

THERMODYNAMIC STUDY OF DECOMPOSITION OF DICHLORODIFLUOROMETHANE IN THERMAL PLASMA

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Decomposition of dichlorodifluoromethane in thermal plasma was investigated theoretically by computing the equilibrium composition of the gas mixtures involving carbon, chlorine and fluorine in presence of argon (which is assumed to be the main plasma gas) and/or in addition of hydrogen and calcium together with hydrogen. The calculations were carried out for the temperature range between 500 and 6000 K and for the total pressure of the system of 1 bar. Use is made of the fact that a thermal plasma is a plasma in (local) thermal equilibrium, which makes possible the theoretical determination of its equilibrium composition at definite temperature by employing Gibbs free energy data for the compounds present in the system and assuming that the equilibrium of the system corresponds to its minimum energy state. The results of calculations show that toxic molecules and radicals can be, under convenient conditions (appropriate temperature and amount of added substances), converted into stable non-toxic species like CaF_2 and CaCl_2 .

Keywords: dichlorodifluoromethane decomposition, thermal plasma, thermodynamic calculation

Introduction

Dichlorodifluoromethane is one of chlorofluorocarbon compounds (CFCs) – freons. Chlorofluorocarbons were synthesized in 1928 and since then, being generally low toxic and chemically inert compounds, they were widely used as the cooling mediums in refrigerators, in spray bottles, etc.. In 1974 Molina and Rowland [1] (with Crutzen, Nobel Prize winners in chemistry for 1995) found that stratospheric ozone layer has been depleted due to chemical reactions of chlorine or fluorine radicals, originating from chlorofluorocarbons (gradually transported up to the ozone layer), with ozone. Since then, the investigations concerning the decomposition methods of chlorofluorocarbons have gained on importance. Among the applied methods, the thermal plasma method is very efficient because of its high temperature; it gives also the opportunity to remove highly toxic products of decomposition (chlorine or fluorine containing molecules or radicals) by introducing into the plasma the gases (besides chlorofluorocarbons) like hydrogen, oxygen, etc., and via chemical reactions which involve chemical species present in the plasma [2, 3].

In this paper decomposition of dichlorodifluoromethane in thermal plasma was investigated theoretically by computing the equilibrium composition of the gas mixtures involving carbon, chlorine and fluorine in presence of argon (which is assumed to be the main plasma gas) and/or in addition of hydrogen and calcium together with calcium. The calculations

were carried out for the temperature range between 500 and 6000 K and for the total pressure of the system of 1 bar. Use is made of the fact that a thermal plasma is a plasma in (local) thermal equilibrium, which makes possible the theoretical determination of its equilibrium composition at definite temperature by employing Gibbs free energy data for the compounds present in the system and assuming that the equilibrium of the system corresponds to its minimum energy state. The results of calculations show that toxic molecules and radicals can be, under convenient conditions (appropriate temperature and amount of added substances), converted into stable non-toxic species like CaF_2 and CaCl_2 .

Method of calculation of equilibrium composition

Two basic approaches are used to determine the composition of the complex mixtures at high temperatures. In the first one the thermodynamic equilibrium constants for the decomposition and ionization reactions together with the mass conservation law and electrical neutrality are employed to determine equilibrium composition [4]. The second method based on minimization of the Gibbs free energy was used in this paper. The calculation of the equilibrium gas mixture compositions under condition of constant pressure is carried out using the method of White *et al.* [5], extended for the mixtures containing charge particles [6]. It is based

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on the fact that the equilibrium of the system corresponds to its minimum energy state. The free energy G of the system is the sum of the chemical potentials, μ_i , multiplied by the mole fractions, x_i , of its components,

$$G = \sum_{i=1}^n x_i \mu_i \quad (1)$$

where n and x_i are the numbers of chemical species and their mole fractions that has to be determined. The set of x_i values leading to the equilibrium can be obtained by solving the equation

$$\delta G = 0 \quad (2)$$

at the fulfilled mass balance condition

$$\sum_{i=1}^n a_i x_i = b_j; \quad j=1, 2, \dots, m \quad (3)$$

where m represents the number of elements in the system, a_i is the number of atoms of element j in the molecule i , and b_j is coefficient proportional to the percentage (or mole fraction) of the element j in the system. The quasineutrality of a system containing also charge species is ensured by the condition

$$\sum_{i=1}^n q_i x_i = 0 \quad (4)$$

where q_i represents the charge of species i . According to the method of White *et al.*, the mole fractions x_i are calculated by an iterative procedure. One starts with any set of positive numbers x_{i0} which satisfy Eqs (3) and (4) and builds the 0th-order approximation for G . The free energy is then expanded into a Taylor series up to the quadratic terms in $x_i - x_{i0}$. The conditions (3) and (4) are taken into account with help of Lagrange

multipliers π_j . A minimization of the free energy leads to a system of linear equations that determine the improved values for x_i and thus a new approximation for G . The procedure is repeated until convergence is achieved. It should be noticed that the dimension of the system is $(m+1)$, i.e. it depends only on the number of the elements in the system. The concentrations of the species in traces can be calculated using the equation:

$$z_i = \exp \left[- \left(\frac{G}{RT} \right)_i - \ln p + \sum_i a_i \pi_j \right] \quad (5)$$

where p , T , R are total pressure in the system, temperature and gas constant, respectively.

Applying the method described the equilibrium compositions of Ar/C/Cl/F, Ar/H/C/Cl/F and Ar/H/Ca/C/Cl/F gas mixtures were calculated in the temperature range between 500–6000 K, at total pressures of 1 bar. Ar/C/Cl/F gas system should relate to thermal plasma obtained introducing dichlorodifluoromethane into argon as main gas plasma; Ar/H/C/Cl/F and Ar/H/Ca/C/Cl/F gas systems relate to argon/hydrogen (Ar/H₂) thermal plasma in addition of dichlorodifluoromethane and of dichlorodifluoromethane with calcium (Ca), respectively. Mole amounts of the elements present in the system [b_j from Eq. (3)] and their ratios were chosen in order to simulate particular plasma in present of dichlorodifluoromethane. The properties of the systems (elements present, mole amounts and mole ratios, species considered in the calculations) have been summarized in Table 1. The equilibrium partial pressures (what is equal numerically to the mole fractions under total pressure of 1 bar) of up to 85 species (atoms, ions, molecules, molecular ions, radicals) (Table 1), whose

Table 1 Properties of the gas mixtures

Chemical elements present in the system	Chemical species considered in calculations	Mole fractions of the elements present in the system
Ar, C, Cl, F	e ⁻ , C, C ⁻ , C ⁺ , C ₂ , C ₂ ⁻ , C ₂ ⁺ , C ₃ , C ₄ , C ₅ , C ₆ , Ar, Ar ⁺ , F, F ⁻ , F ₂ , Cl, Cl ⁺ , Cl ⁻ , Cl ₂ ⁺ , Cl ₂ , ClF, ClF ₃ , ClF ₅ , CCl, CClF ₃ , CCl ₂ , CCl ₂ F ₂ , CCl ₃ , CCl ₃ F, CCl ₄ , CF, CF ₂ , CF ₃ , CF ₄ , C ₂ Cl ₂ , C ₂ Cl ₄ , C ₂ Cl ₆ , C ₂ F ₂ , C ₂ F ₄ , C ₂ F ₆	Ar/0.95 C/0.01 Cl/0.02 F/0.02
Ar, H, C, Cl, F	e ⁻ , C, C ⁻ , C ⁺ , C ₂ , C ₂ ⁻ , C ₂ ⁺ , C ₃ , C ₄ , C ₅ , C ₆ , Ar, Ar ⁺ , F, F ⁻ , F ₂ , Cl, Cl ⁺ , Cl ⁻ , Cl ₂ ⁺ , Cl ₂ , ClF, ClF ₃ , ClF ₅ , CCl, CClF ₃ , CCl ₂ , CCl ₂ F ₂ , CCl ₃ , CCl ₃ F, CCl ₄ , CF, CF ₂ , CF ₃ , CF ₄ , C ₂ Cl ₂ , C ₂ Cl ₄ , C ₂ Cl ₆ , C ₂ F ₂ , C ₂ F ₄ , C ₂ F ₆ , HF, HCl, CHCl, CHClF ₂ , CHCl ₂ F, CHCl ₃ , CHF, CHF ₃ , CH ₂ ClF, CH ₂ Cl ₂ , CH ₂ F ₂ , CH ₃ Cl, CH ₃ F, C ₂ HCl, C ₂ HF, CH, CH ₂ , CH ₃ , CH ₄ , C ₂ H, C ₂ H ₂ , C ₂ H ₄ , H, H ⁻ , H ⁺ , H ₂ , H ₂ ⁺ , CH ⁺ , C ₂ H ₃ , C ₂ H ₅ , C ₂ H ₆ , C ₃ H, C ₄ H, C ₅ H, C ₆ H, C ₃ H ₂ , C ₄ H ₂	Ar/0.87 H/0.08 C/0.01 Cl/0.02 F/0.02
Ar, H, C, Cl, F, Ca	e ⁻ , C, C ⁻ , C ⁺ , C ₂ , C ₂ ⁻ , C ₂ ⁺ , C ₃ , C ₄ , C ₅ , C ₆ , Ar, Ar ⁺ , F, F ⁻ , F ₂ , Cl, Cl ⁺ , Cl ⁻ , Cl ₂ ⁺ , Cl ₂ , ClF, ClF ₃ , ClF ₅ , CCl, CClF ₃ , CCl ₂ , CCl ₂ F ₂ , CCl ₃ , CCl ₃ F, CCl ₄ , CF, CF ₂ , CF ₃ , CF ₄ , C ₂ Cl ₂ , C ₂ Cl ₄ , C ₂ Cl ₆ , C ₂ F ₂ , C ₂ F ₄ , C ₂ F ₆ , HF, HCl, CHCl, CHClF ₂ , CHCl ₂ F, CHCl ₃ , CHF, CHF ₃ , CH ₂ ClF, CH ₂ Cl ₂ , CH ₂ F ₂ , CH ₃ Cl, CH ₃ F, C ₂ HCl, C ₂ HF, CH, CH ₂ , CH ₃ , CH ₄ , C ₂ H, C ₂ H ₂ , C ₂ H ₄ , H, H ⁻ , H ⁺ , H ₂ , H ₂ ⁺ , CH ⁺ , C ₂ H ₃ , C ₂ H ₅ , C ₂ H ₆ , C ₃ H, C ₄ H, C ₅ H, C ₆ H, C ₃ H ₂ , C ₄ H ₂ , Ca, Ca ⁺ , CaCl, CaCl ₂ , CaF, CaF ₂ , CaH	Ar/0.89 H/0.04 C/0.01 Cl/0.02 F/0.02 Ca/0.02

Gibbs (free) energy data were available [7], were calculated in the temperature range between 500–6000 K for gas phase system. Gibbs free energy data and other thermodynamic properties of substances can be obtained experimentally like in [8] or can be computed theoretically as in [9].

Results of calculations

The equilibrium composition of Ar/C/Cl/F gas mixture presented in Figs 1–4 relates to the particular mixture that consists of 0.95 moles of Ar, 0.01 moles of C, 0.02 moles of Cl and F each, at the total pressure of 1 bar. These mole numbers and their ratios were chosen in order to simulate Ar thermal plasma with 1% of dichlorodifluoromethane. In the calculation 44 species (atoms, molecules, radicals, ions, electrons) are taken into consideration. The equilibrium partial pressures of some stable chlorofluorocarbons (CCl_2F_2 , CClF_3 , CCl_3F , C_2Cl_2), as a function of temperature, are shown in Fig. 1. In Fig. 2 are shown partial pressures of carbon in atomic and molecular forms (C_2 , C_3 ...) and partial pressures of some radicals (CF , CCl , CF_2 ..).

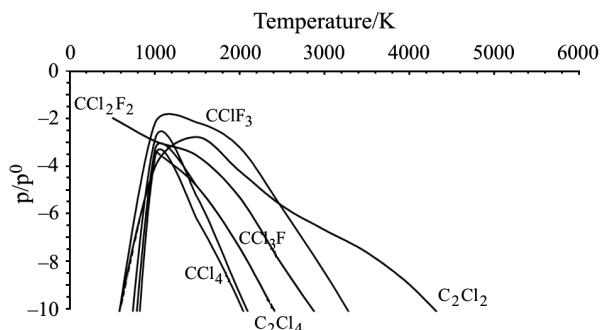


Fig. 1 Equilibrium partial pressures of some chlorofluorocarbon compounds in Ar/C/Cl/F gas system, as a function of temperature; Ar=0.95 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

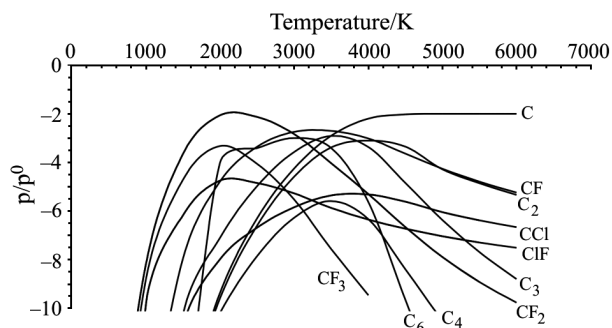


Fig. 2 Equilibrium partial pressures of carbon in atomic and molecular forms and of some carbon, chlorine and fluorine containing radicals in Ar/C/Cl/F gas system, as a function of temperature; Ar=0.95 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

Equilibrium partial pressures of fluorine and chlorine in atomic (F, Cl) and molecular forms (F_2 , Cl_2) are presented in Fig. 3 and partial pressures of ions are shown in Fig. 4. From the results presented in Figs 1–4 it can be seen that practically the only one existing compound at 500 K is CCl_2F_2 molecule. At 1000 K different chlorine and/or fluorine containing methane and ethane derivatives (CClF_3 , CCl_3F , C_2Cl_4 , CCl_4) as well as chlorine in molecular (Cl_2) and in atomic form (Cl) appear in the gas mixture. Among of them CClF_3 and Cl_2 are of the highest partial pressures. It can be noticed from Fig. 2 that up to 1500 K carbon and chlorine or fluorine containing radicals, carbon in atomic and molecular forms are present in the gas mixture in a very small amounts. At 2000 K CClF_3 still exists in the system with considerable partial pressures besides CF_2 and CF_3 , the last one being present in the system, comparing to CF_2 , in smaller amount. At $T \geq 2000$ K chlorine is present in the gas mixture in atomic form (Cl). At temperatures between 2500 and 4000 K dominant carbon containing forms (with respect to their concentrations in the gas mixture) are atomic carbon and carbon containing molecules (C_2 , C_3 , C_6). CF radical also appears but with lower partial pressure. At $T \geq 3000$ K

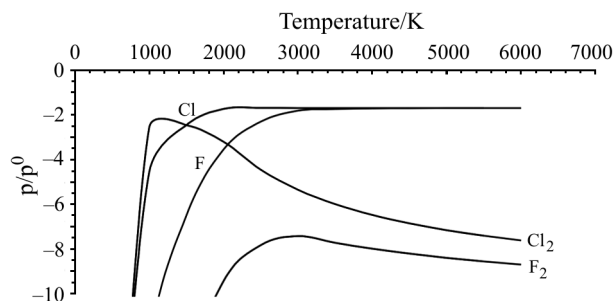


Fig. 3 Equilibrium partial pressures of chlorine and fluorine in atomic and molecular forms in Ar/C/Cl/F gas system, as a function of temperature; Ar=0.95 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

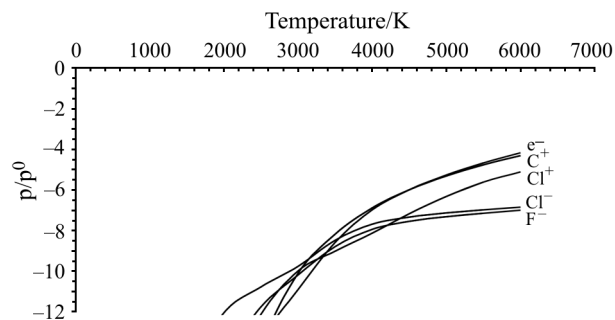


Fig. 4 Equilibrium partial pressures of electrons and some ions in Ar/C/Cl/F gas system, as a function of temperature; Ar=0.95 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

fluorine is present in the gas mixture in atomic form (F) and at $T \geq 4000$ K all carbon containing species are converted into atomic carbon. Partial pressures of ions and electrons are quite low even at 6000 K ($\sim 10^{-4}$ bar), Fig. 4, reflecting the fact that the atoms considered (C, Cl, F) have high ionization energy, among of them carbon is of the lowest one (11.2 eV) and practically all electrons (under conditions estimated) are due to ionization of carbon atoms.

The equilibrium composition of the Ar/H/C/Cl/F gas mixture presented in Figs 5–7 relates to the particular mixture consisting of 0.87 moles of Ar, 0.08 moles of H, 0.01 moles of C, 0.02 moles of Cl and 0.02 moles of F and at the total pressure of 1 bar. With chosen mole numbers and their ratios we simulate Ar/H₂ thermal plasma with 1% of dichlorodifluoromethane. In calculation 78 species (atoms, molecules, radicals, ions, electrons) are taken into consideration. The equilibrium partial pressures of dichlorodifluoromethane (CCl₂F₂), chloromethane (CH₃Cl), fluoromethane (CH₃F), some hydrocarbons (CH₄, C₂H₂, C₂H₄), carbon in atomic and molecular forms (C, C₂, C₃,...), as a

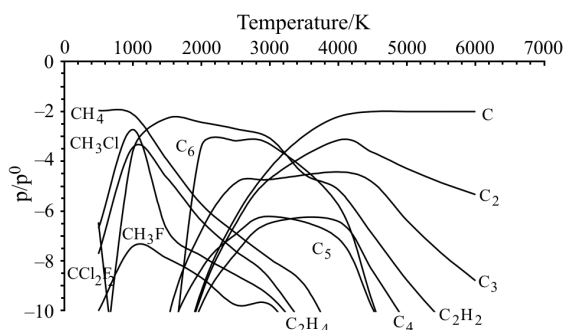


Fig. 5 Equilibrium partial pressures of some hydrocarbons, their chlorine and fluorine containing derivatives and carbon in atomic and molecular forms in Ar/H/C/Cl/F gas system, as a function of temperature; Ar=0.87 moles, H=0.08 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

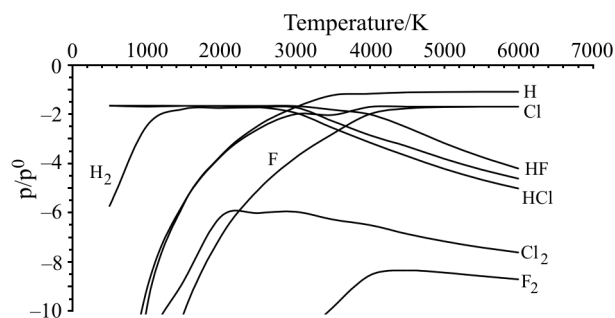


Fig. 6 Equilibrium partial pressures of hydrogen, chlorine and fluorine atomic and molecular forms in Ar/H/C/Cl/F gas system, as a function of temperature; Ar=0.87 moles, H=0.08 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

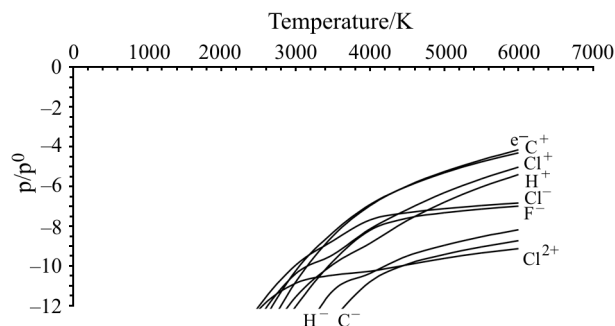


Fig. 7 Equilibrium partial pressures of some ions and electrons in Ar/H/C/Cl/F gas system, as a function of temperature; Ar=0.87 moles, H=0.08 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

function of temperature, are shown in Fig. 5. In Fig. 6 are presented partial pressures of hydrogen, chlorine and fluorine atomic and molecular forms and partial pressures of ions (C⁺, H⁺...) are shown in Fig. 7. According to Figs 5 and 6, CH₄ is molecule of the highest partial pressures up to the 1000 K, Fig. 5; HCl, HF and H₂, Fig. 6, are molecules of the highest partial pressure from 1000 to the 3000 K exhibiting stability at high temperatures and in broad temperature region. In this temperature region practically total amounts of chlorine and fluorine introduced into the system are in the form of HCl and HF. Between 1000 and 3000 K carbon is present in the gas mixture in the form of acetylene (C₂H₂). Its partial pressure is almost constant in this temperature range. Some carbon containing molecules (C₆) appear in the system but with lower partial pressures, Fig. 5. At $T \geq 3000$ K, practically all amount of chlorine introduced into the system is present in atomic form. Fluorine and hydrogen containing species are almost completely converted into fluorine and hydrogen atoms at $T \geq 4000$ K, Fig. 6. Partial pressures of electrons and ions ($\sim 10^{-4}$ bar at 6000 K) are similar to those in the Ar/C/Cl/F gas mixture because in the both cases the main source of electrons is ionization of carbon atoms.

The equilibrium composition of the Ar/H/Ca/C/Cl/F gas mixture presented in Figs 8–11 relates to the particular gas mixture consisting 0.89 moles of Ar, 0.04 moles of H, 0.02 moles of Ca, 0.01 moles of C, 0.02 moles of Cl and 0.02 moles of F at the total pressure of 1 bar. With chosen mole numbers we simulate Ar/H₂ thermal plasma with 1% of dichlorodifluoromethane and 2% of calcium. In calculation 85 species (atoms, molecules, radicals, ions, electrons) are taken into consideration. The equilibrium partial pressures of calcium containing compounds, as a function of temperature, are shown in Fig. 8. The equilibrium partial pressures of some hydrocarbons (CH₄, C₂H₂, C₂H₄), carbon in atomic and molecular forms (C, C₂, C₃,...) and

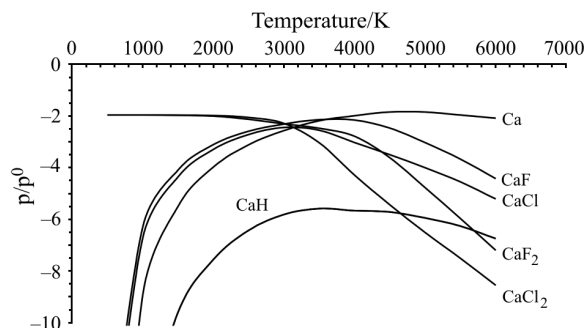


Fig. 8 Equilibrium partial pressures of calcium containing compounds in Ar/H/Ca/C/Cl/F gas system, as a function of temperature; Ar=0.89 moles, H=0.04 moles, Ca=0.02 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

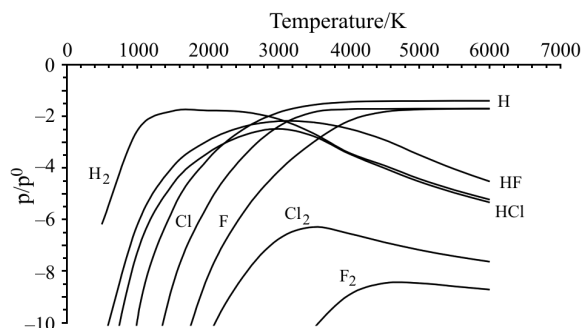


Fig. 10 Equilibrium partial pressures of hydrogen, chlorine and fluorine atomic and molecular forms in Ar/H/Ca/C/Cl/F gas system, as function of temperature; Ar=0.89 moles, H=0.04 moles, Ca=0.02 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

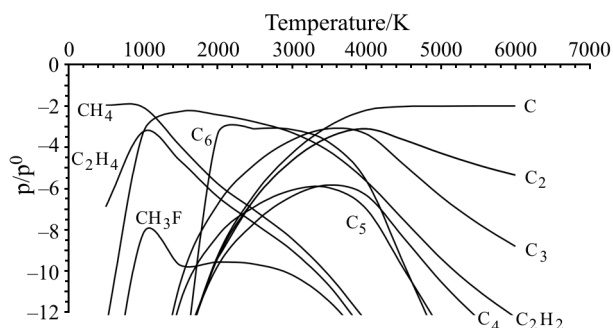


Fig. 9 Equilibrium partial pressures of some hydrocarbons, their fluorine containing derivatives and carbon in atomic and molecular forms in Ar/H/Ca/C/Cl/F gas system, as a function of temperature; Ar=0.89 moles, H=0.04 moles, Ca=0.02 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

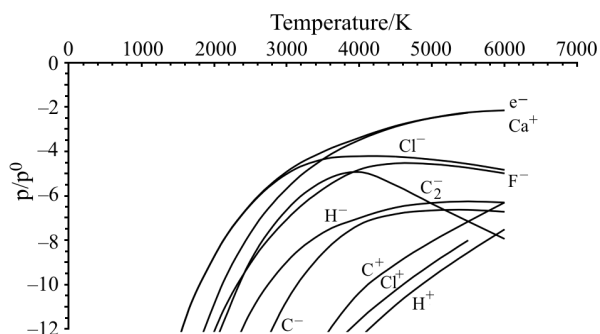


Fig. 11 Equilibrium partial pressures of some ions and electrons in Ar/H/Ca/C/Cl/F gas system, as a function of temperature; Ar=0.89 moles, H=0.04 moles, Ca=0.02 moles, C=0.01 moles, Cl=0.02 moles, F=0.02 moles, $p=1$ bar

fluoromethane (CH_3F), as a function of temperature, are shown in Fig. 9. In Fig. 10 are presented partial pressures of hydrogen, chlorine and fluorine atomic and molecular forms and the equilibrium partial pressures of ions (C^+ , Ca^+ , H^+ ...) are shown in Fig. 11. According to the Fig. 8, at temperatures between 500 and 2800 K, practically total amounts of chlorine, fluorine and calcium introduced into the system are present in the form of CaCl_2 and CaF_2 . Partial pressures of CaF and CaCl radicals are low but increase with temperature. At approximately 3000 K their partial pressures become equal to the partial pressures of CaCl_2 and/or CaF_2 . Chlorine and fluorine are completely atomized at temperatures $T \geq 4600$ K, Fig. 10. At temperatures higher than 4000 up to the 5200 K, calcium is present in the system predominantly as atomic calcium, Fig. 8 and at 5700 K partial pressures of calcium in atomic (Ca) and ionic form (Ca^+) are equal, Fig. 11. Partial pressures of electrons and ions ($\sim 1 \cdot 10^{-2}$ bar at 6000 K, what is 50% of total calcium) in this system (Ar/H/Ca/C/Cl/F) are higher than in the former cases due to the presence

of calcium that is the element with relatively low ionization energy (6.11 eV). All the electrons under the temperature range estimated are due to ionization of calcium atoms.

Among hydrocarbons CH_4 is molecule of the highest partial pressures up to the 1000 K and in this temperature region all amounts of carbon and hydrogen present in the system are in the form of CH_4 , Fig. 9. Between 1000 and 3000 K carbon is present in the system in the form of acetylene (C_2H_2) and hydrogen in the form of molecular hydrogen (H_2) and acetylene (C_2H_2). Fluorine and chlorine containing methane derivatives, except CH_3F , appear with very low partial pressure and cannot be presented in figure within the scale chosen.

Conclusions

From the results of the calculation it can be concluded that in Ar/C/Cl/F gas mixture under chosen conditions (C:Cl:F=1:2:2, 1% of C, 2% of Cl and F, total

pressure of 1 bar) chlorine is completely atomized at $T \geq 2000$ K, fluorine at $T \geq 3000$ K and carbon is completely atomized at $T \geq 4000$ K, Figs 2 and 3. In the temperature range between 2000 and 3000 K different radicals (CF , CF_2 , CF_3) and carbon containing molecules (C_2 , C_3 , C_4) are formed, Fig. 2 and at temperatures between 1000 and 2000 K CCF_3 and Cl_2 are of considerably high partial pressures, Figs 1 and 3.

In presence of hydrogen, Ar/H/C/Cl/F gas mixture, as a most stable molecules, CH_4 , C_2H_2 and C_2H_4 , HCl and HF are formed, Figs 5 and 6. Under chosen conditions (C:Cl:F:H=1:2:2:8, 1% of C, 2% of Cl and F, 8% of H, total pressure of 1 bar) at lower temperatures (up to the 1000 K) carbon is present almost completely in the form of CH_4 followed by smaller amount of C_2H_4 . At higher temperatures, from 1000 to 3000 K, dominant carbon containing species in respect to its amount in the mixture is C_2H_2 , Fig. 5. It is in the agreement with [10] where it was found experimentally that the decomposition (conversion) products of dichlorodifluoromethane and 1,2-dichloroethane introduced into Ar/ H_2 plasma jet are mainly acetylene (C_2H_2), ethane (C_2H_4) and methane (CH_4). In the temperature range between 1000 and 3000 K chlorine and fluorine are present almost completely in the form of HCl and HF, Fig. 6. Although these results suggest that addition of H_2 in stoichiometric amount in respect to CCl_2F_2 leads to the formation of HCl and HF in broad temperature region (Cl_2 and F_2 are, according to the calculations, in negligible amounts) it was found experimentally in [2] that the excess of H_2 to the stoichiometric amount is effective in eliminating Cl_2 . It illustrates the fact that thermodynamic calculations can be very useful for understanding the basic processes in particular thermal plasma processing but they can not explain all the details arising during experiment, because some steps during plasma processing are, or can be, far from equilibrium. Chlorine and fluorine, in this gas mixture are completely atomized at $T \geq 4000$ K.

In the gas mixture containing calcium besides hydrogen, Ar/H/Ca/C/Cl/F, in the temperature range between 1000 and 3000 K, $CaCl_2$ and CaF_2 molecules are

formed instead of (toxic) HCl and HF, Figs 8 and 10. To achieve replacement of HCl (HF) by $CaCl_2$ (CaF_2) definite amount of calcium should be added into the system (stoichiometric one) as it was ensured in the calculation with chosen mole amounts ratios of the elements present in the system (C:Cl:F:H:Ca=1:2:2:4:2). Important carbon containing species (with respect to their partial pressures) are similarly to the Ar/H/C/Cl/F, CH_4 , C_2H_2 and C_2H_4 .

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