Glow Discharge Polymerization

Glow Discharge Polymerization:

Kinetics, Physics and Mechanisms

By

Vladislav Zyn

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ABSTRACT

Countless applications of plasma polymerization, from housekeeping to nanotechnology, with a weak understanding of the mechanism of this process dictate the need to study its theoretical foundations. The content of the book is a detailed description of the stimulation of local mechanisms of polymer synthesis in the main zones of glow discharge by electrophysical collision-type processes specific to each zone. The discharge processes in all zones create their own mechanisms and control the course and local rates of polymerization. The zone mechanisms are so different that the local polymerization rates provided by them in different zones at the same time can differ by hundreds of times. The most powerful cathode mechanism creates polymer structures that obey the law of gas-discharge similarity and contain typical signs of radiation exposure: abnormal over-compaction, compressive stresses, microcraters from ion shocks and micro-explosions.

For researchers, postgraduates and students in plasma chemistry and plasma technology.

INTRODUCTION

Plasma chemical polymerization has become widely known as a method of creating polymer films and coatings for various purposes. This method provides high rates of product formation, good controllability and compatibility with electronic technology. The chemical versatility allows the use of plasma polymers in adhesives, water treatment, biomedicine, and many other fields [*Carneiro de Oliveira J. et al.*: 2021; *Roualdes S. et l:* 2017]**.** In fact, today it is one of the highest-level scientific technologies, which makes it possible to obtain film composite structures. The strongest side of this technology is its controllability and the ability to intervene in the course of the reaction in order to correct it at almost any stage. Much less known is the function of plasma chemical polymerization as a generator of aerosols and fine powders, being formed spontaneously as a by-product of the formation of a polymer film. In literature there is information about the use of plasma-derived polymer aerosols for the synthesis of new powder materials with a unique nanoscale structure and morphology, possessing a variety of physical, chemical and other properties [*Yasuda*: 1988; *Polak*: 1979].

At the same time, the current level of understanding of the mechanisms of plasma reactions does not allow the building of the technological process in an optimal way and usually forces it to rely on luck, previous experience and intuition [*Roualdes S. et al.*: 2017; *Michelmore A. et al.*: 2015]. Plasma polymerization has little in common with classic polymerization. Many side reactions occur during film deposition. This is a consequence of the random nature of plasma dissociation of complex organic molecules by their bonds and the subsequent secondary reactions of synthesis. The chemical diversity of reacting particles inevitably leads to the formation of many different compounds. Several kinetic models of plasma polymerization have been proposed which involve a competitive ablation and polymerization (CAP) mechanism which gives an account of the rather complicated and interrelated influences of fragmented elements in the deposition of plasma polymers (PPs) [*Friedrich J.*: 2011; *Lam D.K. et al.*: 1976; *Yasuda*: 1988].

One of the most significant disadvantages of plasma-generated polymer aerosol is a wide size distribution of formed particles, including the presence of quite large (up to 1-5 microns) ones. When deposited on substrates or embedded in a growing polymer film, the particles form a specific surface relief, the properties of which contain information about the movement and distribution of the aerosol in the discharge volume. Attempts to control the behavior of the aerosol by electrical methods did not yield significant positive results, and this behavior remains largely mysterious and incomprehensible, which is noted in the works of many authors [*Benedikt, Consoli, Schulze, Keudell*: 2007; *Haddow, France, Short, Bradley, Barton*: 2000; *Voronin, Bradley, Fotea, Zelzer, Alexander:* 2007; *Voronin, Alexander, Bradley*: 2006; *Voronin, Zelzer, Fotea, Alexander, Bradley*: 2007; *Swindells, Voronin, Bryant, Alexander, Bradley*: 2008; *Takahashi, Tachibana*: 2001; *Nikiforov, Pankratov, Laguseva, Starovoytova:* 2005; *Slovetsky, Deryugin*: 1987; *Ivanov, Soldatova, Epshtein*: 1985; *Aleksandrov*: 1987; *Ivanov, Lebedev, Polak*: 1981]. As in the case of surface films, the material of the synthesized aerosol is not a polymer in the usual classical sense, like a regular structure with repeating elements. The peculiarity of a substance polymerized in plasma, both a film and aerosol particles, is its irregularity, disorder, rather chaotic combination of different in their chemical structure fragments of the initial monomer. But there can also be small regions of regular classical polymer, moreover, from one initial precursor compound, not one, but two or three different polymers can be formed. Typically, regular or irregular polymer chains are interconnected by the same covalent cross-links as inside the chains. Thanks to this, the entire structure is volumetric-stitched and quite rigid. It is impossible to say in advance whether the materials obtained in this way are good or bad – it all depends on whether the fields of application corresponding to their properties are found for them and what the results of this application will be.

The capacity of empirical approaches to solve these problems is largely exhausted, and therefore, at present, many scientific centers around the world are conducting fundamental research on the physical and chemical aspects of plasma chemical polymerization and its products.

Plasma chemical synthesis has two vectors of further development - applied and fundamental ones. The objectives of the first one are the development of technological methods and the production of new material structures with new valuable properties, primarily in the micro- and nanometer size ranges. This also includes studying the properties of the structures created and developing applications. Various mechanisms existing simultaneously inside a reactor with pulsed glow discharge were discovered depending on the location and operating phase of a period - on or off [*Jebali S. et al.*: 2021].

In this book, polymerization is considered as a process distributed over the internal space of the reactor, including the bulk and surface reaction zones, or media. Three media can be specified in the first approximation: gas phase, aerosol and surfaces. Each medium has its own specific reactions and mechanisms. A more detailed examination reveals a rather complex heterogeneous reaction structure of each of these media. For example, the gas-discharge medium, in addition to being a gas plasma, is divided into a dozen zones with its own mechanisms of purely electrical processes that not only trigger all further chemical transformations, but also significantly affect the course of chemical reactions and determine their rates.

Here are some of the features of this book. It is based on the author's and collaborators' many years of research on the polymerization of organic compound vapours under low frequency glow discharge. Such a discharge retains the structure and basic properties of well studied classical DC glow discharge which actually has time to be established in the discharge gap every half-period. Although most plasma polymerization applications use other types of non-equilibrium discharges, the properties of LF discharge make it an excellent and equally convenient benchmark model as DC discharge, and at the same time it has much greater stability.

The thermodynamic and chemical-kinetic analysis of conditions promoting or preventing the processes of molecular formation of clusters, nano and microstructures that precede the formation of a solid polymer coating or large aerosol particles is carried out. The end of the prepolymerization stage means a fundamental change in the mechanism of polymer assembly. At this stage, there is a transition from a molecular mechanism to a cluster one, and the predominant processes are coagulation of growing particles, and their sedimentation and condensation on surfaces. Examples of concrete studies of the mechanisms of aerosol formation and its gravitational drift, which forms specific spatial distributions of matter, are given, which opens up opportunities for both obtaining the aerosol mass spectrum and isolating monomass particle beams.

The connection between the spatial inhomogeneities of the polymerization mechanism and the primary electrophysical processes of the glow discharge has been investigated. It was found that the full spatial kinetic pattern of polymerization, i.e., the spatial distribution of local polymerization rates throughout the discharge space, reflects well enough the known zonal structure of glow discharge. The discussion of this relationship is one of the main focuses of the book.

The results of kinetic studies of the formation of polymer films on the electrodes of the gas-discharge system and on solid-state substrates located in different zones of the glow discharge are presented. A comparative analysis of the polymerization kinetics in all reactor zones showed that in all these different cases the main stage leading the whole process was exclusively gas-discharge activation of the substance.

One more interesting theme has occurred recently. Polymer synthesis methods using atmospheric plasma polymerization have attracted growing attention in recent years, owing to their high potential for polymer deposition and nanoparticle synthesis for various applications. This theme exceeds the limits of our consideration. Necessary primary information can be found in [*Jang, H.J.; Jung, E.Y. et al.*: 2021].

LIST OF ABBREVIATIONS

HMDSA – **he**xamethyldisilazane,
HMDSO – hexamethyldisiloxane,
HFB – hexafluorobezene,
OMTS –octamethyltrisiloxane,
PTFE – polytetrafluoroethylene,
TFE – tetrafluoroethylrne,
TFM – tetrafluoromethane

CHAPTER I

KINETICS OF PLASMA CHEMICAL POLYMERIZATION

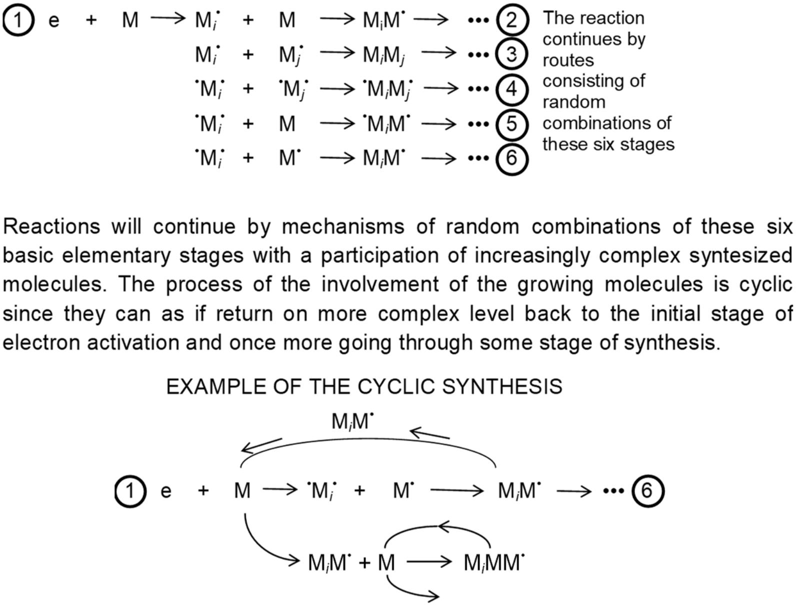
This chapter sets out the fundamentals of a qualitative kinetic analysis of the initial gas-phase stages of prepolymerization, leading to the enlargement of molecules and the growth of nuclei of future polymer particles in the volume of the discharge. The purpose of the qualitative analysis is to process and systematize the primary data of continuous monitoring of the molecular composition of the gas phase during the discharge in monomer vapor. Databases can be any results of measuring molecular concentrations in the system, obtained using proven methods of mass spectrometry, optical spectroscopy or chromatography. The most general, rather abstract scheme is considered, which, nevertheless, is often used in practice. In it, by default, the following conditions are assumed to be fulfilled: 1) the reaction proceeds completely in the gas phase; 2) the discharge and reaction spaces coincide; 3) both spaces are homogeneous; 4) the results of measurements and calculations performed for one point are also valid for all other points of the reactor. In other words, the regime of instant ideal mixing of the gaseous medium is provided for all molecular participants in the reaction, the concentrations of which change simultaneously during the reaction. The feasibility of this assumption for glow discharge conditions is shown in Chapter 2.

1.1. Physicochemical Basics of Gas Discharge Polymerization

Plasma-chemical, or gas-discharge polymerization is a stimulated process in which plasma, mainly its electronic component, plays the role of a stimulator. In the absence of stimulation, the starting gas or monomer vapors are chemically inactive and no reactions occur in them. Polymerization begins only when the discharge is switched on. Not every discharge and not any plasma is suitable for the role of a polymerization activator. It is necessary to provide simultaneously two contradictory conditions: for chemical activation, particles with kinetic energies of several eV are required, which corresponds to a temperature of thousands and tens of thousands of Kelvin. No polymer can withstand such temperatures and is bound to collapse. For the resulting polymer to be preserved, the temperature of the medium should not exceed 500 K. But then the molecules cannot be activated. The necessary conditions are provided only in nonequilibrium discharges, where the temperature of the molecules just has a value of 400–500 K, but at the same time electrons are accelerated by the electric field to energies equivalent to 40,000 K. A similar situation is realized in various types of glow discharges - direct current, low current, high and ultra high frequency. The electrons of these discharges are quite capable of activating gas molecules in collisions. The discharges contain ultraviolet photons, which are also capable of activating molecules, but the efficiency of the photons is much lower, and they do not play a significant role in polymerization.

The molecular mechanism of plasma chemical polymerization, in the crudest approximation, is a two-stage process, at the first stage of which the monomer gas is activated by electron impact, and at the second stage, chemical reactions between the activated molecules and their fragments. A more detailed examination shows that both of these stages have their own rather complex structure and consist of many simpler, so-called elementary stages, which are single collisions of two, less often three, particles. The course of chemical transformations is determined by the properties of active particles. Even for simple molecules, the activation process gives an ambiguous result, when various radicals, ions, and excited molecules can be formed. The chemical reactions they initiate are even more diverse. The totality of all activation and chemical processes constitutes the reaction mechanism, which can include hundreds and thousands of elementary stages. The study of the mechanism allows you to intervene in the course of the reaction and direct it in the right direction, which is of great practical importance. General concepts of the mechanisms of plasma chemical polymerization are reflected in the bicyclic scheme of H. Yasuda, basic elements of which are shown in Fig. 1.1 [*Yasuda*: 1985, p..79].

The scheme is named bicyclic because it includes two types of cyclic reactions: the 1st is based on reactivation of the reaction products of monofunctional active species. The 2nd is associated with the reactions of bifunctional active species such as $\cdot CH_2\cdot$ or $\cdot CF_2\cdot$. In both types of cycles, the reaction can proceed by a fast stepwise mechanism, and under certain conditions, for example, at high pressure and low substrate temperature, also by a chain mechanism - by sequential attachment of monomer molecules. In this case, the monomer must have a structure that allows the attachment, for example, in the form of multiple bonds.



The reaction continues by routes consisting of random combinations of these six stages

Reactions will continue by mechanisms of random combinations of these six basic elementary stages with a participation of increasingly complex syntesized molecules. The process of the involvement of the growing molecules is cyclic since they can as if return on more complex level back to the initial stage of electron activation and once more going through some stage of synthesis.

EXAMPLE OF THE CYCLIC SYNTHESIS

Fig. 1.1. Basic elementary stages and scheme of the radical cyclic step-wise mechanism of plasma polymerization: 1 – activation, 2 - chain, 3 - recombination termination, 4 and 6 - recombination-chain, 5 - chain. The dots indicate free valencies.

The reality of the latter mechanism is evidenced by the IR spectra of the polymer obtained in the plasma of styrene under the conditions indicated above, which are practically identical to the spectra of ordinary polystyrene [*Yasuda*: 1985, p. 80]. In the diagram in fig. 1.1, the chain mechanism is represented by reactions 2 and 5. Reaction 3 is a chain termination during the recombination of two radicals and is a step in the slow activation-recombination mechanism. Continuation of the reaction is possible only after the next activation. Chain 4 gives the same thing, but with the participation of a biradical. Reaction 5 is a stage of a rapid stepwise mechanism with the retention of functionality in the product particle.

Without going into the details of the mechanism, we can try to discuss the basic physical and chemical laws that the process of gas discharge polymerization must follow. This will make it possible to determine what is allowed and what is forbidden under existing conditions, to develop appropriate criteria for comparing experimental results with the theoretical predictions, to classify and select the probable types of reactions, since at present even these rather general issues are unsolved.

1.2. Thermodynamic limits of chain reactions in plasma

Here we consider the question, which remained debatable until the 2010s, about the possibility or impossibility of the chain mechanism of polymerization in plasma. The problem is that the chain mechanism is one of the main ones in ordinary chemical polymerization, but in the conditions of gas-discharge plasma it, as it seemed for a long time, should be prohibited by the laws of chemical thermodynamics. At the same time in plasma the signs of chains were observed experimentally, at least for some monomers: acetylene [*Benedikt*, *Consoli*, *Schulze*, *Keudell*: 2000], acrylic acid [*Haddow*, *France*, *Short*, *Bradley*, *Barton*: 2000; *Voronin*, *Bradley*, *Fotea*, *Zelzer*, *Alexander*: 2007; *Voronin*, *Alexander*, *Bradley*: 2006; *Voronin*, *Zelzer*, *Fotea*, *Alexander*, *Bradley*: 2007; *Swindells*, *Voronin*, *Bryant*, *Alexander*, *Bradley*: 2008], fluorocarbons [*Takahashi*, *Tachibana*: 2001].

Any reversible reaction, such as polymerization, consists of forward and reverse stages. Under isobaric-isothermal conditions, the change in the

Gibbs energy dG is negative for the direct reaction (in this case, polymerization), positive for the reverse reaction (depolymerization), and it is zero in the case of equilibrium and in fact stopping the reaction:

$$dG = dH - T{\cdot}dS = 0 \qquad (1.1),$$

where dH is the enthalpy, or the thermal effect of an isobaric-isothermal reaction, equal to the difference between the enthalpies of products and reagents, T is the temperature, $-T{\cdot}dS$ is the loss of energy due to structural rearrangement (ordering, for example, a decrease in the number of particles) of the system, accompanied by a decrease in its entropy $-dS$. In reality, the energy dG in different reactions and depending on the conditions can be positive, negative, or zero. In the first case, the direct stage of the reaction, polymerization, is blocked by a faster reverse stage, depolymerization, and the reaction as a whole cannot continue. In the second case, $dG < 0$, on the contrary, the direct stage dominates, as a result of which polymerization will occur in the system. In the third case, there is an equilibrium between the rates of the forward and reverse stages, equation (1.1). The system state does not change.

The temperature corresponding to equation (1.1) is denoted as T_c and is called the critical, or upper limiting, or even ceiling temperature of the reaction. It delimits the temperature ranges with positive and negative increments of the Gibbs energy, i.e., areas of predominance of the reverse ($dG>0$) or direct ($dG<0$) reaction. The criterion for the possibility of the development of a reversible reaction in the forward direction, i.e., polymerization, is the decrease in the Gibbs energy, $dG = dH - T{\cdot}dS < 0$. The physical meaning of this limitation is that the removal of energy from the system during the reaction reduces the excitation and thermal motion in it, which is the main destroyer of product molecules, and thereby increases the stability of the final state (products). Low values of the critical (limiting) temperature corresponding to the conditions of plasma chemical polymerization, ~ 100–150 K, for a long time served as the basis for the complete denial of any role of the compound reactions in a gas environment, since its temperature (400-600K) is much higher than the limiting one. In some rather rare cases, polymerization is endothermic and at the same time occurs with a decrease in entropy ($dS < 0$). These systems are characterized not by an upper, but by a lower limiting temperature, below which synthesis reactions are impossible, including polymerization.

There are 4 temperature ranges with their specific features of a polymerization process [*Nikiforov*, *Pankratov*, *Laguseva*, *Starovoitova*: 2005]:

1) if $\Delta H < 0$ and $\Delta S < 0$, then $\Delta G < 0$ only at $T < T_c$, and the polymer can be obtained only at temperatures lower than the ceiling temperature T_c (or upper limit T_{max});

2) if $\Delta H > 0$ and $\Delta S > 0$(polymerization is endothermic), then the polymer cannot exist at temperatures below the lower limit;

3) if $\Delta H > 0$ and $\Delta S < 0$, then it is always positive, and the polymer cannot exist at any temperature;

4) if $\Delta H < 0$ and $\Delta S > 0$ then it is always negative, and the polymer can exist at any temperature.

To the greatest extent, thermodynamic limitations relate to chain reactions. Chain polymerization proceeds by sequentially attaching an entire monomer molecule to a growing active complex of a radical or ionic type. Each act is exothermic and decreases the entropy of the system, since it decreases the number of particles and degrees of freedom. The situation corresponds to condition 1, the reaction has thermodynamic limitations in the form of ceiling temperature at which the rates of the forward (polymerization) and reverse (depolymerization) reactions are equal, and the Gibbs energy change is zero. The reaction in the gas phase can only take place at temperatures below the limit.

The value of the ceiling temperature depends on the total gas pressure in the system, including the reagent gas and the carrier gas. In [*Yasuda H. K*., et al.: 1990], a mathematical expression was obtained that relates the maximum limit (ceiling) temperature and pressure:

$$T_m = \text{const}\cdot \boldsymbol{p}^{\left(\frac{1}{2+n}\right)},\ \ \text{const} = \left({}^{ah}\!/_{Nk^2}\right)^{1/2+n} \qquad (1.2),$$

where n is the order of the reaction; for different types of reactions it is in the range of 0.5-3; a = $8{\cdot}10^{26}$mol^{3}c/K^{3}cm^3, h and k are Planck and

Boltzmann constants, N is the Avogadro number. From here we get a simple ratio between the limit temperatures at different pressures:

$$\frac{T_{m1}}{T_{m2}} = \left(\frac{p_1}{p_2}\right)^{\left(\frac{1}{2+n}\right)}. \qquad (1.3).$$

According to that source, this temperature for the polymerization of methylstyrene is 334 K at a pressure 1 atm and 444 K at 6480 atm. In the same work, the limiting temperature for one of the model reactions in plasma chemical synthesis, $CH_3 + H + M \rightarrow CH_4 + M$, was determined as 869 K at a pressure 760 Torr and 230 K at 1 Torr. The reaction order is $n = 3$. Using the expression (1.3), for a pressure of 0.1 Torr, we find $T_c = 230/(10)^{0.2} = 145$ K. In practice, according to condition 1 in Table 1.1, the chain process in a lower pressure plasma (0.1-100 Pa) at a temperature of 400-500 K and a pressure of 0.1 Torr cannot proceed. In fact, the same can be said not only about chain reactions, but about any recombination reactions that have negative changes in enthalpy and entropy. In particular, in this respect, the recombination of radicals is no better, it must also have its own ceiling temperature and therefore can also take place only at a temperature below the limit. Since the synthesis of the polymer does however occur in plasma at temperatures much above T_c, in spite of the thermodynamic ban, this is usually explained by the participation in an elementary process of a third body or surface, which accept the reaction energy and, as it were, change type of the reaction from exothermic to endothermic. In this last case, there is no critical temperature, these are modes 3 and 4, but if the process ends with the recombination stage and dissociation does not follow, then the entropy of the system decreases, which means the implementation of mode 3, in which the polymer cannot be formed at any temperature. Polymerization by mechanism 3 is not possible. For path 4, there are no bans for synthesis at high temperatures – the reaction is exothermic and is accompanied by an increase in entropy, i.e., dissociation of the product or elimination of a small particle. Such a process can, while remaining exothermic, increase the entropy of the system and thereby transfer the reaction from mode 1 to mode 4, in which it can go at any temperature. The results of the review are summarized in Table 1.1. From the above list of four modes, chain polymerization can only be provided by mode No. 1 at a sufficiently low temperature, below the limit. The limit temperature increases with increasing pressure, but rather slowly, in proportion to $p^{0.2}$ [*Yasuda H. K.*, et al.: 1990].

Table 1.1. Thermodynamically possible modes of synthesis reactions during step polymerization

№	Conditions	Reaction type	Peculiarities	Feasibility
1	$\Delta H < 0$, $\Delta S < 0$	Exothermic recombination	Participation of third body	Possible at T below $T_c \sim p^{0,2}$
2	$\Delta H > 0$, $\Delta S > 0$	Endothermic recombination	Dissociation or elimination	Possible at T above $T_c \sim p^{0,2}$
3	$\Delta H > 0$, $\Delta S < 0$	Endothermic recombination	No T_c	Impossible at any T
4	$\Delta H < 0$, $\Delta S > 0$	Exothermic recombination with decay	No T_c. Dissociation or elimination	Possible at any T

The above consideration brings us to conclusion, shared by many authors, that in the conditions of a conventional glow discharge, the enlargement of particles in the gas phase by the mechanism of a simple binary collision R + R → RR is impossible. First of all, because the gas temperature exceeds the upper limit T_c. Chain gas-phase synthesis of the polymer is also impossible, even more [*Yasuda H.K.*: 1985, p. 53, 62]. Therefore, the appearance of a polymer aerosol in the plasma is explained either by the formation of nuclei through trimolecular reactions, or by the desorption of polymer particles formed on solid surfaces and electrodes. However, at the beginning of the 21st century, many works appeared in which both types of "illegal" processes were experimentally observed – both chain reactions and gas-phase polymerization [*Benedikt, Consoli, Schulze, Keudell*: 2007; *Haddow, France, Short, Bradley, Barton*: 2000; *Voronin, Bradley, Fotea, Zelzer, Alexander*: 2007; *Voronin, Alexander, Bradley*: 2006; *Voronin, Zelzer, Fotea, Alexander, Bradley*: *2007*;

Swindells, Voronin, Bryant, Alexander, Bradley: 2008; *Takahashi. Tachibana:* 2001]. All this pointed to the insufficiency of the traditional thermodynamic approach to the interpretation of experimental results and the need to develop and apply new concepts, primarily ideas about the non-equilibrium nature of plasma chemical polymerization processes.

1.3. Extending polymerization limits in non-equilibrium discharges

As mentioned above, within the framework of equilibrium thermodynamics, it is not completely clear how much one can rely on the criteria formulated for isolated systems in a state of equilibrium or close to equilibrium, and in which all changes are due to internal processes and occur in isothermically isobaric (Gibbs) or isothermically isochoric (Helmholtz) conditions. The change in the Gibbs energy for the direct reaction is negative, for the reverse – positive, and in the boundary case of equilibrium and stopping the reaction, the dG is equal to zero:

$$dG = dH - T_c{\cdot}dS = 0. \qquad (1.4).$$

The plasma chemical system obviously does not meet the listed requirements. The system is not isolated, but it exchanges with the environment by matter (in form of electron flows through it, their attachment and ionization), energy and entropy, which enters in some amount and leaves in another amount together with the electron flow. The system is non-isothermal and non-equilibrium, the temperature of the molecules is 400-500 K, while the electrons have 40,000 K, and there is a permanent exchange between them according to the same points listed above. Changes in the system with a discharge do not occur by themselves, but solely under the action of the discharge. In any case, some published experimental results do not fit into the specified thermodynamic criteria. Small deviations from equilibrium are reflected in the fact that the Gibbs energy either increases (*dG* is positive, and pumping occurs), or decreases (*dG* is negative, and spontaneous relaxation or reaction occurs). The physical meaning of this restriction was discussed above. The heat released during a chain reaction makes the thermal motion very intense, and the excitation of the molecules is large, so much so that all this combined makes it impossible for the stable existence of the synthesis products. There are two reasons for this: 1) an increase in the rate of the reverse reaction with an increase in temperature, and 2) the decay of excited product molecules through channels other than the reverse. These are different situations. The first is characteristic of purely chemical systems that are in equilibrium or close to equilibrium. The Gibbs criterion applies only to them. Its zero value means that the forward and reverse reaction rates are equal. With a positive result dG, the reverse reaction is faster than the direct one, what blocks the reaction as a whole because the reverse stage is always a response to direct one.

In a plasma-chemical system, the picture is much more complicated, several conditions necessary for determining and even formulating thermodynamic functions are not met at once, whether it is the Gibbs energy, or the Helmholtz energy, or entropy. For example, a glow discharge system used in polymerization includes electrical and chemical subsystems. There is no balance in it either between subsystems or within subsystems. The Gibbs criterion is simply irrelevant to this situation due to the possible remoteness of the product state from equilibrium. Recall that the relation (1.4) is a condition of thermal equilibrium in the system and is valid for isothermal conditions and equilibrium states. As to the plasma chemical polymerization system, the question immediately arises: what isothermicity can we talk about in a medium where the temperature of molecular particles is 400K, and the temperature of electrons is 40000K? What temperature should anyone prefer? If we restrict ourselves only to the chemical subsystem, then it is clear that it is open, and any thermodynamic characteristics in it will be determined not only by internal processes, but also by material, energy and entropy exchanges with the external environment, which is difficult or even impossible to take into account. Second question: What is the temperature of molecules and radicals? There are two types of them - primary radicals, formed as a result of electron impact, and secondary ones, formed as a result of chemical collisions of the primary ones with molecules. It is not at all obvious that they will all have the same temperature. Even one molecule can have several temperatures at different degrees of freedom - translational, vibrational, rotational. What the thermometer shows is the average result of the interaction and energy exchange between the thermometer and those components of the environment that are involved in such an exchange. To answer the question of what these components are and what their interaction with the thermometer is, it is necessary to reveal the mechanism of the processes occurring, which generally lies outside the boundaries of thermodynamics. Primary radicals are formed as a result of collisions of an equilibrium molecular medium with an accelerated low-entropy electron flux. Therefore, the formation of radicals can be accompanied not by an increase, as occurs in chemical reactions, but by a decrease in entropy. The discharge medium during its activation by electrons does not relax, but, on the contrary, is pumped up and goes further from equilibrium. The new state of the medium, in which ions, radicals and free electrons appear, is capable of independent chemical relaxation (reaction), and for this reason it should be recognized as low-entropy in comparison with the initial (or final) state. The fact that as a result of the passage of the discharge current, the entropy of the system moves away from its maximum is indicated by the fact that reactions are beginning in an initially chemically passive system, i.e., chemical relaxation processes are being started that always raise entropy. During the activation of the medium, its temperature may also change. It is a typical situation, often considered in synergetics, of an open system through which a low-entropy flow of matter (electrons) and energy passes. In the case under consideration, this is an ordered directed flow of accelerated electrons. The behavior of the system will depend on how intense the mentioned flows are and whether they lead the system much away from equilibrium. In particular, with large deviations, the formation of dynamic dissipative structures is possible what was really observed and will be described in Chapter 4.

L.S. Polak drew attention to the inadequacy of the Gibbs and Helmholtz criteria to the modern understanding of plasma-chemical processes and suggested the need to develop new criteria based on the ideas of Lyapunov's mathematical theory of stability [*Polak*: 1979]. In his book "Nonequilibrium Chemical Kinetics" on page 45 it is noted that the nonequilibrium state of a system cannot be characterized by the concept of "entropy" in the sense of Clausius, which is applicable only to characterize equilibrium or near-equilibrium states. A non-equilibrium generalized analogue of entropy is the Lyapunov function, which characterizes the system's ability to undergo relaxation changes, which has the same mathematical properties as entropy. The generalized Lyapunov entropy in disequilibrium differs from the classical entropy and is equal to it only in equilibrium.

The plasma-chemical system is not limited only to the chemical part, it consists of several subsystems: chemical, or molecular, electronic, external environment and a source of electrical energy. It can be considered isolated only as a combination of all four parts. The most important subsystems – the chemical and electronic ones – are open and exchange both electrons and energy with each other, as well as electronic subsystems exchanging with a current source. Let us especially emphasize the fact that the interaction between subsystems is not limited to only energy exchange. Material exchange also takes place. The chemical subsystem can absorb electrons in the processes of their adhesion to molecules or, conversely, supply them to the electronic subsystem in the processes of ionization. The change in the entropy of a chemical subsystem occurs in two ways: through its production within the subsystem in the course of chemical transformations d_iS and through its consumption from the outside, from the electronic subsystem in the course of electron-molecular collisions d_eS. In the approximation of a purely thermal reaction mechanism and the Maxwellian energy distribution of molecules, we can estimate the first part as d_iQ/T using the standard enthalpies of substances and measuring or setting the gas temperature. The second part is the difference between the entropy consumed by molecules in collisions with electrons and the entropy transferred by electrons in collisions with molecules. If we assume that the energy transferred by electrons to molecules is equal to the energy received by the molecules, then the difference in entropies will be due to the fact that the electronic and chemical subsystems have different temperatures. In a glow discharge, the temperatures of electrons are 30-40 thousand K, and of molecules - 400-500 K. Therefore, $d_eS = d_eQ / T - d_eQ / T_{el}$. The Gibbs energy change will be $dG = d_iQ - T_c\ (d_iQ / T + d_eQ / T - d_eQ / T_{el})$. In fact, the energy of electrons goes to excite not only translational, but also electronic, vibrational and rotational motions in molecules, as well as their dissociation and ionization, each species with its own energy and temperature. The thermal mechanism of chemical reactions assumes only the translational movement of the molecules responsible for the reaction. Taking into account all types of excitations, the change in entropy

$$d_eS = d_eQ_{tr}/T + d_eQ_{el}/T_{el} + d_eQ_{vib}/T_{vib} + d_eQ_{rot}/T_{rot} + d_eQ_{dis}/T_{dis} + d_eQ_{ion}/T_{ion} \quad (1.5).$$

Here we had to insert new indices to denote the types of motion or excitation that consume the incoming energy: tr - translational, el - electron, vib - vibrational, rot - rotational, dis - dissociation, ion - ion. Without even going into the details of the calculation, we can say that the estimation of the critical temperatures of reactions according to equation (1.4) seems to be a very far from reality simplification. Therefore, it would be a mistake to draw conclusions about the details of reactions based on the Gibbs and Helmholtz criteria. Equation (1.5), perhaps, is closer to reality in terms of its general structure, but it contains a large number of undefined quantities and, for this reason, is also of little use for specific assessments of conclusions. Much more reliable conclusions can be drawn from direct observations of chemical processes or their kinetics. Using pulse discharges for this purpose made it possible to separate chemical processes from electrical ones and observe in the intervals between the pulses a purely chemical evolution (relaxation) of the plasma molecular subsystem as a result of reactions induced in it only (for details see 3.4).

1.4. Basic concepts of chemical kinetics used

Unlike conventional chemical systems, any plasma-chemical system is always energetically open, since it constantly consumes energy from an external source. Therefore, in the general case, there is no equilibrium in such systems. They can contain large groups of both excited and fast particles, primarily charged ones, which receive energy not as a result of thermal collisions with other particles, but directly from an external source of electrical energy. Such particles will not fit into classical distributions typical for equilibrium conditions. In principle, with any change in the pumping conditions, the nonequilibrium distributions of particles over the velocities and levels of internal excitation can change. In equilibrium chemical kinetics, the question of a change in the distribution of internal excitation states does not arise, and a change in the particle velocities manifests itself as a change in the temperature of the system. A simple bimolecular reaction in this case is written as follows:

$$A + B \rightarrow C + D \qquad (1.6),$$

and the reaction rate for generation of the substance C is

$$dC/dt = K{\cdot}A{\cdot}B \qquad (1.7),$$

where A, B, C are the concentration of substances, and K is the rate constant depending on temperature according to the Arrhenius law. From the point of view of nonequilibrium kinetics, an elementary act will be the collision of particles A and B in states k and l, leading to the formation of particles C and D in states m and n:

$$A_k + B_l \rightarrow (K_{mn}^{kl}) \rightarrow C_m + D_n \text{ ,,} \qquad (1.8),$$

where K_{mn}^{kl} is the reaction rate coefficient. The classical reaction rate for substance C, written earlier as (1.7), will now be equal to the sum of the transition rates between the states k, l of the original molecules and the states m, n of the finite molecules of type C.

$$\frac{\partial C}{\partial t} = \sum_k \sum_l \sum_m A_k \cdot B_l \int q_m^{kl} \cdot f_A^v \cdot f_B^v \cdot v_{AB} \cdot dv_A \cdot dv_B \qquad (1.9).$$

Here q_m^{kl} – a total cross section of the transition (1.8); index n is excluded because it refers to the substance D which is absent in this case, and the transitions to n-levels are not considered. A_k and B_l are concentrations of the substances A and B in the states k and l, f_A^v and f_B^v - velocities distribution functions of the reagents A and B; v_{AB} – relative velocity of reagent molecules. The level molecular concentrations