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Some Computer Programmes for the Calculation of Chemical Equilibrium Composition, with Application to Combustion and Propulsion Systems

by

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SUMMARY

This Note describes computer programmes which are used in the solution
of problems arising in the combustion of rocket fuels. The chemical elements
considered in the combustion reactions are limited to carbon, hydrogen,
oxygen, nitrogen, chlorine and aluminium. A non-reactive additive may also be
included. The programmes allow for considerable variation in the conditions
governing the combustion, and they can be used to determine the specific
impulse and discharge coefficient of a propellent.

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1 INTRODUCTION

The calculation of the equilibrium composition of a chemical system at high temperature has application in several fields, including the theoretical study of rocket propellent performance. The six-element problem concerning carbon, hydrogen, oxygen, nitrogen, chlorine and aluminium has been programmed for the Mercury computer, and although the programmes were written with special reference to rocket propellents it is considered they have wider application. The Mercury programmes are the main subject of this report, but an earlier programme for the Deuce computer is described in Appendix 5.

Since the original publication of this report, as R.A.E. Technical Note Math. 88, some changes have been made to the six-element programmes. In particular, the pressures considered in the calculations concerning isentropic expansions (cases 4 and 5) can be chosen by the user, and in fact, a series of expansions (or compressions) to selected pressures can be calculated. Formerly, only expansions to one atmosphere were considered.

It may be of interest to note that a later programme is now available to calculate the equilibrium composition of a general system which is not restricted to the present six elements. This programme (R.A.E. 283) can be used on either the Mercury or Atlas computers, but for large chemical systems Atlas is more suitable. At present, equilibrium compositions at specified temperature and pressure, or at specified enthalpy and pressure, are calculated, but the programme is being further developed.

Fig.1 of the original report has been omitted as it is not considered to be of general interest.

2 GENERAL DESCRIPTION OF THE PROBLEM

In this section we consider, in general terms, the purposes to which the Mercury programmes can be applied, before proceeding to a more detailed description in the following sections.

The performance parameters of a rocket propellent can be computed from its physical and chemical properties, provided that certain assumptions are made as to the nature of the products of combustion. The programme described in this Note was made for this analysis in the case of propellents containing the elements carbon, hydrogen, oxygen and any selection from chlorine, nitrogen, aluminium and a non-reactive additive. Although the programme was not designed to work on mixtures containing only oxygen and hydrogen, satisfactory results are also obtained for this case. The range of temperature to which the programmes may be applied is from $500°K$ to $5000°K$.

The composition of the propellent is specified by an atom ratio for each element present, i.e. the ratio of the number of atoms of each element to the number of atoms of hydrogen*. For a propellent containing all six elements,

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*Propellents are often specified by percentage weights of chemical compounds. Appendix 4 gives a description of a programme which accepts data in this form and computes from it the atom ratios which are required as input to this programme.

the existence of twenty-three products of combustion in a state of chemical equilibrium is considered.

The quantities involved in the computations are the amounts of these products of combustion together with the following properties of the efflux: pressure, temperature, enthalpy, entropy, molecular weight, specific volume and specific heat.

Depending on which application of the programme is required, different items in this list are postulated as conditions of the reaction, whilst the remainder are computed from the composition of the efflux.

The programme may be employed in any of the ways described in the following five paragraphs. The numbers given to the paragraphs are included in the input data so as to direct the programme through the path appropriate to the selected application.

(1) This is the simplest application of the programme. The pressure and temperature are specified, and the computation finds the products of combustion and some thermodynamic properties of the system under conditions of chemical equilibrium. The principal use for this application is in the construction of i - V (Enthalpy - Specific Volume) charts. An example of such a chart, from Ref.1, is shown in Fig.2.

(2) The primary purpose here is to determine the combustion temperature, assuming isenthalpic conditions. The pressure and the enthalpy of the constituents at 25°C are specified, together with an estimate of the combustion temperature. The computation is basically the same as in case 1, but involves an extra iteration in which the temperature is adjusted until the resulting enthalpy of the products of combustion is equal to that of the unburnt constituents.

(3) This application is of a similar nature to case 2 above, except that equilibrium conditions are required at a particular entropy instead of enthalpy. The pressure and entropy are specified and the programme adjusts the estimate of temperature until the entropy of the products of combustion reaches the required value.

(4) Here the programme is used to determine the specific impulse of a propellant when chemical equilibrium is maintained throughout an isentropic expansion to an exhaust pressure of one atmosphere absolute. The specific impulse is computed from the change in enthalpy between the combustion chamber and the exhaust. Case 4 must follow a case of type 2, for it is case 2 which provides the entropy value for the low pressure equilibrium and the initial enthalpy from which the specific impulse is found. Apart from the derivation of this data and the small additional calculation involved, case 4 is essentially the same as case 3, in that a target entropy is achieved by an iterative procedure based on temperature.

(5) This is also a calculation of specific impulse, but the assumption is made that the expansion from the combustion chamber to an exhaust pressure of one atmosphere is so rapid that no chemical changes can take place. In

other words the chemical composition at the exhaust is identical to that in the combustion chamber. The term "frozen composition" is used to describe this concept. The case 5 calculation must follow immediately after the case 2 to which it relates. The results of case 5 comprise only the thermodynamic properties, the composition being by definition in identical proportion to that given by case 2.

The expansion from the rocket chamber to the exhaust is unlikely to occur under either of the ideal assumptions made in case 4 or 5, but both calculations are often required as they give the bounds between which the practical results should occur.

There is another calculation that is sometimes required when an isentropic expansion is considered. As the provision of this extra feature increases the computing time by a factor of about ten, it has been made available in a separate version of the programme, which is used only when this additional computation is thought to be really necessary. The calculation, which is described in section 9, determines the "discharge coefficient"; this coefficient is proportional to the maximum value of the ratio of flow velocity to flow specific volume attained during expansion. The pressure and temperature at which this maximum occurs are also determined, and these are termed the throat pressure and temperature. An equivalent flow characteristic, termed "characteristic velocity" in the field of liquid propellent rocketry, is designated by the symbol C^*. However, the symbol C_D and the term "discharge coefficient", as used in the solid propellent rocket field, are used here. C_D and C^* are related by $C^* = g/C_D$, where g is the acceleration due to gravity.

3   THE NATURE OF THE EQUATIONS TO BE SOLVED

The products of combustion that are thought to play a dominant part in the chemical reactions were chosen by R.P.E. This decision was made from well established knowledge of work in this field, aided by spectrographic analysis of flames in the laboratory. In order to consider these products of combustion, it is necessary for certain thermodynamic data to be provided. In fact, for each item a table was supplied giving enthalpy and entropy values from 300°K to 5000°K at intervals of 100°K. The details of the way in which this data is employed is given in Section 4.

Before considering the complete set of equations which are involved in this problem, it may be helpful to consider the types of relationships that are used.

The products are assumed to be in a state of chemical equilibrium and so equations can be formed expressing relationships between the amounts of the constituents present in the combustion.

For example, the reaction

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$
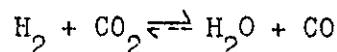
will give the following equation, in which the partial pressure of one item is expressed in terms of the others by the law of mass action. The brackets around the chemical symbols are used to indicate the partial pressures of those items.

$$(H_2) = K \frac{(H_2O)(CO)}{(CO_2)}$$

K is the equilibrium constant, the value of which varies with the temperature of the reaction.

There is a limit to the number of such equations which can be usefully considered. If the system contained r elements and produced n kinds of constituents in the efflux, then there would be (n - r) non-redundant equations of this type. For example, in a three element system of carbon, hydrogen and oxygen, let us suppose that altogether there are ten products of combustion to be considered, comprising the three original elements in their monatomic form and seven new products. There will be seven non-redundant equations; these could be constructed in a variety of ways, but the equations below are constructed by expressing each of the new products in terms of the basic constituents.

$$C + O \rightleftharpoons CO$$

$$C + 2O \rightleftharpoons CO_2$$

$$C + 4H \rightleftharpoons CH_4$$

$$O + O \rightleftharpoons O_2$$

$$O + H \rightleftharpoons OH$$

$$O + 2H \rightleftharpoons H_2O$$

$$H + H \rightleftharpoons H_2$$
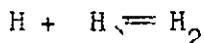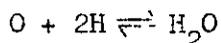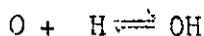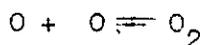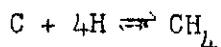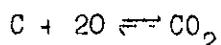
The particular reactions considered in the problem are not all in the above form, in which only atoms appear on the left hand side. In all cases, however, (n - r) non-redundant equations can be constructed.

In addition to these equations of chemical equilibrium, there are also equations of material balance; i.e. the material present in the propellent will be found in exactly the same quantities in the products of combustion. For example, the atom ratio of oxygen to hydrogen of the propellent will equal the ratio of the sum of the partial pressures of the constituents containing oxygen, to the sum of the partial pressures of the constituents containing hydrogen; providing these partial pressures are weighted according to the number of oxygen or hydrogen atoms respectively in the molecules of the constituent gases*. The notation ΣO, ΣH etc. will be used to denote the weighted sum of the partial pressures of the constituents for the respective elements.

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*It is assumed that all gases are ideal, i.e. they obey the laws of Boyle and Charles.

The material balance equations for the carbon, hydrogen, oxygen system shown above would be as follows:-

$$\frac{(CO) + 2(CO_2) + 2(O_2) + (OH) + (H_2O) + (O)}{4(CH_4) + (OH) + 2(H_2O) + 2(H_2) + (H)} = \Sigma O/\Sigma H = O/H$$

and

$$\frac{(CO) + (CO_2) + (CH_4) + (C)}{4(CH_4) + (OH) + 2(H_2O) + 2(H_2) + (H)} = \Sigma C/\Sigma H = C/H .$$

The symbolism O/H, C/H etc. is used to represent the given atom ratios of the propellent.

There will be $(r-1)$ equations of this nature in a general system, giving a total of $(n-1)$ equations to describe the amounts of n products of combustion. The particular solution required is the one for which the sum of the partial pressures of these gases in chemical equilibrium is equal to a prescribed amount- the pressure specified in the input data.

The system considered so far has been confined to gaseous products of combustion. However, certain products may be present in a solid or liquid phase. The carbon referred to in the previous paragraphs was assumed to be gaseous; we will now discuss the treatment if it is also considered to exist in the solid form. The existence of a condensed phase (solid or liquid) is indicated if a mass action equation shows a partial pressure of the gaseous phase greater than its saturated vapour pressure at that temperature. When this occurs, the saturated vapour pressure is the measure of the gaseous content, and the amount of the condensed phase may be found from the appropriate material balance equation. In the case of carbon, the number of gram-atoms of solid carbon can be calculated from:-

$$C_{(solid)} = \Sigma H . C/H - \Sigma C_{(gaseous)} .$$

i.e. the amount of carbon present in the mixture minus the amount contained by the gaseous products.

Hence

$$C_{(solid)} = \left\{4(CH_4) + (OH) + 2(H_2O) + 2(H_2) + (H)\right\} . C/H$$

$$- \left\{(CO) + (CO_2) + (CH_4) + (C_{gas})\right\}$$

where (C_{gas}) is the saturated vapour pressure at the appropriate temperature.

The justification for assessing the condensed phase in terms of partial pressures is that the volume of gas involved is taken to be RT (Universal Gas Constant × Absolute Temperature). Hence from the ideal gas equation, PV = nRT, the partial pressure of a gas is numerically the same as n, the number of gram molecules of the gas.

4   THE EVALUATION OF THE EQUILIBRIUM CONSTANTS

The equations described in the previous section must be solved at a specific temperature, as the equilibrium constants involved in these equations are functions of temperature. These constants are derived within the programme as described in the following paragraphs whenever a temperature change is involved in the computation.

For each product of combustion, the Rocket Propulsion Establishment provided tabulated data connecting enthalpy I, in calories/mol and temperature T in degrees Kelvin. Polynomials were fitted to these tabular values by a least squares method, but an abcissa of t = T/1000 was used so that the coefficients stayed within a manageable range. The order of the polynomial fitted could be varied and for each set of coefficients produced, the maximum residual error was recorded. The lowest order polynomials which gave errors not exceeding 2 calories/mol were the ones chosen to represent the enthalpy functions of each product of combustion.

Appendix 2 gives the coefficients of the polynomials that are used. They were punched on what is called the main data tape, which is described in Section 10. It can be seen that to achieve this high accuracy of better than 2 calories/mol in the discrepancy between the polynomial representation of enthalpy and the tables which were provided, rather large orders of fit had to be employed. With a polynomial of high order there is a danger that, while providing a good fit at the data points, the polynomial values will oscillate about the presumed smooth curve between them. As the polynomials have to be differentiated, this type of behaviour could not be tolerated. In consequence the following examination was made.

Interpolation with every four successive values in the basic data (which is given at every 100°K) was used to provide values at the 50°K points in the temperature range. These results were compared with those produced by using the polynomial representation of enthalpy and close agreement was found. The order of the discrepancies was $0 \cdot 05\%$ of the change in enthalpy due to a 50°K change in temperature. On this evidence, the assumption was made that the kind of errors sometimes associated with fitting high order polynomials would not arise in this problem.

Entropy values for each product of combustion are also required in order to evaluate the equilibrium constants. At a reference pressure the entropy for temperature T can be evaluated from the following relationship

$$S = \int_{298}^{T} \frac{1}{T} \frac{dI}{dT} \, dT + S_{298}$$

where S_{298} is the entropy at 298°K and at the reference pressure.

This expression can be evaluated by using the enthalpy-temperature polynomial as follows:-

$$I = a_o^{\cdot} + a_1 t + a_2 t^2 + a_3 t^3 + \ldots + a_n t^n$$

$$= a_o + \frac{a_1 T}{10^3} + \frac{a_2 T^2}{10^6} + \frac{a_3 T^3}{10^9} + \ldots + \frac{a_n T^n}{10^{3n}}$$

therefore

$$\frac{1}{T} \frac{dI}{dT} = \frac{a_1}{10^3 T} + \frac{2 a_2}{10^6} + \frac{3 a_3 T}{10^9} + \frac{4 a_4 T^2}{10^{12}} + \ldots + \frac{na_n T^{(n-2)}}{10^{3n}}$$

therefore

$$S = \frac{a_1 \log T}{10^3} + \frac{2 a_2 T}{10^6} + \frac{3 a_3 T^2}{2.10^9} + \frac{4 a_4 T^3}{3.10^{12}} + \ldots + \frac{na_n T^{(n-1)}}{(n-1).10^{3n}} + C'$$

$$= \frac{1}{1000} \left[a_1 \log 10^3 t + 2 a_2 t + \frac{3 a_3 t^2}{2} + \frac{4 a_4 t^3}{3} .. + \frac{na_n t^{(n-1)}}{(n-1)} \right] + C'$$

where C' is the constant term corresponding to the lower limit of integration plus the contribution of S_{298}.

The programme evaluates

$$\frac{1}{1000} \left[a_1 \log t + 2 a_2 t + 3 a_3 t^2/2 + \ldots + na_n t^{(n-1)}/(n-1) \right] + S' .$$

The data for entropy and temperature was also provided in tabular form, and the constant S' was chosen so as to minimise the mean deviation of the calculated and tabular entropy values. However, this deviation was found to be so nearly constant throughout the temperature range that the determination of S' could be made quite adequately from the inspection of a few spot points.

In general the enthalpy curves are smooth. However, in the case of the condensed phase of aluminium oxide, Al_2O_3, there is a discontinuity at the temperature where it changes from a solid to a liquid state. Initially this problem was met by providing a polynomial to represent each part of the curve, and the values of I and S were calculated from whichever of these polynomials applied at the temperature under consideration. This was not found to be entirely satisfactory, and it was decided to use linear interpolation between the values from the two polynomials, over a small temperature range either side

of the melting point; in fact ±20°K. This treatment was considered to give a fair approximation to the true behaviour in this region.

Titanium oxide, TiO_2, was the catalyst originally included in the 6-element combustion problem, and like Al_2O_3 it has a melting point well within the range of temperature for which the programme is applicable. So here again, two polynomials are used with linear interpolation between them for temperatures within 20°K of the melting point. The programming details differ slightly so as to allow the non-reactive additive to be changed without altering the programme. Section 10 describes the data which must be supplied for the additive.

Having established a method for obtaining the values of enthalpy and entropy for each combustion product, the computation of the equilibrium constants may now be discussed, as these are functions of the entropy and enthalpy of the individual items taking part in the chemical reaction under consideration.

For the reaction

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \quad,$$
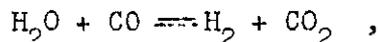
the mass action equation is

$$K_4 = \frac{(H_2)(CO_2)}{(H_2O)(CO)} \quad.$$

Such constants can be evaluated by using the fact that at constant temperature and pressure the "free energy" of a reactive system is a minimum at equilibrium. The "free energy" is the summation of terms involving the enthalpy, entropy and pressure for each of the components in the reaction. This minimum condition requires that

$$\Sigma(ST - I - RT \log_e P) = 0$$

and hence

$$\frac{1}{R}\left[\Sigma S - \frac{1}{T}\Sigma I\right] = \Sigma \log P = \log K \quad.$$

This defines the value of the equilibrium constants. In particular

$$\log K_4 = \frac{1}{R}\left\{(S_{H_2} + S_{CO_2} - S_{H_2O} - S_{CO}) - \frac{1}{T}(I_{H_2} + I_{CO_2} - I_{H_2O} - I_{CO})\right\}$$

where R is the universal gas constant, 1·98719 cal/mol deg. K.

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An example of an equation where the items are not confined to single molecules should clarify the derivation of the equilibrium constants. The reaction

$$2 \, CO_2 \rightleftharpoons 2 \, CO + O_2 \quad ,$$
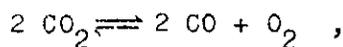
gives a mass action equation

$$K_6 = \frac{(CO)^2 (O_2)}{\cdot (CO_2)^2} \quad ,$$

where

$$\log_e K_6 = \frac{1}{R} \left[(2 \, S_{CO} + S_{O_2} - 2 \, S_{CO_2}) - \frac{1}{T} (2 \, I_{CO} + I_{O_2} - 2 \, I_{CO_2}) \right] \quad .$$

Equilibrium reactions between the condensed and gaseous phases of a compound provide another type of equation. For example let us consider the equilibrium between aluminium oxide and its vapour

$$Al_2O_3 (solid) \rightleftharpoons Al_2O_3 (gas) \quad .$$

In this case the value of

$$\frac{1}{R} \left[S_{solid} - S_{gas} - \frac{1}{T} (I_{solid} - I_{gas}) \right]$$

is equal to the logarithm of the saturated vapour pressure (svp) for this heterogeneous equilibrium, the amount of solid present having no effect,

i.e.
$$K_{19} = Al_2O_3 (svp) \quad .$$

The equilibrium constants associated with reactions concerning the aluminium products are constructed using the enthalpy and entropy of the condensed phase of Al_2O_3. The justification for this and the application of the constants in the mass action equations will become apparent in the following sections.

In view of the fact that it is possible to alter the scheme of combustion in certain cases, the details of computing the equilibrium constants are explained in Appendix 3. The only change requested so far has been to a carbon, hydrogen, oxygen, potassium system.

5   THE REACTIONS CONSIDERED IN THE COMBUSTION

The following list shows the products of combustion that are considered in the problem.

Gaseous products			
CO_2	CO	CH_4	$C_{(gas)}$
H_2O	H_2	H	O_2
OH	O	N_2	NO
N	HCl	Cl_2	Cl
$AlCl$	$AlCl_3$	$AlOCl$	$Al_{(gas)}$
AlO	Al_2O	$Al_2O_{3(gas)}$	

Condensed phases $C_{(solid)}$ $Al_2O_{3}(solid \text{ or } liquid)$

The suffix (solid or liquid) will in future be abbreviated to (s,l).

Two separate versions of the programme have been made which allow the non-reactive additive to be considered in either a condensed state or in a gaseous state. There is no provision for an additive which undergoes a change of state from liquid to gas, but the version of the programme dealing with an additive in the condensed state allows a solid/liquid change.

It is assumed that the partial pressure of aluminium will not reach the saturated vapour pressure and hence the existence of condensed aluminium is not considered. However a check has been included in the programme and an indication is given if this assumption is incorrect. (This check is referred to in Sections 6 and 12.)

The reactions considered in the combustion have been selected to fit into the iterative scheme of solution employed. The iterative scheme is based on three quantities: the partial pressure of H_2O, the ratio of the partial pressures of CO_2 and CO, and the partial pressure of HCl. In consequence, the reactions have been chosen so that, as far as possible, each equilibrium constant is expressed in terms of these three quantities and one other product of combustion.

The reactions and their associated mass-action equations are listed below. The nomenclature for the equilibrium constants will be used throughout the rest of this Note.

1. $C_{(solid)} \rightleftharpoons C_{(gas)}$ $K_1 = (c_{svp})$

2. $2\ CO + \frac{1}{2}\ CO_2 + H_2O \rightleftharpoons 2\ CO_2 + \frac{1}{2}\ CH_4$ $K_2 = \dfrac{(CO_2)^{3/2}\ (CH_4)^{1/2}}{(H_2O)(CO)^2}$

3. $C_{gas} + CO_2 \rightleftharpoons 2\,CO$ $\qquad$ $K_3 = \dfrac{(CO)^2}{(CO_2)(C_{gas})}$

4. $H_2O + CO \rightleftharpoons H_2 + CO_2$ $\qquad$ $K_4 = \dfrac{(H_2)(CO_2)}{(H_2O)(CO)}$

5. $\frac{1}{2}H_2O + \frac{1}{2}CO \rightleftharpoons H + \frac{1}{2}CO_2$ $\qquad$ $K_5 = \dfrac{(H)(CO_2)^{1/2}}{(H_2O)^{1/2}(CO)^{1/2}}$

6. $2\,CO_2 \rightleftharpoons 2\,CO + O_2$ $\qquad$ $K_6 = \dfrac{(CO)^2(O_2)}{(CO_2)^2}$

7. $\frac{1}{2}H_2O + \frac{1}{2}CO_2 \rightleftharpoons OH + \frac{1}{2}CO$ $\qquad$ $K_7 = \dfrac{(OH)(CO)^{1/2}}{(H_2O)^{1/2}(CO_2)^{1/2}}$

8. $\frac{1}{2}O_2 \rightleftharpoons O$ $\qquad$ $K_8 = \dfrac{(O)}{(O_2)^{1/2}}$

9. $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$ $\qquad$ $K_9 = \dfrac{(NO)}{(N_2)^{1/2}(O_2)^{1/2}}$

10. $\frac{1}{2}N_2 \rightleftharpoons N$ $\qquad$ $K_{10} = \dfrac{(N)}{(N_2)^{1/2}}$

11. $2\,HCl + CO_2 \rightleftharpoons H_2O + CO + Cl_2$ $\qquad$ $K_{11} = \dfrac{(H_2O)(CO)(Cl_2)}{(HCl)^2(CO_2)}$

12. $\frac{1}{2}Cl_2 \rightleftharpoons Cl$ $\qquad$ $K_{12} = \dfrac{(Cl)}{(Cl_2)^{1/2}}$

13. $\frac{1}{2}Al_2O_{3(s,l)} + HCl + CO \rightleftharpoons CO_2 + \frac{1}{2}H_2O + AlCl$ $\qquad$ $K_{13} = \dfrac{(CO_2)(H_2O)^{1/2}(AlCl)}{(HCl)(CO)}$

14. $\frac{1}{2}Al_2O_{3(s,l)} + 3\,HCl \rightleftharpoons \frac{3}{2}H_2O + AlCl_3$ $\qquad$ $K_{14} = \dfrac{(AlCl_3)(H_2O)^{3/2}}{(HCl)^3}$

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15. $\frac{1}{2} Al_2O_3(s,l) + \frac{3}{2} CO \rightleftharpoons \frac{3}{2} CO_2 + Al$ $\qquad K_{15} = \dfrac{(CO_2)^{3/2}(Al)}{(CO)^{3/2}}$

16. $\frac{1}{2} Al_2O_3(s,l) + \frac{1}{2} CO \rightleftharpoons \frac{1}{2} CO_2 + AlO$ $\qquad K_{16} = \dfrac{(CO_2)^{1/2}(AlO)}{(CO)^{1/2}}$

17. $\frac{1}{2} Al_2O_3(s,l) + CO \rightleftharpoons CO_2 + \frac{1}{2} Al_2O$ $\qquad K_{17} = \dfrac{(CO_2)(Al_2O)^{1/2}}{(CO)}$

18. $Al(s,l) \rightleftharpoons Al(gas)$ $\qquad K_{18} = (Al_{svp})$

19. $Al_2O_3(s,l) \rightleftharpoons Al_2O_3(gas)$ $\qquad K_{19} = (Al_2O_3\ svp)$

20. $\frac{1}{2} Al_2O_3(s,l) + HCl \rightleftharpoons AlOCl + \frac{1}{2} H_2O$ $\qquad K_{20} = \dfrac{(AlOCl)(H_2O)^{1/2}}{(HCl)}$

Equations (13) to (17) and (20) all describe reactions concerning condensed Al_2O_3 and another aluminium product.

The amount of condensed Al_2O_3 can have no part in a mass action equation; the gaseous equilibrium is between the saturated vapour and the other gases. The relationships listed above for the equilibrium constants K_{13} to K_{17} and K_{20} are derived by combining the equilibrium relation between condensed Al_2O_3 and its vapour with each of the gaseous equilibria. Consider, for example, equation (16), namely:-

$$\frac{1}{2} Al_2O_3 + \frac{1}{2} CO \rightleftharpoons \frac{1}{2} CO_2 + AlO \ . \qquad\qquad (i)$$
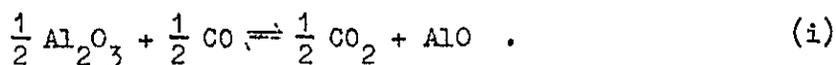
With Al_2O_3 present in a condensed form, the gaseous equilibrium constant K is:-

$$K = \frac{(CO_2)^{1/2}(AlO)}{(CO)^{1/2}(Al_2O_3\ svp)^{1/2}} \qquad\qquad (ii)$$

hence

$$\log K = \frac{1}{R}\left[\frac{1}{2}S_{CO_2} + S_{AlO} - \frac{1}{2}S_{CO} - \frac{1}{2}S_{Al_2O_3(svp)}\right.$$

$$\left. - \frac{1}{T}\left(\frac{1}{2}I_{CO_2} + I_{AlO} - \frac{1}{2}I_{CO} - \frac{1}{2}I_{Al_2O_3(svp)}\right)\right] \cdot \text{(iii)}$$

Equation (19) is:-

$$Al_2O_3(s,l) \rightleftharpoons Al_2O_3(gas) \tag{iv}$$

giving

$$K_{19} = \left(Al_2O_3\ svp\right) \tag{v}$$

and

$$\log K_{19} = \frac{1}{R}\left[S_{Al_2O_3(s,l)} - S_{Al_2O_3(svp)} - \frac{1}{T}\left(I_{Al_2O_3(s,l)} - I_{Al_2O_3(svp)}\right)\right] \cdot$$
$$\dots \text{(vi)}$$

Hence, from equations (ii) and (v), we have:-

$$\left(K\,K_{19}^{1/2}\right) = \frac{(CO_2)^{1/2}\,(AlO)}{(CO)^{1/2}}$$

and from equations (iii) and (vi),

$$\log\left(K\,K_{19}^{1/2}\right) = \frac{1}{R}\left\{\left(\frac{1}{2}S_{CO_2} + S_{AlO} - \frac{1}{2}S_{CO} - \frac{1}{2}S_{Al_2O_3(s,l)}\right)\right.$$

$$\left. - \frac{1}{T}\left(\frac{1}{2}I_{CO_2} + I_{AlO} - \frac{1}{2}I_{CO} - \frac{1}{2}I_{Al_2O_3(s,l)}\right)\right\} \cdot$$

The term $\left(K\,K_{19}^{1/2}\right)$ is denoted by K_{16} in the previous list.

The equilibrium constants K_{13} to K_{17} and K_{20} are derived using the entropy and enthalpy of Al_2O_3 solid or liquid; but when the equilibrium constants are expressed as ratios of partial pressures then Al_2O_3 does not occur explicitly. Conversely, from these mass action equations, the partial pressures of all the aluminium products (with the exception of Al_2O_3) can now be expressed as

functions of an equilibrium constant and the three basic quantities on which the iterative scheme depends. This, of course, simplifies the solution. However, the assumption has been made that Al_2O_3 exists in condensed form. If during the iterative process it becomes apparent that this is not so, and that Al_2O_3 exists in gaseous form only, then different reactions must be considered and a different scheme of solution employed (see Section 7).

6   THE PROCEDURE USED IN THE MAIN COMPUTATION

The "main computation" described here is the derivation of the partial pressures of the gaseous products of combustion, and the amounts of the components in a condensed state, which satisfy the equations described in Sections 3 and 5. In other words, the problem is to find the components of a chemical system in equilibrium, whose collective composition is that of the propellent, and such that the sum of the partial pressures equals the value specified in the input data.

The procedure is based on using estimates for the partial pressures, or the ratio between partial pressures of certain components. The quantities which are estimated are:-

y = the partial pressure of steam   = (H_2O)

a = the ratio of the partial pressures of
       carbon dioxide and carbon monoxide   = $(CO_2)/(CO)$

x = the partial pressure of hydrogen chloride = (HCl)

The estimates are themselves derived by the programme, by assuming that the combustion is a simple system involving only H_2O, CO_2, CO, H_2, N_2 and HCl in the gaseous state and Al_2O_3 in the condensed state.

The first phase of the computation is the adjustment of the HCl estimate by an iterative process until the calculated ratio $\Sigma Cl/\Sigma H$ agrees with the ratio Cl/H specified in the input data. To do this it is necessary to evaluate the partial pressures of all the products which contain chlorine or hydrogen, and also, as is shown later, all the products which contain carbon.

The partial pressures of H_2, H and OH can be found directly from equations (4), (5) and (7) (Section 5).

We have

$$(H_2) = K_4\, y/a$$

$$(H) = K_5 (y/a)^{\frac{1}{2}}$$

$$(OH) = K_7 (ay)^{\frac{1}{2}} .$$

Now

$$\Sigma H = (HCl) + 2(H_2O) + 2(H_2) + (H) + (OH) + 4(CH_4)$$

and the only item in this expression which has not yet been found is the partial pressure of CH_4. In order to obtain this partial pressure it is necessary to calculate the amounts of all the carbon products.

The "carbon calculation" consists essentially of expressing the various carbon products in terms of the partial pressure of CO. The carbon to hydrogen material balance can then be used directly to find the value of the partial pressure of CO, and when this value is substituted back in the expressions for the other carbon products this completes the "carbon calculation". However, this calculation is invalidated if solid carbon is present. This condition exists if the calculated partial pressure of C_{gas} exceeds its saturated vapour pressure. In this case the calculated (C_{gas}) is replaced by (C_{svp}). The partial pressure of CO and hence those of the other carbon products are recalculated from (C_{svp}). The material balance equation is now used to determine the amount of solid carbon present.

The "carbon calculation" can be shown as follows.

From the expression for "a" and equations (2) and (3)

$$(CO_2) = a(CO) \tag{i}$$

$$(CH_4) = \frac{K_2^2 y^2}{a^3} (CO) \equiv A(CO) \tag{ii}$$

$$(C_{gas}) = \frac{1}{aK_3} (CO) \equiv B(CO) \tag{iii}$$

where A and B represent $K_2^2 y^2 / a^3$ and $1/aK_3$ respectively.

Now

$$\frac{C}{H} = \frac{(CO) + (CO_2) + (CH_4) + (C_{gas})}{(HCl) + 2(H_2O) + 2(H_2) + (H) + (OH) + 4(CH_4)} \tag{iv}$$

$$= \frac{(CO) \{1 + a + A + B\}}{(HCl) + 2(H_2O) + 2(H_2) + (H) + (OH) + 4A(CO)}$$

giving

- 17 -

$$(CO) = \frac{\frac{C}{H}\{(HCl) + 2(H_2O) + 2(H_2) + (H) + (OH)\}}{1 + a + A + B - 4A\frac{C}{H}} \quad . \qquad (v)$$

This value of (CO) from (v) is substituted in equations (i), (ii) and (iii), and ΣH is evaluated.

then   If (C_{gas}) as calculated from (iii) exceeds (C_{svp}) given by equation (i),

$$(C_{gas}) = (C_{svp})$$

and re-arranging equation (iii) we have

$$(CO) = aK_3(C_{svp}) \quad .$$

Equations (i) and (ii) are now re-evaluated to give (CO_2) and (CH_4) and a revised value for ΣH is obtained.

Equation (iv) is modified to include solid carbon:-

$$\frac{C}{H} = \frac{(CO) + (CO_2) + (CH_4) + (C_{svp}) + (C_{solid})}{\Sigma H}$$

and hence

$$(C_{solid}) = \frac{C}{H}\Sigma H - \{(CO) + (CO_2) + (CH_4) + (C_{svp})\} \quad .$$

We have now reached the stage at which the partial pressures of all the hydrogen bearing products have been found (by a calculation involving the carbon products). The first phase of the computation is continued with the evaluation of the partial pressures of the chlorine products. Equations (11), (12), (13), (14) and (20) give:-

$$(Cl_2) = K_{11} \frac{a}{y} (HCl)^2$$

$$(Cl) = K_{12}(Cl_2)^{\frac{1}{2}}$$

$$(AlCl) = \frac{K_{13}(HCl)}{ay^{\frac{1}{2}}}$$

$$(AlCl_3) = \frac{K_{14}(HCl)^3}{y^{3/2}}$$

$$(AlOCl) = \frac{K_{20}(HCl)}{y^{\frac{1}{2}}} \quad .$$

These values are then substituted in

$$\Sigma Cl = (HCl) + 2(Cl_2) + (Cl) + (AlCl) + 3(AlCl_3) + (AlOCl) \quad ,$$

and the ratio $\Sigma Cl/\Sigma H$ is computed.

There is no doubt that initially there will be a large discrepancy between this quantity and the specified Cl/H value. The estimate of the partial pressure of HCl must be adjusted, until there is agreement to within an acceptable limit. A second value of $\Sigma Cl/\Sigma H$ is obtained using a slightly increased value of HCl. Subsequently linear interpolation, based on the last two values found, is used to obtain further trial values of (HCl), until a satisfactory result for $\Sigma Cl/\Sigma H$ is found.

Each interpolated value of HCl is examined in the programme to ensure that it is positive; a negative value would be rejected and replaced by half the previous value. Such precautions are taken in other similar procedures throughout the programme.

The first phase of the calculation has produced the partial pressures compatible with the C/H and Cl/H ratios of the propellent, but those pressures are based on estimates of (H_2O) and $(CO_2)/(CO)$. In the second phase of the calculation the estimate of $(CO_2)/(CO)$, or "a", is adjusted until the ratio $\Sigma O/\Sigma H$ from the calculated partial pressures agrees with the O/H ratio specified for the propellent. All the remaining products of combustion are involved in this calculation, and for every value of "a" that is tried the previous iterative procedure to find the partial pressure of HCl must be completed.

In the determination of the value of "a" corresponding to the O/H ratio of the propellant, there are two other material balance equations to be satisfied. The N/H balance is quite straightforward as there are only three products of nitrogen considered. The Al/H balance is rather more complicated, but advantage is taken of the fact that condensed Al_2O_3 almost always exists. This condition is inherent in the construction of the equilibrium equations (Section 5), and the Al/H material balance equation gives the amount of condensed Al_2O_3 present. If however, this indicates the absence of condensed Al_2O_3 a different type of solution must be used; this is described in Section 7. Whichever part of the programme is used to determine the partial pressures of the aluminium products, it is assumed that aluminium itself occurs only in the gaseous phase. It is checked in the programme that the partial pressure of aluminium obtained is less than its saturated vapour pressure, but if this check fails no remedial action is taken, although an indication of the failure is given in the results, (see Section 12).

The second phase of the calculation commences with the evaluation of the aluminium products from equations (15), (16), (17) and (19), and using the material balance equation to find $(Al_2O_{3\ s,l})$.

$$(Al_{gas}) = \frac{K_{15}}{a^{3/2}} \qquad (Al_{svp}) = K_{18}$$

$$\text{check } (Al_{gas}) < (Al_{svp})$$

$$(AlO) = \frac{K_{16}}{a^{\frac{1}{2}}}$$

$$(Al_2O) = \frac{K_{17}^2}{a^2}$$

$$(Al_2O_{3\ svp}) = K_{19} .$$

Now

$$\frac{Al}{H} = \frac{(AlCl) + (AlCl_3) + (AlOCl) + (Al) + (AlO) + 2(Al_2O) + 2(Al_2O_{3\ svp}) + 2(Al_2O_{3\ s,l})}{\Sigma H}$$

hence

$$(Al_2O_{3\ s,l}) = \frac{1}{2}\left[\frac{Al}{H}\ \Sigma H - X\right] \qquad\qquad (vi)$$

where

$$X = (AlCl) + (AlCl_3) + (AlOCl) + (Al) + (AlO) + 2(Al_2O) + 2(Al_2O_{3\ svp}) \ .$$

If $(Al_2O_{3\ s,1})$ from equation (vi) is negative the calculation described in Section 7 is used.

Once the Al/H balance has been achieved, either by the above procedure or that of Section 7, the remainder of the second phase of the calculation can be completed. The partial pressures of O_2 and O are found from equations (6) and (8).

$$(O_2) = K_6 a^2$$

$$(O) = K_8 (O_2)^{\frac{1}{2}} \ .$$

The partial pressures of NO and N can be expressed in terms of the partial pressure of N_2. When these expressions are substituted in the N/H material balance equation, the resulting equation is a quadratic for $(N_2)^{\frac{1}{2}}$.

From equations (9) and (10)

$$(NO) = K_9 (O_2)^{\frac{1}{2}} (N_2)^{\frac{1}{2}} = aK_9 K_6^{\frac{1}{2}} (N_2)^{\frac{1}{2}} \qquad \text{(vii)}$$

and

$$(N) = K_{10} (N_2)^{\frac{1}{2}} \ . \qquad \text{(viii)}$$

Now

$$\frac{N}{H} = \frac{2(N_2) + (NO) + (N)}{\Sigma H}$$

therefore

$$2(N_2) + (NO) + (N) = \frac{N}{H} \Sigma H$$

therefore

$$2(N_2) + aK_9 K_6^{\frac{1}{2}} (N_2)^{\frac{1}{2}} + K_{10} (N_2)^{\frac{1}{2}} = \frac{N}{H} \Sigma H$$

therefore

$$2(N_2) + [aK_9 K_6^{\frac{1}{2}} + K_{10}] (N_2)^{\frac{1}{2}} - \frac{N}{H} \Sigma H = 0 \ .$$

With the solution of this quadratic equation and the evaluation of (NO) and (N) from equations (vii) and (viii), the amounts of all the products of combustion have been determined and ΣO can be found.

$$\Sigma O = (CO) + 2(CO_2) + (H_2O) + 2(O_2) + (OH) + (O) + (NO) + (AlOCl) + (AlO)$$

$$+ (Al_2O) + 3(Al_2O_3\ _{gas}) + 3(Al_2O_3\ _{s,l}) \ .$$

The second phase of the calculation is concluded similarly to the first, namely by interpolating for further trial values of "a" until a satisfactory $\Sigma O/\Sigma H$ is obtained. When this has been achieved then a set of partial pressures - and also the amounts of components in a condensed state - have been found, which are in equilibrium and match the composition of the propellant. The total pressure will not however have the required value; in order to achieve this, different values of y, the partial pressure of H_2O, must be tried. The procedure adopted here is again linear interpolation based on two trial values of y. This iteration includes the other two iterations to find the values of (HCl) and $(CO_2)/(CO)$ appropriate to the value of (H_2O) under investigation.

The determination of the composition at a particular temperature and pressure is referred to as the "main computation" throughout this Note.

7   TREATMENT APPLIED WHEN CONDENSED Al_2O_3 IS ABSENT

The procedure used for the determination of the composition, when condensed Al_2O_3 has been shown absent during the main computation, depends on whether or not the mixture contains chlorine. If it does two iterative loops are used. The outer one determines the partial pressures of aluminium bearing constituents, to satisfy the Al/H ratio, based on an estimate of the partial pressure of AlCl. Naturally, the alteration of the pressure of any chlorine compound affects the Cl/H balance, and the inner loop adjusts the (HCl) and other pressures to correspond to the change in the partial pressure of AlCl.

It is necessary to re-arrange the equations in Section 5 so as to include (AlCl) and eliminate $(Al_2O_3\ _{s,l})$. The equations become:-

$$2\,HCl + CO_2 + AlCl \rightleftharpoons AlCl_3 + H_2O + CO \qquad \frac{K_{14}}{K_{13}} = \frac{(AlCl_3)(H_2O)(CO)}{(HCl)^2(CO_2)(AlCl)}$$

$$CO_2 + AlCl \rightleftharpoons AlOCl + CO \qquad \frac{K_{20}}{K_{13}} = \frac{(AlOCl)(CO)}{(CO_2)(AlCl)}$$

$$H_2O + 2\,AlCl \rightleftharpoons Al_2O + 2\,HCl \qquad \frac{K_{17}^2}{K_{13}^2} = \frac{(Al_2O)(HCl)^2}{(H_2O)(AlCl)^2}$$

$$\tfrac{1}{2}\,H_2O + \tfrac{1}{2}\,CO + AlCl \rightleftharpoons Al + \tfrac{1}{2}\,CO_2 + HCl \qquad \frac{K_{15}}{K_{13}} = \frac{(Al)(CO_2)^{1/2}(HCl)}{(H_2O)^{1/2}(CO)^{1/2}(AlCl)}$$

$$\tfrac{1}{2}\,CO_2 + \tfrac{1}{2}\,H_2O + AlCl \rightleftharpoons AlO + \tfrac{1}{2}\,CO + HCl \qquad \frac{K_{16}}{K_{13}} = \frac{(AlO)(CO)^{1/2}(HCl)}{(CO_2)^{1/2}(H_2O)^{1/2}(AlCl)}$$

$$2\,CO_2 + H_2O + 2\,AlCl \rightleftharpoons Al_2O_3 + 2\,HCl + 2\,CO \qquad \frac{K_{19}}{K_{13}^2} = \frac{(Al_2O_3)(HCl)^2(CO)^2}{(CO_2)^2(H_2O)(AlCl)^2} \quad .$$
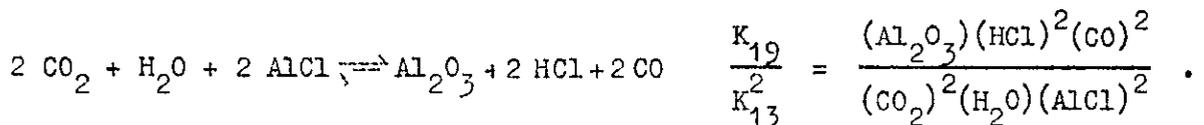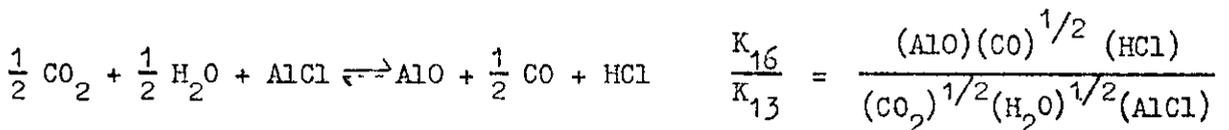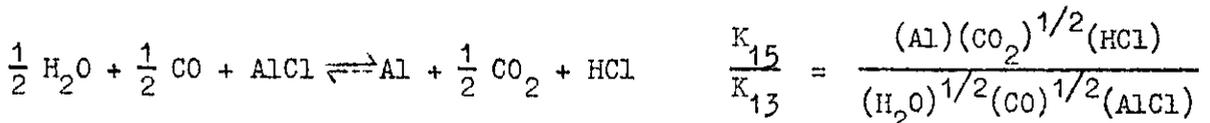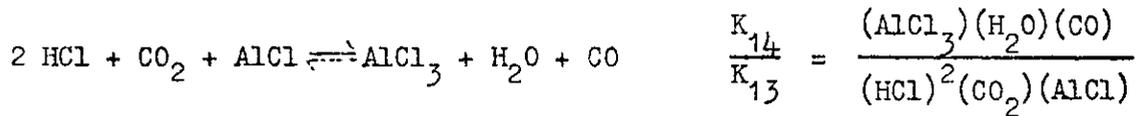
Hence

$$(AlCl_3) = \frac{K_{14}}{K_{13}} \cdot \frac{a}{y}\,(HCl)^2(AlCl)$$

$$(AlOCl) = \frac{K_{20}}{K_{13}} \cdot a(AlCl)$$

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$$(Al_2O) \quad = \frac{K_{17}^2}{K_{13}^2} \cdot \frac{y}{(HCl)^2} (AlCl)^2$$

$$(Al) \quad = \frac{K_{15}}{K_{13}} \cdot \frac{y^{1/2}}{a^{1/2}} \cdot \frac{(AlCl)}{(HCl)}$$

$$(AlO) \quad = \frac{K_{16}}{K_{13}} \cdot \frac{a^{1/2} y^{1/2}}{(HCl)} \cdot (AlCl)$$

$$(Al_2O_{3\ gas}) \quad = \frac{K_{19}}{K_{13}^2} \cdot \frac{a^2 y}{(HCl)^2} (AlCl)^2 \ .$$

An estimate of $(AlCl)$ is made on the assumption that $AlOCl$, Cl and Cl_2 will not be present in significant quantities. Then the relation

$$Cl/H = \frac{(AlCl) + 3(AlCl_3) + (HCl)}{\Sigma H}$$

is used, which reduces to

$$(AlCl)_{estimate} = \frac{\Sigma H \cdot Cl/H - (HCl)}{1 + 3\ a\ K_{14}(HCl)^2/y\ K_{13}} \ .$$

The computation to establish a satisfactory Cl/H balance is identical with that previously described, with the exception of the evaluation of $(AlCl_3)$ and $(AlOCl)$. These are given by the new relationships above. On the completion of this iteration, the remaining aluminium products are computed. Adjustments are made to the value of $(AlCl)$ until the Al/H balance is satisfactory, and then the main computation is resumed at the stage where the partial pressure of oxygen is computed.

If chlorine is absent from the propellent the procedure is simpler, only one iterative loop being used. The determination of the partial pressures of the aluminium compounds is based on the partial pressure of Al_2O which is adjusted until the specified Al/H ratio is achieved. The starting value for the partial pressure of Al_2O is the most recently found value from the normal calculation which assumed $(Al_2O_3 {}_{s,1})$ to be present.

For this computation the equations from Section 5 are re-arranged as follows:-

$$\tfrac{1}{2} CO + \tfrac{1}{2} Al_2O \rightleftharpoons Al + \tfrac{1}{2} CO_2 \qquad \frac{K_{15}}{K_{17}} = \frac{(Al)(CO_2)^{1/2}}{(CO)^{1/2}(Al_2O)^{1/2}}$$

$$\tfrac{1}{2} CO_2 + \tfrac{1}{2} Al_2O \rightleftharpoons AlO + \tfrac{1}{2} CO \qquad \frac{K_{16}}{K_{17}} = \frac{(AlO)(CO)^{1/2}}{(CO_2)^{1/2}(Al_2O)^{1/2}}$$

$$2 CO_2 + Al_2O \rightleftharpoons Al_2O_3 + 2 CO \qquad \frac{K_{19}}{K_{17}^2} = \frac{(Al_2O_3)(CO)^2}{(CO_2)^2(Al_2O)} \qquad .$$
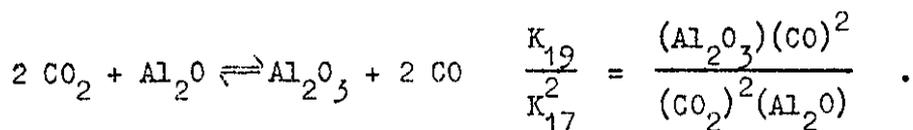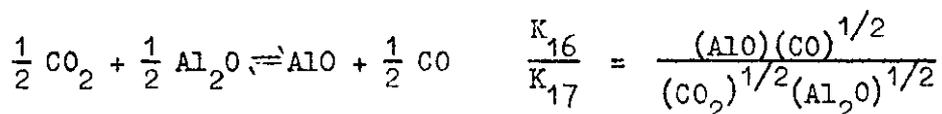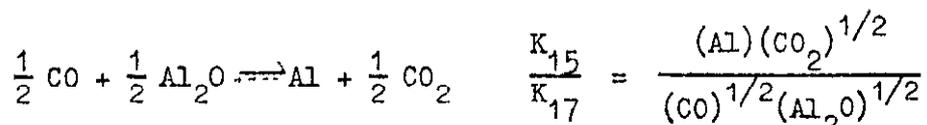
Hence

$$(Al) \qquad = \frac{K_{15}}{K_{17}} \cdot \frac{(Al_2O)^{1/2}}{a^{1/2}}$$

$$(AlO) \qquad = \frac{K_{16}}{K_{17}} \cdot a^{1/2} (Al_2O)^{1/2}$$

$$(Al_2O_3 {}_{gas}) \qquad = \frac{K_{19}}{K_{17}^2} \cdot a^2 (Al_2O) \qquad .$$

Once again, the main computation is rejoined at the calculation of the partial pressure of oxygen.

8   THERMODYNAMIC PROPERTIES

After each application of the main computation, certain thermodynamic properties are found. These are the molecular weight M, the enthalpy i, and the entropy s. In describing the thermodynamic properties the notation used is that the suffix k refers to any one of the products of combustion, whereas the suffix j refers to any one of the gaseous items.

Let p_j = the partial pressure of a gaseous phase

and n_k = the number of moles of a constituent regardless of phase, in a volume $R'T$, where $R' = 82 \cdot 0567$ atm.cm^3/mol.deg.K,

hence $n_j = p_j$.

The thermodynamic properties are calculated from the relationships:-

$$M = \frac{\Sigma \; n_k \; M_k}{\Sigma \; n_k}$$

$$i = \frac{\Sigma \; n_k \; I_k}{\Sigma \; n_k \; M_k} \qquad \frac{cal}{gm}$$

$$s = \frac{\Sigma \; n_k \; S_k - R \; \Sigma \; p_j \; \log_e \; p_j}{\Sigma \; n_k \; M_k} \qquad \frac{cal}{gm \; deg \; K}$$

where R is the universal gas constant, $1 \cdot 98719$ cal/mol deg K.

The programme then proceeds along different paths according to the case number. For case 2 the enthalpy of the propellent is specified, and it is the temperature of the isenthalpic combustion which is required. So far we have merely used the estimate of temperature supplied in the data and found the corresponding value of enthalpy. A further iterative process is used now to find the combustion temperature. Another trial value of temperature is used and then interpolation until the required value of enthalpy is obtained. This iteration includes the evaluation of the enthalpy and the entropy of all the constituents at the new temperature, and the evaluation of the equilibrium constants, before the main computation is started. The final values of i, s and T are placed in special stores, as they will be required if a case 4 or 5 follows this calculation.

In cases 3, 4 and 5 the path taken is similar to that of case 2, but for these cases the mixture must satisfy a value of entropy instead of enthalpy. This entropy is specified by the input data for case 3; for cases 4 and 5 it is the stored value mentioned in the previous paragraph. As the gaseous composition for case 5 is the same as that for the preceding case 2, the main

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computation is bypassed, and only the changes of entropy with temperature are involved in the iteration.

Case 1 proceeds directly to the next part of the programme which is common to all five applications. It is the computation of the specific volume, V, and the specific heat, C_p, of the mixture. We have

$$V = \frac{R'T}{\Sigma\, n_k\, M_k} \qquad \frac{cm^3}{gm}$$

$$C_p = \frac{\Sigma\, n_k\, \dfrac{dI_k}{dT}}{\Sigma\, n_k\, M_k} \qquad \frac{cal}{gm\ deg\ K} \quad .$$

The derivatives for the latter quantity are obtained analytically from the polynomial representations of the enthalpies. For constituents where the enthalpy is represented by two polynomials, the derivative is calculated from the one which applies at the temperature concerned. The practice described in Section 4 of representing enthalpy by a linear function over the range lying 20°K either side of the melting point is not involved.

In cases 4 and 5 there is a further requirement, to calculate the specific impulse of the propellent. Multiplying the change in enthalpy from the combustion chamber to the exhaust (in calories per gram) by the mechanical equivalent of heat, we get the kinetic energy of the efflux per unit mass. If v is the velocity, we get

$$\tfrac{1}{2} v^2 = J(i_c - i_e) \quad erg/gm$$

giving

$$v = \left[2J(i_c - i_e) \right]^{1/2} = 9147{\cdot}7(i_c - i_e)^{1/2} \quad cm/sec .$$

The actual value required, specific impulse, is v/g,

$$S.I. = 9{\cdot}328(i_c - i_e)^{1/2} \quad sec .$$

After these quantities have been evaluated the print routine is entered. The format of the results produced for the various applications of the programme is described in Section 12 and Figs.3 and 4.

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9   THE CALCULATION OF THE DISCHARGE COEFFICIENT

This calculation is sometimes required when the isentropic expansion between the combustion chamber and the exhaust is studied. Consequently it is applicable to cases 4 and 5, which deal with isentropic expansion to one atmosphere under maintained or frozen equilibrium conditions respectively. As mentioned in Section 3, there are separate versions of the programme which include the discharge coefficient calculation as the computing time is much increased by its inclusion.

Let us summarise the computation which has been completed up to the point at which the discharge coefficient is required. A case 2 will have been computed, in other words the temperature has been found which gives a specified value of enthalpy, and the entropy associated with combustion at this temperature will have been evaluated. After these results have been punched a case 4 or 5 calculation will have followed, yielding the temperature which gives the same entropy as that obtained in case 2 at a pressure of one atmosphere. However these results are not punched until after the discharge coefficient has been calculated.

We will now explain the derivation of the discharge coefficient, and then describe the approach used by the programme to compute it.

At some point during the isentropic expansion between the combustion chamber and the exhaust, the ratio of the gas velocity to the specific volume passes through a maximum. The position at which this occurs is called the throat. The temperature and pressure at the throat are required, together with the discharge coefficient, C_D, which is directly proportional to the maximised ratio.

The defining equation for C_D is:-

$$\dot{m} = C_D A_t P_c$$

where $\dot{m}$ = mass flow

and A_t = area of cross-section at the throat.

Now, continuity demands that anywhere in a static flow

$$\dot{m} = A v/V$$

where A = area of cross-section

V = specific volume

Substituting for $\dot{m}/A$ at the throat, where $A = A_t$ and v/V is a maximum, we have

$$\left(\frac{v}{V}\right)_{max} = C_D P_c \qquad \text{where} \quad C_D \text{ is in sec}^{-1} \quad \text{and} \quad P_c \text{ in gm wt/cm}^2$$

or

$$\left(\frac{v}{V}\right)_{max} = 1033{\cdot}23 \, C_D P_c \qquad \text{where} \quad P_c \text{ is in atmospheres.}$$

In the previous section v, the gas velocity, was shown to be $9147{\cdot}7(i_c - i)^{\frac{1}{2}}$ cm/sec, and V, the specific volume to be $R'T/\Sigma n_k M_k$ cm^3/gm. Hence

$$\frac{v}{V} = \frac{9147{\cdot}7}{82{\cdot}0567} \frac{\Sigma \, n_k M_k (i_c - i)^{\frac{1}{2}}}{T}$$

and at the throat, when v/V is a maximum, we have

$$C_D = \frac{1}{1033{\cdot}23 \, P_c} \frac{9147{\cdot}7}{82{\cdot}0567} \frac{\Sigma(n_k M_k)_t (i_c - i_t)^{\frac{1}{2}}}{T_t}$$

or

$$C_D = 0{\cdot}107895 \frac{\Sigma(n_k M_k)_t (i_c - i_t)^{\frac{1}{2}}}{P_c T_t}$$

where suffix t indicates values at the throat.

Also, let

$$Q = 0{\cdot}107895 \frac{\Sigma(n_k M_k)_x (i_c - i_x)^{\frac{1}{2}}}{P_c T_x}$$

where suffix x indicates values at any point during the expansion. Q is referred to as the discharge coefficient function, C_D is the maximum value of this function.

The programme is already orientated to seek a temperature giving a specified value of entropy at a particular pressure. To find C_D, we shall require several such calculations at different pressures, until we find the pressure which gives Q its maximum value i.e. the pressure which gives dQ/dP equal to zero.

To start with we need estimates of dQ/dP at two pressures. We can immediately evaluate Q at a pressure of one atmosphere as an isentropic expansion to this pressure has been calculated. By definition Q is zero at P_c, the combustion chamber pressure. If we calculate isentropic expansions to pressures $P_c/3$ away from these extremes and evaluate Q at these pressures, we can obtain crude estimates of dQ/dP near to $P_c/6$ and $5\,P_c/6$. Interpolation is made from these values for the pressure corresponding to a zero value of dQ/dP. Let this pressure be P_r. Then to get a good estimate of dQ/dP at this pressure, isentropic expansion to $P_r - \delta$ and $P_r + \delta$ are calculated. From experience gained with this problem δ has been chosen as $0 \cdot 025$ atmospheres. Successive interpolations between the last two results for pressure and dQ/dP are made until a pressure giving an acceptably small value of dQ/dP is found. This pressure is then taken as being the throat pressure P_t, and an evaluation of isentropic expansion to P_t gives the final assessment of the throat temperature T_t, and the discharge coefficient C_D. The results obtained earlier for the isentropic expansion to one atmosphere are then punched with the information concerning the throat conditions appended.

Fig.6 shows an example of the variation of the discharge coefficient function (which we have called Q) with pressure, under maintained equilibrium conditions. It also shows the variation of dQ/dP with pressure, and the variation of the temperature required to give isentropic expansion. This example appertains to the same propellent for which results are shown in Figs.3 and 4. It was chosen as it shows clearly the irregularity of the value of dQ/dP in the region of the change of state of Al_2O_3. Such irregularities could lead to the prediction of impossible pressures in the interpolation for zero dQ/dP. This is avoided by replacing any pressure which lies outside the range of the problem by an arbitrary value.

10 THE DATA TAPES

There are two groups of data which must be supplied to the programme. The first, which is referred to throughout this Note as the "main data tape", is used without alteration for most problems. It contains the basic information which the programme requires about the products of combustion.

An annotated version of the main data tape is shown in Appendix 2. It starts with thirty-two sets of figures with a certain similarity. The first twenty-three sets correspond to the gaseous products of combustion. They are given in the order shown in Fig.3, which gives the format of the results. Each set of figures comprises the degree and coefficients of the enthalpy polynomial, followed by the constant S'. Section 4 explains how the constant S' and the enthalpy polynomial are used to obtain values of entropy. Each set is terminated by the repetition of the degree of the polynomial.

The remaining nine sets refer, in order, to the following:-

Solid carbon

Solid aluminium

Liquid aluminium

Two sets of zeros. (These are spare positions which could be used for data on two other combustion products, if any modification was made to the programme.)

Solid titanium oxide

Solid aluminium oxide

Liquid aluminium oxide

Liquid titanium oxide

The next thirty-two numbers on the data tape are the molecular weights of the constituents in the same order as used previously.

The main data tape is terminated by five numbers which are concerned with the non-reactive additive. In order they are:-

(1) Melting point T_{MP} °K

(2) Enthalpy at $(T_{MP} - 20)$ I cal/mol

(3) Increase in enthalpy between $(T_{MP} - 20)$ and $(T_{MP} + 20)$ ΔI cal/mol

(4) Entropy at $(T_{MP} - 20)$ $\bar{S}$ cal/mol deg K

(5) Increase in entropy between $(T_{MP} - 20)$ and $(T_{MP} + 20)$ ΔS cal/mol deg K

Clearly the main data tape will have to be altered if a different additive is used. For a new additive in the condensed state, the necessary changes may be summarised as follows:-

(a) replace enthalpy polynomials and entropy constants for $TiO_2(s)$ and $TiO_2(l)$ by corresponding sets of data for the new additive,

(b) replace the molecular weight of TiO_2 by the molecular weight of the new additive. This occurs in two positions,

(c) replace the last five numbers by the appropriate values for the new additive.

Where information is only available for one phase, and the consideration of this single state is thought to be the best approximation that can be

- 31 -

achieved, then the new data replaces the appropriate set for TiO_2. The molecular weight is again changed (two positions), and the melting point is made either very low or very high according to whether the new data refers to a liquid or a solid state. No further alteration is then necessary to the last four numbers on the tape. A different programme tape must be used for a gaseous additive, as it will contribute to the total pressure of the system. The relevant data is included as if the additive were liquid, and any small number is used as the melting point.

The second data tape contains information relating to the particular analyses which are required. The first number specifies the type of analysis; case 1, 2 or 3. The atom ratios of the propellant are then given in the order

C/H   O/H   N/H   Cl/H   Al/H   and   Extra/H .

(This last ratio is, in fact, the ratio of the number of molecules of the non-reactive additive to the number of hydrogen atoms.) If either this quantity or any element is absent from the propellant, zero must be punched in place of the ratio. The additional data necessary to complete the specification of an analysis varies according to the case number. For case 1 it is the values of temperature and pressure at which equilibrium is to be considered. Further similar calculations for the same propellant may be specified merely by punching further pairs of values of temperature and pressure, but before another propellant can be used the case number must be punched again on the tape. If several sets of temperature and pressure are to be applied to two propellants the data is punched on the tape in the following order:-

$$1 \quad r_1 \; r_2 \; r_3 \; r_4 \; r_5 \; r_6 \qquad T_1 \; P_1 \; T_2 \; P_2 \; T_3 \; P_3 \; \cdots\cdots\cdots\cdots\cdots \; T_m \; P_m$$

$$1 \quad r_1' \; r_2' \; r_3' \; r_4' \; r_5' \; r_6' \qquad T_1' \; P_1' \; T_2' \; P_2' \; T_3' \; P_3' \; \cdots\cdots\cdots\cdots\cdots \; T_n' \; P_n'$$

For case 2 the additional data following the atom ratios comprises a set of three numbers; an estimate of the temperature of combustion (this need not be particularly accurate, ±600°K is adequate), the required pressure in the combustion chamber, and the enthalpy of the propellant at 298°K. Further sets of values for these three quantities may follow, although probably the only useful variation would be to alter the pressure of the combustion. The data tape to instigate such calculations for two propellants would be punched thus:-

$$2 \quad r_1 \; r_2 \; \cdots\cdots\cdots \; r_6 \qquad T_1 \; P_1 \; i_1 \qquad T_1 \; P_2 \; i_1 \; \cdots\cdots\cdots$$

$$2 \quad r_1' \; r_2' \; \cdots\cdots\cdots \; r_6' \qquad T_1' \; P_2' \; i_1' \qquad T_1' \; P_2' \; i_1' \; \cdots\cdots\cdots$$

The structure of the data tape for applications of case 3 is exactly similar to that described for case 2 above, except that the third number in each set following the ratios is a value of entropy. The temperature is an estimate of the temperature at which the specified pressure and entropy will be achieved. Hence, the data will be in the form:

$$3 \quad r_1 \ r_2 \ \cdots\cdots\cdots \ r_6 \qquad T_1 \ P_1 \ s_1 \qquad T_2 \ P_2 \ s_2 \ \cdots\cdots\cdots$$

$$3 \quad r_1' \ r_2' \ \cdots\cdots\cdots \ r_6' \qquad T_1' \ P_1' \ s_1' \qquad T_2' \ P_2' \ s_2' \ \cdots\cdots\cdots$$

The other applications of the programme, cases 4 and 5, only occur following a case 2 calculation. Case 5, which gives the thermodynamic properties resulting from an isentropic expansion to a pressure of one atmosphere without change of chemical composition, is computed if 5 is punched on the data tape. The expansion to one atmosphere with chemical equilibrium maintained is case 4: as in the preceding case, only the number 4 has to be punched. Clearly, if the calculations are required under both frozen and maintained equilibrium conditions, they must be calculated in this order, i.e. the numbers 5, 4 are punched. The data tape to do such calculations for two propellents would be:

$$2 \quad r_1 \ r_2 \ \cdots\cdots\cdots \ r_6 \qquad T \ P \ i \ 5 \ 4$$

$$2 \quad r_1' \ r_2' \ \cdots\cdots\cdots \ r_6' \qquad T' \ P' \ i' \ 5 \ 4$$

There is no limitation on the number or order of the sets of data for the various applications of the programme that may be punched to make up a data tape. The only proviso is that all such tapes must be terminated by the number 1,000,000.

11   THE OPERATION OF THE PROGRAMME

Four programmes are available. They are written in the Mercury PIG 2 programming code.

Programme 201 - Computation does not include the discharge coefficient; this programme is suitable if the non-reactive additive remains in a condensed state.

Programme 202 - Discharge coefficients are computed for cases 4 and 5; again the additive must be in the condensed state.

Programme 203 - Similar to 201, but with a gaseous non-reactive additive.

Programme 204 - Similar to 202, but with a gaseous non-reactive additive.

After running the selected programme into the machine, with the hand-switch setting appropriate to the type of input, the main data is run in with a "prepulse". After the main data tape has been read in, the machine again comes to a stop. At this point it is essential to set the handswitches. The handswitch setting is used for two purposes as described in the following paragraphs.

(1)   To control the accuracy to which the calculation is performed.

In the calculation there are several iterative processes, which continue until certain quantities derived in the computation, attain - to within limits - specified values. Each iterative procedure, with the exception of the discharge coefficient computation, continues until

$$\left| \frac{c - k}{k} \right| < E$$

where   c = computed value

         k = specified value

and   E = $10^{-(p+1)}$

The value of p is set in binary on the least significant end of the hand-switches. Initially it is usually set to 6, but it may be varied during the programme. The operator reduces the value if the computation seems unduly lengthy. Care must be taken to avoid allowing p to fall below the new value being set while the handswitches are being altered. If the operator forgets to set a value for p the iterations will continue indefinitely. However, as soon as this is noticed, and p is set up, the programme will behave normally.

A value of dQ/dP less than E/10 is the criterion applied to the iterative process for finding the discharge coefficient, as described in Section 9.

(2)   To control the printing of the results.

(a)   To obtain a "full print-out" keys 8 and 9 are set level.

(b)   If key 9 is up, then a "short print-out" is produced. In this the details of the gaseous composition are omitted.

(c)   With keys 8 and 9 up, a "very short print-out" is produced. Here the results comprise only the atom ratios and thermodynamic properties.

These variations in the form of the results are illustrated in Figs.3 and 5.

After the handswitches have been set, the data tape containing information about the particular mixtures is fed into the machine with a "prepulse", and the data for one calculation is read. As the calculation proceeds various hoots with recognisably different frequencies indicate the progress of the calculation. Normally, several medium frequency hoots occur at short intervals followed by a hoot of low frequency.

The medium frequency note occurs on each occasion that a set of partial pressures has been computed, i.e. when the O/H ratio has been satisfied. The low frequency note sounds when the partial pressures add up to the required figure specified by the input data. If the calculation is of type 1, the results will be punched at this stage. For cases 2, 3 and 4 this general pattern of behaviour is repeated for each temperature change in the computation. In case 5 the gas composition is fixed, so that only low frequency notes are heard.

If the programme used computes a discharge coefficient, the derivative of a function of pressure is evaluated. On each occasion that a derivative is computed, a very high note of short duration is emitted.

The main variation in this pattern of notes occurs when Al_2O_3 appears to be present only in gaseous form. On these occasions a long low frequency note is sounded. Condensed Al_2O_3 is seldom absent in the final results, but relatively often the computation finds that only the gaseous form exists during the early stages, before the iterations have made much improvement to the estimated values.

At the start of certain cases another sequence of hoots is used to indicate that the procedure for finding estimates of (H_2O), $(CO_2)/(CO)$ and (HCl) has failed. This consists of four hoots, in the sequence low, high, low, high. The machine then waits for a "prepulse". A data tape must be placed in the reader with estimates punched on it. On the "prepulse", this data is read and the programme continues. If a similar failure occurs on a subsequent case, the characteristic sequence of hoots will be heard but the programme will not stop this time and wait for a data tape; it uses instead the guesses read in previously.

The programme continues from one case to the next automatically, until the number 1,000,000 is read at the end of the data tape. A new data tape may then be put in the tape reader, and a prepulse allows the computation to continue. This tape, however, must start with a case number and a set of atom ratios.

Although it is fundamental to the problem that the material balance equations are satisfied, the atom composition of the products of combustion are checked against the input data, before the results are punched. If there is a discrepancy the symbol of the offending ratio is punched out, followed by an X, and the machine stops. The most probable reason for this is that the value set on the handswitches to control the accuracy was too small. After such a failure the programme can be made to proceed with a new case of type 1, 2 or 3, by giving a prepulse.

The operating times for this programme are by no means constant; they will vary from one mixture to another, but particularly they depend on the case number. The following list gives the order of the times for the different applications:-

    Case 1 .... 20 sec

    Case 2 .... 80 sec

    Case 3 .... 80 sec

    Case 4 .... 80 sec,   with C_D ...... 12 min

    Case 5 .... 50 sec,   with C_D ...... 10 min,

These figures do not include the time taken to punch the results.

    If for any reason the programme has to be restarted, the procedure (with the standard PIG 2 input routine) is as follows:-

Set key 8 up

Press the initial transfer button

Return key 8 to normal

Tap handswitches 1, 3 and 2 in that order.

The programme is then ready to accept data, starting with a case number of 1, 2 or 3.

12   PRESENTATION OF THE RESULTS

    In this section the variation in the form of the results for the several applications of the programme will be described. Figs.3 and 4 show sets of results obtained by using programme 202, for a mixture which contains all six elements and an additive (TiO_2). There are three sets of results. The first gives the composition and temperature in the combustion chamber for the given values of pressure and enthalpy. This is followed by the thermodynamic properties resulting from an isentropic expansion to one atmosphere with the composition unchanged. Finally, the new composition and thermodynamic properties are shown when chemical equilibrium is maintained during the expansion. In other words, the three sets of results correspond to cases 2, 5, and 4. Programme 202 includes the calculation of the discharge coefficient.

    The first line gives a position where a reference number for the particular results can be filled in by hand, and a value for E which is referred to in Section 11. The next three rows contain the starting information for the problem. The first two give the composition of the mixture in atom ratios; the third gives the pressure at which the combustion is considered, together with a quantity depending on the case number as follows:-

Case 1 .... Temperature

Case 2 .... Enthalpy

Case 3 or 4 ... Entropy

The two main columns of figures which are printed next give the breakdown of the gaseous composition computed for the propellent*. The amount of each item is given in two ways. In the first column the amount is expressed as the number of moles per mole of gas, (which is often called the proportional partial pressure), and in the second column as the number of moles per 100 grms of propellent.

These quantities may be defined as:-

$$\frac{p_j}{\Sigma\, p_j} \quad\text{and}\quad \frac{100\, p_j}{\Sigma\, n_k M_k} \,.$$

The totals of these two columns are given next, followed by two other totals which also relate to the gaseous phases, but in which each item is weighted by its molecular weight to give the number of grams per mole of gas and per 100 grms.of propellent i.e. the gas totals as set out in the results are:-

$$\frac{\Sigma\, p_j}{\Sigma\, p_j} \qquad \frac{100\, \Sigma\, p_j}{\Sigma\, n_k M_k}$$

$$\frac{\Sigma\, p_j M_j}{\Sigma\, p_j} \qquad \frac{100\, \Sigma\, p_j M_j}{\Sigma\, n_k M_k} \,.$$

Similar results showing the amounts of the condensed phases are then printed. They are expressed in the same units as the gaseous products:-

$$\frac{n_k}{\Sigma\, p_j} \quad\text{and}\quad \frac{100\, n_k}{\Sigma\, n_k M_k} \,.$$

The totals for the whole mixture including the condensed phases follow, in a similar manner to that used for the gas totals

$$\frac{\Sigma\, n_k}{\Sigma\, p_j} \qquad \frac{100\, \Sigma\, n_k}{\Sigma\, n_k M_k}$$

$$\frac{\Sigma\, n_k M_k}{\Sigma\, p_j} \qquad \frac{100\, \Sigma\, n_k M_k}{\Sigma\, n_k M_k} \,.$$

*Teleprinters at R.A.E. have only capital letters, so the symbols CI and AI have been used to represent chlorine and aluminium, this being preferred to CL and AL. If the output tapes are printed on teleprinters with small letters then the chemical symbols will appear somewhat peculiar, e.g. hci represents hydrogen chloride.

The mixture totals are omitted if no condensed phases are present. This completes the information about the composition.

Clearly, the printing must vary with the type of propellent, for the programme has been designed to work on mixtures which do not contain all the elements that are allowed. In these cases certain items cannot be present, and all reference to them is omitted.

It was mentioned in Section 2 that satisfactory results are obtained when the programme is applied to mixtures containing only oxygen and hydrogen; this is so, but the printed results, whilst being quite understandable, contain some irrelevant items.

In Section 6, a check on the value of the partial pressure of aluminium was mentioned. If this pressure exceeds the saturated vapour pressure, this fault is indicated by a row of asterisks following the symbols for aluminium.

If the computation gives a negligible value for the moles per mole of gas of any particular product, (less than 10^{-20}) then the value found for this product is replaced by a dash when it is printed. If, on the other hand, the conditions of combustion are such that a particular item exists only in the gaseous phase then zeros are printed opposite the condensed phase of this item.

The printing of the results continues with a list of thermodynamic properties. The first two of these vary with the application of the programme; they are as follows:-

Case 1   enthalpy, entropy

Case 2   temperature, entropy

Case 3 and 4   temperature, enthalpy

Next, the molecular weight, specific volume and specific heat are printed. This concludes the results for cases 1, 2 and 3. For case 4 the specific impulse is printed, and if either programme 202 or 204 was used the list is concluded by the discharge coefficient, throat pressure and throat temperature.

At the bottom of Fig.3 the results of the case 5 calculation, the isentropic expansion with frozen equilibrium, are given. The value of entropy is not quoted, for by definition it must be the same as that shown in the previous results for case 2. When either programme 201 or 203 is used the results for case 5 are listed in a single column.

The full printing of the results is rather lengthy, so two shortened versions have been provided. Fig.5 shows the application of both shortened forms of printing to the results of the case 2 which are given in full in Fig.3. The choice of the form of printing is made by the selection of switches on the console during the operation of the programme. Section 11 gives full details of this facility.

ACKNOWLEDGEMENTS

LIST OF REFERENCES

No.	Author(s)	Title, etc
1	Williams, W.H.	Thermodynamic charts for tho combustion products of nitric acid and kerosone. A.R.C. R & M No. 2982. July, 1950.

THE ORGANISATION OF THE PROGRAMME

List of routines in the order in which they occur on the programme tapes.

Chapter 1

R101 Reciprocal subroutine
R112 Square root subroutine
R114 Logarithm subroutine
R104 Exponential subroutine
R119 Read to accumulator subroutine
R118 Read to short accumulator subroutine

R11 Reads the main data tape
R12 Reads second data tape and controls type of calculation
R14 Calculates enthalpy and entropy values for temperature T.

Chapter 2

R21 Calculates equilibrium constants at temperature T
R22 A subroutine used by R21
R23 Calculates the initial estimates for H_2O, CO_2/CO and HCl

R24 Rescue routine, hoots and reads estimates from tape.

Chapter 3

R31 The start of the main computation, computes H_2, H and OH

R32 The start of the HCl – Cl/H loop
R33 Calculates products of chlorine and aluminium
R34 Calculates and tests Cl/H ratio, and computes an improved estimate for HCl
R35 Calculates partial pressure of gaseous additive
R36 Computes remaining products of combustion
R37 Entered if condensed Al_2O_3 is absent, hoots and jumps to R81

R38 Calculates and tests O/H ratio, and computes an improved estimate for CO_2/CO

R39 Computes and tests ΣP, and computes an improved estimate for H_2O.

Chapter 4

R40 Calculates M, i and s for the efflux at temperature T
R42 Tests i and computes an improved estimate of temperature
R43 Tests s and computes an improved estimate of temperature
R41 Checks the atom ratios of calculated composition
R44 Computes specific heat and specific impulse.

Chapter 5

R50 A store for the binary characters used by the main print routines
R509 Subroutine for fixed point printing
R510 Subroutine for floating point printing
R52 A subroutine used by R51 to print a line of results
R51 The main print routine, giving gas composition.

Chapter 6

R60 A further store for binary characters used in printing
R53 Completes printing of the results.

Chapter 7

R71 Print routine for additional results from case 4
R72 Print routine for case 5 results.

Chapter 8

R81 The start of the calculation used when condensed Al_2O_3 does not exist, for propellents containing chlorine
R82 Calculates products of chlorine and aluminium
R83 Calculates and tests Cl/H ratio and computes an improved estimate for HCl
R84 Computes the remaining aluminium products, tests Al/H ratio and computes an improved estimate for AlCl
R88 The calculation used when condensed Al_2O_3 does not exist, for propellents which do not contain chlorine.

Chapter 9

R91)
R92) Discharge coefficient calculation.

READ MAIN DATA
READ CASE NUMBER
IDENTIFY TYPE OF CALCULATION

CASES 1,2 & 3

READ RATIOS

READ A NUMBER

TEST WHETHER A TEMPERATURE
OR A NEW CASE NUMBER

CASE N°   TEMP

READ PRESSURE

CASE I   CASE 2 OR 3

READ TARGET I OR S
RESPECTIVELY

CASE 4 OR 5

SET TARGET PRESSURE = I

SET TEMP ESTIMATE = $T_c - 800°K$

SET TARGET ENTROPY = S_c

4   5

SET PARTIAL PRESSURES
EQUAL TO PROP^L PRESSURES

CALCULATE I's, S's & K's FOR TEMPERATURE REQ'D.

CASES 1−4   CASE 5

CALCULATE ESTIMATES FOR H_2O, CO_2/CO & HCl
USING RESCUE ROUTINE IF NECESSARY

MAIN COMPUTATION

(TARGET PRESSURE HAS NOW BEEN ACHIEVED)
CALCULATE THERMODYNAMIC PROPERTIES

CASE I   CASES 2, 3, 4 & 5

TEST I OR S

SAT^Y UNSAT^Y

MODIFY ESTIMATE
OF TEMPERATURE

COMPLETE THERMOPROPERTIES
INSPECT HANDSWITCHES &
PRINT RESULTS ACCORDINGLY

CASES 4 & 5, WHEN C_D IS REQ'D.

CALCULATE C_D FUNCTION
TEST WHETHER C_D MAX^M HAS
BEEN FOUND

YES   NO

MODIFY
TARGET PRESSURE

− − − − APPLIES ONLY TO C_D PROGRAMME.

SCHEMATIC DIAGRAMS OF THE PROGRAMME
A. GENERAL ORGANISATION

COMPUTE H_2, H, OH

TEST FOR SOLID CARBON
& COMPUTE C (GAS), CH_4
CO_2 & CO BY APPROPRIATE
METHOD

TEST FOR PRESENCE OF Cl/H

YES   NO

COMPUTE Cl, Cl_2

TEST FOR PRESENCE OF Al/H

NO   YES

COMPUTE Al Cl, AlOCl, $AlCl_3$

TEST $\Sigma Cl/\Sigma H$ EQUAL TO Cl/H

NO   YES

MODIFY ESTIMATE
OF HCl

TEST FOR PRESENCE OF Al/H

NO   YES

COMPUTE Al, AlO, Al_2O
Al_2O_3 (GAS) ASSUMING
Al_2O_3 (SOLID) TO BE PRESENT

OBTAIN RESIDUE OF Al_2O_3 (SOLID)

ABSENT

COMPUTE O, O_2

TEST FOR PRESENCE OF N/H

NO   YES

COMPUTE N, N_2, NO

TEST $\Sigma O/\Sigma H$ EQUAL TO O/H

NO   YES

MODIFY ESTIMATE
OF CO_2/CO

COMPUTE Σp & TEST IF
EQUAL TO REQ'D VALUE

NO

MODIFY ESTIMATE
OF H_2O

YES

END OF "MAIN COMPUTATION"

TEST FOR PRESENCE OF Cl/H

YES   NO

ESTIMATE AlCl

ESTIMATE Al_2O

TEST FOR SOLID CARBON &
COMPUTE C(GAS), CH_4, CO_2
& CO BY APPROPRIATE METHOD

COMPUTE Cl, Cl_2, $AlCl_3$ &
AlOCl

TEST $\Sigma Cl/\Sigma H$ EQUAL TO Cl/H

NO   YES

MODIFY ESTIMATE
OF HCl

COMPUTE Al, AlO, Al_2O
& Al_2O_3 (GAS)

TEST $\Sigma Al/\Sigma H$ EQUAL TO Al/H

NO   YES

MODIFY ESTIMATE
OF AlCl

COMPUTE Al (GAS), AlO
& Al_2O_3 (GAS)

TEST $\Sigma Al/\Sigma H$ EQUAL TO Al/H

YES   NO

MODIFY ESTIMATE
OF Al_2O

B. THE MAIN COMPUTATION

THE MAIN DATA

(i) Enthalpy polynomial coefficients and entropy constants.

8
-9·61705616, 4
4·93175019, 3
8·58702954, 3
-4·89191325, 3
1·88266930, 3 CO_2
-4·78322239, 2
7·66414821, 1
-6·99321566, 0
2·76311831,-1
52·5044
8

10
-2·85857306, 4
7·95141899, 3
-3·91172625, 3
7·06224119, 3
-6·05115823, 3
3·17418390, 3   CO
-1·08174964, 3
2·40603019, 2
-3·37129813, 1
2·70162749, 0
-9·43930014,-2
58·4128
10

11
-2·00404872, 4
6·96481093, 3
-3·50562585, 3
1·97590650, 4
-2·05455701, 4
1·25162165, 4
-5·08224610, 3 CH_4
1·41447170, 3
-2·66913826, 2
3·26498860, 1
-2·33508918, 0
7·40901178,-2
53·0032
11

6
1·70222670, 5
4·92977190, 3
9·02859061, 1
-8·56419074, 1   C(gas)
3·57036815, 1
-5·74814821, 0
3·28949256,-1
43·6857
6

8
-6·01811863, 4
8·11235618, 3
-1·06918375, 3
2·59156236, 3
-1·37468769, 3 H_2O
3·90792679, 2
-6·44000884, 1
5·79948686, 0
-2·21307142,-1
55·2582
8

10
-2·02690265, 3
6·52108791, 3
1·55812609, 3
-2·88649837, 3
3·04215026, 3
-1·77315662, 3 H_2
6·31279671, 2
-1·41527357, 2
1·95677838, 1
-1·52755373, 0
5·15933024,-2
38·4620
10

1
5·06080447, 4
4·96795491, 3   H
33·4050
1

10
-1·97918740, 3
6·44994631, 3
6·25551033, 1
2·76488584, 3
-3·29517300, 3
2·02215019, 3 O_2
-7·52505961, 2
1·76335533, 2
-2·55116163, 1
2·08607145, 0
-7·38422590,-2
56·5165
10

8
7·11561146, 3
8·02067509, 3
-2·27506347, 3
2·34219375, 3
-1·09989615, 3   OH
3·00883169, 2
-4·88937349, 1
4·38744492, 0
-1·67785044,-1
54·6720
8

8
5·79575195, 4
5·53533340, 3
-8·13215532, 2
6·74383872, 2
-3·39038974, 2   O
1·04373999, 2
-1·91665176, 1
1·93622635, 0
-8·29450508,-2
45·5762
8

10
-2·18085934, 3
7·99189499, 3
-3·75195835, 3
6·26608654, 3
-5·02891103, 3
2·48908400, 3 N_2
-8·05525583, 2
1·71112988, 2
-2·30153845, 1
1·77842302, 0
-6·01517587,-2
56·9907
10

10
1·96005025, 4
8·02607718, 3
-3·85968822, 3
7·29721164, 3
-6·43544235, 3
3·43553037, 3   NO
-1·18219524, 3
2·64083173, 2
-3·70295754, 1
2·96235511, 0
-1·03158934,-1
61·5792
10

6
1·11528365, 5
4·99747933, 3
-5·51851221, 1
4·83878648, 1   N
-2·11346711, 1
4·26604817, 0
-2·79078170,-1
42·6875
6

10
-2·42608731, 4
7·95579591, 3
-2·95922282, 3
3·98662933, 3
-2·49513032, 3
9·22089472, 2   HCl
-2·05772454, 2
2·55478278, 1
-1·17484287, 0
-7·10124617,-2
7·46494778,-3
55·5538
10

10
-2·20681810, 3
6·31616890, 3
5·03117658, 3
-5·82505841, 3
4·42216801, 3
-2·22668389, 3   CL$_2$
7·48997560, 2
-1·66184219, 2
2·33236148, 1
-1·87484004, 0
6·57314172,-2
58·5681
10

10
2·75422088, 4
3·84914888, 3
4·19041788, 3
-5·69609928, 3
4·49995084, 3
-2·27986197, 3   Cl
7·62469381, 2
-1·67405017, 2
2·32308154, 1
-1·84501110, 0
6·39151129,-2
42·2368
10

8
-1·37804273, 4
7·48169362, 3
2·11391435, 3
-1·76781387, 3
8·96090900, 2   AlCl
-2·78707107, 2
5·18757320, 1
-5·29553945, 0
2·27791673,-1
62·4346
8

11
-1·42039335, 5
1·05234920, 4
1·94731352, 4
-2·56645148, 4
2·24794090, 4
-1·34541231, 4   AlCl$_3$
5·57065753, 3
-1·59211288, 3
3·07913015, 2
-3·84346956, 1
2·79223247, 0
-8·96286928,-2
78·5432
11

11
-5·78266924, 4
5·72516812, 3
1·78508328, 4
-2·24252717, 4
1·89486703, 4
-1·10221729, 4
4·45791514, 3   AlOCl
-1·24922301, 3
2·37585727, 2
-2·92347726, 1
2·09799406, 0
-6·66408845,-2
58·1727
11

7
7·59741425, 4
5·18555988, 3
-2·64625471, 2
1·77134394, 2   Al(gas)
-6·83343026, 1
1·51614489, 1
-1·80792228, 0
9·14503023,-2
45·7289
7

8
1·50208607, 4
5·64086525, 3
4·11181165, 3
-3·04913942, 3
1·42871553, 3   AlO
-4·19405314, 2
7·47437903, 1
-7·38040636, 0
3·09382846,-1
56·8987
8

11
-4·07245300, 4
8·31453457, 3
1·22229448, 4
-1·66648331, 4
1·49714559, 4
-9·13787618, 3
3·84297299, 3   Al₂O
-1·11243567, 3
2·17465179, 2
-2·73975794, 1
2·00681687, 0
-6·48985689,-2
68·8850
11

11
-1·52329632, 5
-1·67797063, 3
4·87512485, 4
-5·70113095, 4
4·55890385, 4
-2·54025465, 4
9·92806458, 3   Al₂O₃(gas)
-2·70528886, 3
5·02565668, 2
-6·06036475, 1
4·27256210, 0
-1·33570327,-1
45·9257
11

10
1·00482812, 2
-3·44635744, 3
1·40064799, 4
-1·48371816, 4
1·11651005, 4
-5·80301380, 3
2·04672030, 3   C(solid)
-4·77911461, 2
7·04738882, 1
-5·93008454, 0
2·16699854,-1
-9·52443
10

2
-1·60511905, 3
4·94035720, 3   Al(solid)
1·47976180, 3
11·8659
2

1
3·10999450, 2
7·00000038, 3   Al(liquid)
17·505
1

```
O    O    O    O)  Spare
O    O    O    O)  positions
```

```
6
-2·28412456,  5
 4·28951057,  3
 2·45737268,  4
-2·47903840,  4          TiO₂(solid)
 1·43046473,  4
-4·34245719,  3
 5·38584491,  2
 5·440
6
```

$TiO_2(solid)$

```
9
-4·01104731,  5
-2·71147313,  4
 1·60555473,  5
-2·87837286,  5
 3·39317044,  5          Al₂O₃(solid)
-2·64942723,  5
 1·35855826,  5
-4·39539892,  4
 8·13114267,  3
-6·55238810,  2
-87·7415
9
```

$Al_2O_3(solid)$

```
1
-3·94505003,  5
 3·50000019,  4          Al₂O₃(liquid)
51·795
1
```

$Al_2O_3(liquid)$

```
1
-2·22520000,  5          TiO₂(liquid)
 2·14000009,  4
37·042
1
```

$TiO_2(liquid)$

```
0

0

0

0
```

Data used
if Argon
replaces
TiO₂

TiO_2

```
1
-1·482,  3          Argon
 4·968,  3
42·995
1
```

(ii) <u>Molecular weights</u>

44·011	CO_2
28·011	CO
16·043	CH_4
12·011	C
18·016	H_2O
2·016	H_2
1·008	H
32	O_2
17·008	OH
16	O
28·016	N_2
30·008	NO
14·008	N
36·465	HCl
70·914	Cl_2
35·457	Cl
62·437	$AlCl$
133·351	$AlCl_3$
78·437	$AlOCl$
26·98	Al
42·98	AlO
69·96	Al_2O
101·96	Al_2O_3
12·011	C
26·98	Al
26·98	Al
0	–
0	–
79·9	TiO_2
101·96	Al_2O_3
101·96	Al_2O_3
79·9	TiO_2

Data used if
Argon replaces
TiO_2

39·944 (beside TiO_2 row 79·9)

39·944 (beside TiO_2 row 79·9 last)

(iii) <u>Supplementary data for additive</u>

TiO_2 Argon

TiO_2		Argon	
2100	Melting point T_{MP} °K	o	zeros
-193958	Enthalpy at $(T_{MP}-20)$ in cal/mol	o	punched here,
16806	Increase in enthalpy between $(T_{MP}-20)$ and $(T_{MP}+20)$ cal/mol	o	for a gaseous
45·12	Entropy at $(T_{MP}-20)$ cal/mol deg K	o	additive
8	Increase in entropy between $(T_{MP}-20)$ and $(T_{MP}+20)$ cal/mol deg K	o	

APPENDIX 3

THE PROGRAMMING FOR THE EQUILIBRIUM CONSTANTS

We first give a brief description of the arrangement of the data in the store during the computation.

Throughout the programme it is necessary to store the values of certain quantities pertaining to each of the individual constituents considered in the combustion. Separate "pages" in the computing store have been allocated to partial pressures, enthalpy values, entropy values and equilibrium constants. In general the order in which the items are stored within the page is the same and corresponds to the order used in printing the results and the listing of the main data tape.

The pages are allocated as follows :-

Specific heat .... Page 17 (except during the C_D calculation)

Molecular weight ..... Page 19

Partial pressure ..... Page 23

Entropy .... Page 26

Enthalpy .... Page 29

The values relating to the gaseous quantities occupy stores from 0·0 to 0·44 in each page. The stores for the remainder are as follows :-

$C_{(solid)}$ .... ·46

$Al_{(solid)}$ .... ·48

$Al_{(liquid)}$ .... ·50

$TiO_{2(solid)}$ ...... ·56

$Al_2O_{3(solid)}$ ..... ·58

$Al_2O_{3(liquid)}$ .... ·60

$TiO_{2(liquid)}$ ..... ·62

The programme will overwrite a store originally holding the value appropriate to the liquid phase with the corresponding value for the solid phase if the temperature under consideration is below the melting point of the constituent, or with an interpolated value if the temperature is within 20°K of the melting point. The temperature itself is stored in 28·2.

The equilibrium constants are stored in page 31; K_r occupies store 31.(2r) with the exceptions of K_1, K_{18}, K_{19} and K_{20} which are stored in 31·36, 31·40, 31·60, 31·0.

Data read in for a particular case may be found in page 25, from 25·0 onwards.

The way in which the values of enthalpy and entropy are stored enables the equilibrium constants to be readily computed. Routines 21 and 22 are used for this. Routine 21 contains sections of programme apertaining to each one of the chemical equations considered in the system. Routine 22 is applied to each section of R21. The following explanation applies to equation (7)

$$\frac{1}{2} H_2O + \frac{1}{2} CO_2 \rightleftharpoons OH + \frac{1}{2} CO \quad .$$
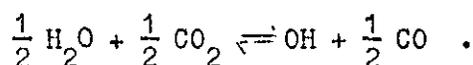
The expression derived for $\log_e K_7$ is:-

$$\log_e K_7 = \frac{1}{R} \left\{ \left(S_{OH} + \frac{1}{2} S_{CO} - \frac{1}{2} S_{CO_2} - \frac{1}{2} S_{H_2O} \right) - \frac{1}{T} \left(I_{OH} + \frac{1}{2} I_{CO} - \frac{1}{2} I_{CO_2} - \frac{1}{2} I_{H_2O} \right) \right\} \quad .$$

The programme commences in Routine 21 by setting an address in B3. It is the address of the start of the next group of instructions which sum the values of enthalpy of the products of combustion from Page 29, (B2 is zero at this stage). After setting an address in B1, although this is not used in this first part, control is transferred to Routine 22.

On entry to R22, with B2 equal to zero, the programme continues by multiplying the sum of the enthalpy terms (left in the accumulator) by - $1/T$. This value, $-\Sigma I/T$ is stored and B2 is reduced by 96; control is then returned to R21.

The group of instructions which was used previously to sum the enthalpy values, now operates on the entropy values from page 26, as all this group of instructions are modified by B2. Once again an address is set in B1 and control transferred to R22.

This time, B2 is found non-zero and the jump to label 2 is made. B2 is reset to zero in readiness for the next computation. The value of $-\Sigma I/T$ stored previously is added to ΣS which is now in the accumulator. This expression, multiplied by $1/R$ is the logarithm of the equilibrium constant.

By means of the address set in B1, the exponential subroutine always returns to the final order (x) of the section of R21, which stores the equilibrium constant K_r in 31·2r.

The section of programme in R21 is as follows:-

(i)	103	1*	Set B3 to the address of instruction (ii)
(ii)	402	29·16	OH ⎱ On the first application the enthalpy
(iii)	422	29·16	+OH ⎪ values are summed. On return from
(iv)	422	29·2	+CO ⎰ R22, B2 has been altered, so that
(v)	432	29·0	$-CO_2$ ⎪ entropy values are summed.
(vi)	432	29·8	$-H_2O$ ⎰
(vii)	500	v1	$\frac{1}{2}\,\Sigma$ .... (v1 represents 0·5)
(viii)	101	2*	Set B1 to the address of instruction (x)
(ix)	590	v/22	Jump to R22
(x)	410	31·14	Store the equilibrium constant.

Instructions (i), (viii), (ix) and (x) appear in all the sections of R21. The remaining instructions are particular to the equation above.

Routine 22, with some annotation is shown below:-

R22		(On the first entry B2 = 0)
172	0	Set B_{test} = B2
080	v2	If $B_{test} \neq 0$, jump to label 2
510	28·4	Multiply ΣI by $-1/T$
410	28·8	Store $-\Sigma I/T$ in 28·8
132	96	Set B2 to -96
593	0	Jump to address held in B3, i.e. $inst^n$ (ii) of R21
102	0 (2	Set B2 to zero
420	28·8	Add on enthalpy contribution to ΣS
500	28·6	Multiply by 1/R, giving $log_e K$ in the accumulator
590	v/104	Enter exponential subroutine, then return to address Held in B1, i.e. $inst^n(x)$ of R21

-

APPENDIX 4

A PROGRAMME TO CALCULATE THE ATOM RATIOS

The performance analysis programmes, described in the main text of this Note, work in terms of the "atom ratios" of the propellent. Sometimes these ratios are not given directly, in which case they must be derived from data on the percentage by weight of the various constituent compounds. The computation required, although simple, soon becomes tedious if the propellent contains many compounds, or if they are of complex chemical composition. Also, an error at this stage would completely invalidate all further work.

A Mercury Autocode programme, R.A.E.205 has been made to do the required calculation. It also computes the initial enthalpy of the propellent, as this is required for most calculations. The output tape may be used directly as the "special data" input tape for programmes 201-204. It can deal with propellents containing up to 100 compounds.

The basic data supplied to programme R.A.E.205 starts with m, the number of chemical compounds, followed by a matrix giving the breakdown of these compounds into the six elements concerned, in the order H, C, O, N, Cl and Al. For example if the first compound was NH_4ClO_4, then the first row of the matrix would be 4, 0, 4, 1, 1, 0. A particular compound is referred to by its "item number", item number 1 referring to the first compound specified in the matrix, item 2 to the second, etc.

The heats of formation of the m compounds are given next (in calories/grm). They are followed by data for the non-reactive additives. Several additives may be listed but only one may be included in any particular propellent. The number of additives listed is given first and is followed by a group of three numbers for each additive. They are:

(i)   an item number i where m < i < 100,

(ii)   the molecular weight of the additive,

(iii) the heat of formation of the additive.

The data described so far will remain unchanged for many applications of the programme, the only likely change being to add further compounds. This involves altering m, adding further rows to the matrix for the composition of the new compounds and specifying their heats of formation. In view of this, it is suggested that the additives should be allocated item numbers from 99 downwards, to avoid the necessity of re-allocating their item numbers each time further compounds are appended.

The remaining data supplied to this programme relates to the particular propellents under investigation. For each propellent there are two types of information required, firstly its composition and secondly the types of analysis

required by Programmes 201-204. The composition is specified by a series of pairs of numbers - the item number of a compound and the percentage* of this compound present in the propellent. The composition data is terminated by the number 100 punched on the tape. Then follows the data specifying the types of analysis required, which is punched in exactly the same format as for Programmes 201-204, described in Section 10, but the atom ratios and also the heat of formation for cases of type 2 are omitted. In fact, the output from this programme (205) consists of this data appropriately interspersed with atom ratios and initial enthalpy (heat of formation). The data is terminated by an asterisk (*), except for the last propellent when the number 1,000,000 is used instead.

Data for Programme 205

(i)   Basic data

m

$$\begin{bmatrix} a_1 & \cdots & a_6 \\ & & \\ & (m \times 6) & \end{bmatrix}$$

The number of compounds from which a series of propellents is to be constructed.
The $(m \times 6)$ matrix giving the atomic content of the compounds, the six columns corresponding to the elements H, C, O, N, Cl, Al.

$$\left.\begin{array}{c} h_1 \\ . \\ . \\ . \\ h_m \end{array}\right\}$$

The heats of formation of the m compounds in cal/gm.

k

The number of additives (k < 10).

$$\begin{bmatrix} i_r & M_r & h_r \\ . & . & . \\ . & . & . \\ & (k \times 3) & \end{bmatrix}$$

The item number, molecular weight and heat of formation of each additive.

---

*Proportional numbers other than percentages may be used to describe the composition of the propellent.

(ii) <u>Data for each propellent</u>

Propellent (A)

$$i \qquad x_1$$

Pairs of numbers giving composition (item number and percentage)

100   Indicates end of composition data.

2   T   P   5   4   Specifies analysis of type 2, 5 and 4.

$*$ Indicates end of data for propellent A.

Propellent (B)

$$1 \qquad x_i$$

Composition

100

$1 \quad T_1 \quad P_1 \quad T_2 \quad P_2 \ \dots \ T_n \quad P_n$ Specifies analysis of several cases of type 1.

1000000   Indicates end of data for propellent B and that B is the last propellent.

APPENDIX 5

THE DEUCE 5-ELEMENT PROGRAMME

The Deuce programme, which was made in 1958, uses a similar technique to the Mercury programme.

A temperature and the atom ratios C/H, O/H, N/H and Cl/H are specified, together with a range of pressures at which equilibrium is to be considered. In fact, the computation is limited to that described as case 1 in the Mercury programme.

Fourteen products of combustion are considered;   they are

$$H_2O, \; CO_2, \; CO, \; O_2$$

$$H_2, \; OH, \; O, \; H, \; N_2$$

$$NO, \; N, \; HCl, \; Cl_2, \; Cl \; .$$
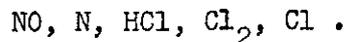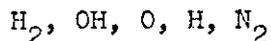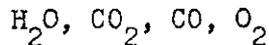
Methane and carbon are not included.

There are three iterative procedures (similar to those described in Section 6), based on the quantities H_2O, CO_2/CO and HCl.

The partial pressures of the gases at equilibrium and the enthalpy, entropy, specific volume, molecular weight and Σplog p are punched out on cards, which are listed on a proforma, an example of which is given overleaf.

The basic data for the enthalpy and entropy of the constituents involved is provided not by polynomials in terms of temperature, but by sets of values at discrete points in the temperature range. In fact, for every $100°K$ between $1000°K$ and $4000°K$, there are batches of punched cards for the values of enthalpy, entropy and equilibrium constants which are required. On each application of the programme the cards appropriate to the temperature involved must be selected and placed with the other data.

The results obtained for a typical 5 element propellent, shown in 5.2, may be compared with the adjacent results obtained for the same mixture by means of the Mercury programme. The gaseous compositions are in reasonable agreement; the slight discrepancies are probably due to differences in the equilibrium constants. In the Mercury programme these constants were computed, whereas for the Deuce programme, values to four significant figures were provided. Despite the discrepancies in composition there is good agreement between the thermodynamic properties.
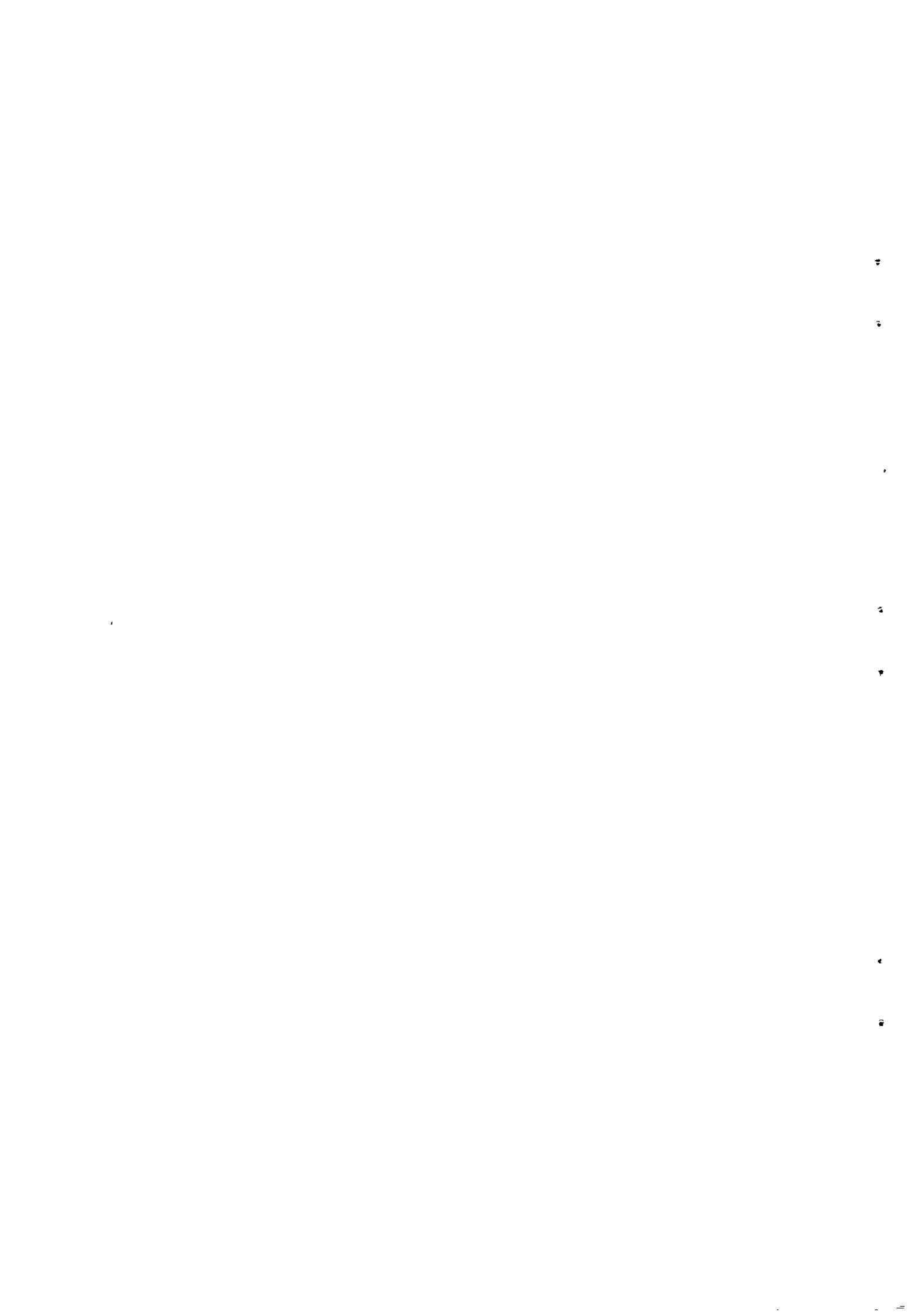
PROPELLENT REF. _____

PROPELLENT ATOM RATIOS		PRODUCT ATOM RATIOS
1.781589 −1	C/H	1.781589 −1
6.476850 −1	O/H	6.476850 −1
1.613439 −1	Cl/H	1.613439 −1
1.613439 −1	N/H	1.613439 −1

PARTIAL PRESSURES (ATM)		MOLE FRACTIONS
2.920859 +1	H_2O	4.292496 −1
7.115326 +0	CO_2	1.045668 −1
7.097233 +0	CO	1.043009 −1
1.088303 −1	O_2	1.599371 −3
4.031839 +0	H_2	5.925194 −2
7.796561 −1	OH	1.145783 −2
3.704714 −2	O	5.444450 −4
3.162512 −1	H	4.647629 −3
6.386578 +0	N_2	9.385719 −2
9.795959 −2	NO	1.439614 −3
3.474856 −5	N	5.106605 −7
1.219781 +1	HCl	1.792591 −1
4.800203 −3	Cl_2	7.054382 −5
6.637359 −1	Cl	9.754265 −3

$\sum P$	6.804569 +1	$\sum P \log P$	1.729597 +2
i^* (cal/gm)	−5.464431 +2	v (cc/gm)	1.435819 +2
S (cal/gm °K)	2.426564 +0	M (gm/mole)	2.519618 +1
$T°$	3.000000 +3		

APPENDIX 5-2

C/H	O/H	N/H	Cl/H
0.178159	0.647685	0.161344	0.161344

PRESSURE 68.0457   TEMPERATURE   3000.00

	NUMBER OF MOLES IN 1 MOLE OF GAS	NUMBER OF MOLES IN 100 GMS OF PROPELLENT
CO_2	1.04539, -1	4.14898, -1
CO	1.04330, -1	4.14068, -1
CH_4	1.26241, -10	5.01032, -10
C	5.86980, -12	2.32963, -11
H_2O	4.29291, -1	1.70379, +0
H_2	5.92207, -2	2.35038, -1
H	4.64653, -3	1.84413, -2
O_2	1.59912, -3	6.34666, -3
OH	1.14471, -2	4.54317, -2
O	5.44500, -4	2.16103, -3
N_2	9.38576, -2	3.72506, -1
NO	1.43960, -3	5.71355, -3
N	5.10673, -7	2.02678, -6
HCl	1.79255, -1	7.11436, -1
Cl_2	7.05895, -5	2.80158, -4
Cl	9.75871, -3	3.87307, -2

GAS TOTALS
(MOLES)	1.00000, +0	3.96884, +0
(GMS)	2.51963, +1	1.00000, +2

CONDENSED
PHASE

C	0	0

ENTHALPY	-5.46459, +2
ENTROPY	2.42659, +0
MOLECULAR WEIGHT	2.51963, +1
SPECIFIC VOLUME	1.43581, +2
SPECIFIC HEAT	4.50325, -1

APPENDIX 5-3

REF. NO.   E = 1.0, −7

C/H	O/H	N/H	Cl/H	Al/H	EX/H
0.178159	0.647685	0.161344	0.161344	0.051413	0.002893

PRESSURE   68.0457   ENTHALPY   −561.2000

	NUMBER OF MOLES IN 1 MOLE OF GAS	NUMBER OF MOLES IN 100 GMS OF PROPELLANT
CO_2	6.44794, −2	2.39604, −1
CO	1.42981, −1	5.31314, −1
CH_4	7.20289, −10	2.67658, −9
C	7.46208, −11	2.77290, −10
H_2O	3.72594, −1	1.38455, +0
H_2	1.08928, −1	4.04773, −1
H	1.12239, −2	4.17079, −2
O_2	1.27058, −3	4.72146, −3
OH	1.51231, −2	5.61973, −2
O	9.24665, −4	3.43604, −3
N_2	9.31362, −2	3.46093, −1
NO	1.60545, −3	5.96583, −3
N	1.70990, −6	6.35395, −6
HCl	1.75076, −1	6.50578, −1
Cl_2	5.94321, −5	2.20848, −4
Cl	1.23726, −2	4.59762, −2
AlCl	1.60103, −4	5.94941, −4
$AlCl_3$	4.88567, −5	1.81551, −4
AlOCl	5.89925, −6	2.19215, −5
Al	1.14917, −6	4.27029, −6
AlO	8.25526, −6	3.06764, −5
Al_2O	8.15312, −7	3.02968, −6
Al_2O_3	2.93523, −9	1.09073, −8

GAS TOTALS		
(MOLES)	1.00000, +0	3.71598, +0
(GMS)	2.36010, +1	8.77010, +1

CONDENSED PHASES

C	0	0
Al_2O_3	2.98214, −2	1.10816, −1
EXTRAS	3.36880, −3	1.25184, −2

MIXTURE TOTALS		
(MOLES)	1.03319, +0	3.83932, +0
(GMS)	2.69108, +1	1.00000, +2

TEMPERATURE	3200.39
ENTROPY	2.34924, +0
MOLECULAR WEIGHT	2.60463, +1
SPECIFIC VOLUME	1.43413, +2
SPECIFIC HEAT	4.46596, −1

FROZEN EQUILIBRIUM EXPANSION TO 1 ATMOSPHERE ABSOLUTE   E = 1.0, −7

TEMPERATURE	1587.48	SPECIFIC IMPULSE	2.50505, +2
ENTHALPY	−1.28240, +3	DISCHARGE COEFF.	6.39484, −3
SPECIFIC HEAT	3.98863, −1	THROAT PRESSURE	3.83914, +1
SPECIFIC VOLUME	4.84057, +3	THROAT TEMPERATURE	2.90998, +3

FIG.3. RESULTS FOR CASES 2 AND 5 USING PROGRAMME 202

C/H	O/H	N/H	C1/H	A1/H	EX/H
0.178159	0.647685	0.161344	0.161344	0.051413	0.002893

PRESSURE   1.0000   ENTROPY   2.349237

	NUMBER OF MOLES IN 1 MOLE OF GAS	NUMBER OF MOLES IN 100 GMS OF PROPELLENT
CO_2	9.43341, $^{-}$2	3.42723, $^{-}$1
CO	1.17860, $^{-}$1	4.28195, $^{-}$1
CH_4	1.69267,$^{-}$10	6.14962,$^{-}$10
C	1.40004,$^{-}$18	5.08647,$^{-}$18
H_2O	3.73018, $^{-}$1	1.35520, +0
H_2	1.26418, $^{-}$1	4.59288, $^{-}$1
H	1.00727, $^{-}$4	3.65949, $^{-}$4
O_2	1.50162, $^{-}$8	5.45552, $^{-}$8
OH	1.86057, $^{-}$5	6.75959, $^{-}$5
O	1.13790, $^{-}$8	4.13407, $^{-}$8
N_2	9.60833, $^{-}$2	3.49078, $^{-}$1
NO	3.53949, $^{-}$7	1.28592, $^{-}$6
N	6.79773,$^{-}$12	2.46967,$^{-}$11
HC1	1.92046, $^{-}$1	6.97717, $^{-}$1
Cl_2	1.85287, $^{-}$7	6.73162, $^{-}$7
C1	1.20230, $^{-}$4	4.36803, $^{-}$4
AlC1	2.54864, $^{-}$9	9.25940, $^{-}$9
$AlCl_3$	2.06371, $^{-}$7	7.49762, $^{-}$7
AlOC1	6.93619,$^{-}$12	2.51997,$^{-}$11
Al	2.95564,$^{-}$14	1.07381,$^{-}$13
AlO	2.14326,$^{-}$13	7.78661,$^{-}$13
Al_2O	1.46257,$^{-}$16	5.31361,$^{-}$16
Al_2O_3	8.40595,$^{-}$20	3.05395,$^{-}$19

GAS TOTALS
  (MOLES)   1.00000, +0   3.63308, +0
  (GMS)   2.41278, +1   8.76582, +1

CONDENSED
PHASES

C	o		o
Al_2O_3	3.06173, $^{-}$2		1.11235, $^{-}$1
EXTRAS	3.44567, $^{-}$3		1.25184, $^{-}$2

MIXTURE TOTALS
  (MOLES)   1.03406, +0   3.75683, +0
  (GMS)   2.75249, +1   1.00000, +2

TEMPERATURE   1772.64
ENTHALPY $^{-}$1.31537, +3
MOLECULAR WEIGHT   2.66182, +1
SPECIFIC VOLUME   5.28458, +3
SPECIFIC HEAT   4.08866, $^{-}$1

SPECIFIC IMPULSE   2.56168, +2
DISCHARGE COEFF.   6.30585, $^{-}$3
THROAT PRESSURE   3.89582, +1
THROAT TEMPERATURE 2.99359, +3

FIG.4. RESULTS FOR CASE 4 USING PROGRAMME 202

REF. NO.   E = 1.0, -7

C/H	O/H	N/H	Cl/H	Al/H	EX/H
0.178159	0.647685	0.161344	0.161344	0.051413	0.002893

PRESSURE   68.0457   ENTHALPY   -561.2001

GAS TOTALS
  (MOLES)   1.00000, +0   3.71598, +0
  (GMS)   2.36010, +1   8.77010, +1

CONDENSED
PHASES

C   o   o
Al2O3   2.98214, -2   1.10816, -1
EXTRAS   3.36880, -3   1.25184, -2

MIXTURE TOTALS
  (MOLES)   1.03319, +0   3.83932, +0
  (GMS)   2.69108, +1   1.00000, +2

TEMPERATURE   3200.39
ENTROPY   2.34924, +0
MOLECULAR WEIGHT   2.60463, +1
SPECIFIC VOLUME   1.43413, +2
SPECIFIC HEAT   4.46596, -1

FIG.5. SHORTENED VERSIONS OF RESULTS
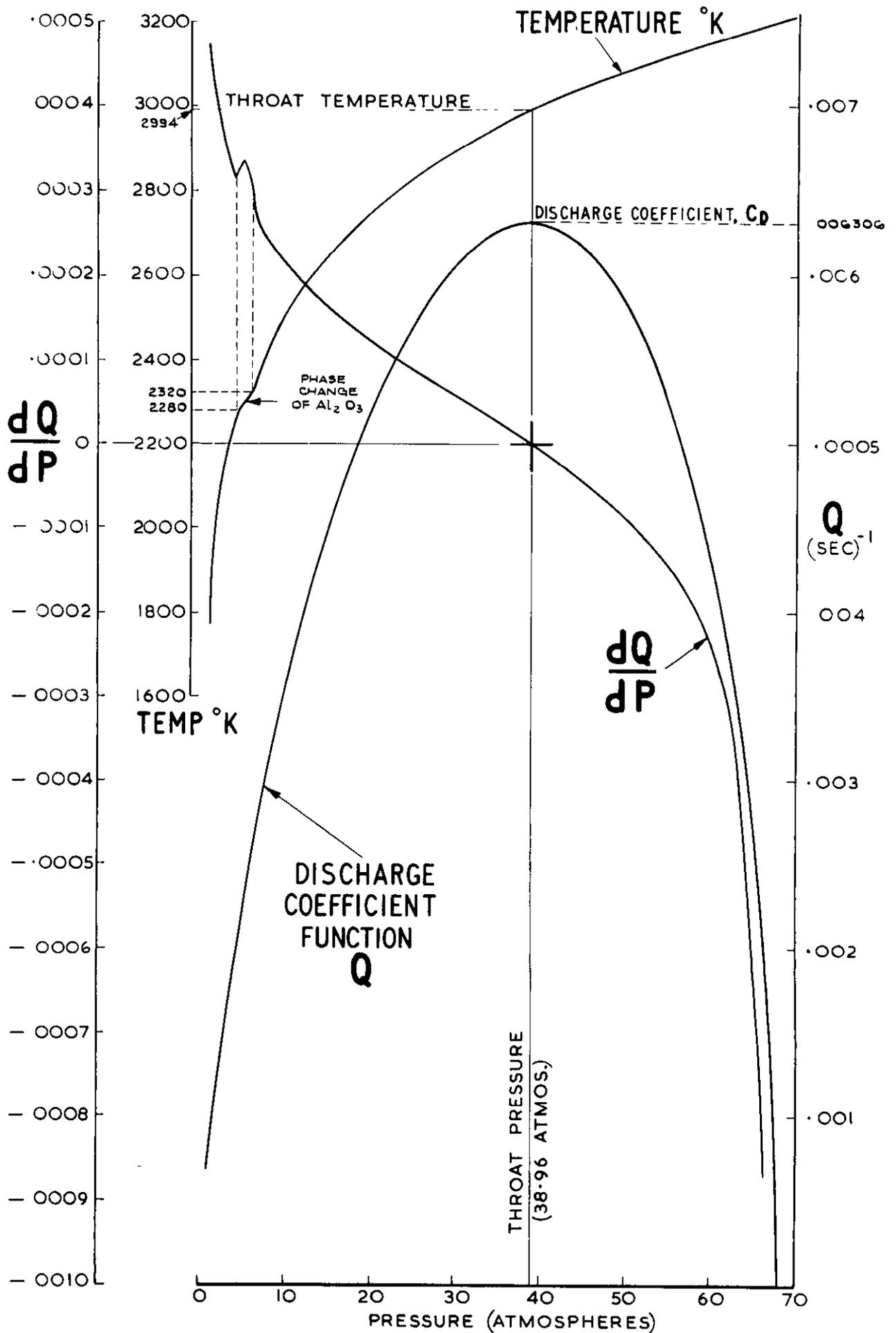
FIG. 6. AN EXAMPLE OF A DISCHARGE COEFFICIENT
FUNCTION AND ITS DERIVATIVE.