# CHAPTER 4

## THERMODYNAMICAL CALCULATIONS

### 4.1. INTRODUCTION

This chapter is devoted to the theoretical calculation of the propellant performance, bases on the thermodynamical properties of potassiumnitrate and sugar. A comparison of these results with the measurements will give knowledge about the efficiencies at which the propellant is consumed and at which the gases are transformed into kinetic energy. With this approuch, one is also able to find the optimum mixture of potassiumnitrate and sugar and derive properties of the gases which are otherwise very difficult to measure.

### 4.2. THE COMBUSTION PRODUCTS

When sugar is oxidised, the following products can be generated:

- carbon-oxygen combinations: C ; CO ; $CO_2$
- hydrogen-oxygen combinations: H ; OH ; $H_2O$ ; $H_2$
- oxygen combinations: O ; $O_2$ ; $O_3$
- nitrogen-oxygen combinations: N ; NO ; $NO_2$ ; $N_2$
- potassiumcontaining product: KOH

In fact it is not straight foreward that KOH is produced. From the possible list of combinations, one can say that $KNH_2$ , KOCN ,KCN and $KHC_2$ have little possibility to be created, while $K_2O$ decomposes at 350°C. $K_2CO_3$ is the other possible candidate, but calculations have shown that in that case the results are too far away from what is measured.

The reaction equation can be written as follows:

$$\alpha KNO_3 + \beta C_{12}H_{22}O_{11} \longrightarrow a\,CO + b\,C + c\,CO_2 + d\,H_2O + e\,H_2 + f\,OH + g\,O + h\,O_2 + i\,O_3 + j\,N + k\,N_2 + l\,NO + o\,NO_2 + p\,KOH + q\,H$$

The amounts of these products are interrelated and depend upon the pressure and the temperature. Below 1600°C only CO ; $CO_2$; $H_2O$ ; $H_2$ ; $N_2$ and KOH seem to appear. The reaction equation than becomes:

$$\alpha KNO_3 + \beta C_{12}H_{22}O_{11} \longrightarrow a\,CO + c\,CO_2 + d\,H_2O + e\,H_2 + k\,N_2 + p\,KOH$$

Between these products there exists an equilibrium equation:

$$K_1 = \frac{N_{CO} \cdot N_{H_2O}}{N_{CO_2} \cdot N_{H_2}} \qquad CO_2 + H_2 \rightleftharpoons CO + H_2O$$

In this equation that is independent of pressure, N denotes the concentration of the product in the mixture.

## 4.3. THERMODYNAMICAL PROPERTIES

In this study the following thermodynamical characteristics are needed:

### 4.3.1. heat of formation at 298°K ($\Delta H_v^{298°K}$)

$CO$ : - 26.416 kcal/mole

$CO_2$: - 94.052

$H_2O$: - 57.7979

$H_2$ : 0

$N_2$ : 0

$KNO_3$: - 118.08

$KOH$ : - 102

$C_{12}H_{22}O_{11}$: - 414.8 (see 4.3.1.1.)

#### 4.3.1.1. calculation of the heat of formation of sugar.

In literature we didnit found the value for sugar. What we found is the change in enthalpy when sugar is completely oxidised . With this data we can calculate the heat of formation:

$$12\ C + 11/2\ O_2 + 11\ H_2 \xrightarrow{(1)} C_{12}H_{22}O_{11} \xrightarrow{(2)} 12\ CO_2 + 11\ H_2O$$

$$(3)$$

Road (3) gives:

$$12\Delta H_v^{CO_2} + 11\Delta H_v^{H_2O} = - 1764.4 \text{ kcal}$$

Road (2) gives: - 1349.6 kcal

Consequently the heat of formation is: $\Delta H_v^{sugar} = - 414.8$ kcal/mole

### 4.3.2. specific heat at constant pressure ($C_p$)

$CO_2$ : $10.34 + 0.00274\ T - 195500\ T^{-2}$ cal/mole

$CO$ : $6.6 + 0.00081\ T$

$H_2$ : $6.62 + 0.00081\ T$

$H_2O$ : $8.22 + 0.00015\ T + 0.00000134\ T^2$

KOH : 18

$N_2$ : $6.5 + 0.001\ T$

4.3.3. other thermodynamical data

| | Mol.W | dens. $g/cm^3$ | fusion cal/mole | Meltpt °C | Bpt °C | vaporis. cal/mole |
|---|---|---|---|---|---|---|
| $CO_2$ | 44.01 | – | – | – | – | – |
| CO | 28.01 | – | – | – | – | – |
| $H_2$ | 2.016 | – | – | – | – | – |
| $H_2O$ | 18 | – | – | – | – | – |
| KOH | 56.11 | 2.044 | 1980 | 360.4 | 1320 | 30 850 |
| $N_2$ | 28.02 | – | – | – | – | – |
| $KNO_3$ | 101.1 | 2.11 | – | 333 | 400* | – |
| sugar | 342.132 | 1.588 | – | 170* | 186* | – |

* decomposition

## 4.4. COMPOSITION OF THE COMBUSTION GAS

The composition of the gas will depend upon the composition of the propellant mixture and upon the combustion temperature.

A material balans for each element yields:

potassium : $\alpha = p$

nitrogen : $\alpha = 2\ k$

oxygen : $3\alpha + 11\beta = a + 2\ c + d + p$

carbon : $12\beta = a + c$

Hydrogen : $22\beta = 2\ d + 2\ e + p$

The concentration of each product can be written as:

$$N_{CO} = \frac{a}{N} \quad ; \quad N_{CO_2} = \frac{c}{N} \quad ; \quad N_{H_2O} = \frac{d}{N} \quad ; \quad N_{H_2} = \frac{e}{N}$$

With $N = a + d + e + c + k$

Since KOH is a liquid, its concentration in the gas phase can be neglected.

The equilibrium equation can now be written as:

$$K_1 = \frac{[a][d]}{[c][e]}$$

We have now at our disposal 6 equations with 6 unknowns (all in function of $\alpha$ and $\beta$ ).

We can now write:

$a = 12\beta - c$
$d = 2\alpha - \beta - c$
$e = 12\beta - 5/2\alpha + c$

If we put:

$12\beta = \lambda$
$2\alpha - \beta = \eta$
$12\beta - 2.5\alpha = \delta$

the equations become:

$a = \lambda - c$
$d = \eta - c$
$e = \delta + c$

$$K_1 = \frac{(\lambda - c)(\eta - c)}{(\delta + c)c} \qquad \text{with } \log K_1 = 0.16 - \frac{222}{T°K}$$

From this we can solve c ( the $CO_2$ concentration)as a function of the temperature and as a function of the composition of the propellant.

$$CO_2 : c = \frac{-(K_1\delta + \lambda + \eta) + \sqrt{(K_1\delta + \lambda + \eta)^2 + (K_1 - 1)\lambda\eta 4}}{2(K_1 - 1)}$$

$H_2$ : $e = \delta + c$
$CO$ : $a = \lambda - c$
$H_2O$ : $d = \eta - c$
$N_2$ : $k = \frac{\alpha}{2}$
$KOH$ : $p = \alpha$

At temperatures aboven 1600°C these equations no longer hold and significant errors can be made, since other compositions can be formed and since the composition is no longer pressure independent.

## 4.5. THE HEAT OF REACTION AT 298°K ( $H_R$)

The heat of reaction depends upon the composition of the propellant and of the composition of the gas at equilibriumtemperature T. The heat of reaction is the sum of the heat of formation for any product, taking into account its amount in the gas when equilibrium is reached. It is the heat that is delivered by the reaction of $\alpha$ $KNO_3$ with $\beta$ sugar to CO, $CO_2$ ... at 25°C ( 298°K).

$$H_R = a\Delta H_v^{CO} + d\Delta H_v^{H_2O} + e\Delta H_v^{H_2} + k\Delta H_v^{N_2} + c\Delta H_v^{CO_2} + p\Delta H_v^{KOH} - \alpha\Delta H_v^{KNO_3} - \beta\Delta H_v^{sugar}$$

## 4.6. THE REACTION TEMPERATURE ($T_o$°K)

The heat of reaction $H_R$ is used to heat up the combustion products to the reaction temperature $T_o$. For this we need to express the heat content or enthalpy of the reaction products as a function of temperature.

$$H = \int_{298}^{T_o} \left[a\,C_{p\,CO} + d\,C_{p\,H_2O} + e\,C_{p\,H_2} + k\,C_{p\,N_2} + c\,C_{p\,CO_2}\right] dT + p\,H_{KOH}^{T}$$

The enthalpy of KOH can be written as:

$$H_{KOH}^{T} = \int_{298}^{633.4} C_{pKOH(s)}\,dT + 1980 + \int_{633.4}^{1593} C_{p\,KOH(l)}\,dT + 30\,850 + \int_{1593}^{T_o} C_{pKOH(g)}\,dT$$

(s),(l) and (g) stand for the solid,liquid and gasphase.

The reaction temperature $T_o$ will be found by simultaneously solving the following expressions:

- a , d , c , ... in function of T
- $H_R$ in function of T
- H in function of T

## 4.7. THE MEAN SPECIFIC HEAT RATIO ( $\gamma$ )

By definition $\gamma = \frac{Cp}{Cv}$ , or for ideal gases: $\gamma = \frac{Cp}{Cp - R}$

R being the ideal gas constant.

Knowing the composition of the gas:a,c,d,..., at the combustion-temperature, one can calculate the mean specific heat ratio:

$$\gamma = \frac{a\,C_{pCO} + c\,C_{pCO_2} + d\,C_{pH_2O} + e\,C_{pH_2} + k\,C_{pN_2} + p\,C_{pKOH}}{a\,C_{pCO} + \ldots p\,C_{pKOH} - R\,(a + c + d + e + k + p)}$$

## 4.8. RESULTS

The results of the calculations are given in the next tabel and in the following figures. It shows for instance that the exhaust velocity reaches a maximum around 60% $KNO_3$. This is partly due to the fact that from that composition on the combustion temperature remains stable since a lot of energy is needed to evaporate KOH. For the calculation of the characteristic velocity the so called frozen flow theory was used. This means that all the characteristics of the gas remain constant during expansion

RESULTS OF THE THERMODYNAMICAL CALCULATIONS

| % $KNO_3$ | 40 | 50 | 55 | 60 | 65 | 68 | 69 | 70 | 71 | 72 | 73 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T_o$ °K | 690 | 1120 | 1340 | 1560 | 1590 | 1590 | 1590 | 1590 | 1590 | 1590 | 1600 |
| H kcal/100g | 15,6 | 30,9 | 38,7 | 46,6 | 54,6 | 59,5 | 61,1 | 62,8 | 64,4 | 66,1 | 67,8 |
| mol/100g: | | | | | | | | | | | |
| CO | 1,7197 | 1,2656 | 1,0279 | 0,7812 | 0,5179 | 0,3526 | 0,2959 | 0,2384 | 0,1797 | 0,1199 | 0,0587 |
| $CO_2$ | 0,3848 | 0,4881 | 0,5504 | 0,6218 | 0,7097 | 0,7698 | 0,7914 | 0,8139 | 0,8374 | 0,8622 | 0,8883 |
| $H_2O$ | 0,2311 | 0,3549 | 0,4061 | 0,4483 | 0,4738 | 0,4819 | 0,4830 | 0,4832 | 0,4824 | 0,4804 | 0,4770 |
| $H_2$ | 1,5001 | 1,0054 | 0,7686 | 0,5410 | 0,3300 | 0,2107 | 0,1724 | 0,1351 | 0,0988 | 0,0638 | 0,0300 |
| $N_2$ | 0,1978 | 0,2473 | 0,2720 | 0,2968 | 0,3215 | 0,3363 | 0,3413 | 0,3462 | 0,3512 | 0,3561 | 0,3611 |
| KOH | 0,3956 | 0,4946 | 0,5440 | 0,5935 | 0,6429 | 0,6726 | 0,6825 | 0,6924 | 0,7023 | 0,7122 | 0,7221 |
| M | 22,578 | 25,934 | 28,018 | 30,464 | 33,380 | 35,412 | 36,147 | 36,911 | 37,710 | 38,542 | 39,414 |
| $\gamma$ | 1,3452 | 1,2978 | 1,2720 | 1,2447 | 1,2258 | 1,2143 | 1,2102 | 1,2060 | 1,2017 | 1,1972 | 1,1920 |
| $u_{th}$ m/s | 1143 | 1608 | 1800 | 1975 | 2138 | 2231 | 2261 | 2292 | 2321 | 2352 | 2382 |
| $C^*$ | 745 | 897 | 951 | 991 | 961 | 937 | 928 | 920 | 911 | 902 | 897 |
| $\theta_{50}$ | 0,7960 | 0,7697 | 0,7529 | 0,7325 | 0,7166 | 0,7061 | 0,7022 | 0,6981 | 0,6938 | 0,6892 | 0,6837 |
| $\theta_{25}$ | 0,7498 | 0,7227 | 0,7054 | 0,6848 | 0,6688 | 0,6583 | 0,6544 | 0,6503 | 0,6461 | 0,6415 | 0,6361 |

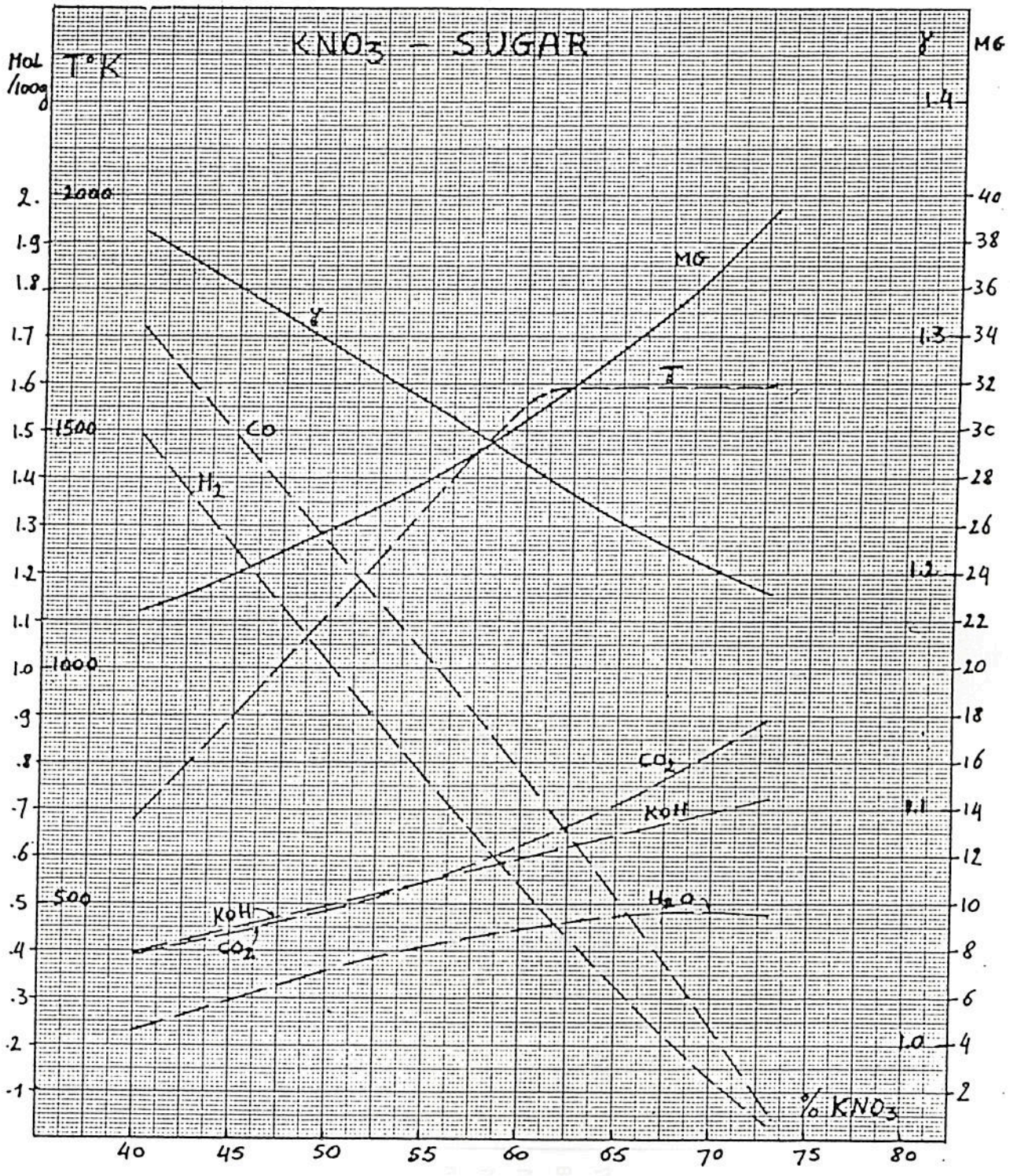


Fig.4.1. Results from the thermodynamical calculations.

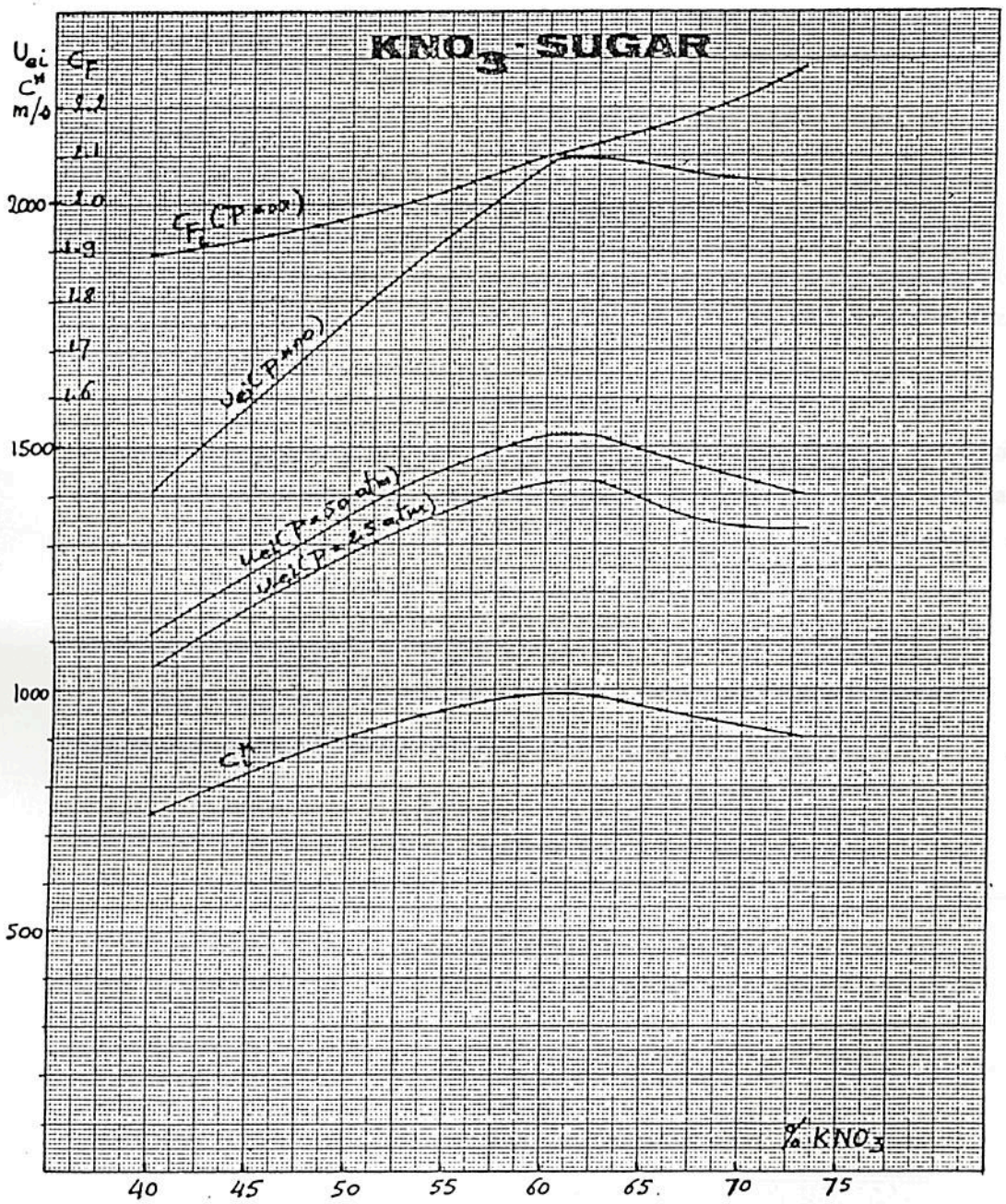


Fig.4.2. Characteristics of the propellant under ideal circumstances.