THERMODYNAMIC ASPECTS OF AN OZONE SYNTHESIS PROCESS IRREVERSIBILITY IN A PHENOMENOLOGICAL FRAME

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A b s t r a c t. The paper presents results on considerations on irreversibility and a non-equilibrium character of phenomena that accompany ozone synthesis in real conditions. As a result, a set of assumptions for a model irreversibility and a non-equilibrium character of an ozone generation process in silent discharges has been formulated.

K e y w o r d s: ozone generation process, entropy production, non-equilibrium phenomena, thermodynamic stimuli, generalized flow.

INTRODUCTION

Ozone generation process belongs to a group of processes characterized by a high energy-consumption rate. During the ozone synthesis process electrical energy utilization for the process does not exceed 10% [1-4], while the remaining part of the supplied energy gets converted into heat that is unproductively carried away to the environment. When the process is run in a conventional way the above mentioned phenomena are accompanied by a substantially elevated thermal state of a substrate gas in the discharge zone [6,7].

At the same time it is worth noting that a real ozone generation process in the physical-chemical and thermal (i.e. thermodynamic) sense is a non-equilibrium process and its description within the domain of classical thermodynamics makes a model theoretical approximation. However, a 'classical' description of an ozone generation process is useful at considering non-equilibrium phenomena and especially when the phenomena occur among equilibrium systems.

The presented research work deals with the above mentioned problem scope and concerns searching for effective methods of ozone generation at temperatures lower than 273K.

CHARACTERISTIC PROPERTIES OF AN OZONIZATION PROCESS REGARDED FROM A THERMODYNAMIC -THERMAL POINT OF VIEW

A discharge gap in the considered ozonizer is a space bounded by electrode surfaces and inlet and outlet cross-sections and it forms a natural area (limited zone) for the ozone synthesis reaction environment. It makes a particular kind of a chemical reactor where chemical processes run under the influence of silent discharges in a substrate gas (oxygen or air). Silent discharges form as a result of the presence of an electrical field of an adequately high potential difference level that surrounds the reaction area.

Enthalpy of an ozone formation out of oxygen according to a totaled reaction is 142.32 kJ/O_3 mole (the data concern a theoretical synthesis process that runs in a quasi-static - equilibrium way).

In reality, energy that is supplied to generate 1 mole of O_3 out of molecular oxygen contained in the air is much greater and it gets into a substrate gas with fluxes of charges accelerated in an electrical field that accompany silent discharges.

Part of the energy gets utilized directly for the ozone synthesis reaction (as an indispensable energy). Its remaining part (much greater than the former one) gets converted into heat in a dissipative process which follows from the properties of the process.

Heat released in a reactor (in a hypothetical extreme case the reactor is surrounded by adiabatic walls) with no possibility to perform any mechanical work, according to the 1st principle of thermodynamics, would increase the internal energy level which would be accompanied by a significant growth of gas temperature. The temperature growth can also be observed in the case of an insufficient heat abstraction from the reaction environment zone [7]. Hence it is necessary to cool down the reaction zone as well as to reduce the substrate gas temperature. The real physical-chemical change and the accompanying thermodynamic change are of non-equilibrium character and so is the process of cooling down the reaction environment zone. Even in steady states reactors operate in an irreversible way causing energy dissipation and especially of driving energy.

OBJECTIVE AND SCOPE OF THE RESEARCH

The presented research work has aimed at formulating assumptions for a description of irreversibility and a non-equilibrium character of processes that occur in a reaction environment during an ozone generation out of a substrate gas (oxygen or atmospheric air) at temperatures lower than 273K.

The research scope has included:

- an analysis of equilibrium thermodynamic and thermal processes that accompany ozone generation out of atmospheric air at reduced temperatures;
- determination of assumptions for formulating a description of an non-equilibrium model of processes occurring in a reaction environment during ozone generation.

A MODEL OF ENERGY CHANGES OCCURRING IN AN OZONIZER GAP AT REDUCED TEMPERATURES

To analyze the above formulated problem energy phenomena occurring in an infinitesimal batch of a substrate gas have been considered - a substrate gas batch that has been subdued to a physical-chemical change in an electrical field and moved along the x- coordinate in the gap with a mean velocity – w_{avg} , with its thermodynamic and calorific parameters averaged out along the gap length (Fig. 1).

From the viewpoint of classical thermodynamics the problem of energy changes can be described by the following equation [3]:

$$d\dot{H}_n + d\dot{H}_{O3} + d\dot{H}_r = d\dot{H} + d\dot{L}_{el},$$
(1)

For to take into account an effect of the generated ozone quantity on energy conversions within a specific environment of reactions proceeding with the participation of an electrical field a notion of a modified relative rate of conversion (α) referred to the synthesis reaction has been introduced. The mass is variable along the ozonizer gap length and the conversion rate α. is variable as well. To express the mentioned variations a new notion "c" has been introduced and it refers to ozone concentration variations depending on the gas residence duration in the discharge gap described according to the Vasiliev formula [10], which allows an ozone mass flux in the following form:

$$\dot{m}_{O3}(x) = S \cdot c^m \cdot w_{avg} \cdot \left[1 - \exp\left(-k_1 \cdot \frac{x}{w_{avg}} \right) \right],$$
(2)

where :

$$\alpha(x) = 1 - \exp\left(-k_1 \cdot \frac{x}{w_{avg}} \right)$$
(3)

With the application of the following notions: physical enthalpy of gas, formation enthalpy, heat penetration between the gas and the cooling agent and also of the function (1) an explicit form of the equation of the 1st principle of thermodynamics has been obtained. The equation describes the course of an

infinitesimal conversion of an infinitesimal gas batch that moves in the ozonizer gap and can be written as follows, [3]:

$$\left[\dot{m}_s \cdot c_{pp} + \alpha \cdot \dot{n}_{O3}^m \cdot M_{O3}\left(c_{p0} - c_{pp}\right)\right]dT_x + \left[\dot{n}_{O3}^m \cdot M_{O3}\left(c_{p0} - c_{pp}\right)\left(T_x - T_{od}\right) + \dot{n}_{O3}^m \cdot M_{O3} \cdot \Delta h\right]d\alpha = \quad (4)$$

$$= \left[\frac{E_v \cdot \dot{m}_s}{\rho_p \cdot L} - 2\pi \cdot r_z \cdot k\left(T_1 - T_{cl}\right) \cdot e^{\beta \cdot x}\right]dx$$

where:

$$k = \frac{2}{\pi}\frac{c_{pp}}{L} \cdot \dot{m}_s \cdot \frac{\dfrac{1}{2d}}{1 + \dfrac{\dot{m}_s}{\dot{m}_c}\dfrac{c_{pp}}{c_c}\dfrac{d_c}{d}} \cdot \varphi_s \ , \qquad \beta = -\frac{2\pi \cdot r_z \cdot k}{\dot{m}_c \cdot c_c \cdot b} \ . \quad b = -\frac{1}{\dfrac{T_1}{T_{c2}} \cdot f_b + 1} \ , \qquad f_b = -\frac{\dfrac{T_2}{T_1} - 1}{\dfrac{T_{cl}}{T_{c2}} - 1}$$

$$\varphi_s = 1.0126 - 3.044 \cdot 10^3 \cdot \dot{m}_s$$

Equation (4) has been transformed into the following dimensionless form by introducing dimensionless quantities henceforth called modules:
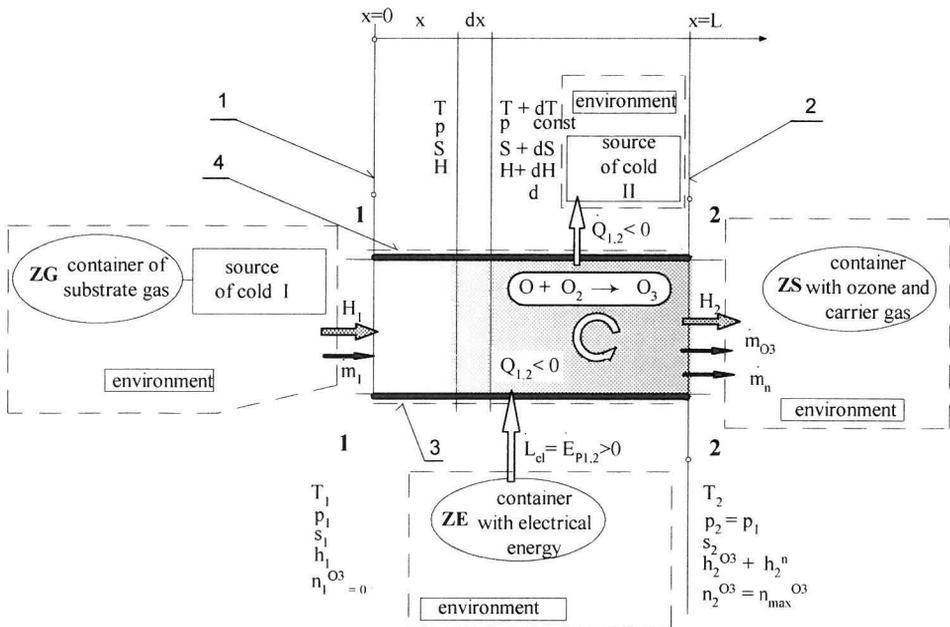
Fig. 1. A model of an open thermodynamic process in the reaction environment [3]
1,2 - abstract walls that allow substance and energy flow; 3,4 - walls that are substance- impermeable and don't allow mechanical work exchange with the environment ; 3 - adiabatic wall; 4 - heat motion to the walls allowed; 3 and 4 - considerable potential difference is applied.

$$d\Theta = \left[M_E - M_{oh} \cdot \left(\frac{k_1 \cdot L}{w_{avg}} \right) \exp\left(- \frac{k_1 \cdot L}{w_{avg}} X_1 \right) - M_Q \cdot e^{\beta \cdot L \cdot X_1} \right] dX_1 ,$$ (5)

with the following boundary condition:

for $X_1 = 0$; $\Theta = \Theta_1 = 1$;   at $T_{od} = T_1$ (6)

After having integrated the equation (5) and having taken into account the boundary condition (6) a particular integral has been obtained in the following form:

$$\Theta(X_1) = 1 + M_E \cdot X_1 - M_{oh} \cdot \left(1 - \exp\left(- \frac{k_1 \cdot L}{w_{avg}} X_1 \right) \right) + \frac{M_Q}{\beta \cdot L} \cdot \left(1 - e^{\beta \cdot L \cdot X_1} \right)$$ (7)

Thus, the distribution of dimensional temperature in the gap can be described by the following function:

$$T_x(x) = T_1 + \frac{E_v \cdot x}{\rho_p \cdot c_{pp} \cdot L} - \frac{\dot{m}_{O3}}{\dot{m}_s} \frac{\Delta h}{c_{pp}} \cdot \left(1 - \exp\left(- \frac{k_1}{w_{avg}} x \right) \right) + \frac{2\pi \cdot r_z \cdot k \cdot (T_1 - T_{cl})}{\dot{m}_s \cdot c_{pp} \cdot \beta} \left(1 - e^{\beta \cdot x} \right)$$ (8)

where the coefficient k_1 depends on the temperature of a substrate gas (oxygen) at the ozonizer inlet which can be described by an experimentally obtained formula in the following form:

$k_1 = 0.0045 \, T_1 - 0.07752$ (9)

Symbol E_v in the previous formulae and in the formula (8) denotes a unit quantity of electrical energy that is indispensable to realize the ozone generation process in real conditions. This quantity at a determined ozonizer geometry is closely and unambiguously related to the obtained ozone concentration c_{O3} by the relation $E_v = E_v(c_{O3})$.

ASSUMPTIONS FOR A NON-EQUILIBRIUM MODEL OF CHANGES OCCURRING IN AN OZONE GENERATION REACTION ENVIRONMENT

Ozone generation in real conditions is an irreversible process and at the same time a non-equilibrium one [2,4,8]. Quality of those conditions can be determined by the following phenomena: a flow of charges and their acceleration in an electrical field crosswise applied to the reactor; a flow of substrate gas along the reactor whose occurrence is simultaneous with a formation, as a result of a physical-chemical reaction over the whole flux area, of a new substance - ozone in a quantity that grows according to the flow direction; dissipation of a part of electrical energy in the substrate gas together with its conversion into heat and the heat abstraction from the reaction zone in an ozonizer.

It is worth emphasizing that silent discharge phenomena (electron flow in gas) and a substrate gas flow that is crosswise with respect to the electrical field direction are of a primary character while the phenomena of heat emission, heating up and cooling down of the gas are secondary. Phenomena of diffusion and thermal diffusion are secondary as well [4, 6].

Steady non-equilibrium states of an ozonizer operation seem to be interesting from a technical point of view. In such states a total entropy change in time and gas fluxes flowing through an ozonizer (reactor) can be expressed by the following relation [5, 9, 10]:

$$\frac{dS_z}{dt} + \frac{dS_w}{dt} = 0 \tag{10}$$

and at the same time:

$$\dot{S}_z = \frac{dS_z}{dt} < 0 \tag{11}$$

$$\dot{S}_w = \frac{dS_w}{dt} > 0, \tag{12}$$

$$\dot{S}_w = \dot{S}_{TZ} + \dot{S}_{TW} + \dot{S}_{CI} + \dot{S}_{CT} + \dot{S}_{EM} + \dot{S}_{EU} + \dot{S}_{\alpha} \tag{13}$$

which means that the whole entropy quantity that has been produced inside the system with an intensity $\dot{S}_w$ gets compensated by an entropy flux outflow through the reactor boundaries to the environment.

Entropy production in a reaction zone results from irreversibility of such phenomena as: electron acceleration and flow as well as their collisions with substrate gas molecules, including oxygen ones, in the electric field ($\dot{S}_{EM} + \dot{S}_{EU}$), physical-chemical phenomena ($\dot{S}_{\alpha}$), heat generation in the discharge micro-zones (dissipation heat); heating up and cooling down of the gas ($\dot{S}_{TZ} + \dot{S}_{TW}$); and diffusion and thermal diffusion of ozone molecules in the gap zone ($\dot{S}_{CI} + \dot{S}_{CT}$).

The course and direction of an ozone synthesis in the mentioned conditions are determined by factors that in the sense of non-equilibrium thermodynamics can be identified with thermodynamic stimuli

Principally, at a phenomenological approach to the problems concerning non-equilibrium phenomena there are two ways of formulating descriptions according to [5, 11], and namely:

- a description that applies a notion of an entropy source efficiency defined as:

$$\Phi_s = \frac{\partial^2 S}{\partial t \, \partial V} \geq 0 \tag{14}$$

- a description that applies a notion of a dissipative function of the following form:

$$\Psi = T \cdot \Phi_s \geq 0 \tag{15}$$

The latter of the mentioned ways seems to be more efficient and that is why it will be applied in the further considerations under a general form of relations between the dissipative function and thermodynamic stimuli.

$$\Psi = \sum_{i=1}^{n} J_i \cdot X_i \tag{16}$$

and at the same time at the first description approximation the following linear relations are fulfilled:

$$J_i = \sum_{j=1}^{n} L_{ij} \cdot X_j \tag{17}$$

If thermodynamic stimuli X are independent then phenomenological factors fulfill the Onsanger dependence[5, 11]:

$$L_{ij} = L_{ji} \tag{18}$$

and the dissipative function takes the following form:

$$\Psi = \sum_{i,j=1}^{n} L_{ij} \cdot X_i \cdot X_j \tag{19}$$

In the case of irreversible and non-equilibrium phenomena that accompany ozone formation in a reaction zone there are mainly stimuli of a scalar character that are conjugate to scalar efficiencies (velocities) which concerns the very ozone synthesis reaction and there are also stimuli of a vector character that follow from equations of energy and heat transfer and mass transport. Figure 2 shows the causal scheme of quantities generating entropy production in the ozone synthesis course.
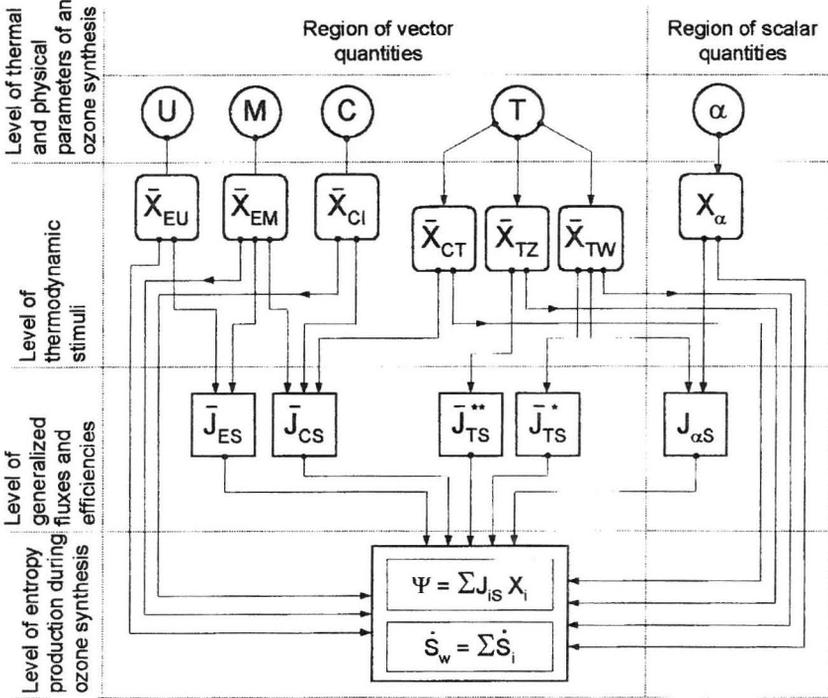
Fig. 2. Causal scheme of quantities generating entropy production in the ozone synthesis course.

According to the earlier accepted description mode, at accepting the dissipative function as its starting point, individual stimuli can be described the following way:

a) Stimuli of temperature :

• temperature stimulus in gas:

$$\overline{X}_{TW} = f_{TW}\left(-\overline{\text{grad}}\,T\right) = -\overline{\text{grad}}\,T \,, \tag{20}$$

generalized conjugate flow can be expressed by the entropy flux density:

$$\overline{J}_{TS}^{*} = L_{TS}^{*}\,\overline{\text{grad}}\,T \tag{21}$$

• temperature stimulus at the reactor wall

$$\overline{X}_{TZ} = f_{TZ}\left(\frac{T - T_s}{\delta_H}\right)\overline{n}_{0S} = \frac{T}{\delta_H}\left(1 - \frac{T_S}{T}\right)\cdot \overline{n}_{0S} \tag{22}$$

generalized conjugate flow can be expressed by the entropy density of a flux that is transferred through the reactor wall::

$$\overline{J}_{TS}^{**} = L_{TS}^{**} \frac{T}{\delta_H}\left(1 - \frac{T_S}{T}\right)\cdot \overline{n}_{0S} \tag{23}$$

b) diffusion stimuli of the ozone substance and tail gas
   • stimulus of isothermal diffusion:

$$\overline{X}_{CI} = -\overline{\text{grad}}\,C \,, \tag{24}$$

generalized conjugate flow expressed by the entropy flux density:

$$\overline{J}_{CS}^{*} = L_{CS}^{*} \cdot \overline{\text{grad}}\,C \,, \tag{25}$$

   • stimulus of thermal diffusion:

$$\overline{X}_{CT} = -\overline{\text{grad}}\,T \,, \tag{26}$$

generalized conjugate flow expressed by the entropy flux density:

$$\overline{J}_{CS}^{**} = L_{CS}^{**} \cdot \overline{\text{grad}}\,T \,, \tag{27}$$

c) stimuli of electron flow in gas:
   • stimulus produced by the potential of an external electrical field:

$$\overline{X}_{EU} = -\overline{\text{grad}}\,U \,, \tag{28}$$

generalized conjugate flow expressed by the entropy flux density:

$$\overline{J}_{ES}^{*} = L_{ES}^{*} \,\overline{\text{grad}}\,U \,, \tag{29}$$

   • stimulus produced by the chemical potential of electrons:

$$\overline{X}_{EM} = -\overline{\text{grad}}\,M_e \,, \tag{30}$$

generalized conjugate flow expressed by the entropy flux density:

$$\overline{J}_{ES}^{**} = L_{ES}^{**}\left(\overline{\text{grad}}\,M + e_e\,\overline{\text{grad}}\,U\right), \tag{31}$$

d) physical-chemical stimulus of the ozone synthesis following from the chemical potential of ozone:

$$X_{\alpha} = A_C = v_{O3}\cdot\mu_{O3}\cdot M_{O3}, \tag{32}$$

generalized conjugate flow expressed by the entropy flux density:

$$J_{\alpha S} = L_{\alpha S}\,X_{\alpha} \tag{33}$$

CONCLUSIONS

The presented considerations have made a basis for formulating a set of assumptions (causes and effects) for elaborating a model of irreversible and non-equilibrium phenomena that accompany an ozone synthesis process in steady states of an ozonizer operation and namely:

1. The main cause of a scalar nature is a thermodynamic physical-chemical stimulus A_C that is described by chemical affinity of an ozone synthesis reaction.

2. Causes of the irreversibility and a non-equilibrium character of an ozone synthesis that exhibit properties of vector thermodynamic stimuli and follow from heterogeneity of the distributions in the gap region of the following factors: electrical potential (U), chemical potential (M), temperatures of gases inside the gap and in the region at a non-adiabatic surface that bounds the gap (T), ozone concentration in the gap (C).

3. The above mentioned (items 1 and 2) stimuli cause effects in a form of generalized flows, conjugate and cross ones, that can be described by vector quantities $\bar{J}_{ES}$, $\bar{J}_{CS}$, $\bar{J}_{TS}^{*}$, $\bar{J}_{TS}^{**}$ and a scalar one $J_{\alpha S}$. The quantities determine entropy production in real conditions of ozone generation through a dissipative function (Ψ).

4. To arrive at a full description of the discussed model it is necessary to formulate forms and relations of phenomenological factors in order to express generalized flows, conjugate and cross ones, and subsequently formulate the final form of the model description.

List of more important symbols

C	- specific heat at constant pressure,	M	- chemical potential
ρ	- density,	M_e	- electrochemical potential
D	- discharge gap size, mm,	p	- pressure
H	- enthalpy,	Q	- heat
J_i	- generalized conjugate flow	s	- entropy
L	- discharge zone length,	T	- temperature
L_i	- phenomenological factor	w_{avg}	- mean mass rate of gas flow in ozonizer gap
$\dot{m}$	- mass flow rate,	α	- rate of conversion

subscript:

s	- dry gas,
c	- cooling liquid,
O_3	- ozone
p	- gas
n	- carrier gas

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TERMODYNAMICZNE ASPEKTY NIEODWRACALNOŚCI PROCESU SYNTEZY OZONU W UJĘCIU FENOMENOLOGICZNYM

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S t r e s z c z e n i e. W pracy przedstawiane są rezultaty rozważań na temat nieodwracalnych i nierównowagowych zjawisk towarzyszących syntezie ozonu w realnych warunkach. Przedstawiono komplet założeń dla modelu nieodwracalnych i nierównowagowych zjawisk towarzyszących syntezie ozonu.

S ł o w a k l u c z o w e: proces wytwarzania ozonu, produkcja entropii, zjawiska nierównowagowe.