

PROBLEMS CONNECTED WITH THE INVESTIGATION OF ELEMENTARY PROCESSES IN LOW-TEMPERATURE PLASMA

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INTRODUCTION

A set of kinetic constants which make it possible to obtain equations for spatial and time functions of particle concentrations (allowance being made, certainly, for macroscopic factors such as mass- and energy exchange) is the main object of investigations on elementary reactions. The number of elementary reaction types encountered in plasma is great, and it is not intended to give here a full account of the present state of the field which is the subject of many monographs.

Considerable work on elementary reactions has been carried out, and yet the chemical and ionization effects can usually be predicted only in a qualitative way. This paper aims mainly at drawing attention to certain problems encountered when attempts are made to work out a quantitative theory for plasma conversions.

The problems connected with radiation transfer will not be considered here, since this is the subject of another plenary lecture. The present authors did not aim at a proportional use of all the results available and many concepts are illustrated, where possible, by data obtained at the Institute of Chemical Physics, USSR.

Experimental investigations of elementary reactions under real conditions for various differently produced plasma types is often very difficult, if at all possible. Thus, attempts are usually made to obtain simple models involving the smallest number of elementary acts susceptible to experimental and theoretical treatment. The elementary reaction kinetic constants thus obtained would then be used for real systems.

The aim and possible applications of the theory in its present form seem to consist in the derivation of formulae for kinetic parameters of real systems, rather than in an *ab initio* calculation of effective cross-sections and rate constants for elementary processes.

All elementary reactions occurring in plasma may be approximately classified as belonging to two types: (i) neutral particle reactions associated with some kind of vibrational energy transfer; these include the main part of purely chemical reactions, such as dissociation $AB \rightarrow A + B$, exchange $AB + C \rightarrow A + BC$, etc.; and (ii) electronic excitation, ionization, and reactions involving electrons, ions, and excited particles. The parts played by the two types of reactions will, certainly, be different, depending upon the plasma production and the nature of the substance.

For low-temperature electric discharge plasma associated with near-atmospheric pressures the electrons and ions will ensure the determination of

the degree of electroconductivity and of the consequent capacity of the system for generation of the Joule heat, whereas the main chemical conversions will proceed by reactions of type (i), with a certain "admixture" of reactions involving excited particles.

The part played by electrons and ions in flames and in many shock waves, though essential in determining the degrees of ionization and electroconductivity, is again unimportant for chemical conversions.

In an approximate way these systems may be called isothermic, in the sense that the temperature of free electrons is close to that of heavy particles.

As the temperature of an electric discharge plasma falls, the system becomes increasingly non-isothermal, i.e. the temperature of electrons becomes considerably higher than that of heavy particles. Meanwhile the "chemical" part of electron reactions gradually increases.

A combined effect is observed in the case of plasma obtained by irradiation where there is a group of very fast electrons responsible for overall ionization and for primary chemical conversions, and a group of slow electrons having a temperature close to that of heavy particles. Here, roughly speaking, the whole set of chemical conversions will be equally accounted for by reactions of both types. Thus, the two latter cases are examples of non-isothermic plasma.

Finally, an interesting kind of plasma is that involving photoionization. It is best represented by the terrestrial ionosphere, where type (ii) reactions play a very important part in chemical conversions, the system being approximately isothermic.

SOME GENERAL PROBLEMS OF THE THEORY OF ELEMENTARY REACTIONS

The rate constant, k , is one of the main kinetic parameters necessary for including a particular elementary reaction in a quantitative description of a complex system. It reduces the expression for the rate of an elementary reaction to the law of mass action.

As is well known for a general case

$$k = \int \sigma(v, \epsilon_i) v f(v_1 \epsilon_i) d v d \epsilon_i$$

where $\sigma(v)$ is the reaction cross section, v the velocity of colliding molecules, $f(v, \epsilon_i)$ the distribution of colliding molecules with respect to velocities and internal degrees of freedom; the latter are defined by a set of ϵ_i parameters.

All quantitative experiments on elementary reactions may, in fact, be classified as those measuring the cross section and its energy dependence, and those using direct determination of k .

Direct determination of the cross section has the advantage of giving a more strict identification of products, and in principle permits extension of the results obtained to any system or any conditions, provided that the distribution function $f(v, \epsilon)$ is known. Unfortunately, the advantage is very limited, as in quasi-isothermic and often in non-isothermic plasma reactions of both the first and second types occur by stepwise vibrational or electronic excitation.

Thus, when attempting to make use of the above mentioned method of determination of constants from the experimental cross sections for elementary reactions, it would be necessary to measure a great number of cross

sections and to allow for a still greater number of their possible combinations in a real system.

Development of the theory for elementary reactions in low-temperature plasma should, consequently, be directed towards evaluation of rate constants for elementary reactions. This would require certain assumptions of energy distribution and of temperature.

The ratio of relaxation to transformation times (τ_r to τ_t) is of great importance for this theory. When $\tau_r \ll \tau_t$ the possibilities of the theory become very considerable. On the other hand at a temperature so high that $\tau_r \simeq \tau_t$, these possibilities will be limited.

It will be noted that the sense of τ_r and τ_t in the $\tau_r \ll \tau_t$ inequality depends upon the type of transformation. For instance, when this is a chemical conversion of a dissociative or exchange type involving no electronically-excited particles, τ_r will be, as a rule, the time of vibrational relaxation τ_v . Whereas, when τ_t refers to thermal ionization, τ_r is the time of relaxation with respect to electronic excitation levels τ_{el} .

The condition $\tau_r \ll \tau_t$ simplifies analysis of reactions in plasma. The processes resulting in redistribution of energy among the degrees of freedom might then be differentiated from chemical reactions with respect to time. Moreover, kinetic equations involving only concentrations may be used for description of dissociation, recombination, and exchange reactions only provided this condition is fulfilled.

For times considerably in excess of that between molecular collisions ($1/z$) it may be taken that certain values of translational temperature, T_M , T_{el} , are characteristic of the heavy and light plasma components, and the distribution functions are Boltzmannian. Then chemical reactions, as well as vibrational and electronic relaxation, will be described by a system of kinetic equations depending on T_M and T_{el} and representing populations of the vibronic states of various components. For t higher than the times of vibrational and electronic relaxation, the system can be further simplified and reduced to a set of equations for concentrations. This simplification reveals the meaning of kinetic coefficients, namely of the rate constants for elementary chemical reactions.

An illustration of this would be the dissociation of AB molecules behind the shock front in a monoatomic gas atmosphere, when the narrow zone of non-equilibrium vibrational relaxation is followed by a broad zone of non-equilibrium dissociation. In this case the kinetics will be described by two independent equations for concentration $N(AB)$ and mean energy $E(AB)$

$$\frac{dN(AB)}{dt} = \frac{-1}{\tau_{diss}} N(AB)N(M) + \frac{1}{\tau_{rec}} N(A)N(B)N(M) \quad (1a)$$

$$\frac{dE(AB)}{dt} = \frac{1}{\tau_v} [E(AB) - E_{eq}(AB)] \quad (1b)$$

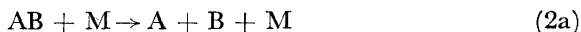
Here $1/\tau_{diss}$, $1/\tau_{rec}$, and $1/\tau_v$ are rate constants for dissociation k_d , recombination k_{rec} , and vibrational relaxation k_v .

Independent changes in concentrations and energy do not mean, however, that a quasi-equilibrium distribution function with respect to vibrational states is characteristic of dissociating molecules at all vibrational

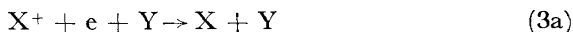
levels. Completion of vibrational relaxation by the moment of the dissociation onset indicates that the distribution function is close to equilibrium only for low vibrational states that are essential for the average vibrational energy of a molecule.

The theory should make possible the calculation of the distribution function over the high energy levels, with subsequent determination of the non-equilibrium rate constant.

The bimolecular dissociation of diatomic molecules and three-body recombination of atoms



as well as the three-body recombination of electrons on ions by collision with atoms, linear non-polar molecules, or electrons



has been extensively treated theoretically.

A system of kinetic equations for populations x_m is the starting point for any calculation (m referring to the m -energy level of a diatomic AB system or an excited atom).

$$\frac{dx_m}{dt} = -\sum_n k_{m \rightarrow n} x_m + \sum_n k_{n \rightarrow m} x_n \quad (4)$$

This system involves rate constants for elementary steps (transition between m and n states) that are calculated from appropriate cross sections with an equilibrium distribution function with respect to velocities of the colliding molecules. As a result of equilibrium distribution over transitional degrees of freedom the principle of detailed equilibrium is fulfilled for each step

$$\frac{k_{m \rightarrow n}}{k_{n \rightarrow m}} = \frac{g_n}{g_m} \exp(-\Delta E_{nm}/kT) \quad (5)$$

Here ΔE_{nm} is the energy difference for n and m states; g_n , g_m are respective statistical weights. When collisions result in transitions only between neighbouring states of a dissociating or recombining system, equation (4) will be reduced to one Focker-Planck equation (6) for diffusion of the system in the energy space

$$\frac{\delta x(\epsilon)}{\delta t} = \frac{1}{2g(\epsilon)} \left[\frac{g(\epsilon)}{kT} \frac{\delta}{\delta t} \langle \Delta E^2 \rangle \left(1 + kT \frac{\delta}{\delta \epsilon} \right) \right] x(\epsilon) \quad (6)$$

Here $g(\epsilon)$ is the density of the dissociating (recombining) system levels. To this approximation, only one function will be characteristic of the kinetics of relaxation, dissociation, and recombination, namely the mean square of energy transferred to the given system per unit time upon collisions with a third molecule ($\delta/\delta t$) $\langle \Delta E^2 \rangle$. This quantity is a function of the molecular

or ion energy ϵ and of the translational temperature T characteristic of the relative distribution of AB and C, or $X^+ + e + Y$.

Calculation of the non-equilibrium rate constant for dissociation of diatomic molecules, making use of the system (eq. 5) was first made by one of the present authors⁵⁴, and Stupachenko and Osipov⁷⁸, under the assumption that only one quantum vibrational transition occurs in collisions. This restriction was rejected later, and a number of approximate methods allowing for multiquantum transitions are known at present (cf. reference 59). These are free of disadvantages of the equilibrium theory making no allowance for perturbation of equilibrium distribution and giving no correct temperature dependence of the rate constant (e.g. the Rice theory⁷⁰). The kinetics of polyatomic molecular dissociation described by eq. (6) was treated theoretically by one of the authors in connection with various models of molecular activation⁵⁵.

Equation (6) was investigated by Pitaevskii⁶⁶, Gurevich and Pitaevskii²⁹, Dalidchik and Sayasov¹⁶, and also by Bates and Khare⁷ with respect to the recombination of electrons and ions. As a result, the Thompson equilibrium theory has been improved, and a number of new effects have been predicted. In discussing the restrictions connected with the concept of diffusion in the energy space, Bates and Khare⁷ have considered recently in detail the transition from a set of equations (4) to a single equation (6).

A quasi-classical description of electronic states of the $X^+ + e$ system appears to be possible for low-temperature plasma, and thus the theories for recombination of heavy particles (atoms) and electrons on ions seem essentially to coincide. The occurrence of a slow step (bottleneck) in the step-wise mechanism of excitation or deactivation is the main characteristic of thermal reactions of this kind. This step corresponds to an energy ϵ^* lower than that of dissociation or ionization by a value of $\delta\epsilon^*$. For decomposition reactions the population of levels of an energy higher than ϵ^* is considerably lower than that for equilibrium. The reverse is observed for recombination. The distribution functions of the two processes are shown in *Figure 1*.

Leaving aside the calculation of constants for models of a particular kind let us discuss the dissociation k_d and recombination k_r constants as qualitative

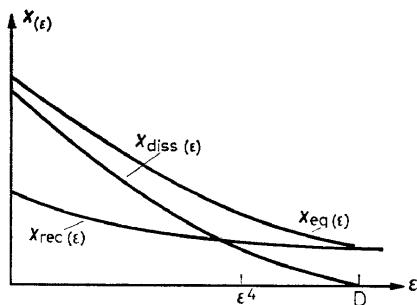


Figure 1. Equilibrium distribution function x_{eq} for vibrational states of the AB molecules: x_{diss} and x_{rec} are non-equilibrium distribution functions in thermal dissociation and recombination.

functions of temperature and interaction characteristics. The dissociation rate constant

$$k_d \simeq z \left[\frac{\langle \Delta E^2 \rangle}{kT} g_d(\epsilon^*) \exp\left(\frac{\delta \epsilon^*}{kT}\right) \right] \frac{\exp(-D/kT)}{Q} \quad (7)$$

Here z is the number of AB and M collisions, $g_d(\epsilon^*)$ is the density of states effective for dissociation[†] and Q is the partition function of the AB molecule. The factor in square brackets fully accounts for perturbation of the equilibrium distribution due to decomposition, while the last factor may be interpreted as an equilibrium distribution function of AB at an energy $\epsilon = D$. A similar expression is valid for recombination, except that the last factor would include the partition functions of recombining particles.

It was found in reducing the complete set of equations (4) or differential eq. (6) in partial derivatives to that for concentration, that non-equilibrium dissociation and recombination constants correspond to a ratio $k_d : k_r = K_{eq}$, when the same degrees of freedom contribute to statistical weights g_d and g_r , the inequality $k_d, k_r \ll 1/\tau_r$ being valid for these degrees of freedom^{59,75}.

The difficulties arising in calculation are directly obvious from the Focker-Planck equation. Firstly, for calculating $\langle \Delta E^2 \rangle$ the interaction potential for the three particles has to be known, and, secondly, the dynamic problem of collisions between M and the bound AB or $X^+ - e$ pair of an ϵ^* energy has to be solved. Only general characteristics of atomic interaction are known at present, and the dynamic problem of inelastic collisions is soluble only for certain rather specific models. The electron-ion recombination is an exception from this point of view: the interaction law is well known and the problem of three-body collisions may be taken as that for a combination of two-body collisions (in view of a very low electron mass as compared to the mass of nuclei). This permits analytical calculation of rate coefficients for electron-ion recombinations in a neutral gas⁶⁶, in plasma with a rather high concentration of electrons²⁹, and in molecular gas plasma¹⁶. The coefficients calculated by making use of the Focker-Planck equation are valid, however, only up to temperatures of several thousand degrees. At higher temperatures the energy ϵ^* corresponding to the rate-limiting step decreases to such an extent that it appears necessary to allow for the discrete nature of the $X^+ - e$ system electronic spectrum. Consequently, the difficulties in calculating $\langle \Delta E^2 \rangle$ increase to the highest extent⁷.

However, only very general relations can be established for rate constants of atom recombination (or dissociation of diatomic molecules), as for instance, the temperature dependence of a rate constant for recombination of atoms in an inert gas⁵⁹ such as $O + O + A$, or dissociation $O_2 + R$. A number of parameters characteristic of such interaction remain unknown. However, these can be determined from independent experimental data obtained at a certain temperature T_0 . The theory would allow an extrapolation of experimental data from low to high temperatures (and *vice versa*). The negative temperature coefficient of the pre-exponential factor of the dissociation constant as calculated theoretically, may be obtained experimentally with very fair agreement for a number of cases. It may be

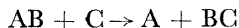
[†] The dimension of $g_d(\epsilon)$ is that of the inverse energy, as follows from definition $Q = \int \exp(-E/kT) g(E) dE$.

said for a general case and a temperature range corresponding to $\tau_r \ll \tau_t$ that the theory makes possible the prediction of k_d and k_r temperature dependences for diatomic molecules, and determination of absolute rate constants with an accuracy to 200–300 per cent.

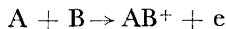
Complications will arise in the case of complex molecules, as there is yet no appropriate information regarding the excited electronic states of polyatomic molecules. When, in very rare cases, the electronic states are known (as for N_2O decomposition), the decomposition rate can be obtained with the same accuracy as for diatomic molecules. It will be noted that the dissociation energy of polyatomic molecules is often determined from the temperature dependence of the rate, and thus represents an additional parameter of the theory (as compared with dissociation of diatomic molecules). When the reaction is adiabatic and the activation energy is known, the dissociation constant may be calculated with an accuracy of one order of magnitude, making use of the statistical theory for chemical reactions.

The reactions for which the rate constants can be evaluated at present, on assumption of certain interaction potentials, are listed in *Table 1*. Theoretical expressions for rate constants may either be taken as a basis for the calculation of rate constants or cross sections, or be used for long range temperature extrapolation of experimental values.

This rigorous approach necessarily excludes a great number of reaction types. Of these let us mention first of all one of the most important elementary chemical processes, namely that of atomic or radical exchange of the type



the ionization by electron impact, ion-molecular reactions, associative ionization



and dissociative recombination. A certain amount of theoretical and experimental work has been carried out on these reactions, but has not yet provided a sound basis for derivation of practically useful formulae.

Finally it will be emphasized once more that the rate constants of the reactions listed in *Table 1* refer to temperatures corresponding to $\tau_r \ll \tau_t$. As the temperature rises, differentiation between "chemical" and "vibrational" or "electronic" relaxation becomes impossible.

For the kinetics of reactions behind the shock front this means that the chemical relaxation starts overlapping that of vibrational relaxation, and the latter, in its turn, coalesces with the wave front. Theoretical treatment of these processes involves attempts to find out (within the scope of certain models) the effect of overlapping on the overall kinetics^{31,45,51,84}. Consequent terms dependent on $E(AB)$ and $N(AB)$ have to be introduced into equations (1a) and (1b), respectively. However, sometimes even these corrections are insufficient for describing the kinetics, so that one is bound to return to the system (eq. 4). Kuznetsov⁴⁵ has found, in particular, that vibrational relaxation starts affecting dissociation at $k_d \simeq (D/kT)^2 k_v$.

In cases of oxygen dissociation, for instance, the $\tau_r \ll \tau_t$ inequality will be fulfilled at $T < 5000^\circ K$. Variations in times of translational, vibrational,

Table 1. Elementary processes the theory of which permits estimation of kinetic rate constants

Types and example of processes	Models adopted in the calculation of rate constants (cross sections)	Range of the theory applicability
1a. Relaxation of molecules in a non-degenerate electronic state $N_2(^1\Sigma_g, v = 1) + N_2(^1\Sigma_g, v = 0) \rightarrow$ $N_2(^1\Sigma_g, v = 0) + N_2(^1\Sigma_g, v = 0) + h\nu$ 1b. Relaxation of molecules in a degenerate electronic state $NO(^2\Pi_{\Omega}, v = 1) + NO(^2\Pi_{\Omega}, v = 0) \rightarrow$ $NO(^2\Pi_{\Omega}, v = 0) + NO(^2\Pi_{\Omega}, v = 0) + h\nu$	1. <i>Vibrational relaxation</i> Molecule represented by: A harmonic oscillator with exponential intermolecular interaction ³² , with the Lennard-Jones potential ⁸⁰ , with the Morse potential ⁷¹ , with an unharmonic oscillator ⁸² Molecule represented by: A harmonic oscillator of a frequency considerably higher than that for splitting of the term ^{56, 58}	$\tau_v \gg 1/Z$
2a. Polarization interaction in the initial and final states $O(^4S) + H(^2S) \rightarrow H^+ + O(^3P_f) + \Delta\epsilon_f$ 2b. Coulomb interaction in the initial or final states $H + Mg^{2+} \rightarrow H^+ + Mg^+ + \Delta\epsilon$ 2c. Exchange and multipole interaction in the initial and final states $Na^*(^2P_f) + Na(^2S) \rightarrow Na^*(^2P_f) + Na(^2S)$	2. <i>Atomic charge exchange or electronic excitation transfer at a small resonance defect</i> Zero approximation terms independent of the interatomic distance V_{12} responsible for charge exchange as an exponential function of R (refs. 57, 18) Linear-crossing zero-order terms V_{12} as an approximate exponential function of distance ^{4, 13} Zero-order terms as a linear or exponential function of R (ref. 64)	$R_0 \gg a_0$ Condition of small resonance defect $\delta\epsilon \ll \mu\epsilon^2/2$ $\delta\epsilon_{min}$ is the minimum splitting of terms involved in transfer

<p>3. <i>Excitation of low atomic states or electronic energy transfer at a great resonance defect</i> Crossing of zero-order terms at a constant non-diagonal matrix element V_{12} (ref. 12) Double-cone type of intersection of adiabatic potential energy surfaces⁶⁰</p>	<p>3a. Electronic excitation in atomic collisions $\text{Na}(^2S) + \text{A}(^1S) \rightarrow (\text{Na}^*(^2P) + \text{A}(^1S)) - \Delta \epsilon$ 3b. Electronic excitation in molecular collisions $\text{Na}(^2S) + \text{N}_2 \rightarrow \text{Na}^*(^2P) + \text{N}_2$</p>	<p>Condition of classical motion of nuclei</p>
<p>4. <i>Thermal dissociation of diatomic molecules and recombination of atoms</i> One-quantum stepwise excitation model at equilibrium rotation distribution^{54, 59} Multiquantum stepwise excitation model at equilibrium rotational distribution⁵⁹ Vibrational theory of dissociation^{59, 86} assuming equilibrium distribution in the reacting system</p>	<p>$\text{O}_2 + \text{A} \rightarrow \text{O} + \text{O} + \text{A}$ $\text{O} + \text{O} + \text{A} \rightarrow \text{O}_2 + \text{A}$</p>	<p>$\omega(\epsilon^*) a_0/\bar{v} \sim 1$ $\omega(\epsilon^*) a_0/\bar{v} \ll 1$</p>
<p>5. <i>Thermal bimolecular dissociation of polyatomic molecules</i> The molecule is represented by a system of oscillators and rotors The rate constant is calculated making use of the statistical theory⁵⁹</p>	<p>$\text{H}_2\text{O}_2 + \text{M} \rightarrow \text{HO} + \text{HO} + \text{M}$</p>	<p>The time of intramolecular energy exchange is considerably shorter than that between collisions</p>
<p>6. <i>Thermal electron-ion recombination</i> Classical motion of an electron over the excited Bohr orbital Energy losses in elastic collision of a recombining electron with an atom⁶⁶ Energy losses in inelastic collisions of a recombining electron with a diatomic molecule (rotational excitation)¹⁶ Energy losses in collisions of a recombining electron with a free electron^{29, 5} Variational theory of recombination⁴²</p>	<p>$\text{He}^+ + e + \text{He} \rightarrow \text{He} + \text{He}$ $\text{He}^+ + e + \text{N}_2 \rightarrow \text{He} + \text{N}_2$ $\text{He}^+ + c + e \rightarrow \text{He} + c$</p>	<p>$\omega(\epsilon^*) a_0/\bar{v} \ll 1$ $\omega(\epsilon^*) \gg 1/z$</p>

and chemical relaxation as a function of temperature behind the shock front are shown in *Figure 2* (cf. Wray⁸⁹). It will be seen that at temperatures

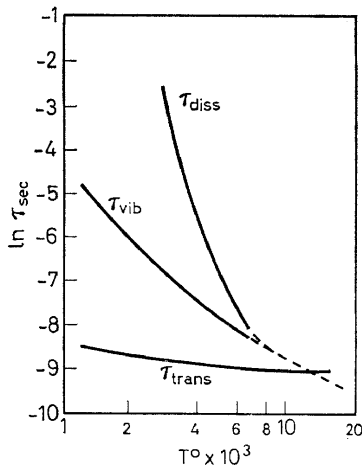


Figure 2. Translational, vibrational, and dissociative relaxation times as a function of temperature behind the shock front in O_2 . The gas density ahead of the front is 1 atm at $T = 273^\circ K$ (according to reference 89)

higher than 6×10^3 – 10^4 the theoretical equations obtained for this case on the assumption that $\tau_r \ll \tau_t$ cease to be valid and there opens up a theoretical *terra incognita*. The same will be observed, at some particular temperature, for any electronic reaction given in *Table 1*.

DETERMINATION OF RATE CONSTANTS FOR CERTAIN TYPES OF ELEMENTARY REACTIONS

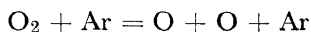
A considerable number of methods for experimental investigation of elementary processes are available at present. However, as mentioned above, the information obtained is considerably less than that required for calculation of overall kinetics for real plasmas. This is due both to experimental difficulties and to the necessity of solving the problems discussed above. Consequently sometimes, determination is made of parameters that can be measured, rather than of those that need to be measured.

Let us consider briefly some of the problems connected with experimental investigation and determination of rate constants for a number of elementary reactions. Attempts will be made to compare experimental data with the reactions listed in *Table 1*, i.e. those coming under a sufficiently strict theory. The present state of experiment and theory will be discussed with respect to other reactions.

1. Thermal dissociation of diatomic molecules

The shock wave method seems to be the best which can be adapted for the determination of the rate constants for thermal dissociation of diatomic molecules. It has been used in measuring dissociation constants for H_2 , O_2 , N_2 , NO , and halogen molecules. However, the accuracy of measurements,

particularly, of the temperature dependence, was far from being satisfactory. For instance, the rate constant for oxygen dissociation by reaction

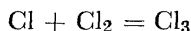


was determined by many researchers and a relation of type

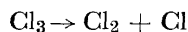
$$k_d = AT^n \exp(-D/kT) \quad (9)$$

was derived (D is the dissociation heat). The n values obtained within the same temperature range ($>5000^\circ\text{K}$) were: -1 (reference 14, 26), $-1/2$ (reference 88), and 0 (reference 87). The theoretical values for diatomic molecules would be -1 , under the assumption that only the vibrational molecular energy contributed to activation. However, the values of $n = -3/2$ (reference 33), -2 (reference 40), and even $-5/2$ (reference 20), exceeding the theoretical value of 1 were obtained by various workers for the rate constant of chlorine dissociation in a chlorine-argon mixture. The discrepancy between theory and experiment might be due to non-fulfilment of the $\tau_r \ll \tau_t$ condition. For halogen dissociation the n value of the empirical equation (9) is found to be essentially higher than unity.

It will also be borne in mind that recombination of chlorine atoms, a process inverse to that of dissociation, seems to proceed according to the scheme³⁹:



Consequently, there is a possibility that the two-step process



might play a certain part in the thermal dissociation of chlorine.

2. Thermal dissociation of polyatomic molecules

The shock wave method is most effective for experimental investigations on thermal dissociation of polyatomic molecules as well. Since, however, primary dissociation is followed by secondary chemical processes, due to interaction between dissociation products and molecules of the initial substance or stable reaction products, it should be made certain that the derived kinetic law corresponds to the primary reaction. Moreover, investigation of thermal dissociation shows that two reaction steps are possible for some three-atomic molecules, that of electronic excitation and that of dissociation, the first being rate-determining. This seems to be the case for the dissociation of sulphur dioxide, where the measured activation energy appears to be lower than the heat of dissociation D and to coincide with the energy of the SO_2 excitation level triplet obtained spectroscopically²⁵.

A two-step dissociation of this kind might be encountered frequently both for three-atomic and for more complex molecules. The absence of reliable experimental data on the kinetics of dissociation of polyatomic molecules, as well as on their spectroscopy, leaves the question open (*see* for example, references 10 and 17).

It will be suggested, however, that due to a great number of degrees of freedom and to a relatively ready intramolecular exchange of vibrational energy, the thermal dissociation of polyatomic molecules should proceed without the electronic excitation step. The exchange probability would increase with the number of atoms in a molecule. For example, the H_2O_2 molecule having apparently no electron levels lower than that of dissociation may be considered as one of a number of polyatomic molecules decomposing according to this scheme. Thus it will be suggested that at temperatures lower than the characteristic temperature corresponding to the lowest H_2O_2 vibrations (1220°K) the rate constant for thermal hydrogen peroxide dissociation will be

$$k_d = A \sqrt{T} \exp(-D/kT) \quad (10)$$

Indeed, k_d measured over a temperature range of 723–932°K appears to be³⁴

$$k_d = 10^{16.8} \sqrt{T} \exp(-47200/kT)$$

the activation energy appearing to coincide with that of H_2O_2 dissociation to 2 OH, known from thermochemical data.

Generally speaking, it may be considered that all reliable experimental results on rate constants for thermal dissociation of di- and polyatomic molecules are in agreement with the theory. However, reliable results are very limited.

3. Exchange reactions

Exchange reactions represent the most widely encountered type of chemical reactions and yet there is no reliable theory for these reactions. In fact, the dependence of the exchange reaction probability, i.e. of the Arrhenius pre-exponential factor, on temperature was considered in general as long as 30 years ago making use of the absolute reaction rate theory²⁸. Later, attempts were made to calculate pre-exponential factors for certain exchange reactions on the basis of this theory. For some reactions, for example, those involving the methyl radical $\text{CH}_3 + \text{RH} = \text{CH}_4 + \text{R}$ (cf. reference 77) the agreement with theory was good, whereas for others, such as $\text{OH} + \text{RH} = \text{H}_2\text{O} + \text{R}$ theory and experiment were in disagreement.

This was evidently due to the insufficiency of the transition state theory. First of all the basic postulate of the rate constant invariance under equilibrium and non-equilibrium conditions cannot be considered as being always valid. Another postulate of the transition state theory, namely the possibility of describing nuclear motion in terms of classical mechanics, cannot be considered as applicable in all cases.

Thus, the temperature dependence of rate constant pre-exponentials for these reactions, the consequent possibility of expressing these constants by one formula over a wide temperature range, and the absolute value of the pre-exponential still need to be investigated. It follows from experiment that for the majority of reactions these values do not exceed the gas-kinetic factor. However, values exceeding the gas-kinetic factor by an order of magnitude

and more were reported³⁶, and it cannot be said for certain whether this is an indication of a drawback of the theory, or of an experimental error.

4. Excitation and ionization of atoms by electrons

Experimental data on effective cross sections for excitation of atoms by electrons are scarce. Direct experiments provide information on transition from the ground state only, theory and experiment coinciding with an accuracy of 200–300 per cent. Thus, in estimating cross sections for transitions between excited levels we had to rely until recently on theory only. And yet it is the transitions between excited states that are most important for low-temperature plasma, since these determine the rate of stepwise ionization.

Calculation making use of the Born method and its most simple modifications (allowance for normalization, exchange, etc.) such as the one suggested by Ochkur⁶¹ for the Born–Oppenheimer method gives qualitatively correct cross section variations, and close to the maximum the excitation functions usually do not differ by more than a factor of two or three, compared to experimental values. The errors in calculating cross sections for ionization from the ground state are approximately the same.

Less certain is the question whether the calculation methods available may be extrapolated to transitions between excited states. However, certain information on scattering of electrons on excited atoms was obtained from experiments on broadening of spectral lines. The theory connects effective cross sections for the broadening and shift of lines with the same S -matrix elements that are responsible for excitation cross sections. Experimental data on broadening of spectral lines are very abundant. Comparison with theory, based on a simple quasi-classical variant of the Born method and carried out by Baranger¹ and Sobelman⁷⁶ has shown good agreement with experiment.

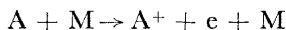
The discrepancy seldom exceeded 30 per cent, and was never above 100 per cent. This seems to be evidence for the applicability of the Born method to transitions between excited states. Anyhow, this should be true for the case when the transferred energy ΔE is considerably lower than that of the electron E . (The condition $\Delta E/E \ll 1$ gives a considerably greater energy range for application of the Born method, as compared with $e^2/hv \ll 1$). Further understanding of the low-temperature plasma should involve the working out of a method for calculating excitation and ionization rate constants. As to excitation and ionization of molecules by electron impact, there is no reliable theory for it even for excitation and ionization from the ground state.

Since the great amount of experimental results on ionization and dissociative ionization (cf. reference 30) available is valid for transition from the ground state only, it cannot be used for calculation of the ionization rate in quasi-isothermic low-temperature plasma. However, it opens up many possibilities for calculating certain rate constants in non-isothermic plasma of a very high electron temperature.

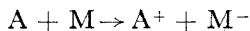
Elaborate investigations on the functions of molecular excitation by electron scattering have been published recently⁴⁸. Unfortunately these are also concerned with transitions from the ground state.

5. Impact ionization

Impact ionization may be described by the scheme



or



Bates and Massey^{2, 6} have considered the theoretical probability of the first reaction. It was suggested that at a favourable intersection of potential energy surfaces for systems $A + M$ and $A^+ + e + M$ the ionization probability will be high even at not too great velocities of the relative motions of A and M . When there is no intersection of potential energy surfaces, the ionization constant will be high only at very high velocities of the colliding particles. However, as the intersection of potential surfaces is responsible for this probability, and a reliable plotting of the surface is impossible, even a qualitative prediction of rate constants for impact ionization of certain A and M is unattainable. It follows that only the experimental method may be relied upon in the determination of these constants.

Direct determinations of rate constants for impact ionization were made in a few cases, and the most reliable results were obtained at high energies (velocities) of particles, exceeding the mean thermal energy for the experimental temperatures by many orders of magnitude. Such are the determinations of cross sections for ionization of alkaline metal atoms upon their collisions with atoms of inert gases or molecules of hydrogen, nitrogen, and oxygen, as made by Dukelskii *et al.*²¹. The minimum energy of alkaline metal atoms was 150–200 eV. Extrapolation of rate constants (cross sections) measured at these energies to those for low-temperature plasma is evidently impossible.

The rate constant for impact ionization of sodium in a hydrogen flame was determined by Sugden *et al.*⁷⁹ and was found to be

$$k_i = A \exp(-eI/kT) \quad (11)$$

where I is the ionization potential. The high value of the effective cross section ($\sim 5000 \text{ \AA}^2$) obtained from the pre-exponential factor in this equation might be due to a stepwise process occurring via excited states of a very great effective radius. Associative ionization might be an alternative⁷⁴ as is explained below.

A convincing argument in favour of impact ionization proceeding by the scheme $A + M = M^+ + M^-$ is the increase in electron concentration in a flame containing an alkaline metal A with addition of halogens to the gaseous mixture (X_2), as shown by Sugden *et al.*⁶⁵. This increase was suggested to be connected with the reactions



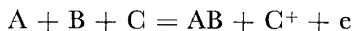
and



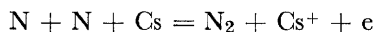
the first being a reaction of the type considered.

6. Recombinative ionization

Thermal ionization is known to proceed also as



This process may be considered as following the mechanism of recombinative ionization. The reaction



studied by Gatz *et al.*²⁴ may serve as an example. Processes of this type may be important only at sufficiently high concentrations of particles involved in three-body collisions. A weak temperature dependence of the reaction rate would seem to be characteristic of these reactions when the recombining particles are of a non-thermal origin.

No theory for recombinative ionization was ever developed.

7. Electronic excitation, electron energy transfer and charge exchange by collisions between atoms and molecules

It would be convenient to classify conversions of translational or vibrational into excitation energy, and energy transfer by collision of heavy particles as belonging to two groups.

The first would involve reactions for which changes in electronic states of colliding particles occur at distances R_0 exceeding atom sizes a_0 . The theory of such reactions occurring by collision of atoms and atomic ions is rapidly developing. Since at great inter-atomic distances the interaction may be calculated with fair accuracy, the theory should be concerned only with the problem of inelastic collision for known interaction potentials. Typical examples of such reactions are given in *Table 1*†.

The cross sections for these processes may be calculated with an accuracy to 100–200 per cent without the introduction of semi-empirical parameters. A calculation of this kind would require knowledge of the approximate wave function of the outer electron. It may be mentioned that the final result is but weakly dependent upon the function parameters. As to the theory involving molecular reactions, it is yet in its initial stage and may claim to estimation of the cross section order only. These problems will be discussed in the section on ion-molecular reactions.

Reactions involving changes of electronic states that occur at a close approach of partners ($R_0 \approx a_0$) would belong to the second group. Since in this case the interaction between atoms is unknown, rather arbitrary parameters have to be introduced into the theory. In principle, these parameters could be obtained from experimental data, and the results of theoretical calculation could be used for temperature extrapolation of the cross section. Unfortunately, this was not done for any reaction.

The attempts to interpret experiments on quenching of sodium fluorescence with argon¹¹ on the basis of the recently developed theory^{1,2} made

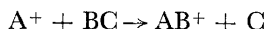
† The resonance charge exchange in atomic collisions most extensively treated theoretically (see, for example, reference 6) will be left aside here. For recent theoretical work let us mention the papers by Smirnov¹² and Bates & Williams⁹ on the $H + H^+$ charge exchange.

use of experimental data obtained at low temperatures⁴⁴. Recent experiments carried out in shock tubes⁸⁵ seem to make doubtful the low-temperature results, yet providing no possibility for determination of theoretical parameters, due to the low accuracy of cross section measurements.

As to the second group of reactions involving molecules only, the cross section order may be predicted here, and this on condition of there being certain information on interaction between partners in electronically excited states. Such is the case, for example, of sodium excitation by collision with a nitrogen molecule. The experimental fact that electronic excitation of sodium follows vibrational excitation of nitrogen³⁸ may obtain an explanation within the scope of a theory⁶⁰ allowing quantitatively for energy transfer from vibrational to electronic levels.

8. Ion-molecular reactions

Two kinds of reactions may occur by collision of slow ions with molecules: exchange of heavy particles and charge exchange. The latter might be dissociative as well. The transfer of heavy particles, *i.e.* reactions of the type



and



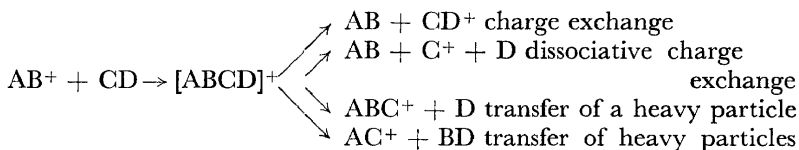
are known to occur by formation of an intermediate often long-lived complex. The initial step and, consequently, the cross section for its formation are accounted for by polarization interaction^{22, 27, 68, 81}. A number of experiments carried out mainly by Lindholm^{50, 43, 15} at energies higher than 10 eV have shown that with polyatomic molecules charge exchange will precede by a resonance mechanism. It would involve the following expression for the effective cross section:

$$\sqrt{(\sigma)} = a - b \ln E \quad (12)$$

Here a and b are parameters dependent upon the wave function of the outer electron.

On the other hand, suggestions have been made that at low kinetic energies both charge exchange and transfer of heavy particles would occur via the formation of an intermediate relatively long-lived complex⁸³.

A number of experiments carried out in the past few years, particularly those using mass spectroscopy and very slow ions^{82, 41} seem to show that the mechanism involving formation of an intermediate complex would be predominant for charge exchange in slow ionic and molecular collisions. Thus, the following scheme should be considered in working out the theory for collisions of ions with molecules



Equation

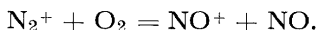
$$\sigma = \frac{2\pi e}{v} \sqrt{\frac{I}{\mu}}$$

is known to be valid for the effective cross section of complex formation²⁷. Here a is the polarisability of a neutral particle, e the ion charge, μ the reduced mass, and v the velocity of relative motion.

Unfortunately the approaches for the calculation of effective cross sections for various channels of complex decomposition are almost unknown. Thus the rate constant obtained from equation (13)

$$k = 2\pi e \sqrt{\frac{a}{\mu}} \quad (13)$$

seems to give the minimum k value. When the reaction occurs essentially by one channel, this value will represent its rate constant. Since the k value is accounted for by polarizational attraction, it is, as a rule, one order of magnitude higher than the "gas-kinetic" number of collisions. Evidence for an activation energy differing from zero was obtained only for one of the many hundreds of ion-molecular reactions studied, namely⁶⁹ for



9. Dissociative recombination

Dissociative recombination $\text{AB}^+ + e \rightarrow \text{A} + \text{B}$ seems to be the fastest of all reactions studied. Its rate constant at room temperature sometimes attains 10^{-6} cm³/sec and does not seem to vary widely for different systems. In other words, if this constant is assumed to be $\sim 10^{-7}$ cm³/sec (at room temperature), it will be reliable to an order of magnitude, though the channels of dissociation of polyatomic molecules cannot be stated *a priori*.

Determinations of the rate constant for dissociative recombination were made in many cases. The method used particularly was that of measuring the rate of plasma decay^{9, 35, 62, 63}. However, unambiguous identification of molecular ions taking part in recombination is possible only for a very simple case, such as for an inert gas. A somewhat clearer picture, though again for relatively simple chemical systems, will be obtained by producing low-temperature plasma by fast electron pulses (a paper by Brodsky and Zagik presented at the Symposium organized during the XXth IUPAC Congress; Moscow; July 1965).

As the temperature of the heavy plasma component increases, the fraction of molecular ions and, consequently, the part played by dissociative recombination of electrons decreases. The temperature corresponding to predominant dissociative recombination will depend, certainly, on the plasma substance, but in general it does not seem to exceed several thousand degrees. The relative temperature dependence of the content of various ions in equilibrium hydrogen plasma, as calculated by Larin and Talrose is shown in *Figure 3*. It will be of interest to note that the contribution from H_2^+ ions will be unimportant within any temperature range. Recombination involving H_3^+ will be predominant at temperatures of 5000–6000°K, while a three-body recombination with H^+ (or radiative recombination at lower

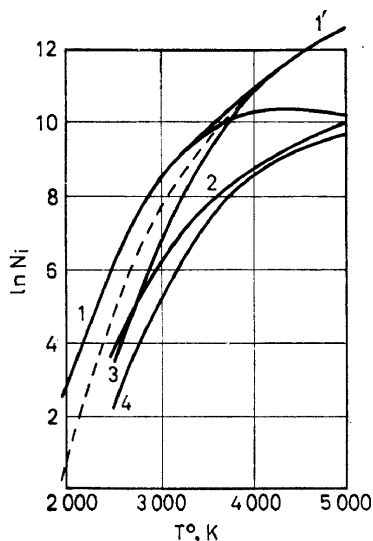
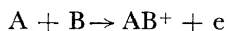


Figure 3. The temperature dependence of ion concentrations at an equilibrium ionization of hydrogen: [1, 1' is the summary concentration of positive ions allowing for H_3^+ ; 1, H_3^+ ; 2, H^- ; 3, H^+ ; 4, H_2^+ ; and the dotted line refers to summary concentration of positive ions without allowance for H_3^+ formation].

pressures) will take place at higher temperatures. It seemed before⁴⁷ that the range of A_2^+ ion appearance would extend to $6-8 \times 10^3$ °K for inert gases as well. However, the affinity of inert gases to their ions and, consequently, the above temperature were found to be lower than was previously thought.

10. Associative ionization

Associative ionization is considered to be a reaction of the type

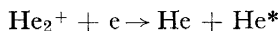


It seems to be of great importance for many plasmas, since its activation energy is lower than that of A or B by the value of the bond energy in the AB^+ ion. It is suggested that the reaction may proceed with participation both of excited and unexcited particles, depending upon experimental conditions. The difficulty encountered in working out both the associative and dissociative ionization theories is that these reactions seem to occur by multiple steps, as shown by a dense spectrum of Rydberg molecular states close to the ionization threshold. The ionization route of reaction



is one of the many routes resulting in excitation. Consequently, the contribution from excited atoms should be allowed for under thermal conditions. Even qualitative determination of the rate constant order for associative ionization would require thorough investigation of potential curves for

Rydberg states of the AB^+ molecule. This was made recently by Mulliken⁵³ for recombination of electrons on He_2^+ . For instance, the reaction



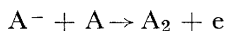
occurs with an activation energy, since only vibrationally excited He_2^+ atoms appear to be effective for recombination. This brings forward another problem which is far from being solved, namely the theoretical investigation of vibrational relaxation for excited electronic states in collisions of molecules with slow electrons. It follows that calculation of the rate constant for associative ionization without allowing for stepwise excitation should be as firmly substantiated as for many of the above cases considered. Nevertheless, for certain evaluations the neglect of intermediate steps might leave unaffected the order of magnitude of the rate constant or its temperature dependence. An analogy with the theory of electronic recombination on atomic ions would be appropriate here: the Thompson equilibrium theory and the Pitaevskii non-equilibrium theory yield the same temperature dependence of k_{rec} . For instance, the semi-empirical calculation of the rate constant for associative ionization $N + O = NO^+ + e$ made by Podlubny⁶⁷ gave the temperature dependence of $k_{a,e}$ as

$$k \sim T^{-1} \exp(-E_0/kT)$$

where $E_0 = 63.5$ kcal/mole. This is rather close to the experimental value reported in the literature⁴⁹

$$k_{a,e} = 3 \times 10^{13} T^{-1/2} \exp(-E_0/kT)$$

It will be of interest to note that electron detachment from negative ions in the reaction



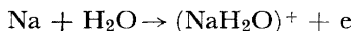
is a more favourable object for the theory, as the negative ions usually involve a single bound state. The approach to calculation of the electron detachment cross section for negative ions, as well as estimation of the cross section are treated by Demkov¹⁹ and Smirnov and Firsov⁷³.

Direct experimental investigation of associative ionization was made by measuring the relative amount of molecular ions formed by collisions of excited with non excited atoms of inert gases in the ion source of a mass spectrometer at low pressures ($\sim 10^{-4}$ mm Hg) (Cf. references 37 and 8). However, until recently, the rate constants and cross sections were determined with insufficient accuracy. Lampe and Hess⁴⁶ have found recently, by using the pulse method worked out at the Institute of Chemical Physics⁸² that the rate constant for the reaction



for an argon level of a lifetime $\tau = 4.8 \times 10^{-7}$ was $4.3 \pm 0.3 \times 10^{-10}$ cm³/sec at a temperature seemingly close to 500°K.

Well-based suggestions were made that associative ionization may essentially increase the ionization rate for systems containing alkali metals, due to reactions of the type



A process of this kind might be responsible for the large effective cross section of Na ionization⁷⁴ (see section 5).

CONCLUSION

It is thought that the theory for processes in low-temperature plasma, particularly for those of importance in chemistry, is in a state requiring a new qualitative step forward both with respect to techniques, and to the scope of theoretical and experimental investigations. The authors will consider their task as fulfilled to an extent measured by their success in convincing the Congress participants that this step should be taken.

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