{-\nu_j^{r''}}} \left\{ \prod_{j=1}^n \left( \frac{y_{je}}{y_j} \right)^{\nu_j^{r''} - \nu_j^{r'}} - 1 \right\} \dots (35)$$

By making the assumption that the mixture is initially very close to equilibrium, so that

$$y_j = y_{je} + \Delta y_j \quad \text{where} \quad \Delta y_j \ll y_{je}$$

then equation (35) reduces to the approximate form

$$\frac{d}{dt} (\Delta y_i) = \sum_{r=1}^N \frac{W_i (\nu_i^{r''} - \nu_i^{r'}) k_b^r}{\rho \prod_{j=1}^n \left( \frac{\rho y_{je}}{W_j} \right)^{-\nu_j^{r''}}} \sum_{j=1}^n \frac{\Delta y_j}{y_{je}} (\nu_j^{r'} - \nu_j^{r''}) \dots (36)$$



The set of equations (36) above, may be solved explicitly to give expressions for  $\Delta y_j$ . However, since the various reactions taking place in a mixture are usually coupled, it is difficult to extract any parameter which gives precise information on the speed of any particular reaction. In order to overcome this difficulty, it is necessary to consider equation (36) in the following form,

$$\frac{d}{dt} (\Delta y_i) = \sum_{r=1}^N \left[ \frac{d}{dt} (\Delta y_i) \right]^r$$

where 
$$\left[ \frac{d}{dt} (\Delta y_i) \right]^r = \frac{W_i (v_i^{r''} - v_i^{r'}) k_b^r}{\rho \prod_{j=1}^n \left( \frac{\rho y_{je}}{W_j} \right)^{-v_j^{r''}}} \sum_{j=1}^n \frac{\Delta y_j}{y_{je}} (v_j^{r'} - v_j^{r''})$$

and then  $\left[ \frac{d}{dt} (\Delta y_i) \right]^r$  is the rate of change of  $y_i$  due to the  $r^{\text{th}}$  reaction alone. By assuming that the remaining  $(N - 1)$  reactions are very slow by comparison with the  $r^{\text{th}}$  reaction, i.e., they are effectively frozen, it follows that for any  $j$ :

$$\Delta y_j = \Delta y_i \frac{W_j (v_j^{r''} - v_j^{r'})}{W_i (v_i^{r''} - v_i^{r'})}$$

and thus

$$\begin{aligned} \frac{1}{\Delta y_i} \left[ \frac{d}{dt} (\Delta y_i) \right]^r &= - \frac{k_b^r}{\rho} \prod_{j=1}^n \left( \frac{\rho y_{je}}{W_j} \right)^{v_j^{r''}} \sum_{j=1}^n \frac{W_j}{y_{je}} (v_j^{r''} - v_j^{r'})^2 \\ &= - \frac{1}{\tau^r} \end{aligned} \quad \dots (37)$$

The parameter  $\tau^r$  is a characteristic reaction time for the  $r^{\text{th}}$  reaction. It is the time taken for a given small deviation from equilibrium of the mass fractions associated with the  $r^{\text{th}}$  reaction to fall to  $1/\exp.$  of their initial values as a result of the  $r^{\text{th}}$  reaction alone, the temperature and density being held constant.

The relative speeds of the various reactions taking place in any mixture can thus be deduced by comparing the magnitudes of the various  $\tau^r$ 's. If, for example,  $\tau^r \gg \tau^q$ , over the range of temperature and pressure likely to be encountered, then the  $r^{\text{th}}$  reaction may be considered to be sufficiently "slow" in comparison with the  $q^{\text{th}}$  reaction, and thus neglected.

The/

The near-equilibrium solution for the  $r^{\text{th}}$  reaction alone, as developed by Penner (Ref.6) and outlined in Section 3.5.1, also yields a characteristic reaction time  $Z^r$ , where

$$\frac{1}{T^r - T} \frac{DT}{Dt} = - \frac{1}{Z^r} .$$

The temperature derivative is the actual temperature gradient occurring in the flow. If  $Z^r$  is evaluated on the basis of equilibrium values of  $\rho$  and  $y_i$ , then it may be shown to be identical to  $\tau^r$ . However, the formulation of the present section is thought to be more relevant here than that outlined in Section 3.5.1, because it defines the characteristic reaction time without reference to any particular flow configuration.

#### 4.2 Criteria based on a sudden-freezing analysis

The  $(n - n_A)$  equations (8) are first written in a form similar to that used in equations (13):

$$\frac{dy_i}{dx} = \sum_{r=1}^N a_i^r X^r \quad \dots (38)$$

where  $X^r$ , which represents the curly bracket in equation (8), is given by

$$X^r = R_f^r - R_b^r$$

and

$$R_f^r = k_f^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r'}}$$

$$R_b^r = k_b^r \prod_{j=1}^n \left( \frac{\rho y_j}{W_j} \right)^{\nu_j^{r''}} .$$

If the  $r^{\text{th}}$  reaction proceeds at an infinite rate and so remains in complete equilibrium, both  $R_f^r$  and  $R_b^r$  are infinite. The difference between these two infinite terms, which is proportional to the net rate of change of  $y_i$  due to the  $r^{\text{th}}$  reaction, must then be determined from equation (10) rather than from equation (8). This argument suggests that, if the  $r^{\text{th}}$  reaction proceeds at a finite rate which is sufficiently fast to remain close to equilibrium, then

$$R_f^r \simeq R_b^r \quad \dots (39)$$

so that

$$\left| R_f^r \right| \gg \left| X^r \right| . \quad \dots (40)$$

If equation (39) is nearly satisfied, then so is the law of mass action equation (10); thus the quantities  $R_f^r$  and  $X^r$  in the criterion (40) may be evaluated on the basis that the  $r^{\text{th}}$  reaction remains in complete equilibrium. Evaluation of  $X^r$  under these conditions requires care. Calculated as the difference between  $R_f^r$  and  $R_b^r$ , where  $k_f^r$  and  $k_b^r$  are infinite according to the above equilibrium approximation, it is indeterminate. However,  $X^r$  is in fact finite even for the infinite rate solution.

4.2.1 Case when number of reactions equals number of molecular species

If the total number of reactions considered,  $N$ , is equal to the number of molecular species present,  $n_m$ , then  $X^r$  can always be found from the system of equations (38) if the  $\frac{dy_i}{dx}$  values are suitably calculated (see below). On the other hand, if  $N > n_m$ ,  $X^r$  cannot be determined in this way because there are more  $X^r$  values than equations (38). The physical explanation of the apparent anomaly is that, when the reactions are all close to equilibrium, the chemical problem is over-specified if  $N > n_m$ , because only  $n_m$  laws of mass action are required to determine the composition. It is not then possible to determine the contributions of the individual reactions to  $\frac{dy_i}{dx}$ . We shall assume in this section that  $N = n_m$  and the development of a criterion for cases where  $N > n_m$  will be postponed until the following section. The criterion (40) for the  $r^{\text{th}}$  reaction to be near equilibrium may be rewritten in the form

$$B^r \equiv \left| \frac{R_f^r}{X^r} \right|_e \gg 1 \quad \dots (41)$$

where the suffix  $e$  indicates that the functions are evaluated with the  $r^{\text{th}}$  reaction in equilibrium. Unlike the criterion of Section 4.1, this equation can only be used as part of a detailed computation of a

particular flow system, because the derivatives  $\frac{dy_i}{dx}$  are required. It is accurate in the sense that the  $r^{\text{th}}$  reaction must always be close to equilibrium if  $B^r \gg 1$ .

Equation (41) is directly applicable to the partial equilibrium method of solution outlined in Section 3.2. At positions where  $B^r$  becomes equal to some number greater than unity (Ref.13 suggests that  $B^r = 20$  is a suitable criterion, but this needs checking for flows with complicated chemistry), an equation (10) is replaced by a corresponding equation (8). No assumptions need be made about the rates of the other  $(N - 1)$  reactions. The derivatives  $\frac{dy_i}{dx}$  are automatically found in the step-by-step integration process, so  $X^r$  can be found from equations (38) (if  $N = n_m$ ) and  $B^r$  then follows.

A criterion similar to (41) may be used to define a region in which the  $r^{\text{th}}$  reaction is nearly frozen, namely;

$$B^r \ll 1 \quad \dots (42)$$

However, this condition is not accurate to the same degree as (41), because the evaluation of  $B^r$  assuming that the  $r^{\text{th}}$  reaction is in equilibrium must lead to errors when this reaction is in fact nearly frozen.

The two conditions expressed by (41) and (42), suggest a criterion (Ref.12), which may be used to define the sudden-freezing points referred to in Section 3.4. Since the sudden-freezing point of a particular reaction lies between the near-equilibrium and near-frozen limits defined by (41) and (42) respectively, we write

$$B^r = Q^r \quad \dots (43)$$

at the sudden-freezing point. The constants  $Q^r$  are expected to be of order unity. Clearly, equation (43) is purely empirical.

Another empirical criterion for the sudden-freezing point has been developed by Hall and Russo (Ref.9) for a binary mixture of atoms and molecules with only one reaction. It has been extended in Ref.14 to deal with a multi-component mixture with one reaction. This criterion leads to results similar to equation (43).

#### 4.2.2 Criterion when the number of reactions is greater than the number of molecular species

In a reacting gas mixture in which  $N > n_m$ , there are more quantities  $X^r$  than equations (38), so the  $X^r$ 's are indeterminate and the criteria given by equation (41) cannot be applied directly. This difficulty may be overcome by a suitable technique of grouping some of the reactions together.

If the members of a certain group of  $n_m$  reactions out of the total  $N$  are all sufficiently fast, then  $n_m$  laws of mass action are available (equations (10)) and the equilibrium composition can be completely specified. Therefore,  $(N - n_m)$  reactions can depart from equilibrium without altering the equilibrium composition. However, if  $(N - n_m + 1)$  of the reactions depart from equilibrium, one of the  $n_m$  laws of mass action must be dropped in favour of a particular differential continuity equation (38). Clearly it is necessary to test all possible groups of  $(N - n_m + 1)$  reactions in order to test when the composition departs from equilibrium. As soon as any one of these groups fails the equilibrium test one of the laws of mass action must be replaced by a differential continuity equation.

In general, there are  $\frac{N!}{(N - n_m + 1)!(n_m - 1)!}$  groups of

$(N - n_m + 1)$  reactions. In order to test these groups of reactions, it is necessary to form further equations from the set of equations (38), by eliminating the unwanted  $X^r$ 's. These equations have the form

$$D_j = \sum_r b_j^r X^r \quad \dots (44)$$

where  $r$  takes the chosen group of  $(N - n_m + 1)$  values and  $D_j$  is a function of the terms  $\rho v \frac{dy_i}{dx}$ . The criterion that all  $(N - n_m + 1)$  reactions have departed from equilibrium is then

$$B_j \equiv \frac{\sum_r b_j^r R_f^r}{D_j} \leq Q_j$$

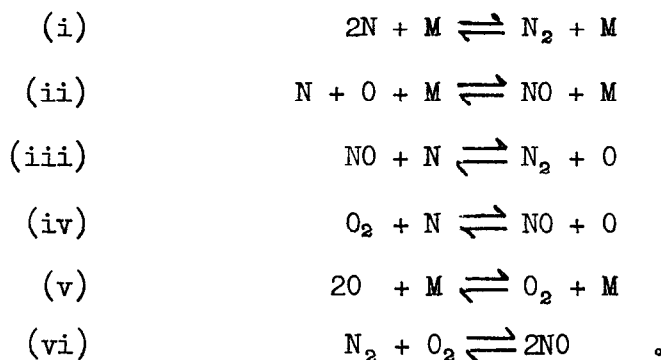
and one of the laws of mass action must subsequently be replaced by either one of equations (38) or (44).

In any reacting system there may be groups of less than  $(N - n_m + 1)$  reactions, for which the reactions remaining when such a group is removed are not linearly independent. Groups of this type will be called "essential groups". For example, a group of less than  $(N - n_m + 1)$  reactions would obviously be an essential group if none of the remaining reactions involved a particular molecular species  $M_i$ . If an essential group departs from equilibrium, one law of mass action must be discarded in favour of the differential continuity equation for  $M_i$ . The equilibrium test for such a group is simply:

$$B_i \equiv \left| \frac{\sum_{r=1}^N a_i^r R_f^r}{\rho v \frac{dy_i}{dx}} \right| \leq Q_i .$$

If an essential group of less than  $(N - n_m + 1)$  reactions exists, then it usually has the effect of reducing the number of equilibrium tests which need to be carried out at each stage in the step-by-step calculations.

In order to clarify the above discussion, we shall illustrate the technique by means of an example. The example chosen assumes six reactions which are likely to be important in air at high temperatures.



In this example  $N = 6$ ,  $n_m = 3$  and  $(N - n_m + 1) = 4$ . The differential continuity equations corresponding to the  $n_m$  molecular species may be written in the form,

$$\frac{dy}{dx} O_2 = a_{O_2}^4 X^4 + a_{O_2}^5 X^5 + a_{O_2}^6 X^6 \quad \dots (45)$$

$$\frac{dy}{dx} NO = a_{NO}^2 X^2 + a_{NO}^3 X^3 + a_{NO}^4 X^4 + a_{NO}^6 X^6 \quad \dots (46)$$

$$\frac{dy}{dx} N_2 = a_{N_2}^1 X^1 + a_{N_2}^3 X^3 + a_{N_2}^6 X^6 \quad \dots (47)$$

From equations (45) and (47) it is apparent that two essential groups are (iv), (v), (vi) involving  $O_2$  and (i), (iii), (vi) involving  $N_2$ . Also, the group (i), (ii), (v) is essential, because the remaining reactions, (iii), (iv), (vi), are not linearly independent ((iv) - (iii) rearranges to give (vi)) and therefore do not provide sufficient information to determine the equilibrium state. These essential groups reduce the number of equilibrium tests which need to be applied initially from fifteen to nine. The groups to be tested initially are tabulated below

1	1	4	1	1	1	2	2	2
2	3	5	2	2	3	3	3	3
5	6	6	3	4	4	4	4	5
			4	6	5	5	6	6

Suppose reactions (i), (ii), (iii) and (iv) constitute the first group of reactions to depart from equilibrium. The criterion which tests this condition is given by equations (46) and (47) on elimination of the terms containing  $X^6$ , i.e.,

$$\rho v \left\{ \frac{dy}{dx} NO - \frac{a_{NO}^6}{a_N^6} \frac{dy}{dx} N_2 \right\} = - \frac{a_{NO}^6}{a_N^6} a_{N_2}^1 X^1 + a_{NO}^2 X^2 + \left\{ a_{NO}^3 - \frac{a_{NO}^6}{a_{N_2}^6} a_{N_2}^3 \right\} X^3 + a_{NO}^4 X^4 \dots (48)$$

The function  $B_j$  is then given by the modulus of all the positive terms on the right-hand side of equation (48) divided by the entire left-hand side of the equation. The step-by-step calculations are then continued by using equation (48) together with the two laws of mass action corresponding to reactions (v) and (vi). Only two equilibrium tests

need/

need now be applied at each stage in the calculation until either reaction (v) or reaction (vi) departs from equilibrium. The test for reaction (v) follows from the elimination of the terms containing  $X^6$  from either equations (45) and (46) or (45) and (47). The test for reaction (vi) follows directly from equation (47).

A similar technique to that outlined above may be carried out if any other of the groups of reactions tabulated above is the first to depart from equilibrium.

## Chapter 5

### Thermodynamic and Chemical Kinetic Data

#### 5. Thermodynamic Data

Once the chemical reactions and species have been chosen, the thermodynamic data  $W_j$ ,  $C_{pj}$ ,  $\Delta H_f^0$  and  $K_p^r$  etc., may be found tabulated in standard works of reference, e.g., Ref.18. The accuracy of this type of information will not be discussed here, such details can be found in the original papers which are usually referred to in the standard works. Errors in the thermodynamic data are likely to be small by comparison with the errors associated with most of the published chemical kinetic data, as we shall see in the next section.

The presentation of tabulated thermodynamic data to a computer might give rise to the problem of computer storage space, thus it may be worthwhile to undertake fitting the data over the likely range of interest, to empirical formulae of the type:

$$C_{pj} = a_j + b_j T + c_j T^2$$

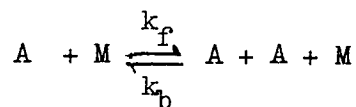
and 
$$K_p^r = A^r \exp(-B^r/T) \text{ etc.,}$$

where  $a_j$ ,  $b_j$ ,  $c_j$ ,  $A^r$  and  $B^r$  are empirical constants.

#### 5.1 Chemical Kinetic Data

Essential requirements for solving the species continuity equations are that the reaction rate parameters  $k_f^r$  and  $k_b^r$  are known. Reliable chemical kinetic data of this type is lacking for the majority of reactions which are likely to be important in the study of non-equilibrium nozzle flows. This must therefore be one of the biggest barriers in the way of carrying out realistic ramjet nozzle performance calculations.

Consider a general three-bodied reaction of the type:



in which M is assumed to be an "inert" third body which can either serve as an energy source for the forward dissociation reaction, or as an energy sink for the backward recombination reaction. To the best of the authors'

knowledge, /

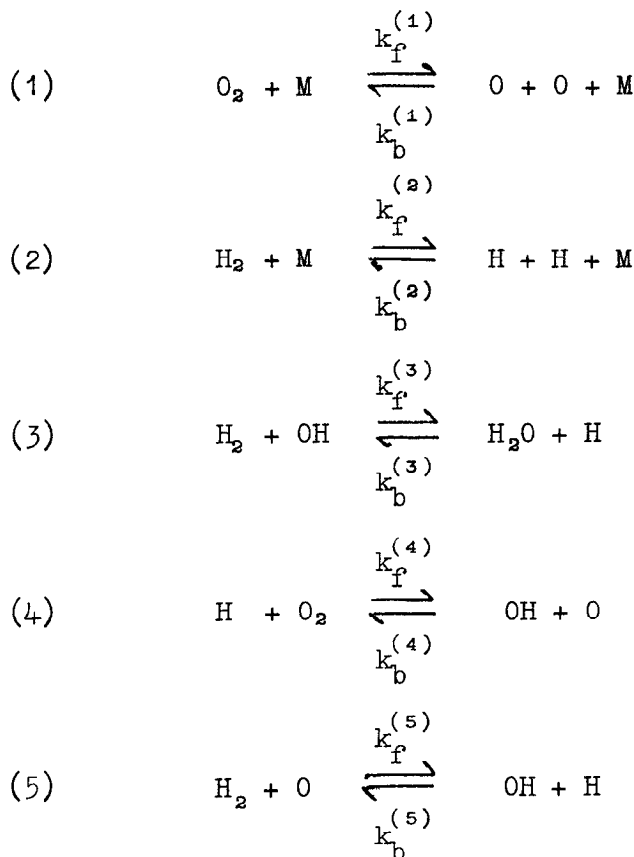


knowledge, only the forward reaction rates have been experimentally observed in reacting gas flows under conditions of interest to the present work (e.g., Refs.19 and 20). The backward reaction rates have then been deduced using equations (10) and the tabulated values of the equilibrium constants  $K_p^r$ . This process involves assuming an equilibrium relationship between  $k_f^r$  and  $k_b^r$ , even when the state of the gas is greatly different from an equilibrium state. The correct relationship between  $k_f^r$  and  $k_b^r$  at conditions removed from equilibrium, appears to be one of the major unsolved problems of chemical kinetics.

Another complication arises because the values of  $k_f^r$  and  $k_b^r$  may differ by as much as an order of magnitude (Ref.21) depending on the nature of the third body. This fact greatly increases the amount of data which ought to be specified, but present knowledge does not permit us to make this refinement in the majority of cases. However it must be noted that errors are bound to arise when we assume that a rate parameter, deduced for a particular third body, can be applied unchanged for all the many third bodies present in the system.

The rate parameters are known also to be functions of temperature, but their variation with temperature has not been predicted in a large number of cases. Much of the available data has been obtained near room temperature, and its extrapolation to conditions of interest here will be very inaccurate.

In order to demonstrate the present limited availability of chemical reaction rate data, some of the reactions which may be involved in a hydrogen ~ oxygen mixture at elevated temperatures will be considered. These reactions are\*



Reaction (1)/

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\* More recent data on the chemistry of  $H_2 \sim O_2$  reactions is provided by several contributions in the Proceedings of the 9th Symposium (International) on Combustion, Academic Press, 1963.



Reaction (1) has been studied extensively. Experimental results at elevated temperatures are reported in Refs.19, 20 and 22, and at room temperature in Refs.23, 24 and 25. Theoretical estimates of the rate parameters are given in Refs.26, 27 and 28. Mathews (Ref.19) has proposed values for the reaction rate parameters based on his interferometric measurements in the non-equilibrium region behind normal shock waves in oxygen. He also reviewed previous work concerned with reaction 1. The values which he gives are

$$k_f^{(1)} = 5.42 \times 10^7 T^{\frac{1}{2}} \left( \frac{59\,380^\circ\text{K}}{T} \right)^3 \exp \left( \frac{-59\,380^\circ\text{K}}{T} \right) \text{ litre mole}^{-1} \text{ sec}^{-1}$$

$$k_b^{(1)} = 18.5 \times 10^{10} T^{-\frac{1}{2}} \text{ litre}^2 \text{ mole}^{-2} \text{ sec}^{-1}$$

for the temperature range  $3\,000^\circ\text{K} < T < 5\,000^\circ\text{K}$ . Both the above results assume the third body to be an oxygen molecule. Mathews suggests that his results are not likely to be in error by more than a factor of two, which is indeed a high degree of accuracy when compared with some of the following data for the remaining reactions. It is noteworthy, however, that even in this case it was not possible to determine the temperature dependence of the rate parameters experimentally, and Mathews was forced to rely on theory for this dependence. The magnitude of Mathews' value for  $k_b^{(1)}$  appears to be greater than the recent theoretical value due to Keck<sup>b</sup> (Ref.28) by a factor of about three at  $3\,000^\circ\text{K}$ , but they are both in very close agreement at  $5\,000^\circ\text{K}$ .

A survey of some experimental values for the recombination reaction rate parameter for reaction (2), suggests that  $k_b^{(2)}$  lies within the approximate range  $(0.1 \sim 2.0) \times 10^{10}$  ( $\text{litre}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$ .) at room temperature with either  $\text{H}_2$  or  $\text{H}$  as the third body, see Refs.29 ~ 33. Bulewicz and Sugden (Ref.34) give an experimental value of

$$k_b^{(2)} = 2.2 \times 10^{10} \text{ (litre}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1} \text{.)}$$

at  $1\,650^\circ\text{K}$  with  $\text{H}_2\text{O}$  as the third body, and Schott (Ref.35) gives

$$k_b^{(2)} = 2.0 \times 10^9 \text{ (litre}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1} \text{.)}$$

at  $2\,100^\circ\text{K}$  with  $\text{H}_2$  as the third body. Two experimental values of the forward reaction rate parameter  $k_f^{(2)}$ , are given by Chesick and Kistiakowsky (Ref.22), these are

$$k_f^{(2)} = 1.5 \times 10^5 \text{ (litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{.) at } 2\,850^\circ\text{K,}$$

and  $k_f^{(2)} = 2.5 \times 10^5 \text{ (litre} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1} \text{.) at } 3\,250^\circ\text{K,}$

both the above results were obtained using mixtures of  $\text{H}_2$  and  $\text{X}_e$ . Comparison of Refs.34 and 35 suggests that the nature of the third body can significantly influence the values of  $k_f^{(2)}$  and  $k_b^{(2)}$ , and clearly their temperature dependence is not known. However, the dissociation energy is quoted (Refs.43 and 44) as  $103.2 \text{ k.cal.}$ , and it would seem reasonable to postulate an Arrhenius form for the reaction rate parameters.

Semenov (Ref.35) quotes Avramenko's (Ref.36) experimentally determined value of the forward reaction rate for reaction (3) as:

$$k_f^{(3)} = 4.2 \times 10^9 T^{\frac{1}{2}} \exp\left(\frac{-10 \text{ k.cal.}}{RT}\right) \text{ (litre . mole}^{-1} \text{ . sec}^{-1} \text{ .)}$$

over the temperature range 600°K ~ 800°K. There appears to be no more experimental data available for reaction (3) at present.

Reaction (4) has been studied by Karmilova et al. (Ref.37), the results of their experiments give

$$k_f^{(4)} = 5.64 \times 10^{10} \exp\left(\frac{-15.1 \text{ k.cal.}}{RT}\right) \text{ (litre . mole}^{-1} \text{ . sec}^{-1} \text{ .)}$$

over the temperature range 733°K ~ 873°K. Shott and Kinsey (Ref.38) have also determined  $k_f^{(4)}$  at 1 650°K, i.e.,

$$k_f^{(4)} = 1.43 \times 10^9 \text{ (litre . mole}^{-1} \text{ . sec}^{-1} \text{ .)}$$

and this is approximately 2.5 times the value given by Karmilova's expression for  $k_f^{(4)}$  extrapolated to 1 650°K. Schott and Kinsey have deduced an Arrhenius form for  $k_f^{(4)}$  by combining a value reported by Baldwin and Walsh (Ref.39), i.e.,

$$k_f^{(4)} = 5 \times 10^6 \text{ (litre . mole}^{-1} \text{ . sec}^{-1} \text{ .)}$$

obtained at 793°K with their own at 1 650°K, to give

$$k_f^{(4)} = 3 \times 10^{11} \exp\left(\frac{-17.5 \pm 3 \text{ k.cal.}}{RT}\right) \text{ litre . mole}^{-1} \text{ . sec}^{-1} \text{ .}$$

The quoted error in the exponent could easily change the value of  $k_f^{(4)}$  by order of magnitude.

Clyne and Thrush (Ref.40) have recently studied reaction (5), and they give the following value for the forward reaction rate parameter

$$k_f^{(5)} = 1.2 \times 10^{10} \exp\left(\frac{-9.2 \text{ k.cal.}}{RT}\right) \text{ (litre . mole}^{-1} \text{ . sec}^{-1} \text{ .)}$$

over the temperature range 409°K ~ 733°K. They claim that the above Arrhenius form fits their results to within 10%. However, there is also evidence (Refs.41 and 42) that the activation energy for reaction (5) is near 6 k.cal.

The values of  $k_f^r$  and  $k_b^r$  quoted above, are not intended to constitute a comprehensive review of the reaction rate data appropriate to hydrogen ~ oxygen reactions. However, they illustrate that a great deal

more/

more fundamental work is still required before all the necessary reaction rate data can be tabulated for a wide range of conditions.

The authors have found references in the literature to the rates of eight more reactions between hydrogen and oxygen, in addition to the five quoted above. For these eight reactions they could only find three sets of experimental results, and all of these had been performed at low temperatures. Rough theoretical estimates were given for the rates of all the other reactions.

The results of theoretical calculations, e.g., Ref.12, indicate that the length of a nozzle required to maintain a reacting gas flow close to equilibrium, is directly proportional to the recombination rate parameter  $k_p$ . Any errors in the value of  $k_p$  would therefore be reflected in the theoretical estimates of required nozzle dimensions. Thus, it would appear unwise to embark on extensive theoretical calculations by a method likely to give great numerical accuracy, until considerably more reliance can be placed on the reaction rate data for the complicated chemical changes that are likely to be involved. The authors believe that some of the approximate methods described in the previous chapter can easily yield a numerical accuracy compatible with present knowledge of most common reaction rates. A first step must be to check the approximate methods against results of more accurate calculations for a system of several reactions.

## Chapter 6

### 6. Conclusions

(1) The formulation of a one-dimensional nozzle flow problem involving arbitrary numbers of species and reactions is mathematically straightforward, and techniques exist for the numerical solution of the resulting equations.

(2) A number of approximate methods of solution have been discussed. The assumptions involved in these methods have been tested for flows with a single chemical reaction, but still require confirmation in cases where several reactions occur. It is necessary, therefore, to perform an accurate integration of the flow equations in a case where several reactions occur, and to compare this result with computations based on the various approximate methods. The most suitable approximate method may be chosen from this comparison.

Concerning the methods of analysis described in Chapter 3, the authors believe that the Partial Equilibrium Technique (3.2) can yield solutions of the governing equations to a high degree of accuracy, if the near-equilibrium criterion (Chapter 4) is sufficiently stringent. Several of the more approximate techniques appear to be attractive, and should be tested against results obtained by the Partial Equilibrium Technique. The Sudden Freezing Analysis (3.4.1) may be more generally applicable than some of the other approximate techniques, as it is not limited by near-equilibrium or near-frozen flow assumptions.

(3) There is a very serious shortage of the chemical kinetic data which is essential for the solution of non-equilibrium nozzle flow problems. Accurate data is completely lacking for the majority of reactions which are likely to occur, and resort must be made to order-of-magnitude guesses and extrapolations over large temperature ranges.

(4) Until very much more accurate kinetic data is obtained, comparatively simple approximate methods of analysis {suitably tested, as described in Conclusion (2) above} may be expected to yield numerical results whose accuracy will be limited by the available data, rather than by the method of computation.

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