A COMPUTER PROGRAM TO PERFORM DATA PROCESSING OF FLAME TEMPERATURES OF PYROTECHNIC REACTIONS

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Abstract

A program is described which enables data processing of theoretical temperatures of flames of pyrotechnic reactions. This software has been developed with simplified mathematics. A very large database of thermodynamic characteristics allows a very important number of different calculations of temperatures.

The program takes into account the phenomena of dissociation of the most important species present in the reactions that we have to use. The results that we obtained with this computer program are very satisfying.

Keywords: calculation of flame temperatures, computer programs, data processing, dissociative reactions, pyrotechnic reactions

Introduction

Computer programs have already been used to perform data processing in the field of pyrotechnics [1–9]. The mathematics involved in this kind of subject can sometimes be complex [10, 11]. Therefore we decided to write a program able to give the flame temperature of pyrotechnic reactions with very good accuracy. The computers are personal models, so the accessibility is total but more powerful ones can be used. We developed some aspects of a relatively unknown but very interesting graphic method [12]. This method was manual, limited to hydrocarbons, and gave random results. So we developed a computerised model of it, and improved its possibilities to give always results with a very good accuracy. This accuracy is directly dependent on the quality of the data included in the thermodynamic database. The algorithmic used process can be easily adapted to solve a lot of problems of modeling in chemical fields (modeling of chemical reactions, kinetics, ...) [13, 14].

Short theoretical aspects

We consider that the flame temperature is the maximum temperature reached by the products of a given pyrotechnic reaction. We emit the following hypotheses:

1) the pyrotechnic reaction is performed at ambient temperature (298 K), initial temperature of the reactants;

2) the energy produced by the reaction is absorbed by the products of the reaction;

3) the pyrotechnic reactions are total;

4) the flame produced is an adiabatic one.

Owing to these quite acceptable hypotheses we can write the well known relation [15–18]:

$$\Delta H_r^o = -\sum_{i=1}^{p}(H^{T_f} - H^{298})_i = -\sum_{i=1}^{p} n_i \left(\int_{298}^{T_f} C_{p_i}dT + \sum L_i \right) \qquad (1)$$

where

ΔH_r^o	enthalpy of the reaction
$(H^{T_f}-H^{298})_i$	warming enthalpy of a product i. It will be called ΔH_i in our work
T_f	flame temperature
p	number of the products of the reaction
n_i	number of moles of a product i
C_{p_i}	heat capacity of a product i (at a constant pressure)
L_i	latent heat of transitions of a product i

Concerning the heat capacities we will write [19]: $C_p = a + b.T + c.T^2$

The coefficients a, b, c are found in the literature [20–25]. They really take into account variations in temperature.

Flame temperature calculation

Considering the starting data and hypotheses, we chose an iterative method which is particularly well adapted for data processing, and which can easily be applied. First, before computing the flame temperature itself, we must know the heat of the reaction. For this the following well known equation is used [15]:

$$\Delta H_r^o = \sum_{j=1}^{p} n_j \, \Delta H_j^o - \sum_{k=1}^{r} n_k \, \Delta H_k^o \qquad (2)$$

where

p Number of products of the reaction

r Number of reactants

n_j Number of moles of a product j

n_k Number of moles of a reactant k

ΔH_j^o Heat of formation of the product j at 298 K

ΔH_k^o Heat of formation of the reactant k at 298 K

For this calculation the computer uses the thermodynamic database that we have included in our system. Then, in a second step, it will have to propose from an initial temperature (fixed at 298 K) an increasing series of temperatures with an interval of 1 K. Then for each temperature T, and for each product of the reaction it will have to evaluate the quantity ΔH_i with the help of the relation (1). Considering the different possible states of a product, several kinds of calculations of the amount of heat ΔH_i can be considered. Our program automatically knows in which physical state a product i is (solid, liquid, gaseous). These calculations are performed for each temperature proposed and for each product i. Then for one of the temperature proposed the following sum is calculated:

$$\Delta H = \sum_{i=1}^{p} \Delta H_i \tag{3}$$

where

p number of the products of the reaction

ΔH heat absorbed by all the products of the reaction

Finally the computer program will perform the following test:

$$\Delta H_r^o = -\Delta H \tag{4}$$

If the answer is positive, the last temperature proposed is considered as the right flame temperature. If the answer is negative, the computer adds one Kelvin to the last temperature proposed and begins again the data processing using the Eq. (1).

Algorithmic features of the flame temperature procedure

When the program is started the user must indicate the amount P of products and the amount R of reactants. So the computer knows the total amount N of chemical compounds of the reaction:

$$N = P + R$$

Then the following operations will be performed N times:

Step 1: A request to the user to give the name of the common atomic element of the family of molecules in which the reactant or the product is included. For example, Carbon is the common atomic element of the molecule family in which CH_4 is included.

A great amount of reactants and product reactions are involved in all our pyrotechnic reactions (> 250). In order to be quick and efficient we built a classification system for all these data. Then we chose to group all the chemical components in families having the same common atomic element. For instance, Sodium (Na) will be the common atomic element of the following family: Na, Na_2O, NaO_2, NaF,... Each family will have a distinct file. Each chemical component of a family will be a record of the family file. And in each record we find the different variables containing the thermodynamic data of the chemical component concerned.

Step 2: The program displays on the screen the complete set of the molecules belonging to the family selected in step 1.

Step 3: A request to the user to select with a line number the molecule involved in the reaction, and its amount of moles.

Step 4: The computer takes on disk memory all the thermodynamic data of the chosen molecule. These data for a given product i are:

- Heat of formation at 298 K
- Coefficients a, b, c of the heat capacity $C_{p(i)}$ in the solid state
- Liquefaction temperature $T_{liq(i)}$
- Latent heat of liquefaction $Chal_{liq(i)}$
- Coefficients a, b, c of the heat capacity $C_{p'(i)}$ in the liquid state
- Vaporization temperature $T_{vap(i)}$
- Latent heat of vaporization $Chal_{vap(i)}$

Coefficients a, b, c of the heat capacity $C_{pi''(i)}$ in gaseous state.

When these operations are done, the computer knows all the thermodynamic data for all the compounds involved in the pyrotechnic reaction. The next step for the computer consists in data processing. Briefly:

Step 1: First temperature proposition by the computer (this proposition is 298 K)

Step 2: Calculations, for each product i, of the heat ΔH_i absorbed at temperature T.

Step 3: Sum, for all the products i, of the heat ΔH_i absorbed by them at temperature T.

Step 4: Test in order to know if $\Delta H_r^o + \Delta H \geq 0$

Step 5: If the test is positive the last temperature T proposed is considered as the flame temperature, which is called T_f. If the test is negative the last temperature proposed is incremented by 1 and the data processing starts again at step 1.

Consideration about the products of pyrotechnic reactions

Owing to the principle of the data processing of a flame temperature based on our calculation we can see that the heat capacities of the reaction products will be affected if they are involved in some equilibrium of dissociation. To simplify the written presentation of chemical species, we will not differentiate between molecules, ions and radicals. Consequently we will use the word "mole" for all these species. For instance, here is a reaction written without dissociation:
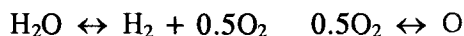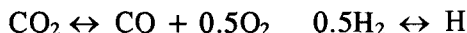
$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$
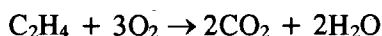
Now, here is the same reaction with some dissociation:

$$C_2H_4 + 3O_2 \rightarrow 2CO + 1.8H_2O + 0.4OH + 1.8O$$
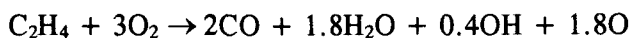
Although in both cases the amounts of atoms grams of C, O and H are not changed, we note that we have 4 moles of products (2 + 2) in the first reaction, but in the second one we have 6 moles of products. So the total heat capacities of the products of these two reactions will be different.

Possible dissociation equilibria of dissociable species

In the pyrotechnic reactions studied the principal products are CO_2, H_2O and N_2. These three species are considered as gaseous. They can be produced independently of one another and also independently of other reaction products. Thus these species will be involved in the following classical equilibria [26]:

$$CO_2 \leftrightarrow CO + 0.5O_2 \qquad 0.5H_2 \leftrightarrow H$$

$$H_2O \leftrightarrow H_2 + 0.5O_2 \qquad 0.5O_2 \leftrightarrow O$$

$$H_2O \leftrightarrow 0.5H_2 + OH \qquad 0.5N_2 + 0.5O_2 \leftrightarrow NO$$

So we can write the following six Equations [5, 12]:

$$K_1 = \frac{p_{CO} \cdot (p_{O_2})^{1/2}}{p_{CO_2}} \tag{6}$$

$$K_2 = \frac{p_{H_2} \cdot (p_{O_2})^{1/2}}{p_{H_2O}} \tag{7}$$

$$K_3 = \frac{p_{OH} \cdot (p_{H_2})^{1/2}}{p_{H_2O}} \tag{8}$$

$$K_4 = \frac{p_H}{(p_{H_2})^{1/2}} \tag{9}$$

$$K_5 = \frac{p_O}{(p_{O_2})^{1/2}} \qquad (10)$$
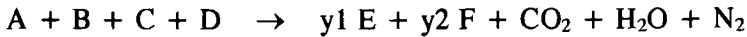
$$K_6 = \frac{p_{NO}}{(p_{N_2})^{1/2} \cdot (p_{O_2})^{1/2}} \qquad (11)$$
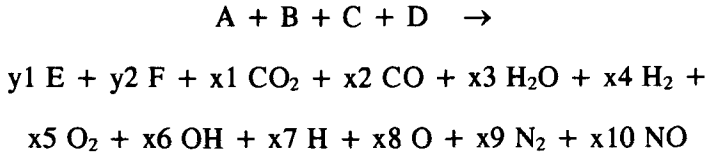
$K_1 \to K_6$ equilibrium constants

$p_{CO_2}, p_{CO}, p_{H_2O}, \ldots$ partial pressures of the species concerned / atm

Remark   we know the $K_1 \to K_6$ values as functions of the temperature.

For example, if we consider the following reaction:

$$A + B + C + D \quad \to \quad y1\ E + y2\ F + CO_2 + H_2O + N_2$$

We have in fact:

$$A + B + C + D \quad \to$$

$$y1\ E + y2\ F + x1\ CO_2 + x2\ CO + x3\ H_2O + x4\ H_2 +$$

$$x5\ O_2 + x6\ OH + x7\ H + x8\ O + x9\ N_2 + x10\ NO$$

A, B, C, D   reactants

E, F   possible reaction products considered as undissociable (ex: KCl)

y1, y2   amount of moles of the undissociable species

CO_2, CO,... dissociable and/or dissociated species

x1, x2   amount of moles of the dissociated species

Remark   the dissociation of species increases with the temperature.

If we could know the x1, x2,... values and inject them into the previous calculation of the temperature of flame we would have access to a very realistic temperature value. As a consequence we developed a theoretical method to perform a data processing able to give the x1 $\to$ x10 values.

Access to the real mole amounts of dissociated species

The presence of CO_2 and/or H_2O and/or N_2 in the products of reaction is directly linked to the presence (or absence) in the reactants of the atoms C, O, N, H. The following six cases have been chosen:

Case 1: Simultaneous presence of C, O, N, H

Case 2: Simultaneous presence of O, N, H

Case 3: Simultaneous presence of C, O, H

Case 4: Simultaneous presence of C, O, N
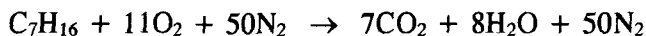Case 5: Simultaneous presence of O, N
Case 6: Simultaneous presence of C, O

According to the case to which a given pyrotechnic reaction belongs the method of access to the real amount of moles will be slightly different.
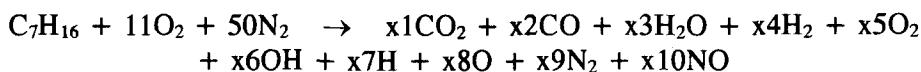
Method of access to the real amounts of moles of dissociated species

The access to the real amount of moles of species is obtained by means of its partial pressure. It is necessary to know the temperature to which the products of a reaction are exposed to calculate their rate of dissociation. In 1943 Damkohler and Edse developed a method to solve this kind of problem [12]. This method was based on successive graphic and random approaches. Briefly speaking the principle was to propose some arbitrary values for some temperatures of a reaction. Then knowing the $K_1 \rightarrow K_6$ constants, the (6) $\rightarrow$ (11) equations, and with graphic considerations they had access to the partial pressures, and to the real amount of moles of dissociated species. All these calculations are very time-consuming and concern reactions which contain only atoms C, O, N, H. We retained only certain means of calculations from this method, and we included original data processing.

In our method we will also propose reaction temperatures, but a clever way is to obtain reaction temperatures automatically. We will take an example of pyrotechnic reaction which belongs to case 1.

$$C_7H_{16} + 11O_2 + 50N_2 \rightarrow 7CO_2 + 8H_2O + 50N_2$$

A more realistic form will be:

$$C_7H_{16} + 11O_2 + 50N_2 \rightarrow x1CO_2 + x2CO + x3H_2O + x4H_2 + x5O_2 + x6OH + x7H + x8O + x9N_2 + x10NO$$

Here there are 10 unknown quantities x1 $\rightarrow$ x10. Thus we must find ten equations to have access to them. In addition to the previous equations (6) $\rightarrow$ (11) we can write others by using some relations with the numbers of atoms. For instance:

$$nC^*/nH^* = 7/16 = 0.4375 \tag{12}$$

$$nO^*/nH^* = 22/16 = 1.375 \tag{13}$$

$$nN^*/nH^* = 100/16 = 6.25 \tag{14}$$

where nC^*, nH^*, nO^*, nN^*: Theoretical numbers of atoms for the reaction considered.

These ratios are constant because for a given reaction the number of atoms of a species is a constant one. Therefore the user will be asked the values of these relations. On another connection there are relations between relative number of atoms and partial pressures of the products of a reaction given by Damkohler and Edse in the book of Gaydon and col. [12]:

$$nC = p_{CO_2} + p_{CO} \tag{15}$$

$$nH = 2 p_{H_2O} + 2 p_{H_2} + p_H + p_{OH} \tag{16}$$

$$nO = 2 p_{CO_2} + p_{CO} + p_{H_2O} + 2p_{O_2} + p_{OH} + p_O + p_{NO} \tag{17}$$

$$nN = 2 p_{N_2} + p_{NO} \tag{18}$$

Remark: There are two interesting properties of numbers of theoretical atoms and numbers of relative atoms. For instance:

$$\text{i)} \quad \frac{nO^*}{nH^*} = \frac{nO}{nH} \tag{19}$$

$$\text{ii)} \quad \frac{nO^*}{nO} = \frac{nC^*}{nC} = \frac{nH^*}{nH} = \frac{nN^*}{nN} \tag{20}$$

These properties will give us a test in order to verify whether the partial pressures given by the data processing are the correct ones. Here is an example of such a test:

$$\frac{nO}{nH} = \frac{nO^*}{nH^*} \tag{21}$$

Lastly we will use the following equation of the total pressure:

$$P = p_{CO_2} + p_{CO} + p_{H_2O} + p_{O_2} + p_{H_2} + p_{OH} + p_O + p_H + p_{N_2} + p_{NO} \tag{22}$$

This last equation will give us a second test for verification of the calculated partial pressure. This test will be:

$$P = P_t \tag{23}$$

where

P Total calculated pressure

P_t Total pressure asked of the user. (This pressure will often be 1 atm.)

We did not choose a direct method of calculations for the system of ten equations with ten unknown quantities. It is the computer itself which proposes the values for two partial pressures. These values will be chosen according to the case to which the pyrotechnic reaction belongs. When these two values are stated, different strategies of data processing are beginning [12]. Figure 1 shows an example of calculation for a reaction containing carbon and oxygen:

A very important remark: It is to be noted that these calculations of partial pressures are made for a given temperature. Once the computer has calculated the ten partial pressures we will have to check their validity, so the following relations must be tested:

$$\frac{nO^*}{nH^*} = \frac{nO}{nH} \quad \text{and} \quad P_t = P \tag{24}$$

If these two relations are proved at the same time, this will mean that the calculated partial pressures are true and that the values proposed by the program were right. The one problem will be, in fact, to be able to propose the right values for these two ratios. In order to better realise this problem we will represent as an example in a three dimensional space (x, y, z) the four quantities p_{CO_2}/p_{CO}, p_{H_2O}, nO/nH and P. The partial pressure p_{H_2O} is put on the X axis, the

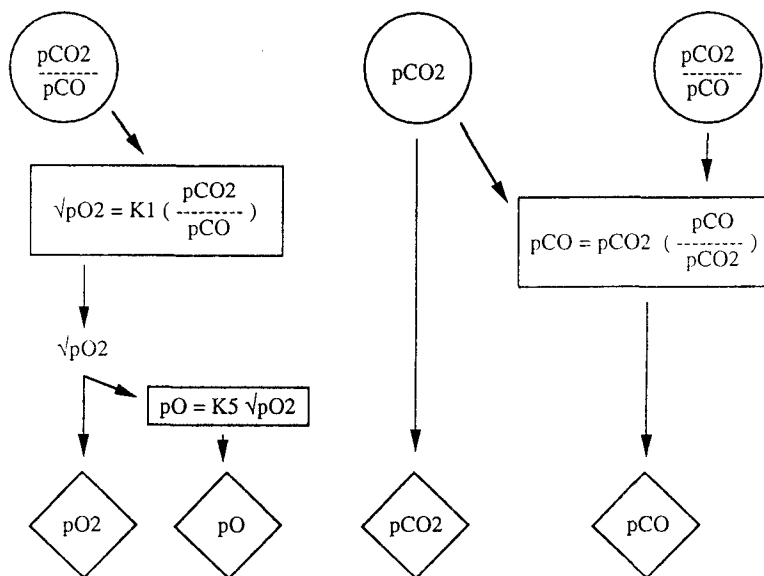
Fig. 1 Example of calculations for a reaction containing carbon and oxygen

ratio p_{CO_2}/p_{CO} on the Y axis and the values of nO/nH as well as those of P on the Z axis (Fig. 2).

The set of values of pressures P and ratios nO/nH determines two distinct areas above the plane (x, y). We drew a small part of it on the above picture (hatched areas). These two areas will cut the $z=P=P_t$ and $z=nO^*/nH^*=nO/nH$ giving two curves (curves 1 and 2) which will pass one above the other at a given time. This phenomenon is inevitable because there is necessarily a value of p_{CO_2}/p_{CO} and of p_{H_2O} for which the calculated pressure P and the calculated ratio nO/nH are equal in the same terms, respectively to the real pressure P_t and to the ratio nO*/nH* as the pyrotechnic reaction exists. This intersection point corresponds to the real values of p_{H_2O} and p_{CO_2}/p_{CO}. Let's have a look from above Fig. 3 in order to better see the intersection of the two curves.

At first sight nothing enables us to know the position of the intersection point A in advance. Indeed, our original method differs from that of Damkohler and Edse [12]. They proposed couples for values of p_{H_2O} and p_{CO_2}/p_{CO}, then tentatively, owing to the values they found for P and for nO/nH, they modified their values of p_{H_2O} and p_{CO_2}/p_{CO}. This method being long drawn out, we pre-
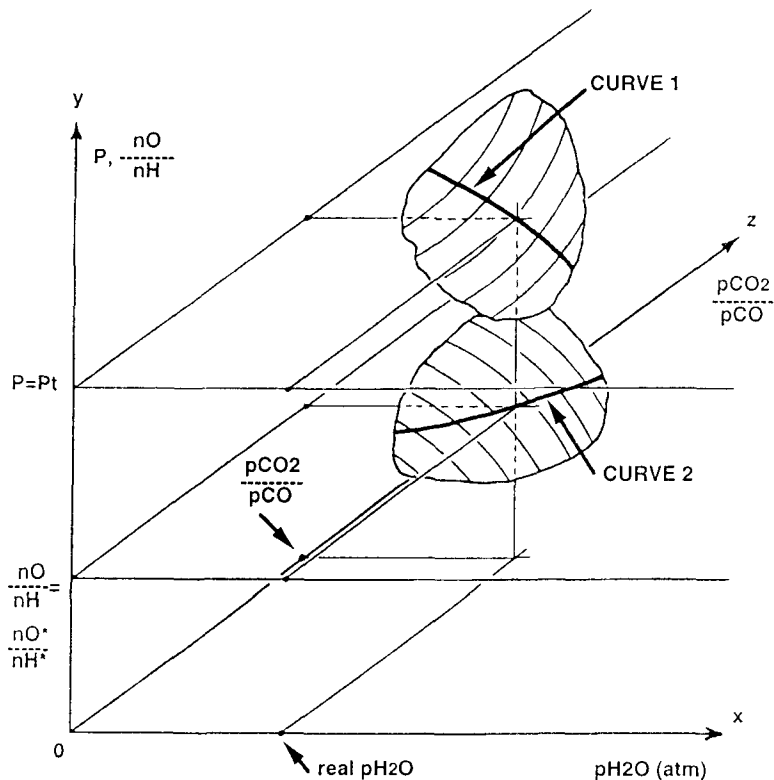

Fig. 2 Three dimensional view of calculations on partial pressures and nO/nH

ferred to create one which we called "scanning". The following two remarks should be borne in mind:

- The value of the pressure p_{H_2O} is such that $0 < p_{H_2O} < P_t$
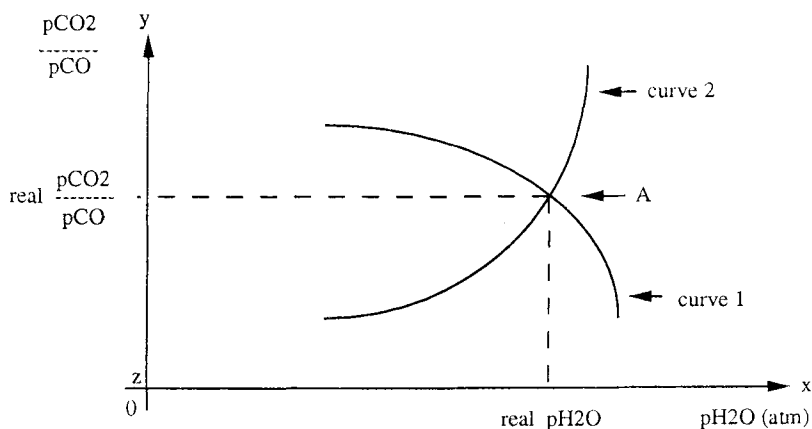- The value of the ratio p_{CO_2}/p_{CO} is such that $0 < p_{CO_2}/p_{CO} < \infty$.

Fig. 3 Visualisation of Fig. 2 from above

The principle of this method consists in proposing values for p_{CO_2}/p_{CO} and for p_{H_2O} according to a systematic methodology. To begin with, the program will set a first series of values and propose them:

- For p_{CO_2}/p_{CO} it will propose in order 1,2,... (increments of 1)
- For p_{H_2O} it will propose $P_t/10$, $2 \cdot P_t/10$, $3 \cdot P_t/10$,...(increments of $P_t/10$)

It is to be noted that the values of p_{CO_2}/p_{CO} will be proposed first and for each of these values, the values of p_{H_2O} will be proposed one after the other. So the first couples of values will be: (1;0,1) (1;0,2) (1;0,3) etc.

This can be visualised as in Fig. 4:

For each couple of values the calculation of partial pressures will be done as described above. Then, each time, the following test will be carried out:

$$P \geq P_t \qquad (25)$$

- If the answer is negative, the propositions of values will continue with the current increments
- If the answer is positive, this means that the last value proposed for p_{H_2O} goes slightly beyond curve 1 (point C on Fig. 5)

In that case the program will:

– Go back to the proposition of the preceding values which is point B (p_{CO_2}/p_{CO} is unchanged, p_{H_2O} alone is incremented).
– Divide the increment of p_{H_2O} by 10
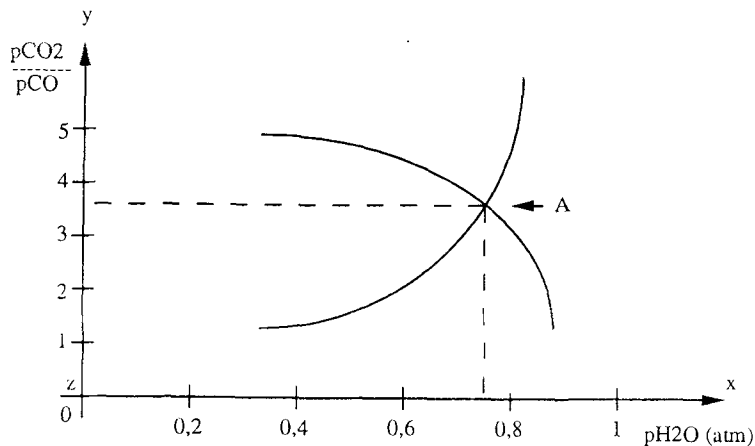– Propose some values from B up to C (p_{CO_2}/p_{CO} constant).

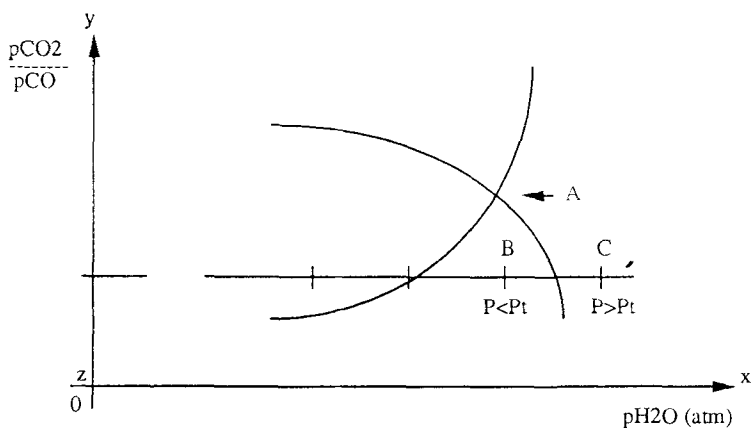Fig. 4 Representation of the values of the two partial pressures

Fig. 5 First framing of the partial pressure of p_{H_2O}

As before, for each couple of values, test (25) will be performed:
– If the answer is negative, the proposition of values continues with the current increments.
– If the answer is positive, this means that the last value proposed for p_{H_2O} goes slightly beyond curve 1 (point D on Fig. 6)

In that case the computer will:

 – Go back to the proposition of the preceding values, point E (p_{CO_2}/p_{CO} is unchanged, only p_{H_2O} is decremented).

 – Divide the increment of p_{H_2O} by 10.

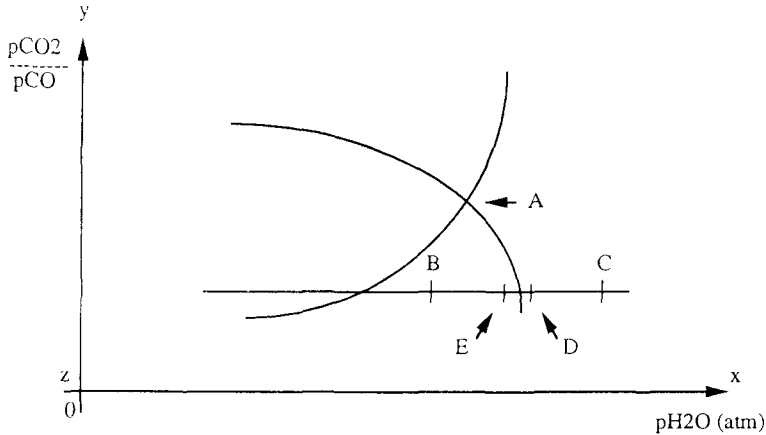 –Propose values from E up to D (p_{CO_2}/p_{CO} a constant)

Fig. 6 Improvement of the framing of p_{H_2O}

For each proposition test (25) will be performed. The set of these operations, framing the curve 1 and dividing by ten the increment of p_{H_2O}, will be performed five times. The relation $P = P_t$ will be checked to the nearest 0.00001, which is more than satisfying for a precise calculation. So, this set of operations constitutes an independent process of the framing of the pressure P_t. Once the value of p_{H_2O} is determined through this process, we will have to check the value of p_{CO_2}/p_{CO}, too. To do so we will use the following test:

$$\frac{nO^*}{nH^*} \leq \frac{nO}{nH} \qquad (26)$$

 – If the answer is negative we increment p_{CO_2}/p_{CO} to one unit and we begin again the framing procedure of the pressure P_t described above.

 – If the answer is positive this means that the last value proposed for p_{CO_2}/p_{CO} goes slightly beyond curve 2 (point B on Fig. 7).

In that case the program will:

 – Go back to the value proposed before for p_{CO_2}/p_{CO} (level C)

 – Divide the increment of p_{CO_2}/p_{CO} by 10

 – Propose new couples (p_{CO_2}/p_{CO}, p_{H_2O}) taking into account the new increment for p_{CO_2}/p_{CO} and applying the framing procedure of P_t.

$$\frac{pCO2}{pCO}$$

$$\frac{nO^*}{nH^*} < \frac{nO}{nH} \quad D$$

$$\frac{nO^*}{nH^*} > \frac{nO}{nH} \quad C$$
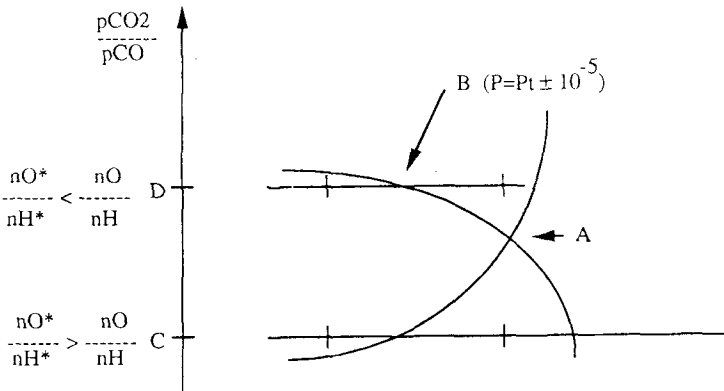
B $(P = P_t \pm 10^{-5})$

A

Fig. 7 Framing of the partial pressure p_{CO_2}/p_{CO}

For each couple proposed test (26) will be performed:

– If the answer is negative the proposition of values continues for (p_{CO_2}/p_{CO}, p_{H_2O}) with the current increment for p_{CO_2}/p_{CO} by using the framing procedure of the pressure P_t.

– If the answer is positive it means that the value proposed for p_{CO_2}/p_{CO} goes slightly beyond curve 2 (level E on Fig. 8).

In that case the program will:

– Go back to the value previously proposed for p_{CO_2}/p_{CO} (level F)

– Propose new couples (p_{CO_2}/p_{CO}) taking into account the new increment for p_{CO_2}/p_{CO} and applying the framing procedure of P_t.

For each couple proposed test (26) will be performed.

The set of framing operations of curve 2 with the division by 10 of the increment of p_{CO_2}/p_{CO} will be executed five times altogether. The relation (26) will be checked to the nearest 0.00001. This set of operations constitutes an independent framing procedure of the value of nO^*/nH^*. When the two framing procedures of the values of nO^*/nH^* and P_t have been realized, we will then have the true values of p_{H_2O} and p_{CO_2}/p_{CO} with a high degree of accuracy. This implies that all the partial pressures resulting from the calculations at that time will be considered as accurate and therefore actual. It should be noted that depending on the results of the pyrotechnic reactions, the initial conditions of the procedures, as well as the verification tests, could be slightly different. But, on the whole, the principle will remain strictly identical. Now that we know the partial pressures of the dissociated species for a given temperature, we have to consider their amount of moles.
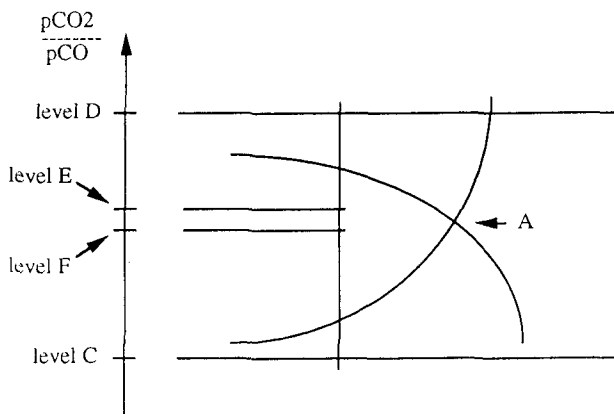
Fig. 8 Improvement of the framing of p_{CO_2}/p_{CO}

Research of the percent of dissociated species from the partial pressures

We will show the method's principle. Let's study a reaction which would give as products of reaction:

$$\ldots \rightarrow nA + pB + qC$$

where

n, p, q   theoretical numbers of moles,
A, B, C   species such as CO_2, CO, H_2O, O_2,...

We will have the two following reactions which will then be respected:

$$p_A + p_B + p_C = P_t \tag{27}$$

$$n + p + q = N \tag{28}$$

where

p_A, p_B, p_C Partial pressures of the species A, B, C
N Theoretical total number of the product moles
P_t Actual total pressure

Then we will adjust the sum of the amount of moles to the P_t pressure value. To do so we write:

$$\frac{P_t \cdot n}{N} + \frac{P_t \cdot p}{N} + \frac{P_t \cdot q}{N} = P_t \tag{29}$$

The quantities of type $P_t \cdot n/N$ thus become amounts of the relative moles. The quantities of type p_A, p_B, p_C are, for their part, the partial pressures calculated by the program. If we consider that the partial pressure of a type of species and the amount of relative corresponding moles are directly linked, we can write, with the help of the relations (27) and (29):

$$p_A = P_t \cdot \frac{n}{N} \tag{30}$$

$$p_B = P_t \cdot \frac{p}{N} \tag{31}$$

$$p_C = P_t \cdot \frac{q}{N} \tag{32}$$

Our unknowns are n, p, q. We know the partial pressures. We need N. In order to get it we will, for instance, take into account the following two reasonings:

– The relative number of the atoms of oxygen nO is proportional to the relative total number of moles and also to the total pressure P_t.

– The number of theoretical atoms nO^* is proportional to the theoretical total number N of product moles.

This can be summed up by:

$$N = \frac{nO^* \cdot P_t}{nO} \tag{33}$$

P_t and nO^* are known, nO is the result of calculation with the help of relation (17). As an example, for relation (30) it will be:

$$n = p_A \cdot \frac{nO^*}{nO} \tag{34}$$

Therefore the theoretical amounts of moles of a species will be obtained by multiplying its corresponding partial pressure by the ratio nO^*/nO. As can be realized, we are thus able to find the dissociated species obtained as well as their respective theoretical amounts of moles, for a chosen case and a given temperature. We will now study a general method to gain access to the flame temperature of a reaction which has dissociable reaction products. In that case they are called dissociated reactions. This method will be seen directly through the algorithmic operations of the program.

Original method to gain access to the flame temperatures of dissociated reactions

In order to illustrate our argument, let us suppose a pyrotechnic reaction which would give us the following theoretical reaction products:

$$... \rightarrow 2ZrF_4 + H_2O + 3CO_2 + 4N_2$$
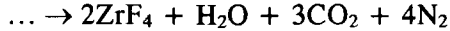
Taking into account all that has already been said, we notice that this is really a dissociated reaction, and therefore we will obtain all the products of dissociation already studied above (CO_2, CO, H_2O, O_2, H_2, etc....). From a computing point of view, the program which enables us to gain access to the flame temperatures of dissociated reactions is the same as that already described for non-dissociated reactions. We "only" added a set of procedures allowing us to find the amounts of moles of the dissociated species as a function of a given temperature (however, this set of procedures consists of 70% of the whole new listing program). This program is called EQ.EXE. Here we note that the preceding version for non-dissociated reaction is called TF.EXE.

As soon as it is started, the program asks the user to enter:

– the number of reactants
– the number of dissociated reaction products

Then, exactly as in the TF program, the user will be asked to specify the physico-chemical characteristics of the reactants and of the products by means of an adapted display. Lastly, the first computation of a flame temperature will be set going. Once it is ended, the values of the reaction heat and the flame temperature will be displayed. Then the user will be asked if he wishes to have a simpler printing of the results. This printing will give the equation of the reaction flame studied. We call T_1 the temperature of the flame concerning the reaction not yet dissociated. This temperature will be an upper limit temperature because we entered the reaction in its undissociated state in the program. Thus the whole of the calorific capacities of the reaction products will be a lower limit, and the flame temperature will be higher. Hence'forth it can be seen that, as soon as any dissociation happens it will always tend to lower the flame temperature. Later on we will use this very important characteristic.

At the next step, the user will be asked if the reaction can produce dissociated species. If the answer is negative the program will stop definitely. If the answer is positive, it will ask the user to specify to which case the reaction belongs. The program will display on the screen the six possible outlines of dissociated species:

1– Carbon, nitrogen, hydrogen, oxygen

2– Nitrogen, hydrogen, oxygen
3– Carbon, hydrogen, oxygen
4– Carbon, nitrogen, oxygen
5– Nitrogen, oxygen
6– Carbon, oxygen

The user will choose one of them, then he will have to enter the number of theoretical atom grams of oxygen nO of the reaction. Next, and according to the case chosen by the user, some ratios will be asked, such as:

Case 1: nC^*/nH^*, nO^*/nH^*, nN^*/nH^*
Case 2: nN^*/nH^*, nO^*/nH^*
Case 3: nC^*/nH^*, nO^*/nH^*
Case 4: nN^*/nC^*, nO^*/nC^*
Case 5: nN^*/nO^*
Case 6: nO^*/nC^*

To conclude, the program will ask the total pressure at which the reaction is supposed to happen. This pressure will practically always be taken as equal to 1 atmosphere. The computation of the amount of moles of the dissociated species will then be automatically started.
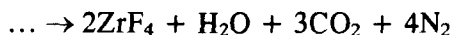
Real amount moles of dissociated species calculation

The program will take and keep in memory the temporary flame temperature T_1 which was found for the reaction not yet dissociated. In the case in which the temperature T_1 would be higher than 6000 K a message would warn the user that this value of 6000 K would be taken for T_1 failing any other one. In fact, we can get access to the constants $K_1 \rightarrow K_6$ up to 6000 K. Next, for the temperature T_1 the program will load the values of these six constants into memory. To do so we entered the value table of the constants into the program depending on the temperature. Moreover we extrapolated the constant values from 5000 K to 6000 K. We created a process which allows, thanks to interpolations, computation of the constants $K_1 \rightarrow K_6$ for every value of temperature within the range from 298 K to 6000 K.

Now the program will initiate the process allowing finding of the partial pressures of dissociated species for T_1. The general method to gain access to these pressures is already described in detail in the preceding chapter. Depending on the case, the arbitrary magnitudes proposed by the program and the magnitude on which tests will be made will be different of course. Once the program has determined the right values for the partial pressures of dissociated species it will compute the amounts of real moles owing to the method already described and which works for every case.

Dissociative reaction flame temperature

Here it is time to summarize the program operations. We had a reaction which would have given us, as theoretical reaction products:

$$... \rightarrow 2ZrF_4 + H_2O + 3CO_2 + 4N_2$$

A first computation of a flame temperature gave us a T_1 temperature. Then, as we assumed that T_1 was the flame temperature we started the process of computing the amounts of real moles of the dissociated species for this temperature T_1. We got for our example:

$$... \rightarrow 2ZrF_4 + x1CO_2 + x2CO + x3H_2O + x4H_2 + x5O_2 + x6O_2 + x7H +$$

$$x8OH + x9NO + x10N_2$$
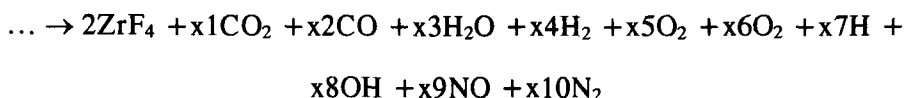
$x1 \rightarrow x10$ being known now for T_1 temperature. Taking into account that T_1 is an upper limit temperature, here we have the highest rates of dissociation for the species concerned. The trick will be now to inject this reaction into the program computing the temperatures of flames, taking into account the whole range of the products of the reaction (here there are 11) and their numbers of real moles (2, x1, x2, x3,...). This will be done fully automatically by the program, which can see the difference between dissociable and undissociable species. Moreover, all the information is stored in memory (number of moles and formulas of the reaction products), it is the program itself which will look for all the physico-chemical characteristics of the products and of the reactants of the considered dissociated reaction in the database. These computations being ended we will get a second flame temperature T_2 which, this time, will be a lower limit for every temperature, because the dissociation rates of the products that the program has considered were upper rates, because the first temperature T_1 was an upper limit too. Thus, we have determined a range of temperature T_1, T_2 within which is the true flame temperature T_f. In order to discover T_f we have to propose some temperatures within this range T_1, T_2 through a particular methodology. Indeed all this can be summed up in the following sequence:

- Step 1: Proposal of a reaction not yet dissociated
- Step 2: Computation of an upper limit temperature T_1
- Step 3: Computation of the amount of moles of dissociated species for temperature T_1
- Step 4: Computation of a lower limit temperature T_2 for the dissociated reaction obtained at step 3

So it may be noted that if we propose a relatively high temperature at step 3, we will get a corresponding lower temperature at step 4. This is the reason why, to begin with, we will propose the following series of high temperatures:

$$T_3 = (T_1 - 1000); \quad T_5 = (T_3 - 1000); \quad T_7 = (T_5 - 1000) \text{ etc...}$$

We will, then, respectively get at step 4 the following corresponding low temperatures:

$$T_4, T_6, T_8 \text{ etc....}$$
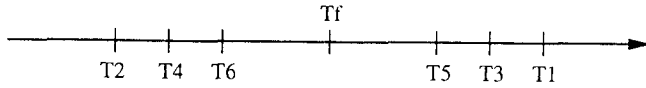
This is illustrated in Fig. 9:

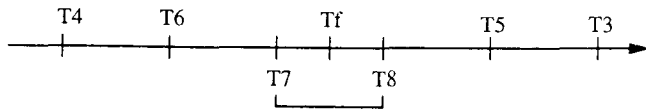**Fig. 9** First framing of temperature T_f

Fig. 10 Crossing of proposed and calculated temperatures

After a while we will get a crossing of the temperatures, that is to say, that the "lower" calculated temperature will be in fact higher than the "higher" temperature proposed. As an example we will have:
Then we will propose in that example the following series of temperatures:

$$T_7 = (T_5 - 100); \quad T_9 = (T_7 - 100) \quad T_{11} = (T_9 - 100) \text{ etc....}$$

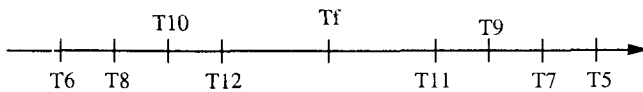We will get the following corresponding temperatures $T_8, T_{10}, T_{12}...$ This is illustrated in Fig. 11.

Fig. 11 Improvement of the framing of T_f

Here again we will get, after a while, a crossing of temperatures. As before we will then modify the decrement of temperatures so that we could propose:

$$T_{13} = (T_{11} - 10); \quad T_{15} = (T_{13} - 10); \quad T_{17} = (T_{15} - 10) \text{ etc....}$$

We will get the corresponding lower temperatures $T_{14}, T_{16}, T_{18},...$ Once again we will get a crossing of temperatures. So we will propose the last following series of temperatures:

$$T_{19} = (T_{17} - 2); \ T_{21} = (T_{19} - 2); \ T_{23} = (T_{21} - 2) \ \text{etc.} \dots$$

We will get the corresponding lower temperatures T_{20}, T_{22}, T_{24}, etc.... When we reach the last crossing of temperatures we will take the higher temperature proposed before and the corresponding calculated lower temperature, and then we will calculate the arithmetical average.

This average will be considered as being the theoretical flame temperature of the considered pyrotechnic reaction. We will have for instance, with a relative accuracy of 1 deg:

$$T_f = \frac{T_{23} - T_{24}}{2} \tag{35}$$

Note: The relative accuracy of the computation will be 1 deg.

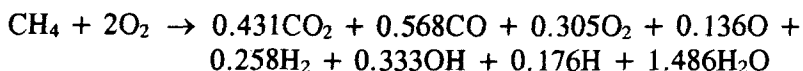## Limits of the method – examples of applications

Damkohler and Edse's method that we improved was limited to hydrocarbon combustions. Now, this type of reaction always produces the same reaction products, that is to say: CO_2, H_2O, N_2. As far we are concerned we widened the range for the reaction products which can be created by a pyrotechnic reaction. But, taking into account the starting hypotheses and especially the use of partial pressures, the reaction products other than CO_2, H_2O, N_2, will have to obey the following conditions:

– They must not be the subject of a dissociation equilibrium
– They must not have the atoms, C, O, N, H so as not to miscalculate the atomic balance
– They must not be gaseous from 298 K to the flame temperature T_f

Obviously these are the limits of the possible choice of the products but the accuracy of the computation which can be obtained is very high. This is why this method is very attractive.
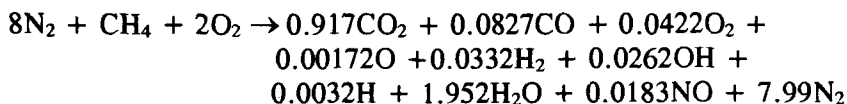
Results

These results were obtained on some test applications such as combustions. When the temperature of experimental flames are known, they are indicated.
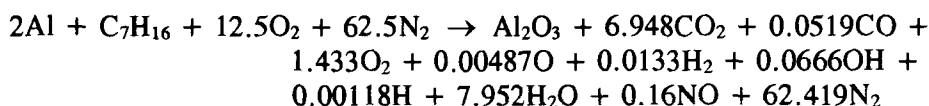
$$CH_4 + 2O_2 \rightarrow 0.431CO_2 + 0.568CO + 0.305O_2 + 0.136O +$$
$$0.258H_2 + 0.333OH + 0.176H + 1.486H_2O$$

$\Delta H = -497.71 \ \text{kJ/mol}$

T(calculated)   3034 K
T(real)   3010 K

$$8N_2 + CH_4 + 2O_2 \rightarrow 0.917CO_2 + 0.0827CO + 0.0422O_2 +$$
$$0.00172O + 0.0332H_2 + 0.0262OH +$$
$$0.0032H + 1.952H_2O + 0.0183NO + 7.99N_2$$

$\Delta H = -849.16$ kJ/mol
T(calculated)   2189 K
T(real)   2222 K

Now this is a real application of our program where the real temperature is unknown:

$$2Al + C_7H_{16} + 12.5O_2 + 62.5N_2 \rightarrow Al_2O_3 + 6.948CO_2 + 0.0519CO +$$
$$1.433O_2 + 0.00487O + 0.0133H_2 + 0.0666OH +$$
$$0.00118H + 7.952H_2O + 0.16NO + 62.419N_2$$

$\Delta H = -6478.28$ kJ/mol
T(calculated)   1946 K
T(real)   unknown

Conclusion

This set of computer programs has brought very interesting possibilities into our theoretical calculations. The methodology of the data processing allows us to obtain results easily with a very good accuracy and without complex mathematical knowledge. These routines give always a right single result because it is a systematic method. For this reason other methods such as Simplex not appears to be suitable. Some improvements will be made in the choice of new dissociable species (for example: SO_2, TiO_2, etc.). The limit to this kind of improvements will in fact be the speed of data processing of the computer itself. We specify that an arithmetic processor is compulsory. For our applications we used an IBM type computer running at 25 mHz.

It is very important to note that these routines can be easily implemented on other kinds of computers such as Unix workstations, with little modifications of the source library. In our laboratory an implementation will be made on a RISC IBM RS 6000 station.

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Zusammenfassung — Es wird ein Programm beschrieben, welches die Datenverarbeitung für theoretische Temperaturen von Flammen bei pyrotechnischen Reaktionen ermöglicht. Diese Software wurde mit vereinfachten mathematischen Methoden entwickelt. Eine sehr große Datenbank thermodynamischer Eigenschaften erlaubt eine sehr bedeutende Anzahl verschiedener Berechnungen der Temperaturen.

Das Programm berücksichtigt die Erscheinung der Dissoziation der wichtigsten Vertreter, die in den zu benutzenden Reaktionen vorkommen. Mit diesem Computerprogramm konnten recht zufriedenstellende Resultate erzielt werden.