

# THERMODYNAMIC ASPECTS OF PROCESSES TAKING PLACE IN A DISCHARGE GAP OF AN OZONIZER

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## 1. Introduction

Energy utilization in ozonizers in the course of ozone synthesis from atmospheric air usually does not exceed 10%. It is a rather small and not a satisfactory efficiency especially when the process is applied on a larger scale because it yields economic problems then. Hence it seems to be important to find ways to improve the efficiency of the process.

An indepth analysis of ozone generation process in silent discharges in an ozonizer requires thorough consideration of thermodynamic and thermal phenomena accompanying the process. It is very important since the rate of ozone generation essentially depends on the thermal state of substrate gas and most of discharge energy is changed into heat in internal sources which can significantly influence the mentioned thermal state.

## 2. Problem and Objectives

Discharge gap of an ozonizer forms a specific plasma chemical reactor (fig.1) [3,5] where chemical and physical processes occur in substrate gas (air, oxygen) under the influence of silent electrical discharges. Silent discharges form in electrical field of sufficiently high intensity surrounding the reaction zone.

Discharges cause ionization of air components including oxygen that is preceded by dissipation of molecular oxygen ( $O_2$ ) into atoms followed by synthesis reactions including ozone ( $O_3$ ) synthesis reaction.

Discharge energy in its indispensable part is directly utilized in the ozone synthesis reaction. The remaining part of energy (much bigger than the first one) is changed into heat by the dissipation process hence energy efficiency of the ozone synthesis process is much less than unity.

Heat released from internal sources distributed in gas flowing through the plasma chemical reactor that is enclosed with adiabatic walls when no mechanical work were possible would increase (according to the 1st principle of thermodynamics) internal energy of gas particles which would be accompanied by significant rise of gas temperature.

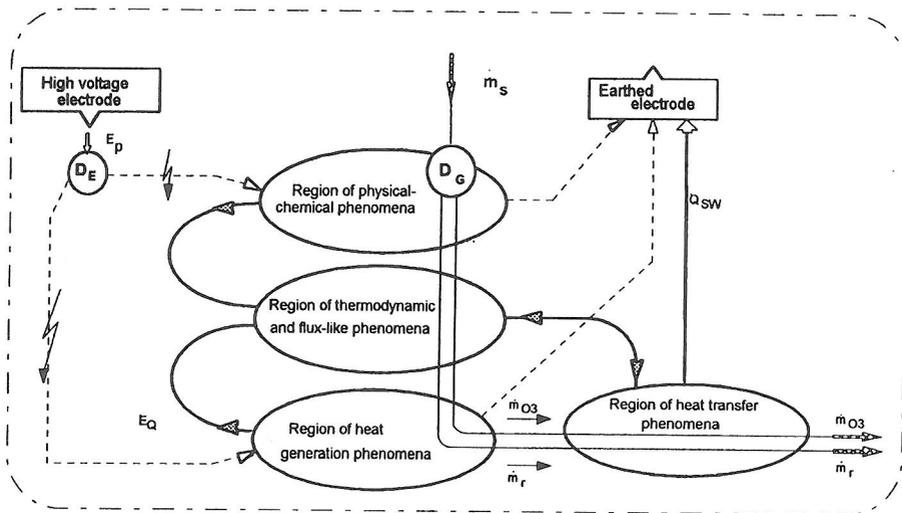


Fig. 1. Arrangement of areas of the most significant phenomena accompanying the ozone synthesis process in ozonizer's discharge gap.

Experimental results show that elevated temperature of substrate gas or temperature rise in reaction zone result in decrease of the zone synthesis reaction advancement. Hence it is not only that an adequate thermal state of substrate gas should be maintained but also the reaction zone should be cooled intensively.

The main objective of the presented research work is thermodynamic analysis of energy processes accompanying ozone synthesis reaction for to trace the mechanism of thermal and calorific effects on the ozone generation process. First of all it requires a correct and precise formulation of the analysed thermodynamic problem and a thermokinetic one closely connected with it.

### 3. Identification of thermodynamic-thermal phenomena occurring in the reaction zone

Ozone synthesis is accompanied by a series of inter-permeating phenomena that makes an analysis of the physical-chemical and energy-conversion aspects of the process rather difficult. The most important regions of the phenomena are the following ones:

- phenomena connected with physical-chemical changes,
- phenomena accompanying the thermodynamic process,
- phenomena connected with heat transfer.

The accepted system of grouping the phenomena has been introduced for to make possible separate modelling of thermodynamic, physical-chemical, and thermokinetic processes. The model of the thermodynamic process is related to physical-chemical processes by the reaction advancement and to the model of heat transfer by the quantity of energy exchanged with the environment in the form of heat.

The discharge gap of a reactor is thus a thermodynamic system enclosed with walls of properties presented in the fig.2.

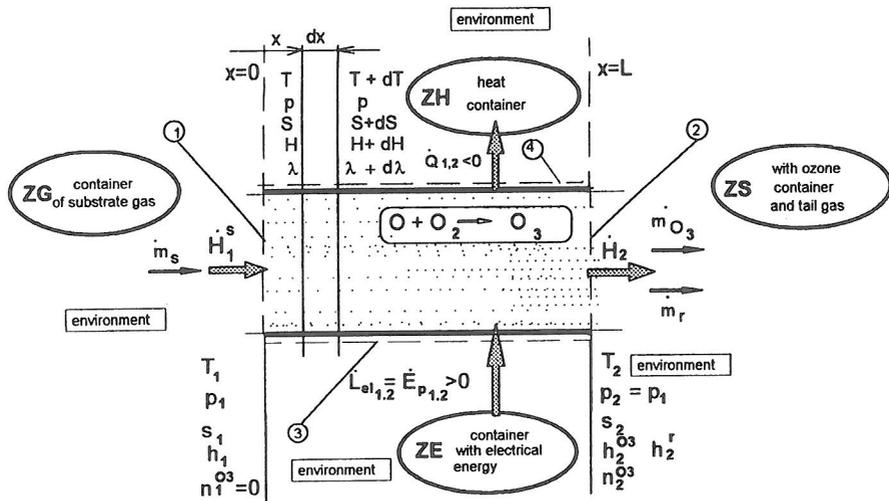


Fig. 2. Diagram of the thermodynamic system of a discharge gap in the considered plasma chemical reactor

1, 2 - walls (abstract ones) let through substance and energy flow

3,4 - walls blocking substance flow and mechanical work exchange with the environment  
 wall 3 - adiabatic one, wall 4 - lets heat transfer through, walls 3 and 4 - considerable difference of potentials is applied

The system cooperates with containers in the environment with the following contents: substrate gas -ZG, ozone and tail gas -ZS , electrical energy- ZE, heat - ZH.

In the gap chemical change of molecular oxygen (e.g. from air) into ozone takes place and it is coupled with thermodynamic process.

Taking into consideration inference based on research [2,3,4] and big concentration of gas molecules it was decided to apply phenomenological approach (substrate gas and ozone are treated as viscous and ideal in the thermal sense).

The ozonization process in the reactor's discharge gap is considered to be an irreversible open thermodynamic process that proceeds without any possibility of performing mechanical work outside but work is supplied in the way of electrical effect in gas (silent discharges) with simultaneous heat abstraction to the environment (coolant).

The course and the direction of the process in the system are driven by forces presented in the diagram 3a.

The gas motion process is a laminar flow of viscous gas in a channel forced by external forcing through and the thermal motion process consists in heat penetration

into gas whose flow is forced by internal heat sources to the coolant through the barrier separating both liquids.

Fig. 3b shows the way the processes are interrelated.

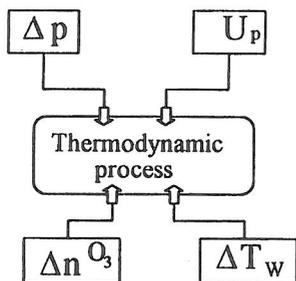


Fig. 3a. Driving forces of the process in the ozonizer's discharge gap

$\Delta p$  - pressure difference between inlet's and outlet's sections

$U_p$  - potential difference in electrostatic field

$\Delta n^{O_3}$  - concentration difference of the ozone synthesis reaction products

$\Delta T_W$  - temperature difference between substrate gas and coolant

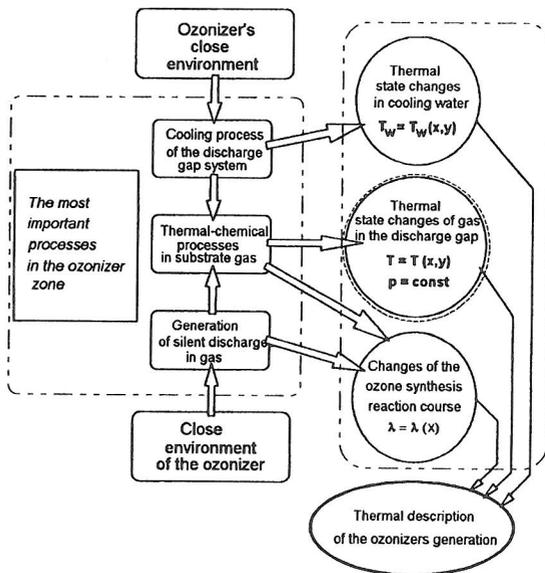


Fig. 3b. Diagram of interrelations of processes occurring in the reaction gap from the viewpoint of thermal-calorific description of an ozonizer.

Formal description of the process referred to the infinitely small change of thermal and calorific states and infinitely small advancement of the reaction and unit quantity of the substance is the following:

$$d\dot{S}(T, \lambda_{O_3}) - \frac{d\dot{H}(T, \lambda_{O_3}) - d\dot{L}_{el}}{T} > 0 \quad \text{at } p = \text{const} \quad (1)$$

$$d\dot{H} + d\dot{Q}_\tau = d\dot{Q} + d\dot{L}_{el} \quad (2)$$

$$d\dot{S} = \left( \frac{\partial \dot{S}}{\partial T} \right)_{p, \lambda_{O_3}} \cdot dT + \left( \frac{\partial \dot{S}}{\partial \lambda_{O_3}} \right)_{p, T} \cdot d\lambda_{O_3}; \quad d\dot{H} = \left( \frac{\partial \dot{H}}{\partial T} \right)_{p, \lambda_{O_3}} \cdot dT + \left( \frac{\partial \dot{H}}{\partial \lambda_{O_3}} \right)_{p, T} \cdot d\lambda_{O_3} \quad (3a, b)$$

$$\dot{H} = \dot{H}^{O_3}(T, \lambda_{O_3}) + \dot{H}^I(T, \lambda_{O_3}) \quad \text{and } x = 0; \quad \dot{H} = \dot{H}_1^S; \quad x = L; \quad \dot{H} = \dot{H}_2 = \dot{H}_2^{O_3} + \dot{H}_2^I \quad (4)$$

$$\text{where: } d\dot{L}_{el} = dE_p; \quad d\lambda_{O_3} = \frac{dn_{O_3}}{v_{O_3}} \quad (5)$$

Specific density of energy generated in thermal way in individual sections of the reaction zone is the measure of action of internal heat sources in the flowing gas. The quantity is formally described by the following dependence:

$$q_v(x_i, \tau) = \frac{\partial \dot{Q}_V}{\partial V} = \frac{\partial E_Q}{\partial V} = \text{const} \quad i = 1, 2, 3 \quad (6)$$

Thermal model of a reactor was elaborated on the basis of the analysis of the operation of laboratory and industrial ozonizers [3,5] with some indispensable simplifications introduced [1,2]. The described model is a simplified Fourier-Kirchoff equation in the following dimensionless form:

$$y(1-y) \frac{\partial \Theta}{\partial \zeta_1} = \frac{\partial^2 \Theta}{\partial y_1^2} \quad (7)$$

with boundary conditions:

$$\Theta(\zeta_1 = 0, y) = 1 \quad \frac{\partial \Theta}{\partial y}(\zeta_1 = 0) = 0 \quad \frac{\partial \Theta}{\partial y}(\zeta_1, 1) + k \cdot \Theta(\zeta_1, 1) = D \quad (8 \text{ a, b, c})$$

where:  $\Theta = \frac{T_{KS} - T}{T_{KS} - T_{KP}}$ ;  $T = t - \frac{1}{2} q_v \cdot y^2$ ;  $\zeta_1 = \frac{x - x_H}{B \cdot d}$ ;  $y_1 = \frac{y}{d}$ ;  
 $D = \frac{1}{2} q_v \frac{d^2}{(T_{KS} - T_{PS}) \cdot \lambda}$ ;  $B = 6 \cdot Pr \cdot Re$ ;  $x_H = d \frac{Re}{20}$

The equation (7) together with the boundary conditions (8) describes the phenomenon of heat motion in the discharge gap of the considered ozonizer (modified Graetz problem).

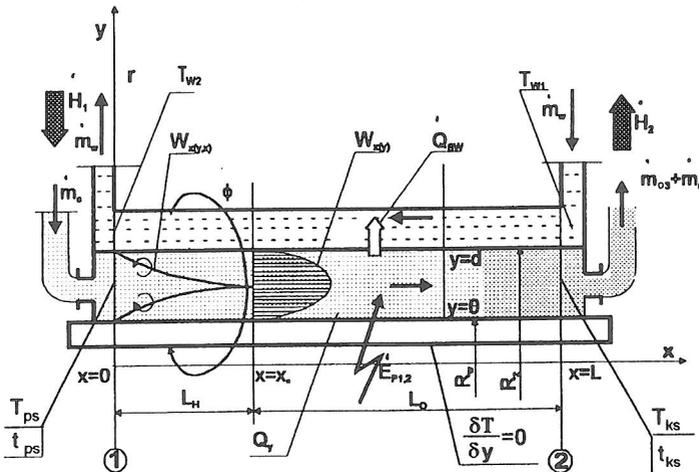


Fig. 4. Diagram of heat motion in the discharge gap of a plasma chemical reactor including the geometry and the flow system of the gas and coolant.

#### 4. Conclusions

The paper presents an attempt to formulate initial description of a thermodynamic process accompanying the ozone synthesis reaction in a plasma chemical reactor taking into account the direction of the course the process.

The discussed process was considered in relation to a thermokinetic process of heat abstraction from the reaction zone. Differential equation systems together with boundary conditions were obtained and they can form a basis for further research work and can be applied to the analysis of thermodynamic-thermal phenomena effect on energy efficiency of the ozone generation process.

#### 5. References

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- [4] Ozonek J., Fijałkowski S., and Pollo I., Analysis of energy losses in an industrial ozone generating instalation, Proceedings of the 11th Ozone World Congress, San Francisco (1993), S-8-6679.
- [5] Schmidt-Szałowski K., Catalic activity of silica in ozone formation in electrical discharges, Plasma Chem. Plasma Proces. 9, 1989, 234-254.

#### List of more important symbols

$\dot{c}_p$  - specific heat at constant pressure, J/kg·K,

$d$  - discharge gap, mm,

$\dot{E}_p$  - energy, J/s

$\dot{H}$  - enthalpy, J/s,

$\dot{m}$  - mass flow rate, kg/s,

$p$  - pressure, N/m<sup>2</sup>,

$\dot{q}_v$  -heat quantity produced in the volume

unit of the discharge gap, J/m<sup>3</sup>·s

$S$  - entropy J/K·s,

$t$  - temperature, °C,

$T$  - temperature, K,

$w$  - velocity, m/s,

$y_1$  - dimensionless value of discharge gap size,

$\lambda$  - gas heat conductivity, J/m·K,

$\zeta_1$  - dimensionless ozonizer length,

#### subscript:

s - dry air,

w - water,

o<sub>3</sub> - ozone

o - environment,

t - tail gas