ERRATUM

The June 1994 issue of *Pure and Applied Chemistry* (Volume 66, No. 6) included the articles 'Theoretical basis of non-equilibrium near atmospheric pressure plasma chemistry' by A. A. Fridman and V. D. Rosanov, and 'Modelling of dielectric barrier discharge chemistry' by B. Eliasson, W. Egli and U. Kogelschatz. Unfortunately, the front pages of these two papers were transposed during production so that the body of both papers was printed out of position within the issue, and given the wrong page numbers and running headlines.

Both articles are reproduced in their entirety on the following pages with the correct page numbers and running headlines. A correct version of the contents page is also reproduced. These pages should be used to replace those in the faulty printed copies.

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Theoretical basis of non-equilibrium near atmospheric pressure plasma chemistry

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Abstract: Theory and modelling of non-equilibrium plasma chemical processes are under consideration. It includes the description of the main fundamental reactions of charged and excited particles, the non-equilibrium physical and chemical kinetics, the models of non-equilibrium atmospheric pressure gas discharges such as gliding arc, microwave, RF-discharge, electron beams, corona e.a., and finally the modelling of the plasma chemical processes of CO_2, H_2S, H_2O, CH_4, metal halogenides dissociation, NO and organic compounds synthesis, and finally the air purification from SO_2, NO_x and volatile organic compounds (VOC).

INTRODUCTION

The high energy efficiency and selectivity could be obtained in non-equilibrium plasma for different types of chemical reactions. Thus for CO_2 dissociation in plasma it's possible to put selectively 90% of total discharge power in CO production when vibrational temperature is about 4000K and translational one in supersonic flow is only 100K. But it's not so easy to choose here the only proper regime and plasma parameters from a lot of possibilities typical for systems far from equilibrium. This is the reason why theory and modelling are so important in non- equilibrium plasma chemistry.

For non-equilibrium plasma modelling we need first of all a description of fundamental reactions of excited and charged particles. The highest energy efficiency in plasma can be provided by vibrational excitation of molecules (1,2). For electron temperature 1-3 eV and for a lot of different molecules the main part of discharge power (up to 97%) is going to vibrational excitation, also the vibrational energy is responsible for overcoming the activation threshold of endothermic chemical reactions. For this reason the vibrationally excited molecules elementary reactions are of the main interest for high efficiency non-equilibrium processes and will be considered here at first.

The same for physical kinetics, vibrationally excited states distribution function is very significant for plasma chemical reaction rates calculation. The so called Treanor effect of overpopulation of highly excited states leads to essential acceleration (3-5 orders of value) of non-equilibrium reactions. As well the centrifugal effect is very important in macrokinetics modelling of non-equilibrium chemical processes taking place in fast rotating discharge plasma. As an example here the non-equilibrium plasma chemical process of hydrogen sulfide dissociation with hydrogen and liquid sulphur production will be considered.

The other important problem is connected with non-equilibrium plasma generation in high power near atmospheric pressure steady state discharges, so in the conditions when such a typical non-equilibrium discharge as glow discharge is unstable. From this point of view the microwave discharge, where non-equilibrium plasma exists in 1000KW near atmospheric pressure units (1,3), is of traditional interest. The gliding arc is the new type of powerful non-equilibrium discharge self sustained for near atmospheric pressure (4). The modelling of this discharge will be considered here as well.

As a result the modelling of the specific non- equilibrium plasma chemical processes will be considered in order to determine the optimal conditions for the highest energy efficiency. The main processes under

consideration will be: carbon dioxide, hydrogen sulfide, water vapour and methane decomposition, nitrogen oxide synthesis, and flue gas cleaning from SO_2 and NO_x.

The main elaborated computer programmes for non-equilibrium plasma chemical processes modelling will be described as well. They are: the programme for statistical calculations with kinetic limitations, the programme for kinetic calculations including sensitivity analysis, the programme of determination of unknown reaction rate constants, the programme for calculation of kinetics and gas dynamics of plasma chemical processes in different types of gas flow.

THE FUNDAMENTAL REACTIONS OF EXCITED MOLECULES IN PLASMA

As it was mentioned above, one of the more significant fundamental reactions in near atmospheric pressure non equilibrium plasma chemistry are the reaction of molecules in the vibrationally excited states. This kind of reactions provides for such molecules as carbon oxide and dioxide, nitrogen, hydrogen, methane, in some cases water, oxygen e.a. the highest value of energy efficiency in organization of plasmachemical processes. For such a reaction modelling we need from the one hand the description of fundamental reaction characteristics, and from the other hand the vibrationally excited states population distribution function and then kinetic reaction rate constant. The analytical formula for such kind of exchange reaction:

$$A + BC(E_V) = AB + C$$
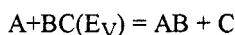
rate constant was obtained as a function of vibrational energy of BC- molecule excited in plasma. The model can be used when activation energy of exchange reaction under consideration is more than vibrational quantum of AB and BC molecules, and also is higher than thermal energy of collision. The approach was made on the base of theory of vibronic terms taking into account that the system can be described by the fixed vibronic term upto the moment of final reactionary reconstruction. The correlation for microscopic reaction rate coefficient Kr(Ev) could be written in this case as follows:

$$K_R(E_V) = K_0(E_V) \exp((aE_V - E_a) / T_0)$$

Here E_a is a fundamental reaction activation energy, $K_0(E_V)$ is not so fast changing pre-exponential factor, T_0 is a translational temperature, and finally a-factor is the main reaction parameter - the so called coefficient of vibrational energy utilisation in overcoming of activation barrier of chemical reaction. One can see that the correlation written above looks like Arrenious one with activation energy reduced on some part of vibrational energy aE_V. For this reason a-factor could be considered as efficiency of vibrational energy in excited molecule reaction.

According the theory under consideration, taking into account Eccart- profile of adiabatic reaction way, the correlation for a-factor can be written as follows:

$$\mathbf{a} = 1 / (1 + (g_r E_{ar}/g_d E_{ad}))^p + (w - w^*)/w$$

Here $E_{ad} = E_a$ is the direct reaction $A + BC = AB + C$ activation energy, and E_{ar} is the activation energy of reverse reaction $AB + C = A + BC$; g_r and g_d are the reverse interaction radiuses for direct and reverse reactions; w and w^* are B-C bond vibration frequencies for free BC molecule and for transition activated complex respectively; factor p = 0.5 for adiabatic reaction and p = 1 for non- adiabatic one. For a lot of reactions interesting for plasma chemical applications the formula mentioned above can be significantly simplified and written only as a function of well known activation energies of direct and reverse reactions:

$$\mathbf{a} = E_{ad} / (E_{ad} + E_{ar})$$

This correlation shows that for endothermic reaction (when $E_{ad} \gg E_{ar}$) the efficiency of vibrational energy in process stimulation is very high - a-factor is upto 100%. On the contrary, for exothermic reactions (when $E_{ad} \ll E_{ar}$) the efficiency of vibrational energy is relatively small - a-factor is close to zero. It proves, hat vibrational excitation of molecules in non- equilibrium plasma can stimulate high efficiency endothermic

chemical processes. It's interesting to remark that according to our correlation the sum of **a**-factors direct and reverse reactions is equal to unit. This result correlates with the well known illustrative Polanyi model of the role of vibrational and translational energy in chemical reactions stimulation.

The correlation described above are very convenient and useful for non-equilibrium reaction modelling. We must note also that this formula is in a good agreement with the existing experiments and complicated numerical computer calculations as well. In the Table 1 you can see examples of a comparison of theoretical and experimental values of **a**-factor for the different types of chemical reactions:

TABLE 1. The efficiency of vibrational excitation energy (**a**-factor) in chemical reaction stimulation.

Chemical reaction	Reaction enthalpy ΔH, eV	Activation energy, E_a, eV	a-factor, experimental	a-factor, theoretical
$F + HF(vib.exc) = F_2 + H$	4,27	4,37	0,98	0,98
$F + DF(vib.exc) = F_2 + D$	4,34	4,44	0,99	0,98
$Cl + HCl(vib.exc) = Cl_2 + H$	1,96	2,04	0,95	0,96
$SCl + HCl(vib.exc) = SCl_2 + H$	2,0	2,1	0,96	0,98
$SO_2Cl + HCl(vib.exc) = SO_2Cl_2 + H$	1,86	1,93	0,96	0,96
$NO + HCl(vib.exc) = NOCl + H$	2,83	2,89	1,0	0,98
$O + OH(vib.exc) = O_2 + H$	3,35	3,35	1,0	1,0
$NO + OH(vib.exc) = NO_2 + H$	1,28	1,28	1,0	1,0
$SF_4 + HF(vib.exc) = SF_5 + H$	3,70	3,74	0,97	0,99
$H + HF(vib.exc) = H_2 + F$	1,39	1,46	1,0	0,95
$Cl + HF(vib.exc) = HCl + F$	1,43	1,49	0,96	0,97
$HS + HF(vib.exc) = H_2S + F$	1,93	1,98	1,0	0,98
$HO_2 + HF(vib.exc) = H_2O_2 + F$	2,03	2,07	1,0	0,98
$NH_2 + HF(vib.exc) = NH_3 + F$	1,39	1,43	1,0	0,97
$SiH_3 + HF(vib.exc) = SiH_4 + F$	1,86	1,86	1,0	1,0
$N_2H_3 + HF(vib.exc) = N_2H_4 + F$	2,61	2,65	0,97	0,98
$CH_3 + HF(vib.exc) = CH_4 + F$	1,43	1,48	0,98	0,97
$C_2H_5 + HF(vib.exc) = C_2H_6 + F$	1,61	1,63	1,0	0,99
$S + CO(vib.exc) = CS + O$	3,70	3,72	1,0	0,99
$CS + SO(vib.exc) = CS_2 + O$	0,91	0,96	0,91	0,95
$SO + CO(vib.exc) = COS + O$	2,26	2,48	0,96	0,92
$CH_2 + CO(vib.exc) = C_2H_2 + O$	2,04	2,17	0,91	0,94
$O + NO(vib.exc) = O_2 + N$	1,39	1,68	0,90	0,86
$O + AlO(vib.exc) = O_2 + Al$	0,11	0,24	0,67	0,65
$H + HCl(vib.exc) = H_2 + Cl$	0,02	0,15	0,30	0,40
$O + HCl(vib.exc) = OH + Cl$	0,03	0,20	0,60	0,54
$OH + H_2(vib.exc) = H_2O + H$	-0,64	0,25	0,24	0,22
$N + O_2(vib.exc) = NO + O$	-1,2	0,3	0,24	0,19

The information about theoretical, numerical and experimental results of fundamental chemical reactions stimulation by molecules excitation in plasma can be taken from (1,5-7). The specific characteristics and role of charged particles fundamental reactions in high efficiency near atmospheric pressure non- equilibrium processes are considered in (1,8-10).

The new activity here is connected with an investigations of complex-ions reactions and ion-cluster catalysis, and their role in mechanisms of oxidation of SO_2, NO_x, VOC and other impurities in air during the plasma chemical purification of industrial flue gases by electron beams, corona, barrier and other discharges.

THE PHYSICAL KINETICS OF NON-EQUILIBRIUM PLASMA CHEMICAL PROCESSES.

For calculation the vibrationally excited states population (or the same- vibrational distribution function), taking into account vibrational excitation, VV- and VT- relaxation processes and chemical reactions, it is convenient to use the Focker- Planck equation for molecule diffusion in the space of vibrational energy:

$$df/dt + d/dE\,(j_{eV} + j_{VV} + j_{VT} + j_R) = 0$$

Here f(E) is the vibrational distribution function; E- is the molecule vibrational energy; j is the molecules flow rates in the space of vibrational energy, corresponding to eV-excitation, VV- and VT- relaxation, and chemical reaction respectively. The simplest VT- flow rate is defined by VT-diffusion coefficient D_{VT} in an energy space:

$$j_{VT} = - D_{VT}(E)\,(df/dE + f/T_0)$$

and gives in the case of j_{VT}=0 the Boltzmann distribution function with the translational temperature T_0. The other relaxation VV- flow rate is defined by VV-diffusion coefficient D_{VV} in an energy space and also depends on vibration anharmonicity coefficient x_e, and vibrational temperature T_V (we must take into account, that in the non-equilibrium conditions under consideration vibrational temperature is essentially higher than translational one):

$$j_{VV} = - D_{VV}(E)\,(df/dE + f/T_V - 2x_eE\,f\,/\,T_0\,h\nu)$$

This flow rate in the case of j_{VV}=0 gives Treanor vibrational distribution function, typical for non-equilibrium plasma (in this correlations hν is the vibrational quantum):

$$f(E) = (1/T_V)\exp(-E\,/\,T_V + x_e\,E^2\,/\,To\,h\nu))$$

The calculations of reaction rates of chemical reactions stimulated by vibrational excitation in non-equilibrium plasma (1,2,7) show that Treanor effect increases the reaction rates on many orders of value and in the same time increases the energy efficiency of plasma chemical processes.

It was shown that high efficiency of chemical reactions provided by vibrational excitation can be reached when the values of vibrational temperature, specific discharge energy input and ionization degree become more than critical one defined by relaxation processes (in the same time translational temperature must be continuously much less than electron temperature and vibrational one). The typical values of these critical parameters are: vibrational temperature at about 2000K, specific discharge energy input at about 0.1-0.2 eV/mol, ionization degree lg(Ne/No) at about -7; also the high level of non- equilibrium must be supported as well as high level of electron temperature T_e = 1-2 eV. It was also shown that the dependence of energy efficiency on specific energy input usually has a maximum at 1 eV/mol. The realization of the conditions mentioned above give the possibility to reduce energy cost of plasmachemical reaction in more than three times with respect to equilibrium organisation of the same reaction. The additional information in this direction will be done later during the consideration of concrete plasmachemical reactions providing by vibrational excitation.

The other big group of plasma chemical reactions is those one with liquid or solid products. As an example here could be considered the hydrogen sulfide dissociation with hydrogen and liquid sulphur production. The details of this important for industrial application plasma chemical process will be discussed later (in the chapter concerned with the modelling of concrete plasma chemical processes). Now we want to emphasize, that for such kind of processes the non-equilibrium conditions can be organized by fast rotation of discharge plasma. When centrifugical effect becomes so strong that condensed products flow becomes faster than reverse reaction rate and heat flow, the energy of products reduces very significantly. The kinetic theory of such kind of processes can be taken in (11,12). To attain this centrifugical effect one need to fulfill the conditions hard enough concerning the velocity Vϕ of plasma rotation:

$$(mV\phi^2 / T_0) \, c(To) \, N^2 \gg 1$$

Here m is a molecule mass, c(To) is a relative concentration of cluster products, and N is their mean size. The realization of the conditions mentioned above give the possibility to reduce energy cost of plasmachemical reaction in more than three - five times with respect to equilibrium organization of the same reaction.

THE MODELS OF NON-EQUILIBRIUM NEAR ATMOSPHERIC PRESSURE DISCHARGES.

Generally two very different kinds of plasmas are used for chemical applications. Hot electrical arc plasmas in thermodynamic equilibrium allow the injection of high power levels, but with low efficiency for chemical reactions. Conversely, cold nonequilibrium plasmas created by conventional glow discharges offer good selectivity and efficiency, but generally at limited power and pressure. In these two general and conventional types of discharge it is impossible to support continuously the optimal parameters mentioned above- the high level of non- equilibrium, high electron temperature and high electron density in the same time.

These parameters can be realized in microwave discharge, where skin-effect permits to get in the same time the high level of electron density and the high electric field (so high electron temperature as well) in the relatively cold gas. Present super high frequency discharge technology can be used to generate dense (lg Ne(electrons/cm3) = 13) non- equilibrium plasma (T_e=1-2eV, T_V=3000-5000K, T_0=800-1500K, and for supersonic flow T_0 =150K and less) at pressures up to 200-300 torr and at power levels reaching 1 MW (1,3). The experimental details and modelling of high power non-equilibrium microwave discharge can be taken in (1,3,13).

Recently a simpler technique offering the similar advantages has been proposed (4,14). The corresponding device, called GlidArc (gliding arc), operates at atmospheric pressure or higher; the dissipated power in non- equilibrium conditions may reach 40 kW per electrode pair. In the simple case of a direct current (4), this discharge is driven by power generator (Vo = 800 V, Imax = 60 A). In series with the generator there is a variable resistor R = 0 - 25 Ohm and also, in order to delay the breaking off of the arc, a selfinductance L = 25 mH.

The discharge starts at the shortest distance (1 - 2 mm) between the electrodes; within a time of about 1 μs there is formation of a low resistance plasma and the voltage between the electrodes falls to a few volts. The small plasma volume is then dragged by the gas flow at a speed of about 10 m/s, and the length of the arc column increases together with the distance and the voltage between the electrodes. The plasma is in thermodynamic equilibrium because the electrical power delivered by the generator is sufficient to compensate energy losses by thermal conductivity κ(T). The dissipated power per unit length of the arc:

$$W = 16\pi \, \kappa(T_0) \, (T_0/I) \, T_0$$

is equal here W= 0.6 KW/cm (for air at gas temperature T_0 = 7 000 K) and doesn't change significantly during the equilibrium arc evolution (I-ionisation potential). Neglecting the selfinductance L in a first approach, Ohm's law may be written here as:

$$Vo = RJ + W \, l / J$$

where l is the length of the arc. This equation gives the solutions for the current J:

$$J = (Vo \pm (\, Vo^2 - 4 \, W \, l \, R)^{0.5} \,) / 2R$$

where only the solution with the + sign has a physical meaning. During this period of thermodynamic equilibrium, the current decreases at the same time as the arc voltage Wl/J and the power Wl increase linearly with the length l. When the length of the arc approaches the critical value:

$$l^* = Vo^2 / (4 \, WR)$$

the current becomes equal to $J^* = Vo/2R$, and the voltage and power both approach their maximum values of $V^* = Vo/2$ and $P^* = Vo^2 / 4R$, respectively. In our case l^* has the numerical value of about 10 cm. Later when $l > l^*$, the heat losses Wl continue to increase, but since the electrical power cannot increase any further it is no longer possible to sustain the arc in thermodynamic equilibrium.

This is the moment of GlidArc transition in the main non-equilibrium regime. The gas temperature will fall rapidly to about 2000 - 3000 K, at the same time as the electron temperature remains at about 1 eV. These conditions are similar to those prevailing in moderate pressure (30 - 200 Torr) high frequency discharges; the plasma conductivity is maintained by stepwise ionisation processes, and the arc can continue its evolution with much smaller heat losses, $W^* = 0.15 - 0.20$ KW/cm (14). Also, it shows that according the formula mentioned above the maximum length lmax that the non-equilibrium arc can reach is 3-5 times more than l^*.

The non-equilibrium arc can continue until the moment when the heat losses W^*lmax become again equal to the maximum power delivered by the generator. The calculation (14) shows that between 75 and 80 % of the total energy injected into the arc is dissipated during the non-equilibrium period (because lmax » l^*). After the break of non-equilibrium discharge it will be a new breakdown and new arc formation. One period of this pulse-periodic process is at about 30msec.

A striking phenomenon occurring during the GlidArc transition in non-equilibrium phase is the sudden increase in arc length. The power of the discharge changes very little in this moment, whereas the temperature decreases rapidly. The length of the arc increases then in the ratio lmax/ $l^* = W / W^* = 3 - 5$ during a time that depends on the thermal conductivity, and that is of the order millisecond.

This sudden increase was fixed experimentally by high speed camera. Thus, in general the major part of the energy dissipated in the GlidArc corresponds to a non-equilibrium plasma state, as well as in microwave discharge. In accordance with discharge parameters this plasma is particularly promising for several chemical applications involving vibrational excitation.

NON-EQUILIBRIUM PLASMA CHEMICAL PROCESSES

In this chapter we shall consider the main results of modelling (and corresponding experimental results) of some concrete non-equilibrium near atmospheric pressure plasma chemical processes, where the highest values of energy efficiency were obtained. Additional information can be taken in (1-3,10,13,15).

Carbon dioxide dissociation $CO_2 = CO + 0,5 \; O_2$, $\Delta H = 2,9$ eV/mol.

This process can be essentially and with a high efficiency stimulated in non-equilibrium plasma by vibrational excitation of carbon dioxide molecules (mode v3). The lowest critical value of ionisation degree lg(Ne/No) is about -6, those of for specific energy input is about 0.15 eV/mol, those of for vibrational temperature is about 2000K, the required electron temperature 1-3 eV.

The highest energy efficiency for subsonic gas flow is 80% (with respect to $\Delta H = 2,9$ eV/mol) and can be attained for optimal specific energy input 0,8 eV/mol. The highest energy efficiency for supersonic (M=3) gas flow is 90% (almost all discharge power is going in selective process of CO production) and can be attained for optimal specific energy input 0,5 eV/mol.

The highest value of energy efficiency of carbon dioxide dissociation was obtained experimentally in non-equilibrium microwave discharge (power- 2KW, pressure 100-200 torr): in subsonic regime the highest efficiency was 80%, in supersonic one 90% in a good agreement with a modelling.

Hydrogen sulfide dissociation $H_2S = H_2 + S(s)$, $\Delta H = 0,2$ eV/mol.

This process can not be stimulated by vibrational excitation because of fast relaxation rate of hydrogen sulfide molecules. The essential deviation from equilibrium can be organized by centrifug·al effect in fast rotating discharge, system. For atmospheric pressure and gas temperature about 1500K, the optimal specific energy input is about 0,4 eV/mol, the required rotation Mach-number not less than 0,6.

The lowest energy cost from modelling is 0,5 eV per H_2 molecule. One need take into account that for equilibrium system even the lowest theoretical limit of this process energy price is 1,8 eV/mol, so 3-4 times more than out of equilibrium.

The highest value of energy efficiency of hydrogen sulfide dissociation was obtained experimentally in fast rotating non-equilibrium microwave discharge (power- 2KW, pressure up to 300 torr): for optimal

specific energy input about 0,4 eV/mol, the lowest energy price was 0.7 eV per H_2 molecule in a good enough agreement with modelling.

The big demonstration unit for such a technology application is working in the gas plant in Russia on the power level 1 MW for treatment 1000 m^3 of hydrogen sulfide per hour.

Nitrogen oxide synthesis $0,5 N_2 + 0,5 O_2 = NO$, $\Delta H = 1$ eV/mol.

This process can be essentially stimulated in non-equilibrium plasma by nitrogen vibrational excitation. The lowest critical value of ionisation degree lg(Ne/No) is about -7, those for specific energy input is about 0.15 eV/mol, those for vibrational temperature is about 2000K, the required electron temperature 1-3 eV.

The highest energy efficiency is about 35% (with respect to $\Delta H = 1$ eV/mol) and can be attained for optimal specific energy input 0,8 eV/mol. The efficiency of this process is lower with respect to carbon dioxide dissociation because of energy losses in exothermic stages.

The highest value of energy efficiency of nitrogen oxide synthesis 30% was obtained in non-equilibrium microwave discharge for specific energy input at about 1 eV/mol in additional magnetic field, operating in the conditions of electron- cyclotron resonance. The results obtained in these experiments are in a good enough agreement with modelling.

Water vapour dissociation $H_2O = H_2 + 0,5 O_2$, $\Delta H = 2,6$ eV/mol.

This process can be somewhat stimulated in non-equilibrium plasma by vibrational excitation of H_2O molecules. The lowest critical value of ionisation degree lg(Ne/No) is about -4, those for specific energy input is about 0.3 eV/mol, those for vibrational temperature is about 3000K, the required electron temperature 1-3 eV.

The highest energy efficiency is 50% (with respect to $\Delta H = 2,6$ eV/mol) and can be attained for optimal specific energy input 0,8 eV/mol. The energy efficiency is limited here first of all by very high vibrational relaxation rate.

The highest value of energy efficiency of water vapour dissociation about 35-40% was obtained experimentally as a result of intensive vibrational excitation in non-equilibrium microwave discharge (power- 2KW, pressure 100-300 torr).

Methane conversion $CH4 = 0,5 C_2H_2 + 1,5 H_2$, $\Delta H = 2$ eV/mol.

This process can be stimulated in non-equilibrium plasma by vibrational excitation of methane molecules. The lowest critical value of ionisation degree lg(Ne/No) is about -6, those for specific energy input is about 0.4 eV/mol., the required electron temperature 1-3 eV.

The lowest energy price of acetylene production here is 5,5 eV/mol, with respect to the minimum value of energy cost in equilibrium plasma about 8 eV/mol. The optimal specific energy input is about 1eV/mol.

The numerous experiments carried out in this direction were considered in (16). Vibrational stimulation of this process in moderate pressure non- equilibrium microwave discharge gave the energy cost 5,8 eV/mol. in accordance with theory.

SO_2, NO_x, and VOC oxidation in air for flue gas purification.

The modelling of these non-equilibrium plasma chemical processes was made for their application in industrial gas cleaning by relativistic electron beams and pulse corona discharge (10, 15). As an example let us consider here the most important one: the small amount of SO_2 oxidation in air by E-beams, where the main problem is the reduction of reaction energy cost.

In the traditional low current density systems the energy cost of purification is 10-20 eV per SO_2 molecule, due to the typical price of active particles in such a linear systems. The reduction of this energy cost becomes possible by organization of negative ion and negative ion clusters chain oxidation processes. This chain process can be realized in the optimal range of E-beam current density and optimal value of air humidity.

The efficiency predicted in modelling for the optimal plasma parameters was 0,3-0,5 eV per SO_2 molecule. The EB-experiments in a good agreement with a modelling show, that for optimal values of

current density and humidity the energy cost decrease up to 0,8 eV per SO_2 molecule, so it was confirmed the effect of non-equilibrium plasma catalytic activity.

In modelling (and in experiments as well) it was also shown that ion-molecular chain processes in droplet phase can also cause an additional reduction of oxidation energy cost.

COMPUTER PROGRAMMES FOR PLASMA CHEMICAL MODELLING

We shall list here our main computer programmes elaborated for non-equilibrium plasma chemical processes modelling:

1. The programme for statistical calculations with kinetic , limitations. This programme permits to make the fast estimation of conversion degrees and energy cost of non-equilibrium plasma chemical processes as well as thermodynamics calculations for equilibrium one.

2. The programme for kinetic , calculations including sensitivity analysis. This programme permits to calculate the complicated kinetical schemes, homogeneous and also heterogeneous taking into account surface reactions and reactions in droplet phase. This programme includes the sensitivity analysis, which gives the possibility to determine the main guiding reactions, the mechanism of plasmachemical process and finally the accuracy of modelling.

3. The programme for determination of unknown reaction rate constants. This programme contains the kinetical data base and also permits to determine theoretically unknown reaction rate constants using additional bank of thermodynamical and spectroscopic data.

4. The programme for calculation of kinetics and gas dynamics of plasma chemical processes in different types of gas flow. This programme permits to describe kinetics and two-dimensional gas dynamics for different types of gas flow and different discharges, including high frequency discharges.

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