Modelling of chemical reactions under nonequilibrium halogenated electrical discharge conditions

D.I.Slovetsky

Institute of Petrochemical Syntheses, Academy of Sciences,
117071, Moscow, Leninsky prospect 29, USSR

Abstract – Statement of the problem and results are discus-
sed concerning modelling of the chemical reactions under
nonequilibrium electric discharge plasma conditions in SF_6,
CF_4, CCl_4 and SF_6+O_2 mixtures. As the base for modelling the
inner plasma parameters as measured are used in line with
the quantitative study of chemical reaction kinetics inclu-
ding reactions with participation of the halogen atoms and
halogenated radicals and molecules.

INTRODUCTION

Halogenated plasmas of electrical discharges are used for generation
of chemically active halogen atoms and halogencontaining radicals to study
the reaction ones with other, gaseous molecules and solids and to develope
plasmachemical processes of material treatment. The plasma chemical etching
of solid materials for example determine today the progress in number modern
technologies particularly in microelectronics.
Mathematical modelling of chemical reactions in plasma is desirable step in
studying reaction mechanism, optimization and development of controllable
plasmachemical processes.
And so the number works deal with modelling of chemical reactions in dischar-
ge plasmas of CF_4, SF_6, CCl_4 and their mixtures with oxygen used widely
for plasmachemical etching (ref. 1-7). Interest in modelling is increased
in time. But the sucsesses are very modest because of modelling in nonequi-
librium plasma is very complicated problem, wich can be solved in diverse
ways with diverse level of detalizaion.
Therefore this report presents the critical analysis of involved problems
including the statement of question, determination of main plasma parameters
influencing on chemical reactions, comparison of calculated results with
experimental data and finally the conclusions about mechanisms of chemical
reactions under halogenated plasma conditions.

THE STATEMENT OF QUESTION

All chemical convertions in nonequilibrium cold plasmas are initiated by
electron-molecular impacts giving rise the dissociation, excitation and
ionization of molecules. Primary products are involved into secondary reac-
tions in bi- and three- molecular collisions.
Rates and directions of chemical convertion are determined by inner plasma
parameters such as the electron density (n_e), and energy distribution fun-

ctions (EEDF), influencing on primery reactions,and heavy particle temperature influencing on secondary reactions.

From the other side electron parameters and gas temperature depend on discharge parameters including electric power, current and the electric field distribution over plasma volume.

Hence the problem of reaction kinetics calculation in plasma is divided into the two interconnected problems: determination of inner plasma parameters at the given external discharge parameters and proper calculation of the chemical reaction kinetics depending on the inner plasma parameters.

To solve the both problems it is necessary to know the mechanisms of main physical and chemical processes in plasma (ref. 8,9). Therefore modelling has to be self-consistent. Completly self-consistent modelling is very complicated and is not performed now even in the simplest cases of dc discharge plasmas of electropositive gases.The first part of the problem namely calculation without chemical reactions is solved now in self-consistent statement only for the rare gases plasmas of dc, HF and microwave discharges (ref. 10-12). In these cases electric field distributions, gas temperature, electron and ion densities, ion compositions and EEDF are calculated (ref. 11).

There are some attempts to include the chemical reactions kinetics into self-consistent calculations for example in argon-monosilane plasma (ref. 13) but very schematic mechanism of convertion is taken into account in this case.

The modelling problem is solved recently in mostly complete statement for the argon-methane plasma of dc glow discharge (ref. 14). In this work the gas temperature is taken only from experimental measurements.

For the electronegative gases such as freons there are the attempts of self-consistent chemical reaction kinetics modelling in the case of CF_4 and CF_4+ O_2, CF_4+H_2 mixtures in HF discharges with parallel plate electrodes (ref.1-2). But in these works electric field distribution is not calculated as the gas heating. In other works inner plasma parameters are not calculated and are not measured. They are given enough arbitrarily (ref. 3), or are evaluated from average specific electric power (ref. 5,6), but in the latter cases gas heating does not taken into account completely. Chemical kinetics calculation results are compared with experimental data only in works (ref. 5,6).

To illustrate the difficulties in solving the self-consistent problem in halocontaining plasmas let us primerily to consider the methods of inner plasma parameters determining, conceptions of ionization, ion-convertion and charged particles decay mechanisms.

GAS HEATING

Gas temperature can be calculated from heat transfer equation taking into account volume heat sources from electric power input. Gas heating in discharges takes place due to energy transfer from electric field to charged particles. Usually main part of the energy is transferred from electric field to electrons, having large mobility. But in the case of electronegative plasmas ion densities can be much more than electron density and significant part of field energy can be transferred directly to the ions.

Energy of charged particles is transferred to the neutral molecules during collisions. In elastic and inelastic electron-manyatomic molecule collisions with rotational and vibrational excitations whole spended energy of elect-

rons is transferred to gas heating. But in the electronic excitation only
part of electron energy can be transferred to gas heating. This part is
equal to the difference between the excitation energy and energy of chemical
bonds breaking up due to dissociation following the electronic excitation.
This part of energy is converted to translational energy of dissociation
products movement. The same sitnation takes place in the case of dissociati-
ve ionization. Dissociation, ionization and excitation energies can be re-
turned to gas heating as result of volume recombination reactions and quan-
ching or can be lost due to heterogeneous reactions and processes. Ions ta-
king the additional energy from electric field transfer it to neutral par-
ticle in ion-molecule collisions. Part of this energy is spended also in
chemical reactions.

Thus the portion of electric field energy input in discharge wich is spended
to gas heating (η) depends on detailed mechanism of physical and chemical
processes in plasma and it is always less than unity. It is necessary to
know electric power and η -value distributions over plasma to calculate
correctly gas temperature. By other words it is necessary to make self-con-
sistent calculations.

Upper limit of gas temperature can be estimated assuming η =1. The value
can be corrected only after investigation of physical and chemical processes
mechanisms. Such a problem is not solved now in any case.

More practic way is using of experimental gas temperatures as measured with
diverse techniques: thermocouples, thermoprobes, spectroscopic (from Doppler
broadening of atomic lines and rotational lines intensities distribution)
(ref. 8,9). Results of measurements (Fig. 1,2) show that η -values for di-
vers gases vary in wide range depending on kind of gas and discharge para-
meters. For example it varies from 0,5 to 0,7 in CF_4 and SF_6 but it is equal
to 0,8-1 in the CCl_4 plasma under the same conditions.

REDUCED ELECTRIC FIELD STRENGTH

Reduced electric field strength (E/N_o) is one of the main macroscopic para-
meter influencing on EEDF and on rate coefficients of electron initiated
processes. It can be calculated in positive culomn of discharges using equa-
tion of electron balance. For electronegative plasma the approximate equa-
tion is:

$$K_i - K_a = \frac{D_e}{\Lambda_e^2 N_o} \quad , \qquad\qquad (1)$$

where N_o is heavy particle concentration, Λ_e is characteristic diffusion
length for electrons, D_e is their diffusion coefficient, strong depending on
negative ion concentration. In the case of the small concentrations electron
diffusion is ambipolar but at large ones ($\alpha = n_-/n_e \longrightarrow \infty$) approximates
to the free electron diffusion value. Rate coefficients for ionization (K_i)
and dissociative attachment (K_a) are calculated using cross sections of this
processes and EEFD. In the case of homogeneouse plasma with small ionization
grade ($\alpha_i = n_e/N_o < 10^{-6}$) EEFD and the coefficients are the functions of
reduced electric field. Then the E/N_o is the inevident solving of equation 1.
The processes of volume ion-electron recombination and associative electron
detachment do not taken into account in eq.(1). For CF_4, CCl_4 and SF_6 plas-

mas these processes give no contribution in electron balance as evaluated
(ref. 9). For heavier fluorocarbons situation can be not the same.

As followed from abovementioned generation and decay mechanisms can be known
for electrons and ions. By the other word solution has to be self-consistent
or at least results have to be compared with experimental data and analized
to check the validity of origin assumption.

Comparison of calculation results with experimental data (ref. 15) for CF_4
(ref. 15) dc discharges shows that at relativly large gas pressures ($N_0 \Lambda_e >$
$0,4 \cdot 10^{16} cm^{-2}$) reduced fields achieve the critical value which corresponds to
the equality

$$K_i = K_a \quad . \tag{2}$$

Electron diffusion gives no contribution in this range. At the smaller $\Lambda_e N_0$
values there are significant differences between experimental data and cal-
culation with diverse assuming about electron diffusion (Fig. 3^a). The free
electron diffusion does not take place in spite of the calculated relative
ion concentration is vary large ($\alpha \sim 100$) (ref. 9). The data of Fig. 3^a show
that both theoretical variants are not valid for E/N_0 calculations.

From the other side the E/N_0 dependence on $\Lambda_e N_0$ is automodel . The values
do not depend on discharge current density (j =5-25 mA/cm^2) and gas pressu-
re (p =25-300 Pa). Hence the neglected secondary ionization processes with
products and excited particles and ion-electron recombination give no
contribution to ionization and electron decay rates. It is the base for E/N
values calculation in homogeneous stady state plasmas using the experimental
curve (Fig. 3^a).

It schould be noted that more sharp dependence of E/N_0 on $\Lambda_e N_0$ at $\Lambda_e N_0 =$
$\approx 0,2 \cdot 10^{16} cm^{-2}$ can be connected with plasma nonhomogeneousity. The latter can
be more significant in the case of parallel plate electrode plasma with
small electrode gap becáuse to influence of byelectrode potential jumps.
Then data of Fig. 3ª schould be used with large precautions. In HF discharge
plasmas nonstationarity schould be taken into account influencing EEDF too.
The latter effect gives for example increasing of $(E/N_0)_c$ values from
$3,7 \cdot 10^{-15}$ to $5 \cdot 10^{-15}$ V·cm^2 for SF_6 HF plasma (ref. 17). The E/N_0 dependence
on $\Lambda_e N_0$ is also automodel for CCl_4 dc glow discharge in wide ranges of j
and p. Critical CCl_4 value is

$$(E/N_0)_c = 3 \cdot 10^{-15} \text{ V·cm}^2 \quad (\text{ref. 16}) . \tag{3}$$

EEDF

EEDF's for halogencontaining plasmas are determined mainly from calculation
in dependence on E/N_0 by solving the Bolzmann equation or direct modelling
by Monte-Carlo technique (ref. 17-19). Cross section sets are matched by
means of the successive approximations. Coinsidence of drift velocities, cha-
racteristic electron energies and ionization rate coefficients as measured
in drift tube experiments is the matching criteria (ref. 18). In line with
EEDF the rate coefficients of all inelastic electron-molecule processes are
calculated which are used for calculations of plasma processes rates. Main
difficulties of calculated value using are E/N_0 values determination in the
discharges and suppositions checking assuming in EEDF calculation. These are
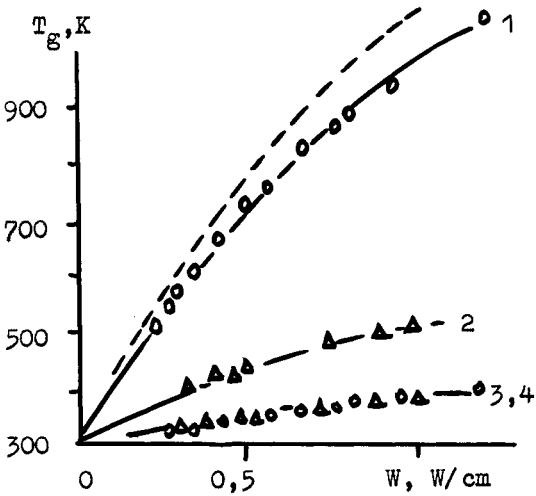plasma locality (homogeneousity), stationarity and small contribution of

Fig. 1. Gas temperatures at the discharge axis (1,2) and walls (3,4) in tubular reactor in CCl_4(1,3),CF_4,CF_4+O_2 (2,4) versus specific discharge power. Dotted line corresponds to the calculation using $\eta =1$ in CCl_4.
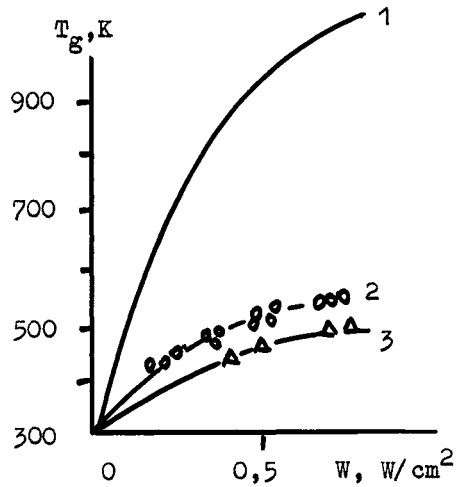
Fig. 2. Gas temperatures at the midle line between the parallel plate electrodes versus specific discharge power in CCl_4 (1), SF_6 (2), CF_4, CF_4+O_2 (3).
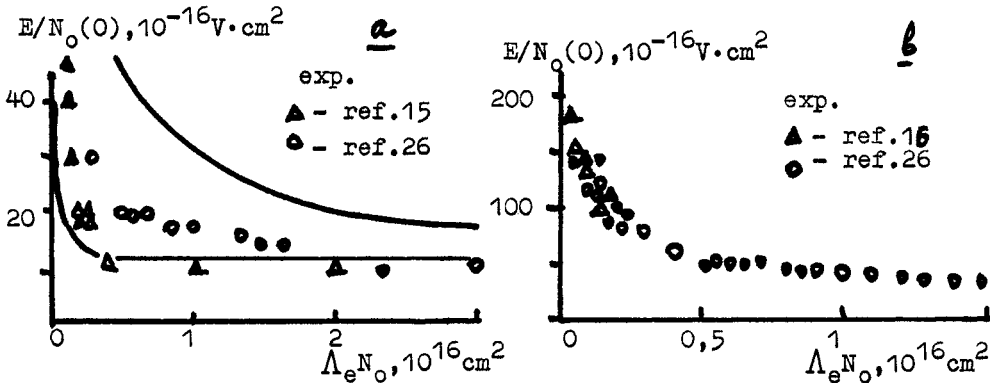

Fig. 3. Reduced electric field vs electron diffusion parameter $\Lambda_e N_0$ in CF_4 (a) and CCl_4 (b) plasmas. The lines are calculated assuming ambipolar ($\alpha \to 0$) and free electron diffusion ($\alpha \to \infty$).
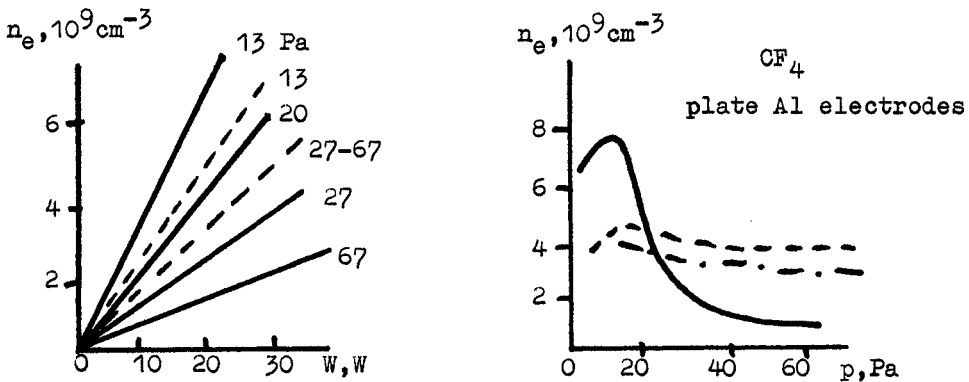

Fig. 4. Total electron densities as measured with micro wave technique (ref. 20) (solid lines) and as calculated (dotted ones) and fast electron densities as measured with spectroscopic technique (pointed-dotted line).

electron-electron and electron-excited particles collisions. Methods for
these processes taking into account are in principle developed and the self-
consistent calculations can be made also in halogenated plasmas. The situa-
tion with nonlocality influence is worse and the problem schould to be sol-
ved for electronegative plasmas.
There are the attempts to measure EEDF in halogenated plasmas with probe
technique. But results are not sistematic and trusty due to failing of theory.

ELECTRON DENSITIES

The electron densities can be calculated theoretically from discharge cur-
rent density equation if the electron drift velocity and E/N_o value are
known. Principle complication in halogenated plasma is the large ion concen-
tration compared with electron one. In the case $\alpha = n_-/n_e \sim V_{de}/V_{di}$ ions
can give comparable contribution to the discharge current. To take this con-
tribution into account it is necessary to know α - value. The problem has
to be solved in self-consistente manner again.
Nevertheless calculated electron densities for CF_4 HF discharges coincide
satisfactory with scanty experimental data (ref. 2,20) (Fig. 4). But relati-
ve dependences on discharge parameters are incorrect. This fact gives no pos-
sibility to use the calculated densities for chemical reaction mechanism in
plasma modelling.

CONCLUSIONS ABOUT INNER PLASMA PARAMETERS

It is necessary to note that inner plasma parameters calculations (such as
electron parameters and gas temperature) are most complicated and made usu-
ally using theories which are not always adequate to the reality.
Therefore modelling of chemical reactions in plasma schould be made using
directly the experimental inner plasma parameters.
As to the electron parameters usual way of EEDF and n_e measurement is not
good for halogenated plasma as shown above. More preferable way is to measu-
re directly the fast electron concentration which completly determine the
rates of inelastic processes initiating chemical reactions in plasma. There
are the spectroscopic methods for the fast electron measurement based on the
line intensities of reference rare gases (as rules argon is used as small
spectroscopic addition to working gas) (ref. 9). Basic assumption of the
spectroscopic method is excitation of the atomic levels by one step electron
impacts and deactivation due to radiation and quenching by molecule impacts.
The excitation mechanism schould be checked before using of the method by
means of special experiments or calculations.
Measured specific rates of the reference line excitation can be used for
calculation of any inelastic electron-molecule process rates if the cross
sections are known including dissociation, ionization and other ones.
Quantitative modelling of chemical reaction in plasma is possible only with
this way because of errors of electron parameters are sufficently small in
this case. Calculated electron parameters errors can be very large as fol-
lows from above discussion particularly in HF parallel plate electrodes
discharges at low pressures (p<50 Pa). In the latter cases calculations
are problematic on account of EEDF nonstationarity and nonlocality and lack
of data concerning mechanisms of ionization, ion convertion, including elec-

tron-ion and ion-ion recombination.

MODELLING OF CHEMICAL REACTIONS IN HALOGENATED DISCHARGE PLASMA

Modelling of chemical reactions in halogenated plasma as shown by above ana-
lysis schould be made using experimental fast electron concentrations and
gas temperatures. The measurements can be carried out in diverse plasmas in-
cluding dc, HF and microwave glow discharge.

Main question of chemical reaction modelling is choice of reaction mechanism
as set of elementary reactions (ref. 9). The procedure consits of looking
over diverse variants with matching of rate coefficients. Validity criterium
of any variant has to be comparison of calculated and measured product kine-
tics. Singling out the reaction rate coefficient in plasma is not trivial
operation.

As rule the values are used as obtained from kinetic analyses in model che-
mical systems for example with mass-spectrometric technique (ref. 5,6). It
is in order because of till recent time particle kinetics are not measured
in plasmas. The measurements become possible now due to development of re-
laxation spectroscopic method for kinetic reaction study (ref. 21).

It is necessary to note in this respect that additional reactions can take
place in plasma due to higher gas and ions temperatures, generation negative
ions, excited particles and specific conditions at the walls and electrode
surfaces. Particularly contributions of volume and surface heterogeneous re-
actions are not known apriory, as the products of molecule dissociation due
to electron impacts. All these questions have to be solved in reaction mo-
delling. Some systems are considered in the next sections. (See also our
reports at this symposium).

SULFUR HEXAFLUORIDE

Detailed experiments were performed with relaxation spectroscopic, mass-spe-
ctroscopic and thermocouple techniques in HF discharge with parallel plate
aluminium electrodes in the range of specific discharge powers from 0,15 to
1,2 W/cm^2 with frequency 13,6 MHz, pressures 16-76 Pa and electrode tempera-
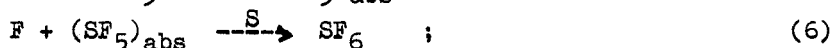ture 300 K. Electrode gap was 1,5 cm.

The spectra of stationary discharge contains atomic fluorine and argon lines
(argon addition was 5%) and some continua which were not identified . Ra-
diation of the molecular fluorine did not observed as the any stable pro-
ducts with mass-spectrometry in flow afterglow (the time of observation was
about 0,5 s after entrance from discharge). Only SF_6 molecules were observed
and the concentrations were the same without and with discharge. The same
facts were observed earlier in work (ref. 4). Modelling of chemical reac-
tions is made by solving equations of heat transfer and chemical kinetics.
Experimental quasistationary gas temperatures and fast electron concenta-
tions are used. Experimental SF_6 dissociation rates due to electron-molecule
impacts are found using argon 750,3 nm line absolute intensity and the ratio
cross-sections of excitation and molecule dissociation. This values are
coincided with the rates of atomic fluorin generation as found from kinetic
curve for F atoms in error limits.

Calculations show that gas temperature rises just after discharge impuls im-

posing to steady state value and drops quickly after discharge out. Characteristic heating times are varied from 1 to 3 ms.

Typical shape of F atom line intensity which represents the kinetic curve of F atom generation in impuls(because of argon line intensity is approximatly constant)and F atom decay during pause are shown in Fig. 5. It is interesting to note that reactions take place in discharge impulses and in pauses at diverse gas temperatures.

Modelling is made with three variants of chemical reactions mechanism . Dissociation is considered to be due to direct electron-molecule impacts with generation of F atoms and SF_5 radicals. This assumptions are in accordance with experimental data namly: F_2 and SF_4 are not observed and SF_6 dissociation rates are proportional to fast electron concentrations depending on discharge power and finally as followed from kinetic curve shapes the dissociation products are recombined quickly with generation only SF_6 molecules (ref. 21). In modelling recombination is assumed to be due to the volume recation with second kinetic order on product concentrations (the first variant) and to the surface reactions with steps :

$$F \xrightarrow{S} (F)_{abs} \quad ; \qquad\qquad (4)$$

$$SF_5 \xrightarrow{S} (SF_5)_{abs} \quad ; \qquad\qquad (5)$$

$$F + (SF_5)_{abs} \xrightarrow{S} SF_6 \quad ; \qquad\qquad (6)$$

$$SF_5 + (F)_{abs} \xrightarrow{S} SF_6 \qquad\qquad (7)$$

(the second variant).

The third variant which is considered to check the one of the assumption contains dissociation into SF_5 and SF_4 radicals in equal quantity and atomic fluorine in respective quantity. It containes also the surface recombination reactions (4-7) for SF_5 and analogical reactions with SF_4 participation.

Volume recombination (the first variant) does not discribe curves of concentration decay in pause where dissociation rate is equal to zero and only recombination of particles generated in impuls takes place. It does not discribe characteristic growth time of the F concentration during impuls (Fig. 5). The best fitting of the calculated and experimental results is observed with heterogeneous recombination (variant N2). The reaction has the first total kinetic order on particle concentration in spite of the small degree of surface covering by absorbed particles. This fact which is not understanding on the first view is explained by the proportionality to the particle concentration of the both stages - absorption and desorption, the latter taking place due to recombination. Without recombination atoms and radicals are absorbed strongly at the surface. Recombination rate coefficient is equal $280^{\pm}20$ s^{-1} and does not depend on gas pressure and discharge power in the whole range. Futhermore the values in pause and impuls are equal what connected with constant electrode temperature.

With the third variant of mechanism containing SF_5 and SF_4 generation it is impossible to match the rate coefficients which would be able to discribe the F concentration decay even in pause. Deviations of calculated curves from experimental first kinetic order curves are less than 15% what is more than error limits.

Moreover reactions modelling in $SF_6 + O_2$ mixture discharge shows that oxydation products observed are correspondent to the SF_5 radical generation.
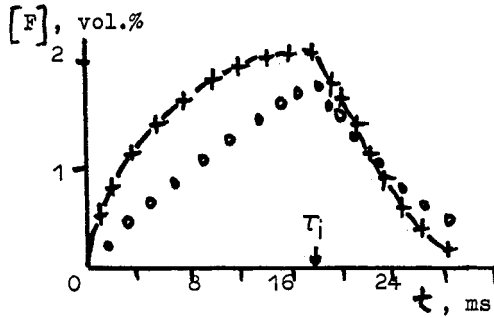
Fig. 5. Kinetic curves for the atomic fluorin formation during
discharge impuls and pause in SF_6 modulated HF discharge with
plate Al electrodes : f=13,56 MHz ; W=1,1 W/cm ; p=76 Pa .
Solid line is experiment, points are calculated assuming recom-
bination reactions of the second kinetic order on the F atom
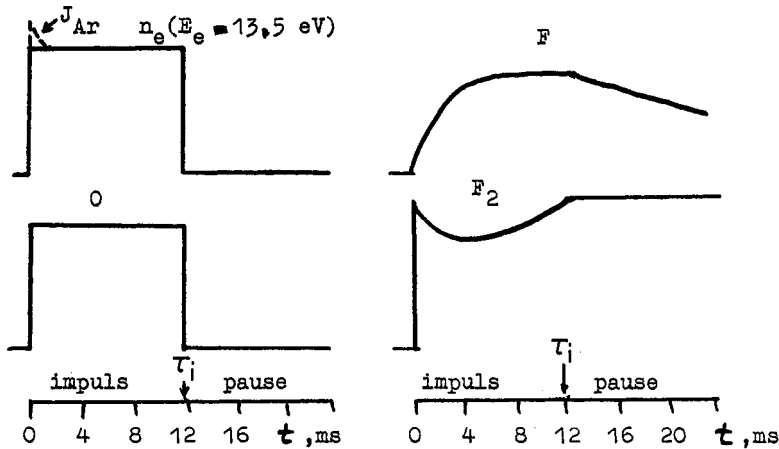concentration (cirles) and of the first one (crosses).

Fig. 6. Kinetic curves (relative concentrations) for the fast
electrons, atomic and molecular fluorine, O atoms in modulated
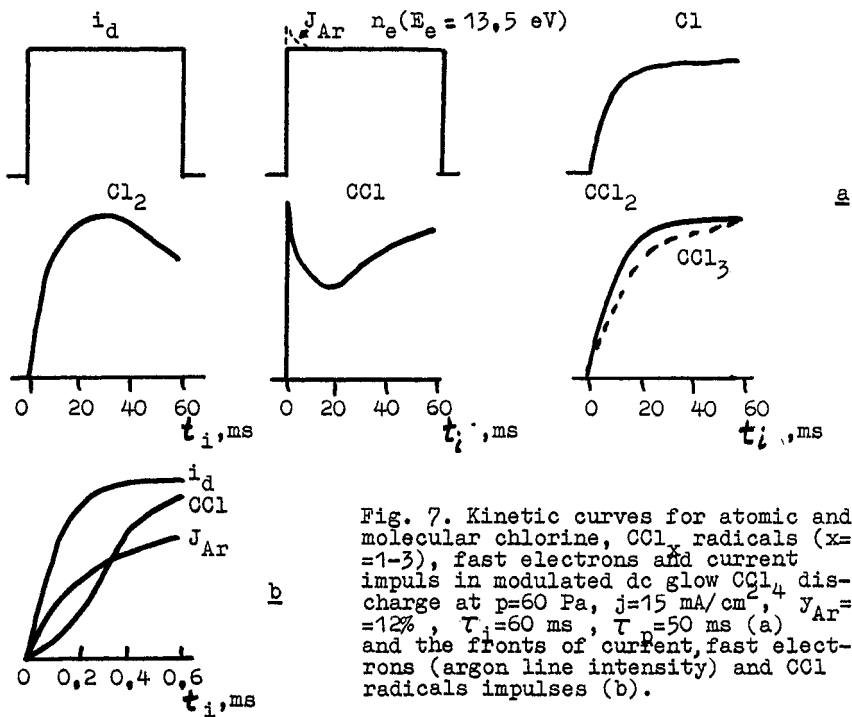HF discharge in 75% SF_6 + 20% O_2 + 5% Ar mixture.

Fig. 7. Kinetic curves for atomic and
molecular chlorine, CCl_x radicals (x=
=1-3), fast electrons and current
impuls in modulated dc glow CCl_4 dis-
charge at p=60 Pa, j=15 mA/cm^2, y_{Ar}=
=12% , τ_i=60 ms , τ_p=50 ms (a)
and the fronts of current, fast elect-
rons (argon line intensity) and CCl
radicals impulses (b).

Primary product is SOF_4 transforming to the SO_2F_2 due to second step of oxidation. SOF_2 molecules which have to be the product of SF_4 oxidation do not observed. Molecular dissociation is shown by modelling to be the result of electron-molecule impacts and to occure through the unstable molecular electronic level excitation. Dissociative attachment gives no sifnificant contribution as it is limited by the molecular ionization having the rates at least by ten times less than the dissociation one.

SF₆ + O₂ MIXTURES

Modelling is made using the results in pure SF_6. Radical oxidation reactions are added in gase phase and absorption of O atoms at the surfaces. Experimental kinetic curves of diverse particle generation and decay are obtained with spectroscopic technique (Fig. 6) (ref. 22). There is increasing of F atom concentration up to maximum at 20% O_2 and then it decreases. O atom and F_2 molecule generation take place. The kinetic curve shapes for the particles are diverse, reflecting various channals of the particles generation and decay.

Including in calculation the SF_5 oxidation reactions

$$O + SF_5 \;---\; SOF_4 + F \;\;(K = (3 \pm 0,5) \cdot 10^{-11} cm^3 s^{-1}) \;(ref. \;23) \qquad (8)$$
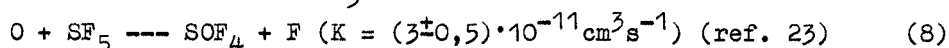
with succeeded reaction

$$SOF_4 + O \;\;---\; SO_2F_2 + F_2 \qquad\qquad\qquad (9)$$

gives the possibility to explain the product composition, the fast front of O atoms generation, F_2 and some additional F atoms generation (Fig. 6).
But taking into account only the reactions (8,9) it is impossible to discribe the experimental data quantitatively.
Particularly the modelling gives no possibility to explaine fast generation and large concentration of O atoms and large ratio of F atom concentration in maxima and without oxygen additions and also relatively small reduction of F atom recombination rates – only in 3 times at 60% O_2 addition. The modelling of the system in progress now but it is very difficult to explaine large experimental material. Nevertheless, modelling gives some new conclusions about generation and decay of F_2 molecules and O atoms.
(See also our report on this symposium).

TETRACHLOROMETHANE

Experiments were carried out in dc glow discharge in CCl_4 (ref. 16). The Cl, Cl_2, CCl, CCl_2 and CCl_3 were identified in the spectra, which had diverse kinetic curves (Fig. 7). Modelling of the chemical reaction allows to suggest new kinetic mechanism. CCl_4 dissociation occurs due to single electron-molecule impacts with generation mainly CCl_2 radicals and atomic and molecular chlorine with equal rates :
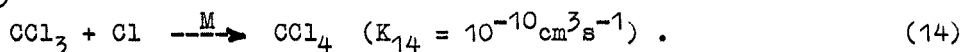
$$CCl_4 + e \;---\!\!\rightarrow\; CCl_2 + 2Cl + e \qquad , \qquad\qquad (10)$$
$$\qquad\qquad\;\; \rightarrow\; CCl_2 + Cl_2 + e \qquad . \qquad\qquad (11)$$

Contribution of CCl_3 radical generation is small :

$$CCl_4 + e \;----\!\!\rightarrow\; CCl_3 + Cl + e \qquad . \qquad\qquad (12)$$
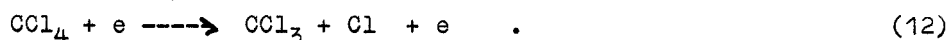
Main channel of CCl_3 generation is gaseous recombination reaction

$$CCl_2 + Cl \xrightarrow{M} CCl_3 \quad (K_{13} = 1,7 \cdot 10^{-12}(300/T)^{2,1} cm^3 s^{-1}) \ . \quad (13)$$
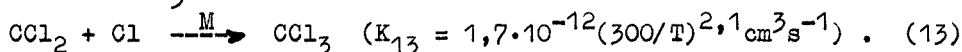
The CCl_3 decays due to fast gase phase reaction

$$CCl_3 + Cl \xrightarrow{M} CCl_4 \quad (K_{14} = 10^{-10} cm^3 s^{-1}) \ . \quad (14)$$

The CCl radical are generated mainly due to chain of reactions

$$CCl_4 + e \longrightarrow CCl_3^+ + Cl^- \longrightarrow CCl_3^* + Cl \longrightarrow CCl + 3Cl \quad (15)$$
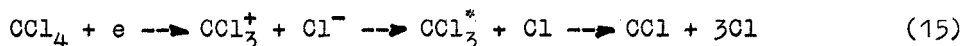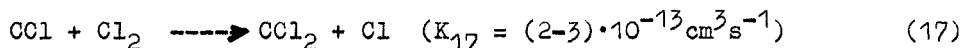
but direct CCl_4 dissociation and dissociative excitation give no significant contribution in opposite to previous supposition (ref. 7).
This chain of reactions (15) explains some delay (0,1 ms) in appearence of excited CCl radicals. Modelling shows that CCl excitation is due to elect-ron- CCl radicals impacts, but is not due to dissociative excitation. Fast CCl generation front and complicated shape of kinetic curves (Fig. 7) ref-lect the fast decay reactions

$$CCl + CCl_4 \longrightarrow CCl_2 + CCl_3 \quad (K_{16} = 3 \cdot 10^{-13} cm^3 s^{-1}) \quad (16)$$

and

$$CCl + Cl_2 \longrightarrow CCl_2 + Cl \quad (K_{17} = (2-3) \cdot 10^{-13} cm^3 s^{-1}) \quad (17)$$
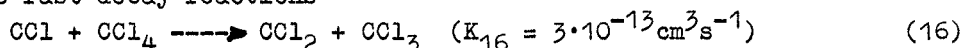
in combination with complex generation reactions. Decay reactions for all the particles in pause between discharge impulses have the second kinetic order on reagent concentrations and take place in gas phase. This fact is proved by differences between the recombination reaction rates in pause (at $T_g = T_{el}$) and impulse (at $T_g \gg T_{el}$) (Fig. 1) what is reflected in different characteristic times (Fig. 8).
The number experimental facts are explained in the frame of suggested new chemical reaction mechanism including the appearence of CCl_3 radical concen-tration maximum in discharge afterglow (ref. 7), diverse dependence of the particle radiation intensity on discharge current nonmonotonic kinetic cur-ves (Fig. 7). It is necessary to strength that formation of C_2Cl_6, C_2Cl_4 and C_2Cl_2 molecules take place as result of radicals recombination at the longer times.
Thuth radicals decay due to diverse recombination reactions or heterogeneousely as for SF_6 and $SF_6 + O_2$ or in volume as for CCl_4 discharges under the approximatly same plasma conditions. Dissociation channals in the-se cases are diverse also, giving or the one of possible radical (SF_5) or the all possible ones (CCl_x - x=1-3).
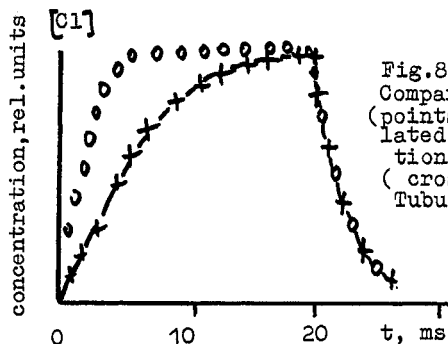

Fig.8.
Comparison of experimental (solid line) and calculated (points) kinetic curves for Cl atoms format on in modu-lated dc CCl_4 discharge, assuming decay due to recombina-tion reactions of the second kinetic order in volume (crosses) and at the reactor walls (circles). Tubular reactor, R=0. 9 cm, p= 27 Pa, j= 15 mA/cm^2.

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Decomposition of CF_4 in discharge plasma was modelling in past most frequently (ref. 1-3,5,6,9). But results of diverse works based on the same experimental results (ref. 23) were opposite including the F atoms decay at the tube surface in reaction having the first kinetic order (ref. 9), or in volume reactions having the second kinetic order (ref. 5,6).

Hence the new experiments are necessary and these are carried out with relaxation spectroscopic technique in dc glow discharge in glass tube (the reactor is the same as used for CCl_4 study). Kinetic curves of F atom decay in pauses between discharge impulses are the first kinetic order ones (Fig. 9). But the rate coefficient is dependent on pause duration (Fig. 9,10).
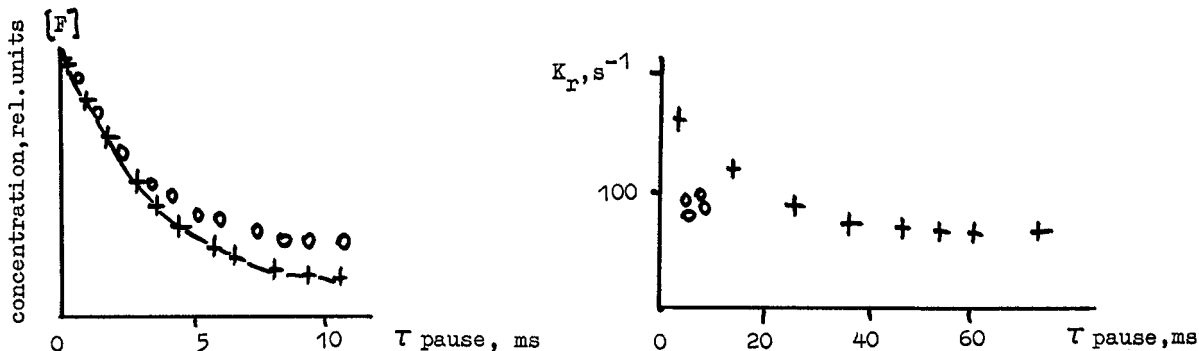

Fig. 9. Kinetic curves for the F atoms decay during pause between discharge impulses in modulated dc discharge. Solid line is experimental data, points are calculated with the first (crosses) and the second (circles) kinetic order recombination reactions. Tubular reactor, R= 0,9 cm, p=27 Pa, j= 25 mA/cm².

Fig.10. Experimental dependence of the F atoms decay rate coefficients in recombination reaction of the first kinetic order on pause duration in CF_4 modulated dc discharge without special treatment (crossed points) and with the special treatment of the tubular glassy reactor walls by helium discharge (open circles).

The complicated picture of decay forces us to carry out control experiments. The discharge tube walls were treated during few hours by helium dc discharge. Just after treating over discharge in CF_4+5% Ar was initiated in the tube. The measured rate coefficient values for F decay after treating were less by 1,5-2 times. With discharging time the values monotonically returned to the untreated values (in limit of ±10%). The experiments prove that the F atoms decay due to heterogeneouse reactions, having the first kinetic order on F concentration. The results confirm the previous conclusions in (ref. 9), but are opposite to conclusions of (ref. 5,6).

In latter works chemical reactions modelling was performed in CF_4 and CF_4+O_2 HF plasmas in tubular HF reactor (ref. 23). Electron density was evaluated from specific discharge power using apriory chosen value of E/N . Gas temperature was equal to the room one. Authors used mechanism composed only from volume reactions. Recombination and oxydation rate coefficients were measured in special setup discharge afterglows at low pressure with mass-spectroscopic technique. They made conclusions on base of thiere experimental kinetic curves that volume reactions of CF_2+F and CF_3+F recombination had the second kinetic order. Modelling gives results satisfactory coinciding with experimental(concentrations of F atoms, and CO,CO_2, COF_2 molecules in the case of CF_4+O_2) at p= 0,5 torr (ref. 23) from their point of view.

But it is necessary to note some incorrectnesses in the works (ref. 5,6). They did not take into account gas heating which had to changed the binary volume reaction rates by many times (up to 4-5). Specific power was determined without observation of discharge dimentions. Our experiments in the same geometry but with glassy tube showed that HF discharge length was more by 2-3 times than electrode length. Thus the evaluated plasma parameters were incorrect. Finally, remeasuring the CF_3+F recombination coefficient in recent works (ref. 24) showed that the value used in (ref. 5,6) was overestimated up to one order and the reaction had the third kinetic order in studied pressure range. Theoretical consideration could not confirm this overestimation and the second kinetic order too (ref. 24).

As result the modelling did not give correct data particularly in dependence on pressure, in variation of F concentration with O_2 addition and without one etc. Direct measuring of F concentration in pure CF_4 at the same parameters give the value less than calculated in (ref. 5) by 2-3 times even at p= 0,5 torr.

From the other side in works summerized in (ref. 9) it was suppoused that main radical and single one is CF_3, though the CF_2 radical radiation was observed in the discharge spectra. In accordance with the results of authors of (ref. 5,6) it is the main product of CF_4 - electron impact dissociation. Hence the modelling of CF_4 and CF_4+O_2 plasmas have to be made from the start. But before this it is necessary to explaine complicated F atom decay observed with relaxation technique (Fig. 9,10).

Thus detailed studying and modelling of chemical reaction kinetic in CF_4 and CF_4+O_2 plasmas show reaction mechanism has to be distinguish significantly from assuming in previous modelling (ref. 1-3,5,6,9).

SUMMARY

In conclusion of the report it is necessary to strength that chemical reactions modelling problems under nonequilibrium halogenated plasma conditions are far from solving in spite of the importance of the systems. It connects firstly with failure of inner plasma parameters modelling. Detailed measurements and development of the discharge theory in electronegative gases are necessary with taking into account nonstationarity, nonlocality of plasmas and negative ions influence on physical and chemical processes in plasma in the first turn on the electron diffusion.

The problem is impossible to solve without detailed study chemical reactions mechanism , charged particle generation and decay and electric field distribution over plasma. The experiments were started and the first results were reported on the Symposium in Tokyo (1987) and ESCAMPIG in Lissabone (1988) using the modern plasma diagnostic techniques. Measurements of inner plasma parameters is obligatory step in the way to the solving chemical reaction modelling problem due to interconnection of the both problems.

One example illustrates above discribed . Gas temperature is one of the main plasma parameter influencing on reaction kinetics. The self-consistent calculations of gas temperatures are not made now in any cases with sufficient correctness.

From the other side portion of energy spend on gas heating is various for the diverse plasmas. For CCl_4 it is more than 0,8 because of the recombina-

tion reactions take place in gas phase. At the same parameters in CF_4 and SF_6 plasmas the η values are less (η =0,5-0,7) because of the chemical energy is spend at the surfaces due to heterogeneous reactions. It is impossible to predict this behaviour apriory. Hence the apriory calculations as in (ref. 1-3) without detailed study is not likely to make today. Evidently the self-consistent modelling of chemical reactions is not possible now for halogenated plasma.

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