ELEMENTARY CHEMICAL PROCESSES AND KINETICS IN A NON-EQUILIBRIUM AND QUASI-EQUILIBRIUM PLASMA

L. POLAK

Institute for Petrochemical Synthesis, Academy of Sciences of the USSR, Lenin Prospekt 29, Moscow V-71, USSR

ABSTRACT

Main problems are considered of the non-equilibrium chemical kinetics which includes plasma chemical kinetics as a particular case. Mechanisms are analysed of plasma chemical reactions occurring under electron impact and through electronic-vibrational excited states. Main equations of plasma chemical kinetics and formulas for the reaction rate factor are discussed. Mutual influence of vibrational relaxation and dissociation is shown to be significant under low temperature plasma conditions. Some approaches are considered for determination of the rate factors for plasma chemical reactions.

INTRODUCTION

Plasma chemistry has developed naturally from the low temperature plasma physics of molecular gases, and especially of their multicomponent mixtures. Plasma chemical reactions (particularly in electrical discharges) usually occur under non-equilibrium conditions and themselves create non equilibrium. Reactions of charged particles and excited molecules play a very important if not principal role; chemical reactions under plasma conditions result in excited particles which have non-equilibrium distributions.

From this the need arose for new developments of certain theoretical ideas* and experimental methods of plasma chemistry.

For a full description of chemical processes (plasma-chemical process in particular), which are usually defined as threshold processes (recombination reactions being the most important exceptions), it is necessary to know $\sigma(kl/ij; \varepsilon)$ the cross section as the function of the translational energy and quantum state; $f(\vec{r}, \vec{v}; t)$ the function of particle distributions by energies and in space; and E_{th} the threshold energy for the reaction; E_{ac}, the activation energy, must also be known, which often is significant from the practical point of view, especially in 'classical' chemistry. Determination of these quantities permits definition of the basic value of the generalized chemical kinetics, k_i the rate factor for the chemical reaction from the ith level,

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* One may recall Bellmann's well-known remark, which states that when building up the theory one must avoid the desert of oversimplifying and the marsh of overcomplicating.

which in the particular limiting case of Arrhenius kinetics is converted to $k(T)$— the chemical process rate constant. Dynamic and kinetic aspects of chemical process descriptions[1-4] are combined in k_i.

SPECIAL FEATURES OF PLASMA-CHEMICAL REACTIONS, THEIR DYNAMICS AND KINETICS

1. Chemical reaction dynamics are described both by the frequency of reacting particle collisions and by the fields affecting them. The total result (very often rather smoothed) of the study in the field of reaction dynamics can be presented as the function, $\sigma(kl/ij; \varepsilon)$.

The 'elementary act' (i.e. collision dynamics) of a chemical process in 'classical' Arrhenius chemistry occurs under the following conditions: the mean energy of the relative motion of colliding particles (molecules) is not above ~ 0.1 eV; the population of the first vibrational level of the ground electronic state predominates over the others; reactions of the following type: $e + M$, $M^{\pm} + M$, $e + M^{-}$, etc. are practically absent; reaction products are not usually excited; elastic collisions predominate over non-elastic ones. In general molecules may be represented as hard elastic spheres.

In the field of interest (plasma chemistry, radiation chemistry, etc.) the situation is quite different: mean molecule energies are $\gtrsim 0.1$ eV; excited molecules are frequently in collision, and chemical reaction products produced by collisions appear often to be in excited states; collisions of molecules with electrons and ions (as well as collisions between molecules) are essential, and there is usually wide difference between translational rates and energy (in the laboratory coordinate system) of the charged particles of small mass (~ 1–50 eV) and those of heavy particles (~ 0.03–2.3 eV), as well as in the vibrational energy of the latter (~ 0.2–0.8 eV). The model of elastic spheres is therefore inapplicable[1,4].

The kinetics of chemical reactions describe the particular type of molecule ensemble behaviour, and this description has a statistical character. Because of this, the kinetic description of ensemble behaviour of various particles is defined, assuming the dynamics of collisions (for instance binary ones) to be known, by molecule quantum level populations and the function for particle distributions by translational energy as well as by ratios of flux probabilities over various channels, for instance

$$M(i)-M(j), \quad M(i)-M'(k),$$

where i, j, k is the totality of molecule quantum state parameters.

In classical chemistry this is not so obvious, as it produces a distribution of a Maxwell type occurring at the initial stage, which at later stages is not (or is only slightly) disturbed by a chemical reaction; the population is considered to be of a Boltzmann type with ground level populations predominating. The transitions of $M(i)-M(j)$ type are therefore disregarded; all the reacting particles have the same mean energy (temperature) giving uniform Maxwell distribution.

In plasma chemistry the situation is different; the initial distribution may

not be of Maxwell type, and the population may not be Boltzmannian. Even when the initial distribution is a Maxwell type it is disturbed by a chemical reaction, and the new distribution produced affects the reaction rate; various reaction components may have distribution functions differing in form and mean energy*, which can change in the course of time with various relaxation times. The transitions of $M(i)-M(j)$ type can no longer be neglected in chemical reaction descriptions; non-elastic collision frequencies are not small by comparison with elastic collision frequencies.
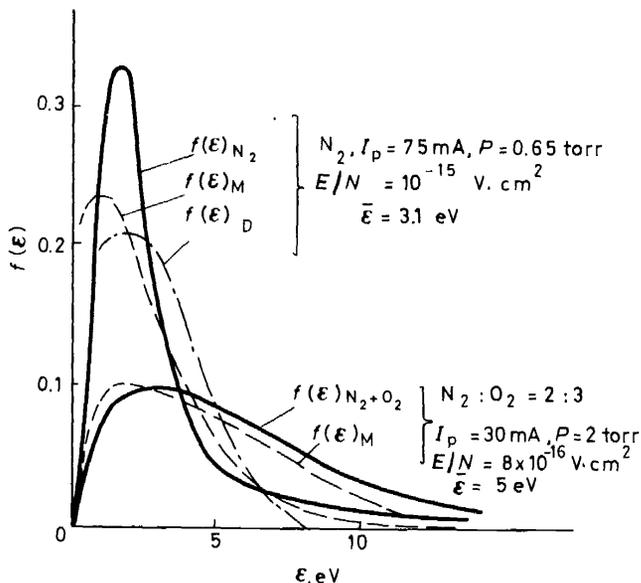
Figure 1. Electron energy distribution under glow discharge conditions in nitrogen and nitrogen–oxygen mixture.

Naturally, the chemical reactions possible in a molecule, and their rates, depend on the structure of the molecule (and for non-monomolecular reactions also on other reaction component structures). This, in particular, prevents the introduction of the term 'reactivity', with respect to molecules. The concept of molecular structure can be formulated differently. For our purpose the following definition is believed to be the best: the structure of a molecule, comprising several atoms, is a system of its quantum levels and space distribution of the component particles.

The problem of connecting reactivity with molecular structure is often considered of paramount importance in 'classical' chemical kinetics. However, it cannot be solved within the limits of the molecular model used.

Automatically, according to the character of the reactions described using generalized chemical kinetics, the problem is being solved within the

* Figure 1 illustrates the functions for electron distributions by energies in glow discharges, measured experimentally.

latter. This, however, takes place when the vague term 'reactivity' is substituted for k_i.

2. Plasma-chemical reactions may be of the non-equilibrium or quasi-equilibrium types. Various types of plasma-chemical reactions are enumerated in *Table 1*.

Table 1. Types of plasma-chemical reactions

	Processes occurring in the system	Characteristics of the system	Process characteristics
Non-equilibrium	Chemical reactions in non-equilibrium systems*	Difference between vibrational and translational temperatures	
		Two subsystems, one Maxwellian and the other non-Maxwellian	Stationary or relaxing
	Non-equilibrium in the system due to the occurrence of chemical reactions	Two subsystems with different temperatures	
		Both subsystems are non-Maxwellian (and non-Boltzmannian)	
Quasi-equilibrium			Stationary or relaxing

* A prominent general feature of non-equilibrium conditions in a gas system or low-temperature plasma is the occurrence of mass, momentum, and energy transfer (or of one of these quantities); this transfer occurs through any small surface element oriented in some way and moving at the speed of the flux (or the mass velocity).

The kinetics of plasma-chemical reactions, as seen from *Table 1*, can be considered as a particular case of non-equilibrium chemical kinetics.

Plasma-chemical reactions in the gas phase (only these reactions will be discussed further) are characterized by the following:

(a) Non-elastic collisions* are more important in 'hot' gases than in 'ordinary' (monatomic) gases, the properties of which are described well by the kinetic theory based upon the consideration of only elastic collisions. The kinetic theory also explains some properties of polyatomic and reacting gases, assuming the non-elastic collision frequency to be small; such a treatment fails when the gas temperature is increased sufficiently.

(b) The difference between the characteristic times of various physical and chemical processes decreases and it becomes impossible to distinguish between the various processes as is possible in classical chemical kinetics.

(c) Chemical kinetics cannot be considered independently of physical kinetics in the field of interest. If the reaction rate exceeds the collision frequency for the momentum-transfer collisions, deviations from equilibrium conditions occur. These can lead to violations of the equilibrium Maxwell–Boltzmann energy distribution and to a relative decrease in density of the highly energetic molecules, owing to the occurrence of chemical reactions.

* Non-elastic electron collision cross sections for many molecular gases may be considered to have maxima both at energies of 1–2 eV and above 4–6 eV due to excitation of vibrational and rotational, and electronic levels, respectively.

The highly energetic 'tail' of the distribution cannot be maintained at the expense of momentum-transfer collisions since the frequency of such collisions is too small. Hence, the basic principles of the simple kinetic theory of chemical reactions and of absolute reaction rate theory are violated. A general solution for the distribution function disturbed by chemical reactions has not yet been found. However, this problem has been studied in some particular cases. The effect of a fast chemical reaction upon the Maxwell–Boltzmann distribution and the effect of the distribution thus produced upon the reaction rate were studied in Ref. 5 using the Monte Carlo method.

There are well known conditions in which translational, vibrational, and rotational temperatures differ and/or various components of a system (electrons, ions, and neutral molecules, for instance) have different temperatures, and/or a system cannot be described at all using the concept of temperature* (non-equilibrium, stationary, and relaxing systems). Strictly speaking, Arrhenius-type kinetics cannot be used in these cases and the ordinary expression for the rate of a chemical reaction is inapplicable.

(d) Multichannel processes should be considered in plasma-chemical kinetics. From the quantum mechanical point of view (we shall consider only two channels for simplicity), in a certain energy range two pairs of particles (A_1, B_1) and (A_2, B_2) can exist, so that there are two independent wave functions which satisfy boundary conditions for a given system. It is known that in a one-channel problem the S-matrix contains all the information about interaction properties of the system, while in a multichannel case a similar theorem has not yet been proved[6]. Moreover, in order to compose the Hamiltonian using the results of scattering all components of the S-matrix should be known for all energies.

(e) The barrier-type nature of the reactions (the existence of an energy barrier opposing the reaction), being peculiar to the Arrhenius classical kinetics, can be completely changed in reactions under plasma conditions. It is necessary to allow for the occurrence of chemical reactions from different quantum levels of the system, and for one of the subsystems as a whole to have above-barrier energy†.

(f) These five special features of plasma-chemical reactions are peculiar to non-equilibrium chemical processes, and chemical reactions under low-temperature plasma conditions are particular (but still important) cases of such processes. In this section some special features of reactions under plasma conditions are discussed briefly.

The degree of ionization is the most important characteristic of a plasma under equilibrium conditions; given the temperature and pressure the degree of plasma ionization may be found using the Saha equation.

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* Strictly speaking, the matter is not just that only the temperature concept is inapplicable in the case of a non-equilibrium system. A complete description of a non-equilibrium system becomes impossible if new concepts are not used: level populations (occupation numbers), characteristics of relaxation over various degrees of freedom, distribution function dependence upon time and coordinates.

† A detailed theory of barrier-type phenomena can be found in Ref. 6.

Ionization processes result from such factors as mutual collisions of heavy particles at high temperatures (energies), their collisions with electrons, photo-ionization, and ion–molecular reactions. A detailed description of all these processes under non-equilibrium conditions necessitates a generalization of the kinetic gas theory for the plasma state. Such a generalization is still under development. In low-temperature plasmas long range collisions occur, due to electromagnetic interaction between charged particles, in addition to ordinary short-range collisions, such as take place in gases. Thus, very small scattering angles and consequently many interactions resulting in small momentum transfer must be considered. Moreover, interaction of charged particles with external electromagnetic fields should also be taken into account[7, 8, 9].

When electron, ion, and molecular gases are not in thermal equilibrium there is energy exchange between electrons and neutral particles and between electrons and ions. The latter occurs through Coulomb-type collisions. Both processes may lead, either directly or through successive steps of excitation, to chemical reactions. The mechanisms and probabilities of these reactions may be studied by plasma-chemical kinetics on the basis of a detailed analysis of all interactions occurring in a system, and using the basic principles of non-equilibrium chemical kinetics.

At present the limited usefulness of Arrhenius kinetics, which are valid only close to equilibrium (for example under small perturbations when a system can still be considered in quasi-equilibrium), is evident. In other words, this type of kinetics can be used when a single value of temperature (being the parameter of the Maxwell–Boltzmann distribution) can be defined for the system*.

Non-equilibrium distribution of reactants takes place, for instance, when the energy is injected pulsewise into the equilibrium system, provided that the condition $\tau_i \ll \tau_{Ch.r}$ is satisfied, where τ_i is the duration of the pulse and $\tau_{Ch.r}$ is the chemical relaxation time (pulse electrical discharges, shock tubes, flash photolysis)†.

The treatment of kinetic problems which depend more upon the molecular

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* In Ref. 10 the temperature as a concept of the kinetic theory is defined from the equation

$$\tfrac{1}{2}m\bar{v}^2 = \tfrac{3}{2}kT \tag{1}$$

This definition has been discussed in the preface to the Russian edition of the book[10] by Bogolyubov, who observed that gases cannot be considered as a generally valid case for the definition. The most general definition of temperature is made assuming it to be the module of the canonical distribution for equilibrium states and the module of approximately canonical distribution for near-equilibrium states. If a state is far from being statistically in equilibrium the concept of temperature is in general inapplicable (cf. Ref. 10, p 58).

† The excitation of reaction products under molecular beam conditions has been studied in Ref. 11, using the reactions of alkali metals with halogen compounds. A kinematic analysis of the angular distribution of the alkali halide molecules produced showed that most of the energy released (equal to the difference between the bond energies of the reactants and products) was contained in the internal excitation of the molecules, and mostly in the vibrational excitation of the newly formed bonds. As the reaction cross section increases from 10Å^2 to 10^2Å^2 the reaction mechanism becomes a 'direct stripping'.

interaction mechanism and molecular quantum level populations* requires far more information about the system[12-20].
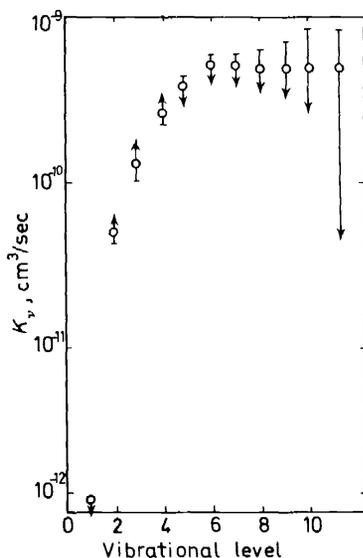
Figure 2. Experimental rate constant dependence on vibrational level numbers up to 10.

Non-equilibrium effects may be observed in a system initially in equilibrium if any processes are occurring at finite rates within the system. Such processes inevitably result in a violation of the Maxwell distribution. In particular, such a violation may be due to non-elastic collisions resulting in mass exchange and internal energy redistribution of colliding particles. Hence, the occurrence of chemical reactions always produces non-equilibrium in a system. This non-equilibrium can be neglected (although with a rather vague degree of accuracy) in the classical Arrhenius kinetics when reaction rates are comparatively small. However, at high temperatures in plasma-chemical processes, in radiation chemistry, shock tubes and other conditions, the effects of these reactions must be taken into account. For instance, thermal dissociation of diatomic molecules is known not only to violate the Boltzmann distribution but also to decrease the vibrational temperature in relation to the translational temperature. These changes

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The importance of the effect of vibrational excitation upon the rate of chemical reaction has been confirmed by the results of experiments[21]. As the vibrational temperature of N_2 molecules is increased from 1000K to 6000K (under $T_{transl} \approx 300K$) the rate constant for the reaction $O^+ + N_2 \rightarrow N_2^+ + O$ increases by forty times (see *Figure 2*). The same change in the translational temperature (under $T_{vibr} = const$) would lead, in accordance with the Arrhenius equation, to a rate constant increase of sixty times. The effects are comparable.

The results of the experiment given in Ref. 22 show cyclopropane (and carbon dioxide) produced by cyclobutanol photolysis to be vibrationally excited at the ground electronic state. The excitation distribution over vibrational levels is non-equilibrium.

affect both dissociation rates and vibrational relaxation processes[*][23]. Non-equilibrium due to a chemical reaction and further occurrence of the reaction under non-equilibrium conditions is the problem to be studied for non-equilibrium, generalized chemical kinetics. The Arrhenius kinetics appear to be an extreme case and thus are believed to be rigorously founded, their applicability limits being clearly defined.

The solution of this problem must be based upon a consideration of the Pauli equation or the Boltzmann equation (or any equation of the Liouville-type). Using one of these equations and taking into account chemical reactions and relaxation processes of the internal degrees of freedom of reacting molecules, specific solutions under various conditions can be obtained, including ordinary chemical kinetic equations and expressions for the rate factors (constants) for chemical reactions.

Three solutions to the problems under discussion may be suggested, allowing for the possibility that a set is found of cross sections $\sigma(\varepsilon)$ for the processes involved; all the required information about the system can be obtained through averaging. These three approaches are quantum-mechanical, classical dynamics, and statistical calculations[26–31].

MECHANISMS OF PLASMA-CHEMICAL REACTIONS

Electron distribution functions: influence upon chemical reaction rates

The influence of non-equilibrium distribution characteristics on chemical reaction rates may be discovered easily under glow discharge conditions in which the main reactions are due to electron–molecule collisions. Let us consider the reaction of CO_2 decomposition in a glow discharge under low pressure (a few torr) and current densities not exceeding 10 mA/cm^2. Under these conditions the rate of thermal decomposition is negligible because $kT_g/\varepsilon_{bond} \ll 1$, where T_g is the heavy particle temperature and ε_{bond} is the energy of the bond CO—O. The results of the work[32, 33] show CO_2 decomposition to result from collisions with electrons:

$$CO_2 + e^- \begin{cases} \nearrow CO_2^* + e^- \to CO + O + e^- \\ \searrow CO_2^- \to CO + O + e^- \end{cases}$$
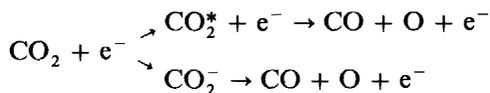
The rate of the reaction resulting in negative ions CO_2^- is low. CO_2 decomposition results from CO_2 molecule excitation into the electronically excited state CO_2^*, the excitation energy exceeding ε_{bond}. The rate of this reaction is given by the expression

$$- dN_{CO_2}/dt = kn_e N_{CO_2}$$

where N_{CO_2}, n_e are the concentrations of CO_2 molecules and electrons,

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* Vibrational relaxation may be characterized in accordance with the theory[24, 25] as follows. (1) Molecules at the higher vibrational levels have lower probabilities per one collision for relaxation than those at the lower levels. (2) Molecules with a high amplitude of vibration (hydrides for example) will relax with high rates. (3) Light molecules are deactivated more effectively than heavy ones. (4) Deactivating molecules having intermediate levels, the V–V process become very probable.

respectively, and k is the rate factor defined as

$$k = \int_{E_{th}}^{\infty} \sigma(\varepsilon)\varepsilon^{\frac{1}{2}} f(\varepsilon)\, d\varepsilon / \int_{0}^{\infty} f(\varepsilon)\, d\varepsilon \qquad (2)$$

$\sigma(\varepsilon)$ is the energy dependent cross section for electronic excitation, and $f(\varepsilon)$ is the electron energy distribution function. The quantity E_{th} is the threshold for electronic excitation.

As the expression (2) shows, the rate factor k must depend on the electron energy distribution $f(\varepsilon)$; conversely, a chemical reaction influences in general the form $f(\varepsilon)$. Under stationary conditions when $f(\varepsilon)$ is constant with time, the main influence on k is the highly energetic part of $f(\varepsilon)$ which is situated over E_{th} independently of the means by which highly energetic electron losses (due to the chemical reaction) occur. The situation is similar in normal Arrhenius-type kinetics, where the expression for k includes the main factor $\exp(-E_{ac}/kT)$, which determines for Maxwellian distribution the portion of highly energetic (chemically active) molecules. In contrast (when the temperature is a measurable quantity determining the distribution), in non-equilibrium kinetics (reactions under glow discharge conditions, for example) the measurable quantity is the distribution function $f(\varepsilon)$.

Under direct current glow discharge conditions the electron energy distribution function $f(\varepsilon)$ depends essentially on the discharge parameters, such as the type of gas, pressure, flowrate, current density, etc. These must be considered when chemical reaction kinetics are studied under these conditions. Using as an example the CO_2 decomposition reaction mentioned above, the authors of Ref. 33 showed that the reaction mechanism could not be elucidated if the function $f(\varepsilon)$ is not known[34-38].

Table 2. Rate factors for CO_2 decomposition

Discharge current I, mA	$n_e \times 10^{-9}$, cm^{-3}	$K_{exp} \times 10^{10}$ cm^3 sec^{-1}	$K_{calc.} \times 10^{10}$ cm^3 sec^{-1}
10	0.66	1.8	—
30	2.0	2.3	1.9
75	4.8	3.4	3.3

The rate factors for CO_2 decomposition are shown in Table 2[33] for a few electron concentrations n_e. These rate factors were measured experimentally, k_{exp} and calculated from expression (2), $f(\varepsilon)$ being measured and cross sections $\sigma(\varepsilon)$ being taken from Ref. 32. The k_{exp} increase with n_e might be attributed to the reaction mechanism change. However, consideration of $f(\varepsilon)$ changes (see Figure 1) observed under the same conditions shows that the reaction mechanism does not change, but that the rate factor increases because of the increased concentration of highly energetic electrons with the discharge current.

Chemical reactions caused by collisions with electrons and those occurring through electronically excited states

The influence of electron collisions upon chemical reactions under low temperature plasma conditions is one of the most important features. For

example, vibrational relaxation rates have been determined for nitrogen and other molecules (CO, CO_2, NO_2, CH_4, etc.) as a function of electron collision rates relative to those with heavy particles[39], starting from relative electron concentrations of 10^{-4}–10^{-3}, even if electrons are no hotter than heavy particles. The effect of electron collisions increases with the difference ($T_e - T_g$) (in discharges at low pressures, for example). The increase of molecular vibrational relaxation rate may lead in some cases to an increase in the dissociation rate of molecules from their ground states. Moreover, the dissociation rate may rise owing to electronic excitation of molecules under electron collisions. Two cases are possible: (1) non-stable states are excited (as for hydrogen and oxygen dissociation[40]; (2) the excitation of stable electronic states is followed by pre-dissociation caused by stable and unstable molecule interactions. In addition to these processes, under various conditions dissociation may occur through a dissociative association of electrons and molecules (this process is not only possible in electronegative gases, but can occur through unstable negative ion formation); such a process takes place in hydrogen under electron energy of 3.7 eV, which is lower than the hydrogen first dissociation potential[41]. Various ion–molecular reactions[42-44] and dissociative recombination of electrons and ions[44,45] may also result in dissociation. Nevertheless, the process of electronic excitation followed by pre-dissociation remains one of the most important in discharges under low pressures, as shown later, with examples (the direct excitation of unstable states may be considered as a particular case of the pre-dissociation having the efficiency of unity).

Fast chemical reactions may lead to lessening of the concentrations of separate vibrational levels, whose reaction rates are above the rates of other deactivation processes. For instance, in a glow discharge of nitrogen the levels of $B^3\Pi_g$ state are under-populated; due to an electron impact from
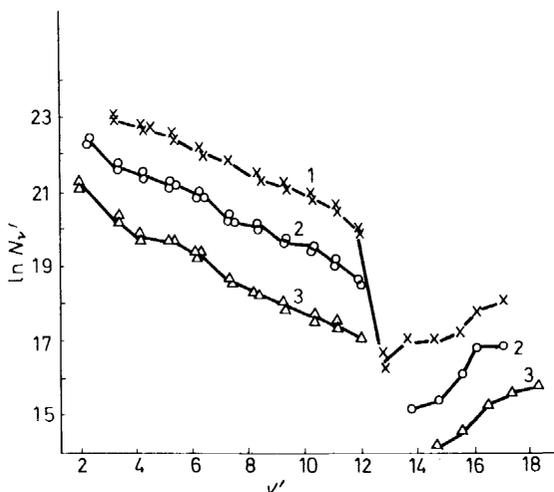
Figure 3. Vibrational level populations of $N_2(B^3\Pi_g)$ in glow discharge versus the number of the level under $p = 3.9$ torr, $d_{tube} = 3$ cm, and various discharge currents i(mA): 1–75; 2–30; 3–10.

the ground state, there was a sharp weakening of $v' \geqslant 13$, above the limit of dissociation (*Figure 3*). This weakening is caused by a fast spontaneous pre-dissociation proceeding at a rate exceeding the rates of radiation dissociation and deactivation by heavy particle impacts.

In general, the contribution of pre-dissociation to molecular dissociation must increase for less symmetrical molecules. The results of studies on the dissociation of methane[46], butane and other molecules[47] indirectly confirm this assertion.

Knowledge of the reaction mechanism (i.e. levels from which dissociation occurs) and corresponding rate factors is essential to the calculation of reaction rate factors under any non-equilibrium and quasi-equilibrium conditions such as radiolysis, photolysis, gas discharges and shock waves.

MOLECULAR DISSOCIATION THROUGH ELECTRONIC EXCITED STATES

Differences between mechanisms and chemical reaction rates taking place in a low temperature plasma and the corresponding mechanisms and rates in ordinary chemical systems are determined mainly by the presence of charged particles, i.e. electrons and ions. Rates of internal degrees of freedom excitation, molecule ionization and dissociation in a plasma are determined by electron collisions at relative degrees of ionization $\sim 10^{-3} - 10^{-4}$, even under conditions when the electron temperature is equal to the temperature of heavy particles. If the electron temperature far exceeds that of heavy particles, as in electric discharges at reduced pressures, rates of excitation, dissociation and ionization are determined by an electron impact under extremely low degrees of ionization indeed.

An electron impact affects most processes which initiate chemical reaction, i.e. molecular dissociation and ionization. As rates of molecular interactions with radicals and ions, resulting from these processes, far exceed the initiation rates, the latter often predominate in the total kinetics of chemical conversions in a plasma.

Molecular dissociation produced by electron impact may proceed without charged particle formation, due to either non-stable or pre-dissociating electron–vibrational level excitations

$$AB + e^- \rightarrow AB^* + e^- \rightarrow A + B + e^- \qquad (3)$$

or due to a direct transition of nuclei composing the molecule, into the continuous spectrum without change in the electron state.

$$AB + e^- \rightarrow A + B + e^- \qquad (4)$$

The following reactions of dissociative formation of charged particles, both positive (dissociative ionization)

$$AB + e^- \rightarrow A^+ + B + 2e^- \qquad (5)$$
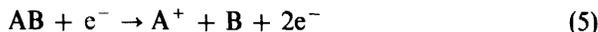
and negative ions (dissociative attachment)

$$AB + e^- \rightarrow AB^- \rightarrow A^- + B \qquad (6)$$

are possible.

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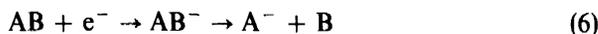
Dissociation is possible in the following cases:

(1) Either excitation of unstable states (with no minima in their potential energy curves); or excitation followed by a transition into the repulsion branch of the potential curve for the stable state, the curve being above the limit of dissociation from this state.

(2) Excitation of stable states, permitting pre-dissociation from some of their vibrational levels, conditioned by interaction of the state with the continuum of unstable states.

(3) Excitation into the stable state followed by a successive transition into the lower state belonging to type 1 or 2.

Unstable electronic states are characteristic of all molecules. For hydrogen and hydrides, in particular, the first triplet states are unstable for halogens— excited singlet states; for other molecules—quintet states etc. For practically all molecules there are cases of spontaneous dissociation of electronic states, above the first potential of their dissociation[48-50]. As well as spontaneous dissociation, pre-dissociation is possible, induced by collisions with other particles—transitions from stable into unstable states caused by collisions.

The lifetime of excited molecules in unstable states, presented as

$$\tau \sim \beta/v_M \sim 10^{-13}-10^{-14} \text{ sec} \tag{7}$$

is well above the characteristic time for electron–molecule collisions,

$$\tau_{col} \sim \beta/v_e \sim 10^{-16} \text{ sec} \tag{8}$$

where β is a characteristic molecular dimension. This is even more true for stable states. For this reason the processes of molecular dissociation [with the exception of process (4)] are considered as two-stage processes, involving excitation of the intermediate state followed by its decay.

The rate factor for dissociation of molecules initially in the level v'' of the electron state m, under electron collisions through excitation of the vibrational level v' of the intermediate state n, is calculated as the product of a rate factor for the intermediate level excitation, (k_{ex}) and the probabilities for a dissociative decay from this level $(Y_{nv'})$:

$$k_D(m, v''; n, v') = k_{ex}(m, v''; n, v') \times Y_{nv'} \tag{9}$$

$$Y_{nv'} = (\Gamma_{nv'} + v^D_{nv'})\tau_{nv'} \tag{10}$$

where $\Gamma^D_{nv'}$ is the probability of spontaneous dissociation, $v^D_{nv'}$ is the frequency of induced dissociation and $\tau_{nv'}$ is the full lifetime for the given level*. The total rate factor for molecular dissociation from the electronic state through the excited electronic vibrational levels m is calculated as follows:

$$k^m_D = \sum_{n, v'} Y_{nv'} \frac{\sum_{v''} N^m_{v''} k_{ex}(m, v''; n, v')}{\sum_{v''} N^m_{v''}} + \sum_k \frac{\sum_{v''} N^m_{v''} \int^\infty_{E_{min}} k_{ex} Y(\Delta E) \, d\Delta E}{\sum_{v''} N^m_{v''}} \tag{11}$$

where $N^m_{v''}$ is the population by the vibrational v'' level of m state.

* Pre-dissociation induced by electromagnetic fields is not considered.

Summation, as fulfilled in (11), is made over all levels permitting pre-dissociation, and in the second term over all unstable states, while integration is made over all energies of the transition into the unstable state. In expressions (9–11) there are no indications of successive transitions. These do not create difficulties but make the equations rather unwieldy.

From the relationship between rate factors for excitation levels and functions for electron distribution by energies,

$$k_{ex}(m, v''; n, v') = \int_{\Delta E^{mn}_{v''v'}}^{\infty} \sigma^{mn}_{v''v'}(E)\,(E/2m)^{\frac{1}{2}} f(E)\,dE \qquad (12)$$

where m is the mass of electrons, the following expression is obtained for cross sections of molecular dissociation through the excited levels:

$$\sigma^m_D = \sum_{nv'} Y_{nv'} \frac{\sum\limits_{v''} N_{v''}\sigma^{mn}_{v''v'}(E)}{\sum\limits_{v''} N^m_{v''}} + \frac{\sum\limits_{v''} N^m_{v''} \int_{\Delta E_{min}}^{\infty} Y_k(\Delta E)\sigma^{m,n}_{v''}(E, \Delta E)\,d\Delta E}{\sum\limits_{v''} N^m_{v''}} \qquad (13)$$

While all vibrational level lifetimes for the excited states contributing to dissociation are dependent on intramolecular (spontaneous) processes, the cross section (13) has the form of a dissociation cross section due to electron impact. When the lifetime is affected by intermolecular interactions* (level quenchings and induced pre-dissociation), the physical sense of cross section (13) as an elementary process cross section is lost.

When methane or other saturated hydrocarbons are excited by electron impact or vacuum ultra-violet radiation intensive transitions into electronic vibrational excited levels are observed, of which some are below the ionization potential, and some auto-ionized[51-54]. The spectra for full electron energy and ionization losses confirm that not all the transitions into auto-ionized states lead to molecule ionization. The excited state depopulation due to spontaneous emission is not effective (the quantum efficiency is less than 10^{-3})[55], despite probabilities for optical transitions under absorption above 10^8 sec^{-1}. Molecular phosphorescence is associated with radiation of dissociation excited products[56]. Because these measurements were made at low pressures (10^{-3} mm Hg), quenching of the excited levels under collisions with other molecules seemed unlikely. The absence of radiation from the excited molecular states can be explained only by the fact that they are all either unstable or stable, but the probability of pre-dissociation from them is rather high compared with that for radiative transitions. In the light absorption and electron energy loss spectra neither rotational nor vibrational structure is indicated (with the exception of ethane, observed to have a vibrational structure in the spectrum)[51]. In Ref. 52 excited states were assumed to be unstable, and the probability of decomposition from the lower triplet state was estimated as $\Gamma^D \sim 3 \times 10^{-15}$ sec^{-1}. Since this value

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* Spontaneous emission probability depends on v^3, where v is the vibration frequency. Thus $\tau_{rad} \sim 1/v^3$ does not depend naturally on the pressure and temperature, while the characteristic lifetime for collisions depends exponentially on the vibration frequency.

Deactivation through emission becomes significant at low temperature only when a collisional deactivation rate is small and the vibration contribution to the specific heat capactiy is negligibly small. Radiative processes are important in the upper atmosphere where the molecular collision rate is extremely small.

is probably overestimated[57] the absence of structure from the spectra can be explained only by high state densities. The above assumption on the role of decomposition in electron level de-excitations was experimentally confirmed for methane. The full cross section of this molecule dissociation, re-established by the data[58], is given in *Figure 4*. By extracting the dissociative
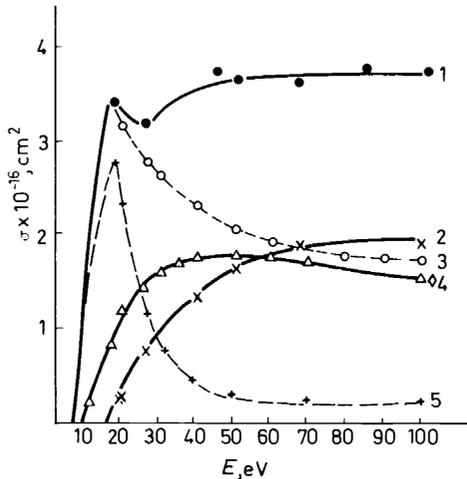
Figure 4. Electron impact dissociation cross section for non-excited methane molecule. 1—total cross section for dissociation[58], the point + is from Ref. 61; 2—dissociative ionization cross-section[59]; 3—total cross section for dissociation through electron-vibrational levels; $\diamondsuit$ from Ref. 61; 4—cross section for dissociation through excitation of permitted transitions; 5—that through the excitation of forbidden transitions.

ionization cross section[59] from this curve 3, the molecular decomposition cross section is obtained through its electronic-vibrational states. Curve 4 is a dissociation cross section through the allowed transition excitation and is calculated by the well-known formula for them using the mean cross sections of light absorption and photoionization[53,60]. The point on this curve at $E = 70$ eV is obtained from comparison of the spectrum for electron energy losses, ionization losses[54] and losses for the allowed transition excitation. *Figure 4* also shows the points for $E = 100$ eV, corresponding to dissociation cross sections, dissociation through electronic vibrational levels and dissociative ionization[*61].

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* As to dissociative attachment[132], this process is defined as a specific one not characteristic for all molecules.

The influence of this process is most essential with halogens, halogen compounds and oxides producing the stable negative ions Cl^-, Br^-, I^- and O^- [133]. For other molecules this process contributes little, compared with the decomposition from electronic excited states (less than ten per cent for CO, CO_2, H_2, N_2 at $E > 1.2$ eV and $T = 300K$).

Since the probability of dissociation being changed depends on the number of the vibrational level v' for a negative ion[134], the cross section value variations may be the more considerable.

For instance, with the temperature increase from 300K to 1000K the value of the first peak of dissociative attachment to N_2O is increased fourfold.

All these results are in satisfactory agreement within the error range of up to 16 per cent[61].

These data show that all reactions for methane molecule excitation not resulting in its ionization lead to dissociation. In this case near the threshold of excitation, the dominant contribution to dissociation makes the dissociation partial cross sections, through excitation of the forbidden optical transitions. Similar conclusions can be drawn for other saturated hydrocarbons.

On the basis of the data known from Ref. 52 on molecular dissociation cross sections due to electron impact through excited electronic vibrational levels, some general remarks on the conditions for these cross section variations may be made. It is practically impossible to determine which state makes the predominant contribution. At high energies of incident electrons the main contribution is from numerous allowed transitions. The role of the Rydberg states, being below the ionization potential, and that of auto-ionizing states are significant.

All the molecules investigated in the Rydberg states, placed below the limit of dissociation, have pre-dissociation so intensive as to prevent molecules from being seen in radiation. While the number of atoms in molecules increases, the cross section excitation maxima for these levels shift into the region of auto-ionizing states[51]. The role of dissociative ionization in full cross sections of dissociation under high electron energies is also more important here. Dissociation cross sections followed by formation of excited products (electron excitation) are usually small compared with the full cross sections of dissociation (*Tables 3, 4*). Cross section calculations for the allowed transitions (including the Rydberg states) are possible, using the Bethe–Born approximation and dependences $\psi(x)^*$, in conjunction with oscillator strengths, light absorption cross sections or photo-ionization.

However, if a molecule has low unstable (hydrogen, methane) or stable states, allowing pre-dissociation (nitrogen), though optical transitions are forbidden, the main contribution to molecular dissociation cross sections by an electron impact, near the threshold of dissociation, is from excitation of these levels. The excitation thresholds of such transitions are lower than

Table 3. Cross section of dissociation of molecules at neutral products and of dissociative ionization[124, 125] $(E = E_D^{max})$

Molecule	E_D^{prod}, eV	E_D^{max}, eV	$\sigma(E_D^{max})$ $(10^{-16}$ cm$^2)$	$E_{diss\ ioniz}^{prod}$, eV	$\sigma_{DI}(E_D^{max})$ 10^{-16} cm^2
H_2	8.8	15–17	0.85	18.08	0
N_2	9.6	70–90	1.78	24.31	0.50
CO	12	35	0.73	22.36	0.15
NO	9	40	1.45	20.1	0.30
CH_4	--	16	3.40	16.5	0
NH_3	11.7	100†	0.28	—	0.97

† Measured only with this electron energy.

*: $\psi(x) = \psi(E/\Delta E) = \exp\left[(\Delta E/E)\ln(E/\Delta E)\right]$.

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Table 4. Cross section of dissociation of molecules by electron impact with excited product formation

Mole-cule	Excited products	E^{prod}, eV	E^{max}, eV	$\sigma(E^{max})$, 10^{-18} cm^2	Refs.
H_2	H(2P)	14.7	50	15.9	64, 69
	H(2S)	14.7	50	7.7	64
	$\sum_{n=3}^{6} H(nP)$	16.6	60	1.2	64
D_2	D(2P)	15.5	50	12.9	64
	D(2S)	15.5	50	6.3	64
	$\sum_{n=3}^{6} D(nP)$	17.4	60	0.96	64
N_2	$\sum N^*$	20	50	13	65
O_2	$O(^3S^0)$	15	100	3	70
	$O(^5S^0)$	14.9	100	1.7	70
CO	$O(^3S^0)$	20.6	110	0.8	70
	$C(^3D^0 + {}^3P^0 + {}^3F^0)$	20.8	110	0.7	70
NO	$O(^5P)$	36	100	4	71
CO_2	$CO(\alpha^3\pi)$	11.46	100	10	70
	$CO(A^1\pi)$	—	30†	1.25	70
	$C(^3D^0 + {}^3P^0 + {}^3F^0)$	26.23	110	3.6	70
	$O(^3S^0)$	21	110	0.76	70
	$O(^5S^0)$	27	100	10	72
	$O(^5P)$	—	100	2	71
H_2O	H(2P)	15.3	50†	28.5	73
	$\sum_{n=3}^{6} H(nP)$	17.3	50†	55.2	73
	$OH(A^2\Sigma_4^-)$	10	16	4	74
CH_4	H(2P)	—	50†	14.5	56
	H(2S)	—	50†	1.55	56
	$\sum_{n=3}^{6} H(nP)$	—	50†	3.8	56
C_2H_6	H(2P)	—	50†	8.5	56
	H(2S)	—	50†	1.5	56
	$\sum_{n=3}^{6} H(nP)$	—	50†	1.2	56
C_2H_4	H(2P)	—	50	9.5	56
	H(2S)	—	50	0.75	56
	$\sum_{n=3}^{6} H(nP)$	—	50	1.2	56
C_6H_6	H(2P)	—	100	15.5	56
	H(2S)	—	50†	0.75	56
	$\sum_{n=3}^{6} H(nP)$	—	50	5.5	56

Table 4.—Cont.

Mole-cule	Excited products	E^{prod}, eV	E^{max}, eV	$\sigma(E^{max})$, 10^{-18} cm^2	Refs.
C_2H_2	$CH(^2\Delta)$	15	110	1.2	74
	$C_2(^3\pi)$	17	100	0.4	74
	$H(3P)$	22	100	1.0	74
C_2N_2	$C(A^2\Pi)$	18.5	95	77	74
NH_3	$NH(^3\pi, v' = 1)$	13	24	7	74

† In these cases the measurements were carried out starting at the mentioned energies of electrons.

those of allowed transitions, and cross section maxima are obtainable under smaller energies of incident electrons. The values for cross section maxima are not less than those of allowed transitions (*Table 5*).

Table 5. Rate coefficients for reactions of dissociation and ionization of molecules by electron impact

$\overline{E}_e = 3$ eV; f_e – Max w; $T_g = T_{v''} = 300$K, $P < 0.1$ torr

Molecule	K, cm^3 sec^{-1}			
	diss. through electr. levels	dissociative ionization	dissociative attachment	ionization
H_2	1.1×10^{-10}	10^{-15}	3.4×10^{-14}	2.5×10^{-12}
N_2	0.5×10^{-10}	1.2×10^{-14}	—	0.66×10^{-11}
CO_2	6.4×10^{-10}	2×10^{-14}	5×10^{-12}	2.2×10^{-11}
CH_4	$\sim 5 \times 10^{-10}$	2.5×10^{-15}	$<4 \times 10^{-13}$	3.4×10^{-11}

This provides the advantage of these level excitations (when they cause dissociation) in molecular dissociation, in electric discharges, in gas and in electron swarms through the excited electron states.

As the number of atoms in molecules increases, the rules for pre-dissociative transition selections between stable and unstable electron states must be weakened, resulting in (as we have seen above in the example of methane and other saturated hydrocarbons) effective dissociation from most of the excited electronic vibrational levels.

It should be noted, however, that intramolecular radiationless transitions which do not cause molecular dissociation, i.e. isomerization, intercombination conversion (under the stable triplet states), can also contribute with an increase in the number of atoms in a molecule under de-excitation of the electronic states[63].

Photodissociation quantum efficiencies of many of the molecules examined—aldehydes, ketones, organic acids, nitrogen, and sulphur-containing organic compounds, organic halogenides, hypochlorites, olefins,

acetylene hydrocarbons, etc., reach 0.5–1 eV[63]. The only exceptions are molecules of benzol, aromatic hydrocarbons and amines, characterized by high luminescence, intercombination conversion and isomerization.

INFLUENCE OF EXCITATION OF INTERNAL DEGREES OF FREEDOM ON ELECTRON IMPACT DISSOCIATION THROUGH ELECTRON-EXCITED STATES

In general cross sections and rate factors for molecular dissociation by electron impact[64, 65] depend on the populations in various vibrational levels of the initial state. In such cases, when the significant contribution is from partial cross sections of dissociation through stable electron states, allowing pre-dissociation either from $\Gamma^D < 10^8 \sec^{-1}$, or from a definite rotational level, there must also be cross section and rate factor dependences upon the temperature for populating by T_j rotational levels.

On the assumption of Maxwell electron energy distributions and Boltzmann populations of vibrational and rotational levels at $M_e^2 \neq f(\Delta E)$ and $T_e \ll \Delta E_{00}^{mu}$ for the partial rate factor for dissociation through the excited stable states n, we have

$$k_D^{mn} \cong 1.7 \times 10^8 T_e^{\frac{1}{2}}(1 + 2T_e/\Delta E_{00}^{mn}) \times |M_e^{mn}|^2 \exp(-\Delta E_{00}^{mn}/T_e) \times \sum_{v'v'} q_{v''v'}^{mn}$$

$$\times \frac{1}{Q_{v''}^m} \exp(-\Delta E_{v'}^m/T_{v''}) \exp\left(-\frac{\Delta E_{v'}^n - \Delta E_{v'}^m}{T_e}\right) \quad (14)$$

and through the unstable states

$$k_D^{mn} \cong 1.7 \times 10^8 T_e^{\frac{1}{2}}(1 + 2T_e/\Delta E_{00}^{mn}) \times |M_e^{mn}|^2 \exp(-\Delta E_{00}^{mn}/T_e)$$

$$\times \frac{1}{Q_{v''}^m} \sum_{v''} \int_0^\infty \frac{dq_{v''}(\Delta E^n)}{d(\Delta E_{v''}^m)} \times \exp\left[-\Delta E_{v''}\left(\frac{1}{T_{v''}} - \frac{1}{T_e}\right)\right]$$

$$\times \exp(-\Delta E_{v'}^m/T_e) d(\Delta E^n) \quad (15)$$

where the temperature is expressed in electron volts, $\Delta E_{v''}^m$ is the vibrational level energy, calculated from the zero vibrational level of the given state,

$$Q_{v''}^m = \sum_{v''} \exp(-\Delta E_{v''}^m/T_{v''})$$

Figure 5 shows the dependences of partial and total rate factors for dissociation through electronic vibrational levels of nitrogen molecules upon the vibrational temperature of molecules in the ground electronic state, calculated from equations (11 and 14) at $\bar{E} = 3$ eV, $p < 0.1$ mm Hg and $T_g = T_j = 300K$.

The dependences for other mean electron energies[66] are analogous. It appears from this figure that the main contribution to dissociation at low vibrational temperatures is excitation of the allowed transitions from $\Delta E > 12.4$ eV and the forbidden transitions into the state $a^1\Pi g$.

With increase in the vibrational temperature, the roles of excitation and subsequent pre-dissociation from the levels of $B^3\Pi g$ and $C^3\Pi u$ states become more significant. Partial rate factors for dissociation through these

levels are comparable in magnitude with rate factors for dissociation through other levels, though under $T_{v''} = 5000\text{--}10000\text{K}$. It is worthy of note that cross sections for dissociation through the triplet states for non-excited molecules are too small to affect the total dissociation cross section[47, 135, 136]. The vibrational temperature variation from 1 000 to 15 000K causes some partial rate factors to increase by more than an order of magnitude, while the total rate factor is increased more than three-fold.
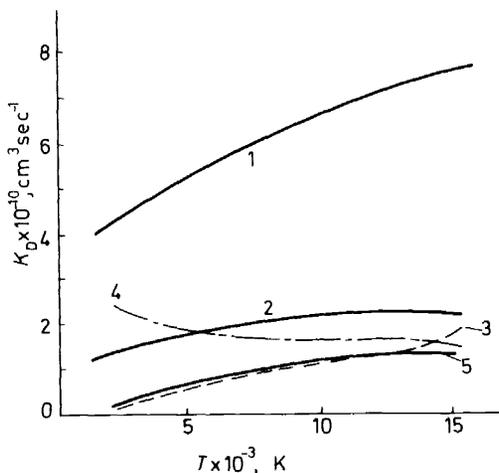
Figure 5. Dependence of nitrogen dissociation rate factors on vibrational temperature under electron impact conditions ($p < 0.1$ torr, $E_e \sim 5\,\text{eV}$, Maxwellian distribution); 1—total K_D; 2—K_i through $a^1\Pi g$, 3—$c^2\Pi u$, 4—$B^1\Pi u$, 5—$B^3\Pi g$ ($v'' \geqslant 13$).

With pressure variation from 0.1 to 10 mm Hg, other parameters being constant, the rate factor for dissociation must decrease 1.5–2-fold, owing to the decrease of the relative probability for dissociation from the state $a^1\Pi g$ and $B^3\Pi g$[67]. This decrease is caused by the competition of the level quenching and pre-dissociation process. The decrease takes place if the pre-dissociation, induced by collisions with other molecules, is assumed to be small under these states. This is apparently true since the induced pre-dissociation is one of the numerous means of quenching these electronic states.

The increase in the molecule rotational temperature to 1000K under $p = 10$ mm Hg, other parameters being constant, should cause k_D to rise by about 30 per cent, because of the dependence of the dissociation probabilities for these states on the rotational temperature.

In the case of hydrogen molecule excitation, the lower triplet state contributes most to dissociation. As shown in expression (15), with the arrangement of the potential curves for the ground and triplet states[68], the increase in vibrational temperature from ambient temperature to T_e, caused by lowering of the dissociation threshold from 8.8 eV (the energy of a vertical transition from the zero vibrational level) down to 5 eV, leads to the 4 to 6-fold increase of the rate factor for dissociation at $\overline{E} = 2\text{--}3$ eV.

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These variations show the significance of the influence of excitation of molecular internal degrees of freedom, characteristic for a low temperature plasma, upon the rate factors for their dissociation by an electron impact through electronically excited states.

The main contribution to hydrogen dissociation under low electron energies correlates with excitation of the triplet levels ($b^3\Sigma_u^+$, $a^3\Sigma g$, $c^3\Pi u$). However, under higher energies of $E \geqslant 50$ eV the partial cross section for dissociation, producing excited atoms, is predominant.

Nitrogen molecule dissociation depends on the influence of stable electronic states, followed by pre-dissociation.

The continuum state excitation $B^3\Sigma_u^-$ (as under the photodissociation process) contributes most to the full cross section for oxygen dissociation through excitation of the electronic vibrational levels by electron impact. Near the dissociation threshold it appears to be the most essential excitation of the forbidden transitions (threshold of 6.1 eV). The corresponding levels can make the predominant contribution under gas discharge conditions.

The auto-ionization levels contribute to the full cross section, approaching 20 per cent with $E \sim 25$ eV and ~ 50 per cent under high electron energies.

The full cross section of dissociation of oxides of nitrogen is the total of the partial cross sections through many electronic-vibrational levels, placed at more or less regular intervals between the first dissociation potential and $\Delta E \sim 18$ eV. Near the threshold of dissociation the main contribution is made by pre-dissociation of $A^2\Sigma^+$, $B^2\Pi$, $D^2\Sigma^+$ states.

Thus, the study of the experimental data on cross sections of various processes resulting in molecular dissociation under electron collisions defines neutral product dissociation as the most typical for all molecules, and as essential for most of them[122].

Dissociation cross section calculations, as fulfilled in the first Born approximation, with the electronic state unchanged, show that this process contributes little to dissociation. Hence, the main contribution to molecular dissociation by electron impact in a low temperature plasma is expected to be made by electronic vibrational level excitation, followed by the decay of the excited states of molecules.

MECHANISMS AND DISSOCIATION RATE FACTORS UNDER GASEOUS ELECTRIC DISCHARGE CONDITIONS

Investigations on mechanisms and rate factors for molecular dissociation in electric discharges through gases attract attention because of their numerous technical applications. Attempts to apply these results for cross-section dissociation calculations, as well as for other non-elastic processes[75, 76] show the solution of the problem to be ambiguous. It can be successful, however, only when the pattern of the cross-section dependence upon the energy is defined beforehand (compare, for instance, the determination of vibrational and electronic excitation of nitrogen molecules[75, 77, 78]). The use of the methods developed for the solution of the problems is impeded by the multichannel character of non-elastic excitation and dissociation, in particular.

Figure 6 shows the dependence of rate factors for hydrogen and carbon

dioxide molecule dissociation upon values ε/N (ε is the electric field, and N the molecular concentration), measured under high frequency[79] and glow discharge conditions[80, 81]. This figure also shows the dependences of coefficient (factor) ratios for hydrogen, methane and ethane[82] dissociation
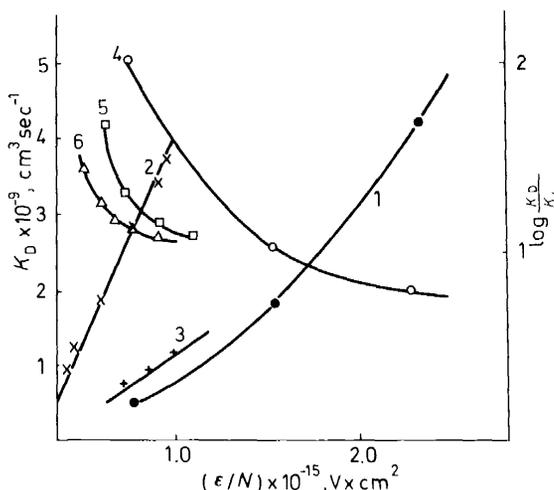
Figure 6. Dissociation rate factors (K_D) and their ratios to ionization rate factor (K_D/K_i) for a number of molecules versus the parameter ε/N. 1—K_D for H_2 from Ref. 79; 2—$10K_D$ for CO_2[80], 3—$10K_D$ for CO_2[81]; K_D/K_i: 4—H_2, 5—C_2H_6[82], 6—CH_4[82].

and ionization on the same parameter. The calculation[83] makes use of hydrogen cross-section dissociation in the approximation of the Maxwell–Boltzmann functions for electron distributions by energies and vibrational populations ($T = 300K$). These calculations show that hydrogen decomposition under specified conditions[79] proceeds as a result of dissociation through electronic-vibrational states. The analogous dependence characters for coefficient (factor) ratios for methane and ethane dissociation and ionization lead to the conclusion that the mechanism of their decomposition under specific conditions[82] is also dissociation through electronic excited levels, and the forbidden transitions with thresholds, being significantly below the ionization potential, are most important. The cross section obtained for methane dissociation by electron impact, as well as those for other saturated hydrocarbons, justifies this conclusion (*Table 6*).

Comparison of the results obtained in Refs 81, 82 on carbon dioxide decomposition, show that, first, decomposition occurs, apparently due to vibrational state excitation of this molecule. However, rate factors for dissociation depend largely on the parameter ε/N as well as on the full discharge current. It has been determined both by calculations[84] and by experiments[86], that electron energy distributions depend essentially not only on ε/N, but also on the degree of vibrational molecule excitation. The calculations for vibrational level populations of nitrogen and carbon monoxide molecules in the ground electronic state (for instance Refs. 87, 88)

Table 6. Cross sections of most probable processes in methane and ammonia

Molecule	Products	$\sigma, 10^{-16}\,cm^2$	Molecule	Products	$\sigma, 10^{-16}\,cm^2$
CH_4	$CH_3 + H$	$1.16 \leqslant \sigma \leqslant 1.2$	NH_3	$NH_2 + H$	$0.07 \leqslant \sigma \leqslant 0.2$
	$CH_2 + H_2$	0.2		$NH + H_2$	0.004
	$CH + H_2 + H$	$0.04 \leqslant \sigma \leqslant 0.08$		$N + H + H_2$	$0.074 \leqslant \sigma$
	$CH_3^+ + H + e$	1.5		$NH_2^+ + H + e$	0.8
	$CH_2^+ + H_2 + e$	0.28		$NH^+ + H_2 + e$	0.09
	$CH_3 + H^+ + e$	$\left.\begin{array}{c} \\ \end{array}\right\}0.04$		$NH + H_2^+ + e$	0.026
	$CH + H_2 + H^+ + e$			$N + H_2 + H^+ + e$	$\left.\begin{array}{c} \\ \end{array}\right\}0.026$
	$C^+ + 2H_2 + e$	0.05		$NH_2 + H^+ + e$	
	$CH + H_2^+ + H + e$	0.02		---	

show them to be essentially different from those obtained according to Boltzmann, and to be defined both by means electron energies and by the degree of ionization and gas temperature in a discharge.

FUNDAMENTAL EQUATIONS OF PLASMA-CHEMICAL KINETICS

It is difficult, at present, to identify an equation to form the basis of non-equilibrium chemical kinetics*. It may be the Liouville, Boltzmann, Pauli, or some analogous equation. The Liouville equation has the advantage of being the integral of mechanics equations. However, it is difficult to apply because of the irreversibility of systems evolution. Moreover, some almost insurmountable obstacles arise from its solution[89-91].

The application of either the Boltzmann[91-93] or the Pauli[94-96] equation necessitates numerical methods and electronic digital computers. This precludes the attainment of general regularities. Nevertheless, it is at present the only means of progress in the solution of non-equilibrium chemical kinetics problems.

Taking into account the difficulties involved in the experiment and interpretation of its results, the importance of using the mathematical experimentation method (the Monte-Carlo method) and analogous approaches becomes evident[5].

The Pauli equation should be taken as a principle for chemical kinetics, at least at present. This conclusion cannot yet be rigorously based, but some serious arguments and discussion can be found in Refs.[94, 96] concerning the importance of this equation for the description of irreversible and relaxation processes (apart from chemical kinetics).

Many methods of solving kinetic problems developed in classical chemical kinetics (the quasi-stationary concentration method in particular) will be used in chemical non-equilibrium kinetics†. Chemical reaction rates will be

* Chemical kinetic calculations are based, generally speaking, upon the many-particle scattering problem.

† Non-equilibrium plasma-chemical processes were observed to be of great importance for amino acid formation in gaseous atmospheres of planets at the stage of a prebiological chemistry (*Figure 7*).

discussed classically within certain ranges of temperature (energy), densities of reactants and of reaction products. However, we are not concerned here with the methods of classical kinetics, which are based upon equilibrium thermodynamics.
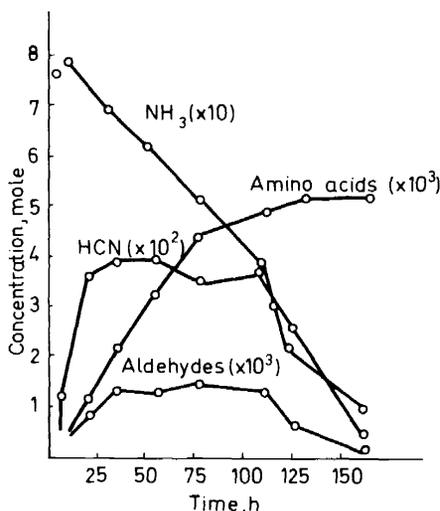
Figure 7. Ammonia, hydrogen cyanide and aldehydes in U-type of Miller device and amino acids in the small cell under the spark effect on the mixture of CH_4, NH_3, H_2O and H_2.

To describe completely the time evolution of a multichannel system, it is necessary to consider excitation and deactivation of all internal degrees of freedom (electronic, vibrational, rotational), the mutual energy exchange between them and the energy transfer from them to the translational degree of freedom. For example, standard kinetic equations do not permit description of the chemical reaction $I + RI \rightarrow I_2 + R$, because the latter can be exothermic and endothermic, and its activation energy can be 20 or 2 kcal/mol depending on whether the ground or first electronic excitation state of atom I is involved[97, 100].

An account of transitions between individual quantum levels modifies the classical equation of chemical kinetics and results in the Pauli equation[1, 95]. We have the Pauli equation for the large-scale matrix of probability density $\rho(n, t)$ for weakly interacting particles to be in set Δn of closely situated states

$$\frac{\partial \rho(n, t)}{\partial t} = \sum_n v_n P_{nn'}, \rho(n, t) - \sum_n v' P_{n'n} \rho(n, t) \tag{16}$$

where v_n is the number of states in Δn, and $P_{nn'}$ is the transition probability per unit of time from $\Delta n'$ to Δn.

This equation permits the development of a new method for the investigation of many-particle system relaxation to the equilibrium state. If a unimolecular reaction occurs in a heat bath of an inert gas the Pauli equation

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may be written as [1, 94, 101]:

$$\frac{dn_i}{dt} = \omega \sum_j P_{ij} n_j(t) - \omega \sum_j P_{ji} n_i(t) - k_i n_i(t) + R_i(t) \tag{17}$$

where $n_i(t)$ is the concentration of reacting molecules at the energy level i at the time t; P_{ij} is the probability of a reacting molecule changing from the state j to the state i owing to a collision with an inert gas molecule; k_i is the rate coefficient (rate constant) for the reaction from the level i, and $R_i(t)$ is the rate of excitation of the level i^*. When there is no excitation, then $R_i(t) = 0$ and equation (15) may be rewritten in a matrix form

$$dN(t)/dt = -IN(t) \tag{18}$$

where $I = [\omega(I - p) + k]$ is the transport matrix; p is the transition probability matrix; k is the diagonal matrix for rate constants; and N is the vector of concentrations. Thus, the problem arises of finding the eigenvalues for equation (18).

Following Ref. 94 some special features of equation (15) are noted:

1. This equation describes the probability density; it is linear and homogeneous.

2. A change in $n_i(t)$ is determined, with balancing between the increase and decrease.

3. The equation may be applied to infinitely large systems provided that at least one of the quantum numbers becomes continuous.

4. The time-dependent quantity $n_i(t)$ has the same value in both the left and right hand parts of the equation. In other words $n_i(t + \Delta t)$ is determined from $n_i(t)$ and does not depend on $n_i(t')$, where $t' < t$ and Δt is much more than a single transition duration; such evolution is called Markovian.

5. Equation (16) describes irreversible motion.

6. The divergence of the transition probability as the system's volume increases to infinity under fixed density conditions is an undesirable feature of equation (16), but may be overcome by analysing real systems.

THE RATE FACTOR FOR NON-EQUILIBRIUM CHEMICAL REACTIONS

The theoretical rate factor (rate constant) for a chemical reaction is a function of the type

$$k \sim k(u, f) \sim k(\sigma, f) \tag{19}$$

---

*Such a process can be described simply (neglecting the molecules of the heat bath) by the following scheme:

$$n_j \underset{\omega P_{ji}}{\overset{\omega P_{ij}}{\rightleftharpoons}} n_i \overset{k_i}{\underset{R f_i}{\longrightarrow}} \text{products}$$

In this case equation (17) takes the form

$$dn_i(t)/dt = \omega \sum_j P_{ij} n_j(t) - n_i(t)(\omega + k_i) + R(t) f_i \tag{19'}$$

where ω is the collision frequency, R is the total rate of production of excited states, and f_i is the probability of the ith excited state being produced.

where u is the potential function for the molecular interaction. The nature of k is rather like that of transfer coefficients, in that many results may be obtained analogously. In general,

$$f = \mathfrak{f}(\vec{r}, \vec{v}, E_{in}; t) \tag{20}$$

where E_{in} denotes molecular quantum level energies and k may prove to be not only a time-dependent but also a density-dependent function. A special study is needed to determine the extent to which the analogy between k and transfer coefficients may be applied (see, for instance, refs. 1, 102, 103).

In general, the rate factor for a chemical reaction, k, depends upon cross sections of corresponding processes, momentum distributions of reactant and product particles and quantum-level populations of molecular internal degrees of freedom[92, 104, 105].

Let us consider an irreversible gas-phase reaction

$$A(i) + B(j) \rightarrow C(k) + D(l)$$

where i, j, k, l are characteristics of the particle quantum states. Relating the reaction rate[1, 2, 106] to the number of collisions between particles $A(i)$ and $B(j)$ yields the expression for the reaction rate factor as

$$k = \sum_{ij} \alpha_i \beta_j \int_{V_A} \int_{V_B} \sigma(ij|l, k; V_{AB}) |V_{AB}| \times F_{A(i)}(V_{A(i)})$$
$$\times F_{B(j)}(V_{B(j)}) \times \mathrm{d}V_{A(i)} \mathrm{d}V_{B(j)} \tag{21}$$

where α_i and β_j are relative densities of particles in quantum states i and j respectively; $\sigma(ij|kl; V_{AB})$ are total cross sections for the corresponding scattering processes (dependent on quantum numbers and velocities of relative motion) considered in the coordinate system of the centre of gravity of the colliding particle; $F_{A(i)}$ and $F_{B(j)}$ are distribution functions (normalized to unity) of A and B particles in i and j quantum states, respectively; $|V_{AB}|$ is the relative velocity module of A and B particles.

The rate factor for the reaction to occur from an ith level may be expressed as follows:

$$k_i = \int_{V_A} \int_{V_B} \sigma(i, j; V_{AB}) |V_{AB}| F_{A(i)}(V_{A(i)}) F_{B(j)}(V_{B(j)}) \, \mathrm{d}\vec{V}_{A(i)} \, \mathrm{d}\vec{V}_{B(j)} \tag{22}$$

If only one of the reactants has internal degrees of freedom,

$$k = \sum_i \alpha_i \int_{V_A} \int_{V_B} \sigma(i; V_{AB}) |V_{AB}| F_{A(i)}(V_{A(i)}) F_B(V_B) \, \mathrm{d}\vec{V}_{A(i)} \, \mathrm{d}\vec{V}_B \tag{23}$$

or briefly,

$$k = \sum_i \alpha_i k_i = \sum_i \tilde{k}_i \tag{24}$$

where $\tilde{k}_i$ is the contribution of the ith level to the gross rate factor, assuming the distribution over vibrational levels α_i to be given. (Here molecules are assumed to have only vibrational level. However, correct treatment requires the inclusion of rotational levels.)

Physical sense of k and k_i

From the physical point of view an essential difference between k_i and k is emphasized. k_i is the fundamental quantity describing any given molecule through the cross section $\sigma(E)$. Strictly, k_i depends upon the molecular interaction potential defined under given quantum states and distribution function $F_i(E; t)$. k_i is the only rate factor for the elementary chemical reaction. The rate factor k, measured in a chemical experiment and defined by equation (21), is always a complex parameter depending on σ and F and upon level populations, and may coincide with k_i only very rarely. Such occasions are most likely under low temperature conditions and for slow reactions (particularly thermoneutral). In general, k depends upon level populations, for example, upon concentrations of molecules in given quantum states. These concentrations vary widely. Evidently k changes with temperature (even under Maxwell–Boltzmann distribution conditions) because of changes in various k_i contributions into k. Thus, a reconstruction of k using k_i gives not an Arrhenius-type but a more complex dependence of k on temperature. At low temperatures the rate factor is determined with the reactions occurring from the lowest level, and the dependence $k = k(1/T)$ coincides asymptotically with that for the first vibrational level. At high temperatures the rate factor changes, and the activation energies also change correspondingly. Therefore, the dependence of log $k \sim 1/T_{tr}$ is not linear but curved. An Arrhenius-type treatment of experimental data is thus physically wrong, especially in such cases as highly exothermic reactions, chain-branching through excited molecules etc., even if translational and vibrational temperatures are equal. The conclusions drawn concerning reaction mechanism changes based upon the bending of the Arrhenius plot are also wrong. In all these (and many other) cases the Arrhenius-type kinetics and its methods of treatment and interpretation of experimental data prevent the correct understanding of the nature of the chemical reactions.

Thus it is shown that the plot of the 'brutto' rate factor $k = \Sigma_i \alpha_i k_i$ of a chemical reaction, as a function of temperature, is not a straight line in Arrhenius coordinates, even if all k_i are described with the Arrhenius-type equations and the Maxwell–Boltzmann distribution[107, 108] exists in the system.

From equation (21) it follows that: (1) k may be determined for any given cross sections and distributions and is not related to the concept of temperature which cannot be defined simply for non-equilibrium systems. (2) k also depends implicitly on time for non-equilibrium processes, since $F_{A(i)}$ and $F_{B(j)}$ are time-dependent. The value of k may be determined using, for instance, the Monte-Carlo procedure[109–111] for any given σ and F.

From k calculations for different non-Maxwellian distributions, making use of the solid ball model, the limits of application of classical chemical kinetics may be found. In particular, these calculations offer possibilities of using the Arrhenius rate constant k_{exp} to interpret the data of chemical kinetic experiments.

The plot of log k as a function of the ratio $\bar{E}_A/\bar{E}_B$ (where $\bar{E}_A$, $\bar{E}_B$ are the energies of A and B species, respectively, averaged over corresponding distributions) is shown in *Figure 8* for a reacting system composed of two Maxwellian gases with different mean energies. Since $\bar{E}_A$ was taken to be

constant and $\bar{E}_B = kT_B$, the ratio $\bar{E}_A/\bar{E}_B \sim 1/T_B$, and therefore the Arrhenius plot shown in *Figure 8* is for the temperature T_B.

These plots differ noticeably from the well-known Arrhenius straight lines. They may be approximated by three or four straight lines with different slopes, particularly for $\beta = 50$, which is somewhat characteristic of classical chemical experiments. The breaks on the corresponding plots for k_{exp} are usually believed to be due to reaction mechanism changes. However, this conclusion is clearly not the only possible one.
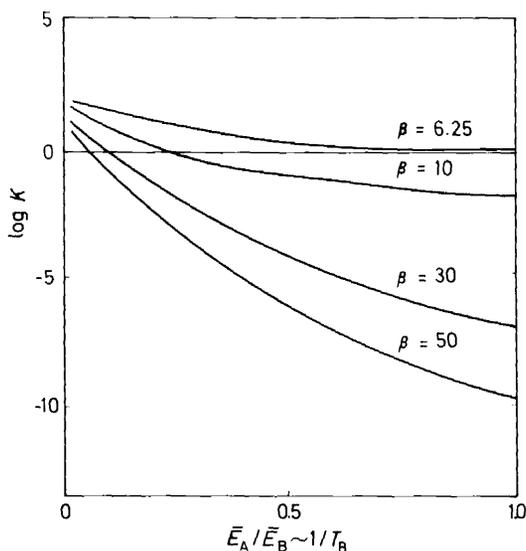
Figure 8. The quantity $\log K$ as a function of $\bar{E}_A/\bar{E}_B$ ($\beta = E_{th}/K T_A$).

The dependences $\log k_i = f(1/T_{tr})$ for various distributions by vibrational levels are shown in *Figure 9* (curves 1–6); curve 7 in *Figure 9* is $k = k(1/T_{tr})$ when there are Boltzmann distributions with $T_{tr} = T_{vibr}$; it is not an Arrhenius straight line.

All these results show that the Arrhenius procedure for describing chemical reactions may lead, even in the simplest cases, to significant errors both in the rate factor k and in the understanding of the chemical reaction mechanism. Thus, three problems arise: (1) The factor k must be found for various more realistic models of molecular structure and interaction using equilibrium and non-equilibrium distributions of the energy and level populations. (2) A procedure must be developed to distinguish between non-equilibrium and Arrhenius reactions under conditions of chemical kinetic experiments. (3) A means must be found to determine E_{th} and k reaction rate factors as functions of energies and level populations. The discussion of problems (1) and (2) is beyond the scope of the present survey. As regards problem (3), some remarks may be made which may be useful in the treatment of non-equilibrium kinetic experimental data. If both subsystems of a non-equilibrium system are Maxwellian, $\bar{E}_A$ and $\bar{E}_B$ are known and k is determined

for a few values of the ratio $\bar{E}_A/\bar{E}_B$. The plot of k as a function of $\bar{E}_A/\bar{E}_B$ should be compared with the plots shown in *Figure 8* (here β is a parameter for the curves shown). The value of E_B may then be determined by the coincidence of the experimental curve and one of the calculated plots. It is interesting to compare the value of E_B with that of E_A obtained from the Arrhenius plot.
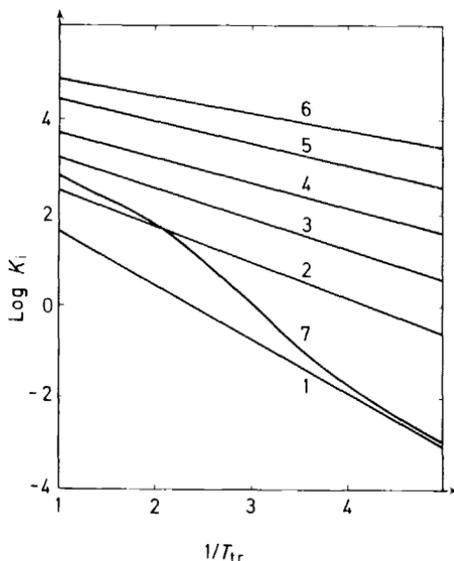
Figure 9. $K_i = f(1/T_{tr})$ is oxygen dissociation rate factor under δ-like distributions of molecules over 1–6 vibrational levels (the curve 7 corresponds to the Boltzmann distribution, i.e. the total rate factor K is determined for $T_{tr} = T_{vibr}$.

To calculate k_i and k, cross sections $\sigma(E)$, distribution functions $f(E)$, and level populations were required. With experimental data $n_i = n_i(t)$, and the reaction assumed to be slow, $F = F_M(1 + \gamma)$, where $\gamma \ll 1$, F_M is the Maxwellian distribution, σ or F may be found using Fredholm's integral equation of the first type[112, 113]. To do this the expression (22) can be used. The problem is formulated for a simple case: comparatively low temperature causes the reaction rates to be slow; the distribution is near-Maxwellian; the reaction occurs mainly from the first vibrational level of the ground electronic state. On the left-hand side of expression (22) is a quantity $(k \pm \Delta k)$ which is determined by a normal chemical kinetic experiment; here (Δk) denotes the error of the experiment. Thus

$$k(T) \pm \Delta k = \int_{E_{th}}^{E_1} \sigma(E) f_M(E)\, dE \qquad (25)$$

where $f_M(E)$ is the Maxwellian distribution, E_{th} is the threshold of the reaction, E_1 is the energy at which the distribution 'tail' is cut off, since the contributions of the molecules with $E > E_1$ to the reaction rate becomes negligible owing to the small and diminishing number of such molecules.

Equation (25) can be solved and $\sigma(E)$ found using one of the known procedures for solving the so-called incorrectly set problems[112]. After $\sigma(E)$ is found for the first vibrational level of the ground electronic state, cross

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sections can be determined for the higher vibrational levels using the Pauli equation and experimental data on the value of k for higher temperatures. A model problem is solved in Ref. 113 and a similar calculation is made for the reaction $CH_3I + I \rightarrow I_2 + CH_3$[113]; electron–ion dissociative recombination $N_2^+(X^2\Sigma_g^+, v = 0) + e^- \rightarrow N(^2D) + N(^2D) + 0.9 \text{ eV}$ is found in Ref. 114, 115; in Ref. 116 the function F is found if $\sigma(E)$ is already known. The procedure of Ref. 113 permits determination not only of $\sigma(E)$, but also of E_{th} (if the latter is not already known).

Recent developments in optical spectroscopy have given rise to the possibility of studying the formation of excited vibrational states, by examining the i.r. fluorescence of reacting molecules and reaction products. Fluorescence spectra investigation is a general method for population determination of various states of reactants and reaction products. The so-called chemical lasers[118] may be considered as particular systems suited for the study of some of the processes mentioned above.

KINETICS OF MUTUAL INFLUENCE OF VIBRATIONAL RELAXATION AND DISSOCIATION[88, 117, 119-134]

To solve the given problem the following main assumptions were made.
1. The medium is homogeneous and isotropic.
2. All particle energy distributions are of the Maxwell type and gas temperature, T_g and electron temperature, T_e do not change with time. Here $T_g \neq T_e$ (for all calculations $T_e = 1 \text{ eV}$ and $T_g = 750K$).
3. The energy of vibrational quantum levels of the $X^1\Sigma_g^+$ state is calculated according to the model of the anharmonic oscillator.
4. The following processes are considered: single quantum vibrational–vibrational processes (V–V) and vibrational–translational (V–T) processes, as well as multiquanta ($\Delta v = \pm 1, \pm 2 \ldots \pm 51$)(e–V) ones.
5. In some of the calculations there are considered to be molecular dissociations and heterogeneous atom recombinations along the sides of the discharge tube. The flux populating the upper vibrational level $v^* = 51$, is assumed equal to that of dissociating molecules, that is $n_{51}(t) = 0$. Atom recombinations on the wall are assumed to occur instantaneously and the molecules formed are assumed to disperse instantaneously according to the populations of their vibrational levels. The molecules produced are mainly vibrationally non-excited, or feebly excited.

To obtain population distributions by vibrational levels it is necessary to solve a system of differential equations of the following type[117]:

$$\frac{dn_{v'}}{dt} = N\langle\sigma v\rangle\{[P_{v+1,v}n_{v,v+1} - P_{v,v+1}n_v] + [P_{v-1,v}n_{v-1} - P_{v,v-1}n_v]\}$$

$$+ \langle\sigma v\rangle\{[\sum_{s=1}^{v^*} P_{v+1,v}^{s-1,s}n_{s-1}n_{v+1} - \sum_{s=1}^{v^*} P_{v,v+1}^{s,s-1}n_s n_v]$$

$$+ [\sum_{s=0}^{v^*-1} P_{v-1,v}^{s+1,s}n_{s+1}n_{v-1} - \sum_{s=0}^{v^*-1} P_{v,v-1}^{s,s+1}n_s n_v]\}$$

$$+ Ne\{\sum_{s=0}^{v^*} k_{s,v}n_s - \sum_{s=0}^{v^*} k_{v,s}n_v\} \qquad (26)$$

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under the initial condition when $t = 0$, $n_v(0) = f(v)$; $v = 0, 1 \ldots v^*$, where n_v is the molecular concentration of the vth vibrational level, v^* is the upper vibrational level (nearest to the limit of dissociation; in the case under consideration $v^* = 51$), N is the molecular concentration, N_e the electronic concentration, $N_e = \alpha \times N$, and α does not change in time,

$$N = \sum_{v=0}^{v^*} N_v(t) \tag{27}$$

(the law of molecule number conservation). Equation 27 naturally occurs in the absence of dissociation and recombination, and acts in the given model of dissociation with instantaneous recombination on the wall. The first figure bracket involves (V–T) process balances, $v + 1 \rightleftarrows v$ level transitions. The second bracket has (V–V) exchange balance, transitions from $s + 1 \rightleftarrows s$, $v + 1 \rightleftarrows v$ levels. The third one has the balance for (e–V) processes. $\langle \sigma v \rangle$ is the average for the gas-kinetic cross section of molecular collisions, obtained from the following equation:

$$\langle \sigma v \rangle = \sigma_{N_2-N_2}^2 \times \left(\frac{8 \pi k T_g}{\mu_{N_2-N_2}} \right)^{\frac{1}{2}}$$

It is assumed that $\sigma_{N_2-N_2} = 3.714$Å, $\mu_{N_2-N_2} = 14\, m_H$.
$P_{v+1,v}^{s-1,s}$ are dimensionless probabilities for (V–V) exchange, calculated according to the Herzfeld theory[119], accounting for the experimental data[120] on (V–V) exchange for CO–N$_2$. $P_{v+1,v}$ are dimensionless probabilities for (V–T) processes, calculated from expressions based on the same theory[121]. $k_{s,v}$ are rate factors for excitation and vibrational deactivation by an electron impact per cm^3 sec^{-1}; the equations for calculation of $P_{v+1,v}^{s-1,s}$ and $k_{s,v}$ are presented in Ref. 88. The probabilities of direct and reverse processes are assumed to be connected by relations of detailed equilibrium for any instant.

The results of the calculations, taking into account assumption 5, are given in *Figure 10*.

Relaxation of population distributions is of specific character here: the higher level populations are significantly reduced by dissociation and deactivation. The solution of the stationary problem confirms that of the non-stationary one with an accuracy of 10 to 15 per cent. The origin of the so-called 'inverse population' gained without the dissociation account at $\alpha = 10^{-7}$ becomes clear (*Figure 11*). At $\alpha = 10^{-3}$, (e–V) processes contribute most to the distribution formation. In the limiting case of (e–V) processes alone the stationary distribution at $t \to \infty$ is considered to be of Boltzmann type with $T_v = T_g$. In contrast, (V–T) processes try to convert the distribution to a Boltzmann type with $T_v = T_g$; (V–V)-exchange is known to provide an intensive flux to populate the higher levels under the given T_v value for the first levels, which is determined by (e–V)-processes at a high degree of ionization. At $\alpha = 10^{-3}$ deactivation of vibrations by (e–V) and (V–T)- processes reduces the flux populating the higher levels due to (e–V)-exchange, even in the absence of dissociation. At $\alpha = 10^{-4}$ the rates of (e–V)-processes are less than those at $\alpha = 10^{-3}$, and (V–T) deactivation does not compensate
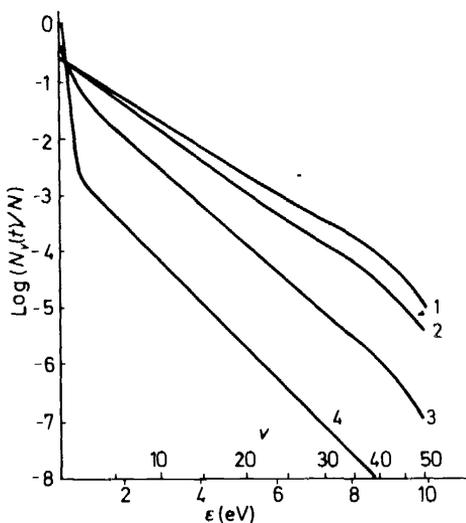
Figure 10. Vibrational levels relative populations for $N_2(X^1\Sigma_g^+)$ versus level number under $N = 10^{-16}$ cm^{-3}, $T_g = 750$K. $T_e = 1$ eV. $\alpha = 10^{-3}$ (taking account of assumption 5): at the following moments of relaxation: $4-t = 10^{-7}$ sec; $3-10^{-5}$ sec; $2-3 \times 10^{-5}$ sec; $1-2 \times 10^{-4}$ sec.
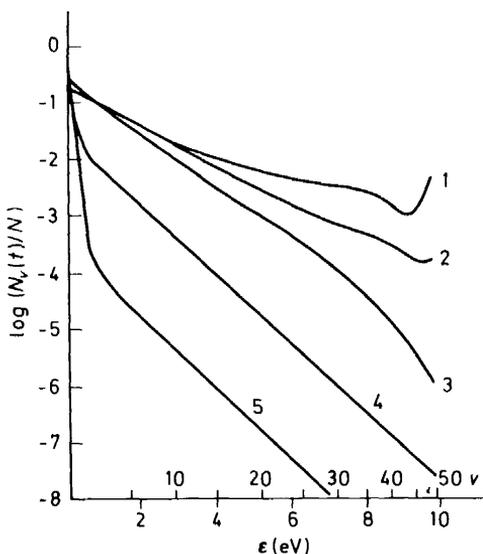
Figure 11. Vibrational levels relative populations for $N_2(X^1\Sigma_g^+)$ versus level number under $N = 10^{16}$ cm^{-3}, $T_g = 750$K, $T_e = 1$ eV, $\alpha = 10^{-4}$ (not considering assumption 5): at the following moments of the relaxation: $5-t = 10^{-7}$ sec, $4-10^{-5}$ sec, $3-2 \times 10^{-4}$ sec, $2-4 \times 10^{-4}$ sec, $1-8 \times 10^{-4}$ sec.
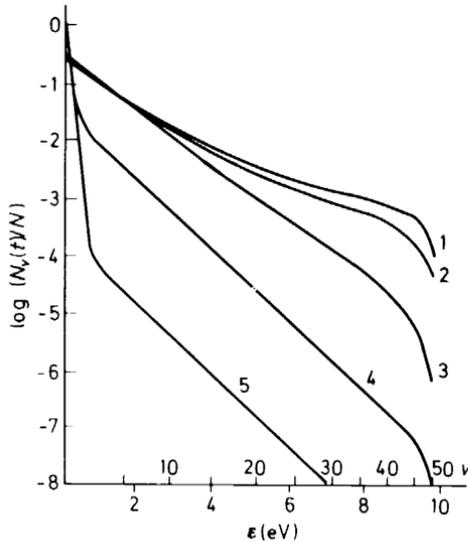
Figure 12. Vibrational levels relative populations for $N_2(X^1\Sigma_g^+)$ versus level number under $N = 10^{16} \, \mathrm{cm}^{-3}$, $T_g = 750\mathrm{K}$, $T_e = 1 \, \mathrm{eV}$, $\alpha = 10^{-4}$ (taking account of assumption 5); at the following moments of the relaxation: $5 - t = 10^{-7}$ sec, $4 - 10^{-5}$ sec, $3 - 2 \times 10^{-4}$ sec, $2 - 4 \times 10^{-4}$ sec, $1 - 8 \times 10^{-4}$ sec.

for the fluxes populating the higher levels due to (V–V) exchange. The dissociation account eliminates the upper level overpopulations at $\alpha = 10^{-4}$. The dependence of the effective vibrational temperature

$$T_{v(0-5)}^{\mathrm{eff}} = (E_5 - E_0)/(\ln N_0/N_5)$$

as defined by the first five levels at $T_g = 750\mathrm{K}$ and $T_e = 1 \, \mathrm{eV}$, on the degree of ionization is shown in *Table 7*. In this case 100 per cent change of (V–V) or (e–V) exchange probabilities causes 12 to 15 per cent variation of $T_{v(0-5)}^{\mathrm{eff}}$.

The calculated $T_{v(0-5)}^{\mathrm{eff}}$ is presented in *Table 7* for comparison with the experimental value obtained by the vibrational T_v^{exp} in Ref. 85.

The agreement between $T_{v(0-5)}^{\mathrm{eff}}$ and T_v^{eff} is satisfactory, considering that the calculation is made for parameters other than the experimental ones ($T_e = 1 \, \mathrm{eV}$, while in the experiment $\bar{\varepsilon} = 2$–$3 \, \mathrm{eV}$ and the distribution function differs from the Maxwell one). Diffusion of vibrational excited molecules

Table 7. Comparison of T_v^{exp} and calculated $T_{v(0-5)}^{\mathrm{eff}}$.

N, cm^{-3}	N_e, cm^{-3}	α	T_g, K	T_v^{exp}, K	$T_{v(0-5)}^{\mathrm{eff}}$, K
7.0×10^{16}	4.4×10^9	6.3×10^{-8}	540	3800	5100
0.9×10^{16}	1.7×10^{10}	1.9×10^{-6}	710	8000	7600
2.7×10^{16}	1.0×10^{10}	3.7×10^{-7}	740	6200	6100
4.3×10^{16}	1.1×10^{10}	2.7×10^{-7}	880	6100	5900
3.2×10^{16}	3.0×10^{10}	9.4×10^{-7}	1200	7600	7100

and their deactivation along the sides of the discharge tube, and some other processes, also are not considered.

To estimate the possible influence of the diffusion of vibrationally excited molecules and their deactivation along the walls of the discharge tube on the population distributions in the vibrational levels of the $X^1\Sigma_g^+$ state, corresponding calculations are made for the stationary problem as follows: $dn_v/dt = 0$.

Equation (26) in this case acquires an additional term

$$\frac{dn_v}{dt} \equiv 0 = \ldots\ldots - \gamma\frac{D}{\lambda^2}n_v$$

$$\frac{dn_0}{dt} \equiv 0 = \ldots\ldots \sum_{v=1}^{v^*} \gamma\frac{D}{\lambda^2}n_v \tag{28}$$

where $\gamma = 10^{-2}$ to 10^{-3} is the accommodation factor, and $\lambda = R_{tube}/2.4$ cm $D = D_0(T_g/300)^{\frac{1}{2}}$ $(2.69 \times 10^{19}/N)$, $D_0(760\,\mathrm{mmHg}, 300K) = 0.231$ cm^2 sec^{-1}. The calculations show that in this range of gas temperatures when $T_g = 300$ to 5000K and ionization degree $\alpha = 10^{-3}$, the influence of the diffusion may be disregarded provided that dissociation and recombination are taken into account (under diffusion conditions when dissociation and recombination are neglected, the variation in the higher level population distributions may be considerable, involving orders of magnitude). At $N \lesssim 10^{15}$ the diffusion must be accounted for.

Thus, the calculations indicate that:

1. Relaxation of population distributions by vibrational levels of the ground electronic state of $X^1\Sigma_g^+$ for the molecule N_2 under the process (e–V) is non-equilibrium in character and proceeds through the sequence of quasi-Boltzmann distributions.

2. The kinetics of vibrational relaxation over various levels and molecular dissociation, accounting for (e–V), (V–V), (V–T) processes, can be calculated by a direct solution of the system of kinetic equations.

3. It was shown that dissociation can essentially affect the population distributions of the upper vibrational levels of the molecule.

4. Velocity ratios for (e–V), (V–V), (V–T) processes under the constant values of T_e and T_g depend on α and vary with time during the relaxation process.

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