EFFECT OF DISSOCIATION ON SPARK IGNITION ENGINES GAS COMPOSITION

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Received July 4, 1985
Presented by Prof. Dr. E. Pásztor

Abstract

The influence of fuel-air ratio, pressure and temperature on the combustion gas composition have been investigated. The paper presents a method for the calculation of the combustion gases mole fractions at different conditions. This helps to a great extent taking the effect of dissociation in the simulation of spark ignition engines.

Introduction

In spark ignition engines it is found that the temperature changes are somewhat different to those predicted by the methods which assume that the combustion reaction proceeds from the initial reactants to the final products of combustion. This is obviously due to dissociation.

For the correct mixture of a hydrocarbon C_nH_m and air the overall chemical reaction can be expressed as

$$C_nH_m + \left(n + \frac{m}{4}\right) O_2 + 3.762 \left(n + \frac{m}{4}\right) N_2$$

$$\longrightarrow n\,CO_2 + m\,H_2O + 3.762 \left(n + \frac{m}{4}\right) N_2$$

At elevated temperature, higher than 2000 K, in the burnt zone the carbon dioxide CO_2 and water vapour H_2O dissociate to form carbon monoxide CO, oxygen O_2, and hydrogen H_2. Furthermore, the molecular oxygen O_2, hydrogen H_2 and nitrogen N_2 dissociate to form atomic oxygen O, hydrogen H and nitrogen N. In addition there will be equilibrium concentration of hydroxyl OH and nitrous oxide NO. Time needed for NO_2 formation is short compared to the time needed for NO[1]**, so the rate of formation of NO is more important than the rate of NO_2. Thus in the burnt zone we have the following species:

$$CO_2, CO, H_2O, OH, H_2, O_2, N_2, NO, H, O \text{ and } N.$$

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** Number in parentheses designate references at end of paper.

The concentration of these various species depends on fuel-air ratio, the pressure and temperature.

The concentrations can be calculated for a certain fuel at different conditions if we can estimate the mechanism of the dissociation process.

Although the combustion in the spark ignition engines occurs without equilibrium we have to assume equilibrium for very short intervals for the calculations of the combustion process. This work is based on the work of Vickland et al. [3] with wide treatment of the problem.

For any system of reactants containing compounds of carbon, hydrogen, oxygen and nitrogen may be represented by the chemical formula $C_wH_vO_yN_z$. The reaction can be written as

$$\begin{aligned} C_wH_vO_yN_z \longrightarrow\ & n_1\,H_2O + n_2\,H_2 + n_3\,OH + n_4\,H + n_5\,N_2 + \\ & n_6\,NO + n_7\,N + n_8\,CO_2 + n_9\,CO + \\ & n_{10}\,O_2 + n_{11}\,O. \end{aligned}$$

If the total quantity of products is n_t. Dividing the above equation by n_t and replacing n/n_t by the mole fraction x, we can write,

$$\begin{aligned} 1/n_t\, C_wH_vO_yN_z \longrightarrow\ & x_{H_2O} + x_{H_2} + x_{OH} + x_H + x_{N_2} + x_{NO} + \\ & x_N + x_{CO_2} + x_{CO} + x_{O_2} + x_O \end{aligned}$$

From which we can write,

$$S \cdot w = x_{CO_2} + x_{CO} \tag{1}$$

$$S \cdot v = 2x_{H_2O} + 2x_{H_2} + x_{OH} + x_H \tag{2}$$

$$\begin{aligned} S \cdot y = x_{H_2O} + x_{OH} + 2x_{CO_2} + x_{CO} + \\ x_{NO} + x_O + 2x_{O_2} \end{aligned} \tag{3}$$

$$S \cdot z = 2x_{N_2} + x_{NO} + x_N \tag{4}$$

$$\Sigma x = 1 \tag{5}$$

The following dissociation reactions are assumed,

$$1/2\ H_2 \rightleftharpoons H$$

$$1/2\ O_2 \rightleftharpoons O$$

$$1/2\ N_2 \rightleftharpoons N$$

$$2\ H_2O \rightleftharpoons 2H_2 + O_2$$

$$H_2O \rightleftharpoons OH + 1/2\ H_2$$

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$

$$H_2O + 1/2\ N_2 \rightleftharpoons H_2 + NO$$

The reaction constants of these reactions can be written in terms of total pressure and the mole fraction of the products as follows, respectively.

$$K_{p1} = x_H \sqrt{P}/\sqrt{x_{H_2}}$$
$$K_{p2} = x_0 \sqrt{P}/\sqrt{x_{O_2}}$$
$$K_{p3} = x_N \sqrt{P}/\sqrt{x_{N_2}}$$
$$K_{p4} = x_{H_2} \cdot x_{O_2} \cdot P/x^2_{H_2O}.$$
$$K_{p5} = x_{OH} \cdot \sqrt{x_{H_2} P}/x_{H_2O}$$
$$K_{p6} = x_{H_2O} \cdot x_{CO}/x_{H_2} \cdot x_{CO_2}$$
$$K_{p7} = x_{H_2} \cdot x_{NO} \cdot \sqrt{P}/x_{H_2O} \cdot \sqrt{x_{N_2}}$$

The present work is divided into two parts. The first one is concerned with the equilibrium constants calculation and the second with the equilibrium concentrations.

A: *Equilibrium constants calculation*

The equilibrium constant is related to the specific Gibbs function and the heat of reaction at certain temperature T as follows:

$$\ln K_p = -\left[\sum\left(\frac{n \cdot g(T)}{R \cdot T}\right)_P - \sum\left(\frac{n \cdot g(T)}{R \cdot T}\right)_R\right] - \frac{\Delta H}{R \cdot T}$$

The heat of reaction ΔH_0 can be calculated for each reaction using the relation,

$$\Delta H_0 = \Sigma n\, h_{0P} - \Sigma n\, h_{0R}$$

The relative Gibbs function for each constituent can be calculated using the method of Benson [1, 2] as follows.

The specific enthalpy h for a substance can be written in a polynomial form as a function of temperature as follows.

$$\frac{h(T)}{RT} = a + b\,T + c\,T^2 + d\,T^3 + e\,T^4$$

The relative specific Gibbs function can be related to the same polynomial coefficient as follows.

$$\frac{g(T)}{RT} = a(1 - \ln T) - b\,T - \frac{c}{2}\,T^2 - \frac{d}{3}T^3 - \frac{e'}{4}T^4 - k$$

Where k is a constant can be calculated using any tabulated data for the Gibbs function. Knowing the heat of reaction at absolute zero and stoichometric coefficient, equilibrium constants can be calculated at different conditions.

B: *Equilibrium concentration of combustion gases*

As mentioned in Vickland paper [3], two independent variables are identified. The first is the ratio of water vapour mole fraction by the hydrogen mole fraction. The second is the reciprocal of the total number of moles of the products.

$$D = x_{H_2O}/x_{H_2}$$

Then,

$$x_H = K_{p1} \sqrt{x_{H_2}}/\sqrt{P} \tag{6}$$

$$x_O = K_{p2} \sqrt{x_{O_2}}/\sqrt{P} \tag{7}$$

$$x_N = K_{p3} \sqrt{x_{N_2}}/\sqrt{P} \tag{8}$$

$$x_{O_2} = K_{p4} \cdot D^2/P \tag{9}$$

$$x_{OH} = K_{p5}\, D \sqrt{x_{H_2}}/\sqrt{P} \tag{10}$$

$$x_{CO} = K_{p6}\, x_{CO_2}/P \tag{11}$$

$$x_{NO} = K_{p7}\, D \sqrt{x_{N_2}}/\sqrt{P} \tag{12}$$

$$x_{CO_2} = S\, D\, w/(D + K_{p6}) \tag{13}$$

$$x_{H_2} = \frac{1}{16}\left[-\left(\frac{Kp_5D + Kp_1}{(D+1)\sqrt{P}}\right) + \sqrt{\left(\frac{Kp_5D + Kp_1}{(D+1)\sqrt{P}}\right)^2 + \frac{8Sv}{(D+1)}}\right]^2 \tag{14}$$

$$x_{N_2} = \frac{1}{16}\left[-\left(\frac{Kp_7D + Kp_3}{\sqrt{P}}\right) + \sqrt{\left(\frac{Kp_7D + Kp_3}{\sqrt{P}}\right) + 8Sz}\right]^2 \tag{15}$$

The consists of the above-mentioned equations consists of the initial estimation of S and D, the computation of the composition, a test for convergence and the readjustment of S and D values for higher accuracy.

Octane C_8H_{18} was chosen and calculations were made for equivalence ratios Φ of 0.8, 1.0, 1.2. Temperature range was from 1400 to 3400 K at pressure values of 1, 10, 20, 40 and 80 bar. Results for C_8H_{18} are shown in figures from (1) to (11). All these results are calculated with accuracy lower than 1%. For the sake of easy plotting of the results values of normal logarithm of mole fraction are plotted against the temperature values.

Method of solution

1— Estimate the values of S and D.

2— Calculate the mole fractions of different gases from equations from (6) to (15).

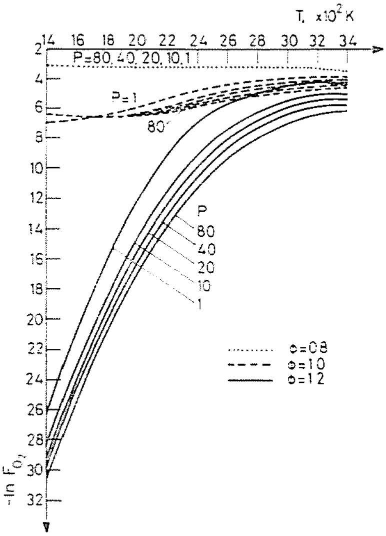

Fig. 1. Mole fraction of molecular oxygen O_2

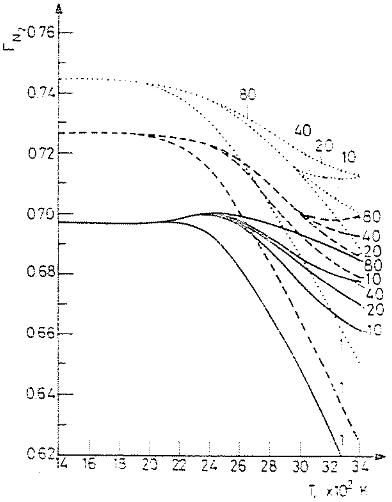

Fig. 2. Mole fraction of molecular nitrogen N_2

3— Test the accuracy of equations (3) and (5).

4— Readjust the values of S and D to obtain reasonable values of accuracy.

The estimation of S and D differs from case to case depending on the temperature, the pressure and the equivalence ratio. The values of S can be assumed using the more stable combustion products (CO_2, H_2O and N_2 are considered only as the combustion products) to calculate the number of mole of the combustion products, S is the reciprocal of the total number of moles.

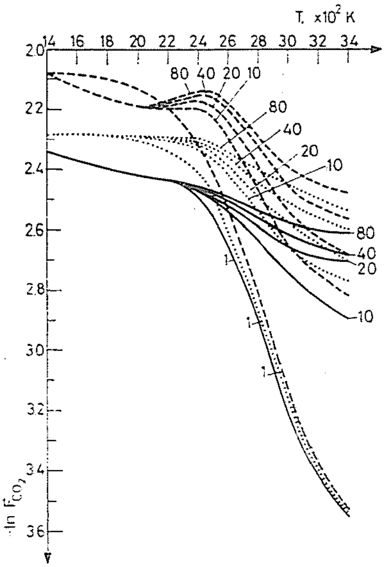

Fig. 3. Mole fraction of carbon dioxide CO_2

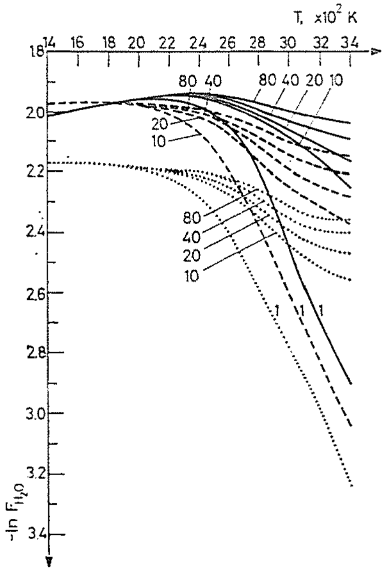

Fig. 4. Mole fraction of water vapour H_2O

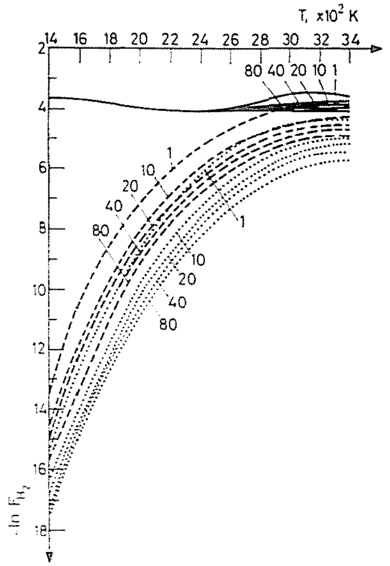

Fig. 5. Mole fraction of molecular hydrogen H_2

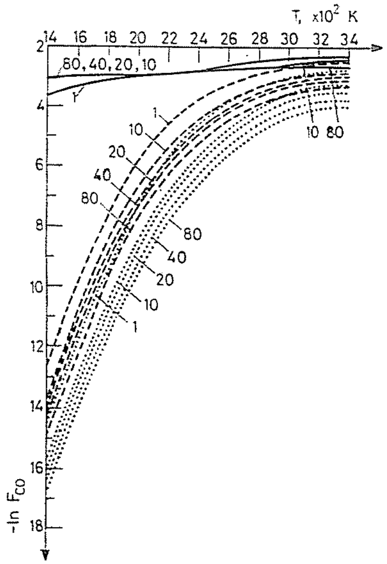

Fig. 6. Mole fraction of carbon monoxide CO

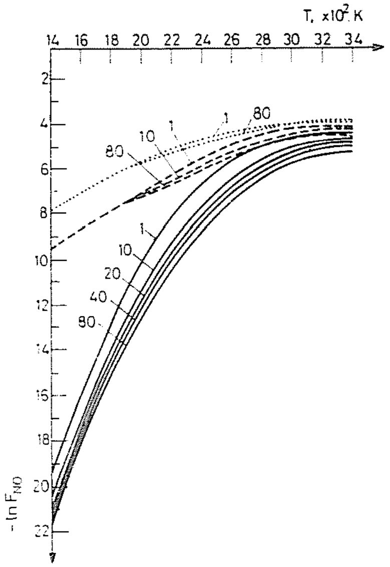

Fig. 7. Mole fraction of nitrous oxide NO

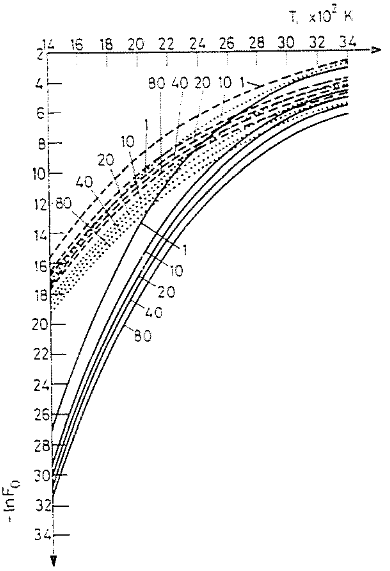

Fig. 8. Mole fraction of atomic oxygen O

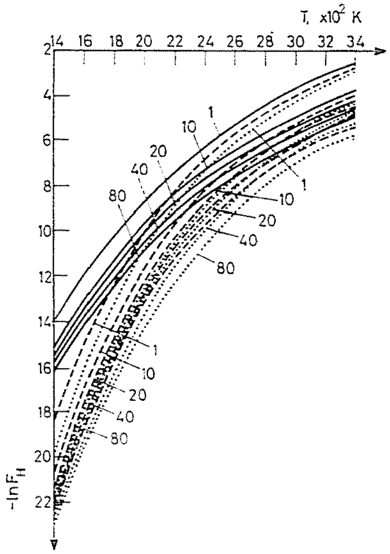

Fig. 9. Mole fraction of atomic hydrogen H

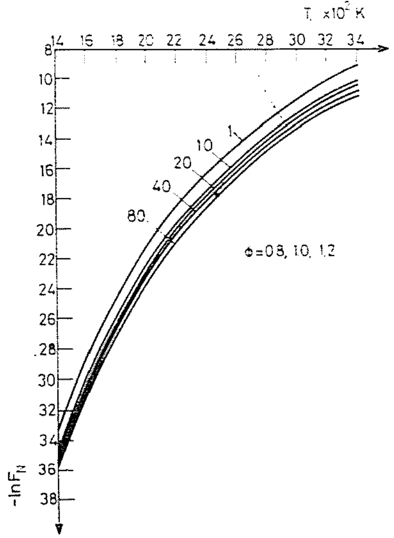

Fig. 10. Mole fraction of atomic nitrogen N

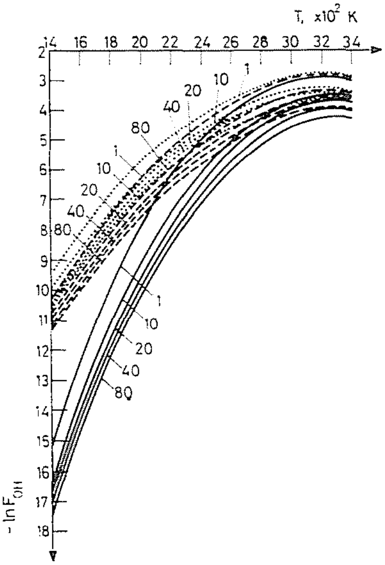

Fig. 11. Mole fraction of hydroxyl OH

To estimate the values of D it is recommended to make a rough calculation with accuracy about 5% to calculate the value of D giving at first positive error and then negative error. Final adjustment of D is made by interpolation. Table (1) shows how much the value of D differs from case to case.

Values of variable D for C_8H_{18}.

Table 1

T K		1400	2000	2400	3000	3400
P bar	Φ					
	1.2	4.979	7.5	8.499	7.892	7.482
80	1.0	0.8 E06	1100	125.3	20.96	15.79
	0.8	0.4 E07	5800	440.9	43.13	29.56
	1.2	4.979	7.499	8.467	7.405	6.652
40	1.0	0.57 E06	811.1	96.62	16.30	12.26
	0.8	0.29 E07	4095	312.2	30.96	21.28
	1.2	4.4979	7.497	8.420	6.605	5.703
20	1.0	0.4 E06	590.4	74.71	12.71	9.444
	0.8	0.2 E07	2892	220.6	22.28	15.21
	1.2	4.979	7.495	8.349	5.728	4.756
10	1.0	0.28 E06	432.3	58.27	9.857	7.212
	0.8	0.14 E07	2045	156.4	16.11	10.83
	1.2	4.979	7.493	8.095	2.901	2.054
1	1.0	0.89 E05	163.5	24.34	3.916	2.552
	0.8	0.46 E06	652.1	50.61	5.371	3.280

Accuracy of results

The accuracy of results depends on the accuracy to which the equations (5) and (7) are satisfied. Vickland [3] stated that results obtained with 1% accuracy in equations (5) and (7) are reliable to within 1% of the total composition for the larger constituents and to within 2% and 3% of each product composition for the smaller constituents.

Experience has shown that if accuracy was shifted to 2% the mole fraction of N_2, CO_2, H_2O and N are not effected so much, but values of mole fractions of O_2, H_2, CO, NO, O, OH and H are seriously effected specially at reduced temperatures 1400 K and chemically correct mixture ($\Phi = 1$), e.g. the mole fraction of O_2 in this case is doubled when the accuracy is shifted from 1% to 2%.

Effect of temperature, pressure or equivalence ratio is easily shown for the eleven gases in Figs from (1) to (11). It is easy to recognize the regions of higher or lower effect for each variable.

Notation

Symbols:

a, b, c, d, e and k are the polynomial coefficients.

x	Mole fraction for different gases.
$g(T)$	Specific Gibbs function at temperature T K.
h	Specific enthalpy.
h_0	Specific enthalpy at absolute zero.
ΔH_0	Heat of reaction at absolute zero.
K_p	Equilibrium constant.
n	Quantity.
P	Pressure .
R	Molar universal gas constant.
S	$1/\Sigma n$.
Φ	Equivalence ratio.

Subscripts:

R	For reactants.
P	For products.

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3. Vickland, C. W. et al.: "A consideration of the high temperature thermodynamics of internal combustion engines". SAE Trans. *170*, 785 1962.

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