

# THERMAL FREEZING IN THE TECHNOLOGY OF AEROSPACE PROPELLANTS

*R. D. Rugescu*

*University "Politehnica" of Bucharest, Romania*

## INTRODUCTION

The unusual behavior of the combustion products of aerospace propellants in the O-N-C-H system is evoked, as manifested during a first round of experimental measurements of chemical composition in 1982. Despite a long series of computational developments and due to these same developments, the strange conflict between the experimental data and the computed imprint of chemical composition ends in the formulation of the freezing temperature hypothesis, proved solid by all the eventual investigations performed by the author.

## 1. THERMOCHEMICAL ISOBAR EQUILIBRIUM

Numerical simulation of the combustion and expansion processes in chemical shifting equilibrium stated the object of a number of studies over the efficiency of aerospace propellants performed by the author since 1962, in the frames of the ADDA program [3]-[14], [15], [16]-[21]. As long as the proprietary computational methods are known and published, it is considered as useful to only reproduce here the unexpected conclusions supplied by the first confrontation of the computed results with the laboratory measurements, as performed in 1982 at CCIT of Chemical Complex in Fagaras, Romania [9], [11]-[13]. These observations are published now for the first time in the international press.

The so-called *particular* thermochemical method developed had manifested a fast convergence in the entire area of temperatures and pressures usually encountered for the homogeneous triple base propellants, from the category of Russian Serebriakov-type cordites [19], nominated as *A-100* and studied at UPB in 1980-1988. The fast convergence is due to the fact that according to this method a computational nucleus with insufficient oxygen is presumed (dominant products), in accordance with the real combustion products of the studied propellant, known to present a considerable

excess of fuel and is typical for these classes of particular computational methods.

The theoretical quantity of oxygen required for the complete combustion of the reducing elements C, H, Pb and Ca is given by

$$A_{ot} = 2 \cdot A_C + A_H / 2 + A_{Ca} + A_{Pb} = 61,2741 \cdot [\text{atoms-gram/kg-propellant}]. \quad (1)$$

On the other hand, the quantity of oxygen actually present in the propellant is equal to  $A_o = 34.28238627$  [gram-atoms/kg-propellant], and this shows that the oxygen is present in insufficient quantity for a complete combustion of fuel elements, namely for the formation of the full combustion products CO<sub>2</sub>, H<sub>2</sub>O and CaO\*. The degree of oxygen deficit is addressed through the coefficient of oxygen "excess"  $\omega_o$  as usual

$$\omega_o = A_o / A_{ot} = 0.5595 \quad (2)$$

which shows that in the propellant *P-100* a quantity of 56% oxygen is only present of the necessary stoichiometrical combustion. The computational method elaborated and experimented is specifically oriented towards such situations and consequently is fast converging when the computational temperatures are not excessively high. The selection of the predominant combustion products (main products) H<sub>2</sub>O, CO<sub>2</sub>, CO, H<sub>2</sub>, N<sub>2</sub>, Pb, CaO\*, CaOH and CaO was confirmed by numerical results at extreme total pressures of 0,1 and 100 atm respectively [9]. At the same time the secondary combustion products of this propellant incorporate in order NH<sub>3</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, HCN a. s. o., in respect with the pressure and mainly the computational temperature.

At high computational pressures ( $p_c = 100$  [atm]) and at low temperatures, also assuming a full chemical equilibrium, a clear tendency of formation of some greater methane CH<sub>4</sub> quantities appears. At 1500°K a 1‰ methane molar concentration would form, which grows up to 1.6% for temperatures lower than 1300°K. Below this temperature the computational method proves inconvenient because

the methane becomes a dominant combustion product, contradicting the hypothesis.

There are enough arguments (for example [2], pg. 158) to consider that at low temperatures the chemical equilibrium in the tendency of formation of some polyatomic molecules from other stable polyatomic molecules cannot be attained and thus remains fictitious. In that regard considerable clarifications may be produced by experimental measurements of the chemical complete composition of the combustion products only. Obviously, the determination of the combustion products' composition directly in the motor and nozzle would be of highest profit, but such experimental installations are not accessible for the moment in Romania. For that reason attention was afforded to the measurement of isochoric combustion products in calorimeters.

## 2. CHROMATOGRAPHIC EXPERIMENTS

In the laboratories of CCIT, where the author had functioned as Laboratory Chief between 1984-1987, measurements of the chemical composition of residual gases in the calorimeter could have been performed, without any special arrangements. This was measured after the constant volume combustion of a given mass of propellant of 6 grams and the cooling of the combustion products up to the ambient temperature.

Measurements upon three different but similar receipts called  $C_1$ ,  $C_2$ ,  $C_3$  were performed, with a loading of the (vacuumed) calorimeter of 21.2765 [kg/m<sup>3</sup>]. The following results were obtained for the concentration of the residual gases CO<sub>2</sub>, CO, H<sub>2</sub> and N<sub>2</sub> in the calorimeter, in molar percent fractions:

**Table 1.**

Type	Test	H <sub>2</sub>	N <sub>2</sub>	CO	CO <sub>2</sub>	Q <sub>v</sub>
C-1	1	22.927	13.657	51.467	12.669	848.04
C-2	2	22.641	13.646	51.283	13.668	850.48
	3	22.829	12.898	51.513	12.766	
C-3	4	22.772	12.861	51.463	12.584	856.22
	5	22.783	12.923	51.582	12.892	
Mean:		22.707	13.149	51.275	12.869	851,58

These measurements contain a small scatter of unknown origin. The measured heat of reaction at constant volume  $Q_v$  is given in [cal/g-propellant]. The chemical composition was measured with a Hewlett-Packard-5840A type gas chromatograph with an 3550A integrator, incorporating a thermal

printer. The column used during those determinations was of "Porapack" type, allowing to retain, besides the four gases already mentioned, the molecular oxygen O<sub>2</sub> also, missing in fact from the combustion products, obvious fact due to the great excess of fuel elements. Unfortunately the given column had not permitted to retain other species as for example NH<sub>3</sub>, CH<sub>4</sub> etc, whose detection in the combustion products presents a high interest for the assessment of the situation of chemical equilibrium in the given system. In those conditions the research was entirely based upon the assertion that the combustion products only present in the calorimeter in gaseous phase are the four species entered in table 1.

## 3. MEASUREMENTS' DISPERSION

Besides some inaccuracies of measurement, the concentrations in the five tests manifest visible dispersions due to the utilization of propellants with different chemical composition. If the error limit for the experimented propellant is of  $\pm 0.5\%$  in mass, giving an elemental composition variation of  $\pm 1.3$  [moli/kg], the scatter limit of measurements for the concentration of combustion products is:

$$\lambda = \pm 1\% \quad (3)$$

These tolerances may be considered as satisfactory for current technological measurements. The main enhancement of this kind of measurements is their repetition for a single propellant receipt and the determination of the water quantity present after burning.

Regarding the accuracy of determinations performed with this apparatus, considering that in the final report the processor of the chromatograph writes the numerical results of the analysis in three decimal digits, in terms of percentage, it is presumed that this is the limit of sensibility of the device. The apparent errors are still higher.

## 4. CONCLUSION OF ANALYSES

Considering the previous observations, the mean percent composition of the combustion products is recorded as valid, in the form given on the last line of table nr. 1. It is also admitted that other combustion products are not forming in concentrations higher than 1:10000 and consequently were not detected by the apparatus.

Comparing the measured values with the results of the thermochemical isobar calculation, it

was observed that they do not correspond, in an apparently surprising manner, neither to the chemical equilibrium at the temperature of nozzle exit, nor to the theoretical temperature from the thrust chamber (order of 2200°K), result that had produced a considerable concern at the first glance. Despite the accuracy of the method, it was roughly considered that the chemical equilibrium is either incorrectly modeled (improbable), or is strongly affected by unconsidered chemical processes. The latest hypothesis is supported by the conclusion that the measured composition is situated between the two limits of shifting equilibrium and frozen chemical equilibrium. Although in the case of the studied propellant (P-100) the performance computation in the two limit cases produce near to each other results, the review of computations through introduction of the effect of a "partial" chemical equilibrium would have considerably enhance the accuracy of predictions.

## 5. THERMAL FREEZING HYPOTHESIS

Well equipped with these results, repeatedly proven during successive experiments, let compare them with the values supplied by the extremal calculation. Provided that the water is excluded from calculations and the concentration of the four main gaseous species is referred to their sum, the image is the one given in the nearby table.

**Table 2.**

Mod	H <sub>2</sub>	N <sub>2</sub>	CO	CO <sub>2</sub>
Frozen equilibrium, 70 bar, 2250°K	21.206	13.927	55.033	9.833
Isochors measurements at 300°K	22.707	13.149	51.275	12.869
Shifting equilibrium, 1 bar, 900°K	32.474	11.935	33.010	22.581
<b>Elongation from 2500°K</b>	<b>13.2%</b>	<b>39.0%</b>	<b>16%</b>	<b>17.1%</b>

The situation recorded in the calorimeter after the combustion and isochore cooling does not coincide with none of the limit hypotheses, while it obviously stands somewhere between the two limits, nearer to the chemically frozen flow hypothesis. A simple, fast linear interpolation shows the degree of elongation (last line of the table 2) from the hypothesis of the chemically frozen equilibrium (first line) at 2250°K. A remarkably good coincidence of the degree of chemical freezing

is observed for the species H<sub>2</sub>, CO and CO<sub>2</sub>, in the limits of 13-17%. In the case of N<sub>2</sub> the approach of 39% is considerably weaker.

This apparently unfavorable result of the first direct confrontation of the thermochemical simulation with the chromatographic experiment had obviously required the development of a more in-depth investigation. At first hand the numerical simulation had to be adapted to the situation of the constant volume combustion, in order to remove potential differences that may appear in the two situations. It is well known for example that the maximal temperatures of the isobar and isochors combustion respectively, for the same propellant, are completely different.

## 6. ISOCHOR COMBUSTION

The details of the computational method elaborated by the author for the study of thermochemistry of isochore combustion are published [9], [11], [12]. The chemical equilibrium was numerically modeled on the basis of equilibrium constants, calculated by the author in previous works [8] and recently published in the collection [22]. We recollect that the main chemical reaction between the dominant species is the water-gas reaction,



the equilibrium of which had made, for that reason, the object of a number of detailed investigations [14], [15], for the first time presented at the conferences [10] and [13], but published for the first time here.

According to the methodology shown in Chapter 4 (Nondissociated composition at  $V, T=ct.$ ) from [9], the working equations obtained through the solution of the system are:

$$\begin{aligned}
 a &= K_{38} - 1, \\
 b &= K_{38}(B'_O + B'_H) + B'_C, \\
 c &= K_{38}B'_O B'_H, \\
 p_{H_2O} &= \frac{b - \sqrt{b^2 - 4ac}}{2a}, \\
 p_{CO_2} &= B'_O - p_{H_2O}, \\
 p_{CO} &= B'_H - p_{CO_2}, \\
 p_{H_2} &= B'_H - p_{H_2O}, \\
 p_{N_2} &= B_N / 2.
 \end{aligned} \quad (5)$$

The usual notations from [20] were used  $C_i = A_i \eta - B_i$  and  $\eta = p_G / n_G$ , respectively

$$\begin{aligned} C'_O &= C_O - C_C - C_{Ca}, \\ C'_C &= C_C - C'_O, \\ C'_H &= [C_H - (1 - \delta_2) C_{Ca}] / 2. \end{aligned} \quad (6)$$

The isochore character of the process is assumed by using the Clapeyron instead of the Dalton equation,

$$\eta = 0.083146 \frac{M_P}{V_I} \left[ \frac{g}{cm^3} \right] \cdot T [^\circ K], \quad (7)$$

where  $M_p$  denotes the propellant mass from the calorimeter and  $V_I$  the free volume of the calorimeter. In the simplified case of non-dissociated composition the total number of moles of combustion products for 1 kg of propellant is known from the beginning,

$$n_\Sigma = A_C + \frac{A_N + A_H}{2} + A_{Ca} = 43.13 \text{ [moles/kg]}, \quad (8)$$

At the loading already mentioned of the calorimeter of 6/282 [g/cm<sup>3</sup>], the results are those reproduced in the nearby table.

**Table 3.** Products of isochore combustion versus temperature

T, °K	H <sub>2</sub>	N <sub>2</sub>	CO	CO <sub>2</sub>	$p_G$ , atm
2500	20.507	13.917	55.848	9.727	190.0
2400	20.684	13.886	55.502	9.927	182.4
2300	20.882	13.852	55.115	10.152	174.8
2200	21.104	13.813	54.679	10.405	167.2
2100	21.355	13.769	54.186	10.690	159.6
2000	21.641	13.719	53.626	11.014	152.0
1900	21.967	13.662	52.988	11.384	144.4
1800	22.340	13.596	52.255	11.809	136.8
1700	22.771	13.521	51.410	12.298	129.2
1600	23.271	13.433	50.430	12.866	121.6
300	35.026	11.375	27.384	26.215	22.8
Test	22.707	13.149	51.275	12.869	-

At the end of gases cooling in the calorimeter the water condensation was neglected, while the composition was referred to the total pressure less the partial water pressure. The total pressure in the calorimeter in isochore conditions and without condensation is obviously directly proportional to the temperature,

$$p_\Sigma = \eta \cdot n_\Sigma = 3.586 \frac{M_P}{V_I} \cdot T \quad (9),$$

namely:  $p_\Sigma = 76.3 \frac{T}{1000}$ . The above results show that the idea of thermal freezing has a real base.

## 7. THERMAL FREEZING

Up to present the notion of chemical equilibrium freezing was more frequently related to the very fast flow through the reactive nozzles. It is fairly known for example the notion of "sudden freezing" (Bray 1961 [2]) in the sense that the available time of gases in the reactive nozzle is very small (order of milliseconds) and consequently the chemical reactions of re-association have no time to develop up to the end. Experiments had confirmed this possibility. The isochore cooling in calorimeters is performing incomparably slower than the flow of the same gases through nozzles either and at the first sight it was expected that the processes of chemical re-association to profit of sufficient time for their development up to the end. On the contrary, it was seen that the low temperatures from within the calorimeter, going up to the normal temperature, have the same "freezing" effect for the chemical reactions. In the calorimeter at 19°C gases were found with a chemical composition corresponding to a frozen equilibrium at a temperature of some 1700°K, regardless how long was the time interval waited from the moment of gas cooling stop and the process of chemical composition measurements. In other words the chemical composition freezing at the level of 1700°K is definitive. This is a striking observation with obvious consequences for the numerical simulations of combustion processes followed by subsequent relaxation of the reaction products in slow transforms.

## 8. THE FREEZING TEMPERATURE

If the presumed hypothesis of thermal freezing, by which we try to explain the conflict between the equilibrium calculations and the chromatographic analyses, is real, then a unique value of the freezing temperature must appear for all the four gases that enter the water-gas chemical reaction. The concentrations of the four gases involved, calculated at the same unique freezing temperature must correspond with the

measurements within the calorimeter. Because the water quantity could not have been measured, the reduction of the unique freezing temperature of the water-gas reaction was performed on the basis of the concentrations of H<sub>2</sub>, CO and CO<sub>2</sub> alone.

Comparing the values of equilibrium computed at different temperatures (table no. 3) with the measured values of the concentrations of the given species it is observed that an obvious concordance of the concentrations at 1671°K appears, with a scatter of  $\pm 36^\circ\text{K}$  only.

**Table 4.** Temperature of concordance equilibrium-measurements.

Chemical species	Temperature
Hydrogen, H <sub>2</sub>	1685°K
Carbon oxide, CO	1707°K
Carbon dioxide, CO <sub>2</sub>	1635°K
Mean and limit error	1671 $\pm$ 36°K

Very close values of the identification temperatures of numerical calculated concentrations with the measured values bring an indubitable confirmation of the thermal-freezing phenomenon. Subsequently using this hypothesis in numerical computations, in regard that the chemical equilibrium is only considered above this temperature, as for lower temperatures a blocked chemical composition be admitted, unusually exact values were obtained for the performances of propellants in the O-N-C-H system. A fair discussion with specialists of the ASTRIUM space center in Landpoldshausen, Germany, in the year 2001 had shown that in the case of the O-H system, largely used by ESA for space propulsion, no similar freezing temperature was observed (yet). Yet immediately after this discussion this research theme had appeared on the site of the center, offered to the doctoral students without any mention regarding the discussion with the present author.

## 9. CONCLUSION

The thermal-freezing hypothesis of chemical reactions of re-association during cooling or nozzle expansion after high temperature combustion was proved as plausible and especially useful in numerical simulations. It may be appreciated that this thermochemical process, yet unveiled upon our knowlege, has an important effect upon applications in the realm of thermochemistry. For the system O-N-C-H the freeezing temperature is unexpectedly high at

1400°K. For the three gaseous species involved in the investigation this value was found with an extremely high level of concordance, the limit of errors being of 36°K. There exist nevertheless a number of reasons why these temperatures do not completely coincide:

- reasons related to foundation of the hypothesis;
- influence of neglected chemical reactions;
- incertitude in composition of propellant samples;
- dispersion of thermochemical functions used;
- errors during chromatographic measurements.

The confrontation of the thermal-freezing hypothesis and of the results obtained on this basis with the sources of mentioned deviations is a problem of perspective yet.

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