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Kinetics and Mechanism of Three-body Recombination of Atoms and Radicals

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The review gives a general account of the results of numerous studies on the simplest atomic and radical reactions which are experimentally found to follow third-order kinetics. A large number of experimental results, arranged systematically in tables and graphs, are quoted and discussed. The principal characteristics of the properties of the reactions of this class (negative temperature dependence of the rate constant, different efficiencies of third bodies, relation between the efficiency and structure, etc.) are analysed. The possible interpretation of these processes on the basis of the simplest theoretical postulates—kinetic collision theory, theory of absolute reaction rates, and other equilibrium theories—are considered.
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I. INTRODUCTION

The hypothesis that elemenatry trimolecular reactions should be encountered very rarely because of the low probability of true three-body collisions arose already in the early stage of the development of chemical kinetics. Thus, according to Trautz [1], trimolecular reactions of the type A + B + C → product do not exist and pseudotrimolecular processes actually involve a complex mechanism: (1) A + B ⇌ AB; (2) AB + C → product. The rate-determining stage in the complex process is the second reaction, which does not affect the rapidly established equilibrium of the first stage. The kinetics of the oxidation of NO and of the formation of nitrosyl bromide and chloride were in fact interpreted from this standpoint.

The statistical calculations of Bodenstein [2], Tolman [3], Kassel [4], and Steiner [5-7] showed that, despite certain difficulties, a quantitative treatment of such reactions is indeed possible on the basis of the hypothesis that a three-body collision takes place in two stages: initially a pair (doublet) is formed and then a triplet following the approach of a third particle. Kassel [4] showed that, by taking into account the interaction between real gas molecules, it is possible to explain the characteristics of the temperature variation of the rate constant of a trimolecular reaction. The rate constant is written in the traditional form:

$$k = z_{\text{eff}} = Ae^{-E/RT} = ze^{-E/RT} \quad , \qquad (1)$$

where A and E are the pre-exponential factor and the activation energy for the trimolecular reaction and z, the number of three-body collisions per cm^3 per second, is calculated from the formulae of Tolman or Kassel:

$$z = 8\sqrt{2}\,\pi^{3/2}d_{12}^2 d_{23}^2 \delta \sqrt{kT}\left(\frac{1}{\sqrt{\mu_{12}}} + \frac{1}{\sqrt{\mu_{23}}}\right) N_1 N_2 N_3 \quad , \qquad (2)$$

$$z = 8\pi l_0^2 \sqrt{\frac{2\pi kT}{\mu}}\left(1 + \frac{\varphi_0}{kT}\right)\left[\int_0^{\rho_0} e^{-E(r)/kT} r^2 dr\right] N_1 N_2 N_3 \quad , \qquad (3)$$

where d_{12} and d_{23} are the gas-kinetic diameters of the doublets, μ_{12} and μ_{23} their reduced masses, N_1, N_2, and N_3 the numbers of molecules per cm^3, l_0 the distance between the particles forming the doublet, ρ_0 the distance between the centre of gravity of the doublet and the third particle, φ_0 the potential energy of the doublet, and $E(r)$ the potential energy at a distance r.

In the theory of equilibrium reaction rates [8,9] the formation of an activated complex from the free reacting molecules also may be preceded by a stage of the equilibrium formation of the binary complex AB with the subsequent formation of the trimolecular complex ABC as a result of the addition of the particle C (AB + C → ABC). The fundamental hypothesis is that equilibrium exists between the complex ABC and the initial reactants, the first equilibrium stage not affecting the equilibrium between the activated complexes and the starting materials A, B, and C. This permits a formal representation of the complex process as an elementary trimolecular reaction. Since three-body collisions between particles occur very rarely, it follows that, for trimolecular reactions to have rates which can compete with bimolecular reactions under certain conditions, they must have low activation energies or actually negative temperature coefficients, as happens in three-body recombination. The hypothesis that simple trimolecular reactions exist has become firmly established in chemical kinetics in connection with the study of the simplest process—the formation of diatomic molecules by the recombination of the atoms (H, O, Br, I, and others). By analysing the potential energy curves for the interaction between atoms, Born and Franck [10], Herzfeld [11], and Polanyi [12] showed that the formation of a stable molecule by the recombination of atoms requires the collision of the mutually approaching atoms with a third particle capable of absorbing the excess energy of the molecule just formed and thus enabling it to be stabilised "in the potential well"†. The transfer of excess energy from the excited molecule to the third particle may depend on the structure of the latter, in particular on the presence in its energy spectrum of resonating levels capable of accepting the excitation energy (vibrational or electronic energy) of the molecule in a collision of the second kind. This may account for specific effects of third bodies, without resorting to hypothesis that the specificity is due to the formation of complexes or intermediate compounds between one of the atoms or radicals and an external particle. The specificity of the effect then follows from the characteristics of the transformation and transfer of the energy of the excited particle, i.e. the transformation of its energy into one of

†Boltzmann [13] drew attention to this even earlier.

the forms of the internal energy of the third particle (vibrational, rotational, etc.), which means that the specificity follows from purely physical considerations. The mechanism of the recombination of atoms or radicals via energy transfer to a third particle is sometimes called in modern literature the "ET mechanism" (the energy transfer mechanism) [14].

The experimental study of the rate constants for three-body recombination of atoms shows that at moderate temperatures they are generally of the order of 10^{15} cm^6 $mole^{-2}$ s^{-1} and are characterised by low negative temperature coefficients, i.e. low negative activation energies in the range 0–5 kcal $mole^{-1}$. However, in some cases much higher rate constants have also been obtained experimentally for atomic three-body recombination reactions, indicating the specificity of the effect of third bodies. These data could not be explained within the framework of the ET mechanism. Furthermore, this mechanism, when applied to the specific effect of third bodies, had already encountered serious criticism in the early work of Rabinowitch [15]. A radical–molecular complex mechanism, called for brevity the RMC mechanism, has been proposed to explain the existence of more powerful effects of third bodies on the recombination of atoms or radicals. In three-body recombination reactions of atoms or radicals involving an RMC mechanism, the participation of a third particle in the process involves its ability to form reversibly with one of the radicals intermediate complexes having an excess excitation energy. This energy may be evolved in collisions between the excited complex and the third particle, after which the normal complex interacts with the radical to yield the product and the chemically unchanged third body. The RMC mechanism can provide a natural explanation of the specific effect of third bodies through the concept of reaction complexes, i.e. within the framework of the concept of homogeneous catalysis, which may accelerate the recombination and can account for the widespread occurrence of recombination with participation of third bodies, which play the role of process catalysts.

The question of the competition between ET and RMC mechanisms in each particular case can be resolved in principle by comparing the lifetimes of the corresponding intermediate species [14]. For example, in the recombination of atoms in the presence of fairly complex (or chemically active) third bodies the intermediate compound of the atom and the third body may be longer-lived thereby facilitating the reaction by the complex mechanism; on the other hand, the recombination of complex radicals in the presence of a simple third body will evidently be faster when the ET mechanism operates. However, these are unusual "limiting" cases. It may be that the lifetimes of the complex formed in the first stages of both mechanisms are comparable on *a priori* grounds and it is difficult to decide qualitatively what are the true relative contributions of the recombination mechanisms (for example in reactions with participation of simple unsaturated molecules).

Below we shall discuss in greater detail the experimental data for three-body recombination reactions of atoms and radicals on the basis of the collision theory, the theory of absolute reaction rates, and certain modifications of these theories.

II. EXPERIMENTAL DATA FOR THREE-BODY RECOMBINATION

During the past ten years special reviews have been devoted to experimental studies on three-body recombination reactions of atoms [16–19]. The most important general features of chemical processes of this type are discussed in the present review. We shall not be concerned with the problem of the three-body recombination of charged particles (ions and electrons), about which many experimental and theoretical papers have also been published recently [20–27,31].

The principal difficulty in the study of three-body recombination is usually the problem of obtaining a fairly high concentration of free atoms. The rapid increase of the number of studies on the kinetics and mechanism of three-body recombination from the middle of 1950's up to the present time is mainly due to the successful assimilation of new effective methods for the production of free atoms. These are flash photolysis [26–31] and the method of shock tubes [31–33]. While the method of flash photolysis permits the direct measurement of the rate constant for the recombination of atoms, in shock tube experiments measurements are made (at high temperatures) of the reverse reaction, i.e. thermal dissociation, and the results must be recalculated in terms of equilibrium constants. Flash photolysis alone is applicable over a fairly narrow range of low temperatures. However, the combined use of flash photolysis together with the shock tube method permits [34] measurements of the rate of recombination at much higher temperatures (the shock tube being used to heat the dissociation gas).

The two methods described are at present the most important in the study of dissociation and recombination processes. Apart from these, the free atoms of light elements are frequently produced by an electrode or electrodeless gas discharge (see for example papers by Canadian workers [35–39]). There exist also a number of different methods for the recording of the concentrations of atoms. Among these the ESR method [40,41], the method of "titration" using a rapid side reaction [42–46], and others have found successful application.

1. Absolute Rate Constants for Three-body Recombination of Atoms‡. Effectiveness of Various Particles as Third Bodies

The interest in three-body recombination reactions of atoms arose to the first place in connection with the problem of the recombination of hydrogen atoms. In the 1930's an extensive series of measurements of the rate constant for this reaction was made close to room temperature (Table 1). The results of these measurements show marked discrepancies because of the imperfection of the method under both static and flow conditions. Nevertheless a great achievement of these early studies was the formulation of the problem of the relative efficiencies of various particles as "third bodies" in the recombination process. However, the initial data on this problem proved to be extremely contradictory: while Steiner in several experimental and theoretical studies [5–7] insists that the

‡The available literature data for the rates of three-body recombination of identical atoms are expressed in two different ways: either in terms of the accumulation of molecules, $d[A_2]/dt = k[A]^2[M]$, or in terms of the consumption of atoms, $-d[A]/dt = k'[A]^2[M]$, where $k' = 2k$. In the present review all the numerical constants refer to the first equation, i.e.

$$k = \frac{1}{[A]^2[M]} \frac{d[A_2]}{dt}.$$

hydrogen atom is less effective than the hydrogen molecule (k_H is not more than 10% k_{H_2}), Senftleben and Reichemeier [47,48] quote $k_H/k_{H_2} \simeq 2000$. At the same time in a series of papers Amdur [49-53] asserts that the effectiveness of the H and H_2 species is comparable and that there are no grounds for expecting a significant difference between them.

Table 1. Rate constants for the recombination of hydrogen atoms: $k = \frac{1}{(H)^2(M)} \frac{d(H_2)}{dt}$.

Room temperature (293-298°K)				High temperatures* (from experiments on dissociation of H_2 in shock tubes)			
third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	$\frac{k_H}{k_{H_2}}$	references	third body M	k at 3500°K, $cm^6\ mole^{-2}\ s^{-1}$	$\frac{k_H}{k_{H_2}}$	references
H	$1.3 \cdot 10^{16}$	0.47	57	H	$3.0 \cdot 10^{15}$	23	63
H_2	$2.8 \cdot 10^{16}$			H_2	$1.3 \cdot 10^{14}$		
				Xe	$4.5 \cdot 10^{14}$		
H	$\sim 1.7 \cdot 10^{17}$	$2 \cdot 10^3$	48	H	$2.2 \cdot 10^{15}$	24	64
				H_2	$9.2 \cdot 10^{13}$		
				Xe	$3.3 \cdot 10^{14}$		
H_2	$9 \cdot 10^{15}$	~ 0.1	5	H	$8.7 \cdot 10^{15}$	12	65
				H_2	$7.1 \cdot 10^{14}$		
				Ar	$1.7 \cdot 10^{14}$		
H_2	$1.6 \cdot 10^{16}$	0.25-1.0	49	H	$9.5 \cdot 10^{15}$	13	66
				H_2	$7.3 \cdot 10^{14}$		
				Ar	$1.7 \cdot 10^{14}$		
H	$8.5 \cdot 10^{15}$	> 50	58	D**	$5.8 \cdot 10^{15}$	41	66
H_2	$1.7 \cdot 10^{16}$	0.3	59	D_2**	$1.4 \cdot 10^{14}$		
H, Ar	$5.6 \cdot 10^{15}$			Ar**	$2.3 \cdot 10^{14}$		
H	$1.02 \cdot 10^{16}$	$\geqslant 10$	52	H	$2.9 \cdot 10^{15}$	3,4	67
H_2	$5.5 \cdot 10^{15}$	$\leqslant 0.1$	7	H_2	$8.6 \cdot 10^{14}$		
				Ar, Kr, Xe	$4.3 \cdot 10^{14}$		
H_2	$1.0 \cdot 10^{15}$		60				
H_2	$0.9 \div 1.2 \cdot 10^{16}$		53	H	$1.4 \cdot 10^{16}$	6,7	68
H_2	$1.18 \cdot 10^{16}$		40	H_2	$2.1 \cdot 10^{15}$		
H_2	$8.9 \cdot 10^{15}$		61	Ar	$2.1 \cdot 10^{14}$		
NO	$1.1 \cdot 10^{16}$		62	Ar	$4 \cdot 10^{14}$***		69

*Most investigators [65-68] who measured the rate of recombination over a fairly wide range of temperatures (mainly 3000-5000°K) noted a decrease of the rate constant, on raising the temperature, in accordance with a T^{-1} law when M is an inert gas. However, Gardiner and Kistiakowsky [64] failed to observe any significant temperature variation in the range 3000-4500°K.

**The values quoted refer to the recombination of deuterium atoms.

***This value was obtained at 1700°K.

It follows from general theoretical considerations [9,54] that a third body M capable of chemical interaction with the recombining atoms (which is the case when M = H) should as a rule constitute a more effective third body. When applied to the reaction under consideration, this point of view is satisfactorily confirmed by later experiments at high temperatures (Table 1, see also Dixon-Lewis et al. [55]) the more self-consistent results of which show that k_H exceeds k_{H_2} on the average by one power of ten. This apparently contradicts the self-evident physical consideration that a larger number of degrees of freedom in the particle M should favour a more effective removal of energy from the recombining pair during its stabilisation in a three-body collision, increasing thereby the rate constant [56]. However, this is true only when particles M which are chemically inert to the recombining particles are compared. In this case the formation of a fairly stable compound H_3 in the interaction between H and H_2 is unlikely (H_2 may be regarded as an inert third body); therefore the above qualitative estimate is inapplicable and the high effectiveness of H as the particle M becomes quite understandable (see also for comparison the data on the recombination of atomic oxygen in Table 2).

The recombination of iodine and bromine atoms has been fairly thoroughly investigated over a wide range of conditions (Tables 4 and 6-8). In practice the role played by the three-body recombination reactions of halogen atoms in photochemical reactions of the type $H_2 + X_2 \rightarrow$ product, where X_2 is a halogen, is very important. The first data on the recombination Br + Br + M → product were in fact obtained by studying the kinetics of the photochemical reaction between H_2 and Br_2. [70-74] The classical experiments of Rabinowitch and coworkers [75-79], designed to investigate the photochemical steady states, marked the beginning of the systematic investigation of the three-body recombination of halogen atoms (iodine and bromine). In these experiments the wide differences between the effectiveness of various atoms and molecules as third bodies were noted for the first time, the absolute values of the rate constants (on the average 10^{15} $cm^6\ mole^{-2}\ s^{-1}$) proving significantly higher than would follow from initial theoretical estimates by Bodenstein [2]. At the same time Rabinowitch [15] suggested that the very high effectiveness of certain complex molecules (he used benzene in his experiments) may be attributed to the formation of a relatively stable atomic-molecular complex.

The dependence of the rate constant on the molecular complexity of the inert third body, mainly on the number of its degrees of freedom responsible for the energy transfer, was particularly clearly demonstrated in the work of Russell and Simons [80]; these workers quote rate constants for the recombination of iodine in the presence of more than thirty different inert gases (Table 4). For example, toluene proved to be 60 times more effective and mesitylene 110 times more effective than argon. Russell and Simons [80] made another interesting observation: they noted that the rate constants vary regularly with the boiling point, critical temperature, and ionisation potential of the inert gas, i.e. with the parameters characterising the strength of intermolecular forces. Fig. 1 illustrates this relation for the variation of $\lg k$ with the boiling point of the substance M as an example.

The existing data for the rates of recombination of the atoms of various halogens on contact with the same inert gas species show that the rate constants are higher for heavier atoms but the differences are not very great. The rates of recombination of I and Br atoms on contact with the same third body are virtually the same over a wide range of experimental conditions [81].

A large number of experimental studies on three-body recombination were stimulated also by interest in the study of chemiluminescence in gases: for example, Berkowitz et al. [82] showed that the intensity of the yellow luminescence of nitrogen depends on the consumption of free N atoms by a third-order rate law with a velocity constant of 7×10^{14} ($\times 10^{\pm 2}$) $cm^6\ mole^{-2}\ s^{-1}$ (see also Reeves et al. [83]); the greenish yellow luminescence of air is due [84] to a trimolecular reaction with participation of O and NO; the

Table 2. Rate constants for the recombination of oxygen atoms and the formation of ozone in three-body collisions.

Low temperatures									High temperatures				
$O+O+M \rightarrow O_2+M$*				$O+O_2+M \rightarrow O_3+M$					$O+O+M \rightarrow O_2+M$				
T, °K	third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	refs.	T, °K	third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	refs.	T, °K	third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	refs.
350	O_2	$3 \cdot 10^{14}$	86	296	O_2	$7.9 \cdot 10^{13}$	$\propto e^{\frac{600}{RT}}$	89	3500	O_2	$2 \cdot 10^{14}$		94
300	O_2	$5 \cdot 10^{15}$	41	296	O_3	$1.8 \cdot 10^{14}$		89	3500	O_2, Xe	$2 \cdot 10^{14}$		95
300	O_2	$1.0 \cdot 10^{14}$	35	296	N_2	$7.4 \cdot 10^{13}$		89	3500	O	$9.9 \cdot 10^{14}$		96
300	NO	$1.85 \cdot 10^{16}$	37	296	CO_2	$1.9 \cdot 10^{14}$		89	3500	O_2	$4.8 \cdot 10^{14}$		96
300	O_2	$1.03 \cdot 10^{15}$	83	296	He	$6.1 \cdot 10^{13}$		89	3500	Ar	$4.5 \cdot 10^{13}$		96
300	O	$3.2 \cdot 10^{15}$	38	296	O_2	$4 \cdot 10^{14}$		84	3500	O_2	$8.4 \cdot 10^{14}$	$\propto T^{-2}$	97
350	O_2	$\leqslant 2 \cdot 10^{14}$	87	296	O_2	$4 \cdot 10^{14}$		90	3500	O	$1.4 \cdot 10^{15}$		98
296	O_2	$1.0 \cdot 10^{14}$	88	350	O_2	$1.1 \cdot 10^{14}$		87	3500	O_2	$4.6 \cdot 10^{14}$	$\propto T^{-0,5\div-2}$	98
300	O	$8.1 \cdot 10^{14}$	40	283	O_2	$6.0 \cdot 10^{14}$		91	3500	Xe	$1.3 \cdot 10^{14}$		98
300	N_2	$1.0 \cdot 10^{14}$	39	300	O_2	$\sim 1.0 \cdot 10^{15}$	$\propto e^{\frac{1800}{RT}}$ or $T^{-3\,4}$	92	3500	O	$1.3 \cdot 10^{15}$		99
300	Ar	$\leqslant 3 \cdot 10^{14}$	39	273	Ar	$2.8 \cdot 10^{14}$		93	3500	O_2	$1.6 \cdot 10^{14}$		99
300	He	$3 \cdot 10^{14}$	39						3500	Ar	$5.2 \cdot 10^{13}$		99
300	N_2O	$1.4 \cdot 10^{14}$	39						3500	Ar	$2.3 \cdot 10^{13}$	$(\propto T^{-1})$	100
300	CO_2, SF_6	$3 \cdot 10^{14}$	39						3500	Kr	$4.6 \cdot 10^{13}$	$\propto T^{-0.5}$	100
300	H_2O	$\sim 5 \cdot 10^{15}$	39						2000	Ar	$2.5 \cdot 10^{13}$	$\propto T^{-1.2}$	101
									2200	O_2	$6.8 \cdot 10^{14}$		102**

*In Kaufman's review [18] $k = 9.8 \times 10^{14}$ was adopted as the best value for $O + O + O_2 \rightarrow 2O_2$ at room temperature. This is lower by a factor of five than the value obtained by extrapolation of the results of measurements in shock tubes.

**The method developed by Kiefer and Lutz [102] permitted the direct measurement of the rate of recombination in shock tubes, instead of its calculation from the rate of the reverse reaction via the equilibrium constant.

intensity of the red-orange luminescence arising from the products of an electric discharge in chlorine also follows a trimolecular law, $\mathcal{J} = k(Cl)^2(Cl_2)$, the $Cl_2(A^3\Pi_{1u}^+)$ molecule being identified as the source of the luminescence [85]. The study of such systems, mainly by producing free atoms from a discharge, has yielded important data on the rates of recombination of oxygen and nitrogen atoms (Tables 2 and 3). The tables also present the results of experiments in shock tubes.

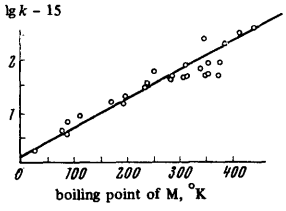


Figure 1. Variation of the rate constant for the recombination of iodine atoms with the boiling point of the substance M. [80]

Examination of the rate constants for the three-body recombination of oxygen atoms at low temperatures (Table 2) shows that they are of the order of 10^{14}–10^{15} when M is an inert gas. Kaufman [18] believes that the best value is 9.8×10^{14} for M = O_2 at room temperature. As the temperature rises, there is a tendency for the constant to fall, which is clearly demonstrated by the results of experiments in shock tubes. The specific effects of various third bodies are also clearly revealed. Table 2 lists the experimental rate constants for the formation of ozone: on the average they are somewhat smaller and are of the order of 10^{13}–10^{14}.

Table 3 lists the rate constants for the recombination of nitrogen atoms on contact with various third bodies. Their order of magnitude differs little from the corresponding values for the recombination of oxygen atoms (at low temperatures), but they vary less markedly with temperature.

Table 3. Rate constants for the recombination of nitrogen atoms*.

T, °K	Third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	Refs.	T, °K	Third body M	k, $cm^6\ mole^{-2}\ s^{-1}$	Type of temp. variation	Refs.
300	N_2, Ar	$6.24 \cdot 10^{15}$		42	298	N_2, N	$2.0 \div 3.5 \cdot 10^{14}$	$dk/dT \geqslant 0$	104
297	N_2	$2.7 \cdot 10^{15}$		43	300	N_2	$5.4 \cdot 10^{15}$		40
297	Ar	$1.6 \cdot 10^{15}$	$dk/dT \leqslant 0$	43	300	N_2	$8.0 \cdot 10^{14}$		61
297	He	$4.0 \cdot 10^{14}$		43	293	N_2	$1.38 \cdot 10^{15}$		105
300	O_2	$6.0 \cdot 10^{15}$		103	293	Ar	$1.9 \cdot 10^{15}$		105
195—400	N_2	$5.7 \cdot 10^{15}$	$dk/dT \simeq 0$	44	293	He	$1.73 \cdot 10^{15}$		105
297	Ar	$2.8 \cdot 10^{15}$		44	3000	Ne	$6.5 \cdot 10^{14}$		106
297	He	$8.2 \cdot 10^{14}$		44	3000	Ar	$3.2 \cdot 10^{14}$	$\propto T^{-0.5}$	106

*The table shows that most investigators found a very small temperature coefficient for this reaction. In the earliest experiments of Forst et al. [107] it was found that $k \propto T^{-4}$ for M = CH_3Cl and CH_3CN.

2. Three-body Recombination involving Di- and Triatomic Particles

Compared with the recombination of atoms, trimolecular reactions in the gas phase with participation of di- and tri-atomic particles, which play an important role in many atmospheric processes, chemiluminescence, and others,

have been less thoroughly investigated and information about them has begun to accumulate mainly in recent years (Table 8). Among processes in this category, the reaction $H + O_2 + M \rightarrow HO_2 + M$, which plays a major role in the kinetics of complex chemical processes, has been most thoroughly investigated. For example, the phenomenon of the upper explosion limit in the chain process of hydrogen combustion and also the classical example of the inhibition of the photochemical reaction between H_2 and Cl_2 by the addition of oxygen are in fact associated with this reaction. The inhibiting effect of O_2 is explained by the fact that the active chain radical (the H atom) combines with O_2 in a three-body collision, yielding the relatively inactive HO_2 radical, which cannot regenerate the H atom at low temperatures [108,109].

Table 4. Effectiveness of various third bodies in the recombination of iodine atoms at room temperature*.

Third body, M	$10^{-15}k$, cm^6 $mole^{-2}$ s^{-1}	Refs.	Third body, M	$10^{-15}k$, cm^6 $mole^{-2}$ s^{-1}	Refs.
Helium	3.3	79	Carbon monoxide	5.42***	122
	1.70	80	Hydrogen iodide	28.1***	122
	3.14	120	Methane	22	79
	1.21	121		8.89	80
	1.41	122	Methyl iodide	150	122
	1.52	123	n-Propane	30.5	80
Neon	1.81	80	Cyclopropane	39.5	80
	3.37	120	n-Butane	35.0	127
	1.67	121	n-Pentane	47.0	79
	1.9**	124	Neopentane	58	125
Argon	6.9	79	2,2-dimethylpropane	43.5	80
	3.63	80	Cyclohexane	54.4	80
	4.39	120	Ethylene	17.1	80
	3.34	121	Tetrafluoroethylene	21.0	80
	4.2	125	Trifluorobenzene	87.8	80
	4.5	126	Benzene	180	79
	2.90	127		87.1	80
	3.65	128		100	122
	2.97	123		79.6	123
Krypton	6.18	120	Toluene	210	80
	4.08	121		194	123
Xenon	6.24	120	Azomethane	187	80
	5.42	121	*p*-Xylene	332	80
Hydrogen	7.3	79	Mesitylene	406	80
	4.77	80		405	123
	4.93	122	Iodine	853	121
Nitrogen	12.0	79		1720	127
	4.52	80		1380	123
Oxygen	19.0	79	Methanol	64.9	80
	6.66	80	Methyl ether	61.9	80
	6.75	123	Methylene dichloride	47.7	80
Water	49.7	80	Carbon tetrachloride	50.8	80
Carbon dioxide	33	79	Ethyl chloride	47.7	80
	13.5	80	Ethyl bromide	80.2	80
	13.4	123	Ethyl iodide	250	80
Nitric oxide	$>4.8\cdot10^{6}$***	122		238***	122
	$3\cdot10^{4}$**	124		261	123

*The results of some studies [79,80,120,125,128] were not corrected for the rapid reaction $2I + I_2 \rightarrow 2I_2$. Therefore the rate constants for relatively ineffective third bodies may deviate from the true values.

**Measured at 60°C

***The values for 50°C are quoted. When M = NO, the rate of reaction is too high for a reasonably accurate determination of the constant.

The $H + O_2 + M \rightarrow$ product reaction was investigated by many workers [110–118] and experimental constants for this reaction, in good mutual agreement, are now available: measurements of Clyne and Thrush [113] in the range 250–800°K and of Getzinger and Schott [115] in the range 1150–1850°K. An interesting feature of this reaction [109,118,119] is a very pronounced catalytic effect of water vapour ($k_{H_2O}/k_{Ar} \simeq 30$ and hardly changes with temperature). This makes it difficult to investigate the upper limit (and particularly its temperature variation), since the presence of even small traces of water vapour in the reaction zone can significantly lower it. Semenov [108] believes that in this case there is a possibility of an unusual chemical interaction involving the formation of the complex $H.H_2O$.

Table 5. Rate constants for three-body recombination involving di- and tri-atomic species.

Reaction	Third body M	T, °K	k, cm^6 $mole^{-2}$ s^{-1}	Type of temp. variation	References
$H + O_2 + M \rightarrow HO_2 + M$	H_2	293	$\sim1.3\cdot10^{13}$		112,118
	O_2	293	$\sim1.3\cdot10^{14}$		112,118
	He	293	$7.6\cdot10^{15}$		113
	Ar	293	$8.0\cdot10^{15}$	$\propto e^{\frac{1500}{RT}}$ or $T^{-1.8}$ (250—800° K)	113
		813	$1.70\cdot10^{15}$		116
		1500	$1.42\cdot10^{15}$	$\propto e^{\frac{1300}{RT}}$ (225 — 1850°K)	115
	H_2O	293	$1.9\cdot10^{17}$		113
		1350	$1.0\cdot10^{17}$		117
$H + OH + M \rightarrow H_2O + M$	Ar	1700	$\sim4\cdot10^{15}$		69
$H + NO + M \rightarrow HNO + M$	Ar	293	$8.7\cdot10^{15}$	$\propto e^{\frac{700}{RT}}$ (250 — 800 °K)	113.129
	H_2	293	$1.48\cdot10^{16}$	$\propto e^{\frac{600}{RT}}$ (230 — 700 °K)	129
	Ne	293	$7.2\cdot10^{15}$		129
	He	293	$6.6\cdot10^{15}$		129
$O + NO + M \rightarrow NO_2 + M$	O_2,N_2,Ar	296	$2.5\cdot10^{16}$		90
	N_2, Ar	296	$2\cdot10^{16}$		84
	CO_2,N_2O	296	$4\div5\cdot10^{16}$		84
	Ar	293	$2.7\cdot10^{16}$	$\propto e^{\frac{1800}{RT}}$ (250 — 800 °K)	113
$NO_2 + NO_2 + M \rightarrow N_2O_4 + M$	N_2	298	$1.4\cdot10^{14}$		130
$Cl + NO + M \rightarrow NOCl + M$	He	293	$3.5\cdot10^{16}$		131
	Ar	293	$3.9\cdot10^{16}$	$e^{\frac{1100}{RT}}$ (270 — 620 °K)	131
	O_2	293	$3.9\cdot10^{16}$		131
	N_2	293	$3.5\cdot10^{16}$		131
	Cl_2	293	$3.4\cdot10^{16}$	$e^{\frac{700}{RT}}$ (270 — 620 °K)	131
	SF_6	293	$3.5\cdot10^{16}$	$e^{\frac{1800}{RT}}$ (270 — 620 °K)	131
$O + SO_2 + M \rightarrow SO_3 + M$	SO_3 (?)	296	$3.0\cdot10^{16}$		90
$O + SO + M \rightarrow SO_2 + M$	Ar	300	$3.2\cdot10^{17}$		132

The rates of reactions of this type (Table 5) have values which are on the whole in the same range of orders of magnitude as the rate of atomic recombination. The negative temperature coefficient in these reactions is fairly small.

3. Temperature Variation of the Rate Constant

An interesting and important feature of three-body recombination reactions, which distinguishes them from other elementary reactions, is a negative temperature coefficient of the rate constant, i.e. a negative effective activation energy $E = RT^2(d\ln k/dT)$. This fact has been established quite reliably for the vast majority of reactions of this class (see Tables 1–3, 5, and 6 and Fig. 2). Qualitatively the two possible two-stage recombination mechanisms can account for the negative activation energy. It arises because the probability of the breakdown of the intermediate complex increases with temperature faster

Table 6. Experimental temperature variation of the rate constants for the three-body recombination of iodine atoms (the constants are expressed in cm^6 $mole^{-2}$ s^{-1} and the activation energies E in cal $mole^{-1}$).

Third body M	Temp. range, °K	Empirical formula	Refs	Third body M	Temp. range, °K	Empirical formula	Refs.
Helium	293—523	$7.6\cdot10^{14}\exp(400/RT)$	123	CO_2	293—523	$6.7\cdot10^{14}\exp(1750/RT)$	123
		$4.7\cdot10^{11}\,T\exp(1400/RT)$	123			$7.4\cdot10^{11}T\exp(2400/RT)$	123
	323—543	$1.41\cdot10^{15}(298/T)^{0.60}$	122		1000—1600	$1.6\cdot10^{14}(1000/T)^{4.74}$	133
		$4.8\cdot10^{14}\exp(660/RT)$	122			$1.3\cdot10^{14}\exp(9460/RT)$	133
	1000—1600	$5.3\cdot10^{14}(1000/T)^{3.85}$	133	$n\text{-}C_4H_{10}$	298—493	$3.5\cdot10^{16}(298/T)^{2.16}$	127
		$1.04\cdot10^{13}\exp(7960/RT)$	133			$2.3\cdot10^{15}\exp(1650/RT)$	127
Argon	293—523	$3.1\cdot10^{14}\exp(1300/RT)$	123	CH_3I	323—543	$2.3\cdot10^{17}(298/T)^{2.24}$	122
		$3.3\cdot10^{11}T\exp(2000/RT)$	123			$1.50\cdot10^{15}\exp(2550/RT)$	122
	298—1600	$2.98\cdot10^{15}(298/T)^{1.33}$	127	C_2H_5I	293—523	$4.23\cdot10^{15}\exp(2400/RT)$	123
		$4.7\cdot10^{14}\exp(1130/RT)$	127			$4.4\cdot10^{12}T\exp(3100/RT)$	123
	1060—1860	$7.4\cdot10^{14}(1000/T)^{1.90}$	134	C_6H_6	293—523	$4.32\cdot10^{15}\exp(1700/RT)$	123
	1000—1600	$7.3\cdot10^{14}(1000/T)^{1.77}$	133			$4.4\cdot10^{12}T\exp(2400/RT)$	123
		$7.6\cdot10^{13}\exp(4560/RT)$	133		323—543	$1.0\cdot10^{17}(298/T)^{2.53}$	122
Hydrogen	323—543	$4.93\cdot10^{15}(298/T)^{1.48}$	122			$3.9\cdot10^{15}\exp(1970/RT)$	122
		$6.6\cdot10^{14}\exp(1220/RT)$	122	Toluene	293—523	$1.87\cdot10^{15}\exp(2700/RT)$	123
Nitrogen	1000—1600	$1.03\cdot10^{14}(1000/T)^{1.38}$	133			$2.0\cdot10^{12}T\exp(3400/RT)$	123
		$1.37\cdot10^{14}\exp(4240/RT)$	133	Mesitylene	295—427	$3.4\cdot10^{14}\exp(4100/RT)$	123
	1060—1860	$7.08\cdot10^{14}(1000/T)^{1.91}$	134			$3.6\cdot10^{11}T\exp(4800/RT)$	123
Oxygen	293—523	$5.1\cdot10^{14}\exp(1500/RT)$	123	I_2	293—523	$5.3\cdot10^{11}T\exp(5300/RT)$	123
		$5.3\cdot10^{11}T\exp(2200/RT$	123		298—1600	$4.5\cdot10^{10}T^{3/2}\exp(5320/RT)$	127

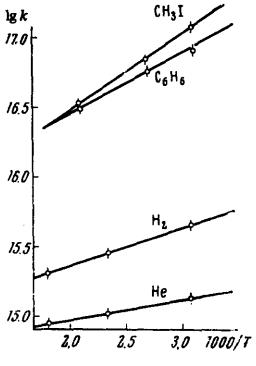


Figure 2. Temperature variation of the rate constant for the recombination of iodine atoms at moderate temperatures [122].

than the probability of the two-body collisions in both stages of the process.

The development of the experimental shock tube technique greatly extended the range of the known temperature variation of the constants. The results of the measurements of the variation of k with T are usually expressed either in terms of the exponential function $k = Ae^{-E/RT}$ ($E < 0$) or in terms of the power function $k = B/T^n$ ($n > 0$) [or $k = B'(T_0/T)^n$] (Table 6). However, more careful measurements showed [135,136] that there is a difference between the parameters E and n obtained at low (flash photolysis) and high (shock tubes) temperatures. Thus Russell [135] concluded that in the formula $k = B/T^n$ for the recombination of I and Br atoms in the presence of inert gas species at high temperatures one should use the average value $n = 1.5$, while at low temperatures the experimental data are best described by the same formula but with $n = 3$. These values are only approximate and are by no means consistent with all the experimental data. It is difficult to speak of the exact values of n or other parameters, since the results obtained at high temperatures may involve considerable errors and do not agree well with one another (see Table 6). However, there is no doubt about the actual complexity of the temperature variation, but it must now be recognised that hardly any elementary chemical reactions may be more or less satisfactorily characterised in terms of the Arrhenius function (or even less so a power function) with constant parameters over a wide range of temperatures [137] §.

The absolute values of the effective activation energies in these reactions are low and vary from zero to (minus) 5 kcal $mole^{-1}$. For example, Strong et al. [126] obtained the following activation energies in the flash photolysis of halogen–inert gas mixtures in the temperature range 25–160°C: −1.4, −2.0, and −1.2 kcal $mole^{-1}$ respectively for the recombination of I atoms in argon, Br atoms in argon, and Br atoms in molecular oxygen. Analysis of the experimental data carried out by Bunker and Davidson [17] showed that the negative temperature coefficient is higher for the gases which are more effective at low temperatures Hence here again there is a correlation between E and the boiling points, critical temperatures, etc. This conclusion is not confirmed by the earlier results of Russell and Simons [80], which are less reliable as regards the temperature variation, since these workers did not allow for the high effectiveness of I_2 as a third body (see p. 597).

According to Husain and Pritchard [138], the variable negative activation energy can be readily interpreted in terms of the ET mechanism if it is assumed that the collision with a third particle leads to the deactivation of the already formed excited ("latent") molecule only when the energy of the relative motion of the recombining particles lies in the range between two critical values ϵ_0 and ϵ_1 (above ϵ_1 there is no deactivation). Then the recombination rate constant should be

$$k = z[\exp(-\epsilon_0/RT) - \exp(-\epsilon_1/RT)] \quad (4)$$

Differentiation of this expression shows that k will decrease with increasing temperature if $\epsilon_0 < RT$ and $\epsilon_1 - \epsilon_0 \ll RT$. It is reasonable to put $\epsilon_0 = 0$; then if one adopts, for example, $\epsilon_1 = 0.1$ and 0.5, we obtain for the recombination

§In the present case one of the possible reasons for this is also the fact that the relative contributions of the ET and RMC mechanisms may vary with temperature.

reaction respectively $E_{300-400} = -0.68$ and -0.51 kcal mole^{-1} and $E_{1000-2000} = -2.72$ and -2.53 kcal mole^{-1} (the subscripts to E denote the temperature ranges). The numerical values thus obtained are extremely plausible, despite the simplified nature of the model: they give a temperature coefficient of the right order of magnitude, the absolute value of which increases at high temperatures in agreement with the results of the majority of the experiments.

4. Energy Distribution Among Recombination Products. Repeated Dissociation and Its Effect on the Temperature Variation of the Rate Constant

In the light of the latest experimental and theoretical data for energy transfer processes, it is fairly reliably known that the conversion of vibrational energy into translational energy, i.e. a process of the type

$$A_2'(v = n) + M \rightarrow A_2'(v = n - 1) + M + Q$$

(a single prime denotes a vibrationally excited molecule) is extremely difficult and is much slower than the transition from one vibrational level to another. The effective deactivation of A_2' requires a very large number of thermal collisions, i.e. it takes place with a very long relaxation time. Therefore it is logical to expect that an elementary exothermic reaction leads to the formation of vibrationally excited molecules, which are then gradually deactivated by collisions with the inert gas molecules. This is confirmed by a series of experiments with elementary bimolecular and termolecular reactions of the type $A + BC \rightarrow AB' + C$ and $A + B + C \rightarrow AB' + C$. For example, according to data of McGrath and Norrish [139], the reaction of atomic oxygen with ozone takes place as follows: $O + O_3 \rightarrow O_2'(v = 17) + O_2$. Cashion and Polanyi [140-143] and also Charters and Polanyi [144], who studied the reaction $H + Cl_2 \rightarrow HCl' + Cl$, arrived at analogous conclusions: the energy distribution among the products formed proved to be displaced from the Boltzmann distribution towards higher vibrational levels. Among termolecular reactions, we may quote as an example the recombination of nitrogen atoms, for which it has been shown [141,145,146], that the N_2' molecule forms at the level with $v = 4$. Villermaux [147] investigated from this standpoint the recombination of hydrogen atoms by a thermal-kinetic method, which is based on the following simple idea: if the energy evolved in the recombination is instantly transferred to translational-rotational degrees of freedom, then the rate of evolution of heat should be equal to the rate of disappearance of atoms (known from other experiments); otherwise the rates are different. The experiments in fact showed that the latter is the case.

Polanyi [148] suggested that, since the recombination product is a vibrationally excited molecule A_2, its repeated dissociation (redissociation) at higher vibrational levels may play an important role. Polanyi made an approximate calculation of the probability of repeated dissociation at 300° and 600°K, assuming that the distance between adjacent vibrational levels close to the dissociation threshold is constant and that there exists a characteristic probability of the change in the quantum number by the same amount, which is independent of temperature. Calculation showed that the total probability of redissociation at all levels in the second and third collisions is 0.175 at 300°K and 0.29 at 600°K. This corresponds to a decrease with increasing temperature in the component of the recombination which definitely contributes to the negative temperature variation of the rate constant. Polanyi obtained an effective activation energy $E = -0.85$ kcal mole^{-1} in the range 300–600°K. The value thus predicted is smaller by a factor of 2–3 than the experimental activation energy, but it may be that, as a result of the above assumptions, it constitutes a lower limit.

Repeated dissociation is only one of the factors contributing to the negative temperature variation, but it is evident that, when this phenomenon is correctly taken into account, complete understanding of the experimental values may be greatly facilitated.

5. Deviations from the Termolecular Law. Anomalously High Efficiencies of Certain Third Bodies

The first experiments on the recombination of atoms showed that the termolecular law holds exactly. However, in 1954–1955 Christie and coworkers [121,149], having revised the results of their earlier study [120] on the recombination of iodine atoms in the presence of noble gas atoms by experiments over a wider range of conditions, observed deviations from the simple relation $d[I_2]/dt = k_M[I]^2[M]$ when the concentration ratio $[I_2]/[M]$ was varied (Fig. 3).

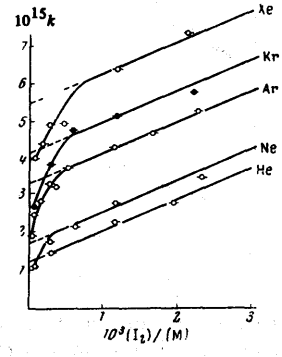


Figure 3. Deviations from the termolecular law in the recombination of iodine atoms [150].

The experimental results showed that the effective rate constant for the formation of molecules is a linear function of the ratio $[I_2]/[M]$ over a wide range of the latter, the relation showing a sharp variation at low values of $[I_2]/[M]$.

In the first series of experiments [120] the variation of the rate constant with $[I_2]/[M]$ was apparently masked by a "thermal effect". Since the recombination process is exothermic, the gas mixture is heated in the course of this process. The exact value of the heat evolved ΔQ depends on the average wavelength of the light absorbed; if we adopt $\Delta Q = 60$ kcal per mole of iodine as the maximum value and assume that the process is adiabatic, we can estimate the increase of temperature: $\Delta T = 3 \times 10^4 \Delta[I]/c_V[M]$, where $\Delta[I]$ is the change in the concentration of free iodine atoms and c_V the heat capacity of the third body M which is present in excess. For a monatomic gas, $\Delta T = 10^4\Delta[I]/[M]$ and, when $[M] = 100$ mmHg and $[I]_0 = 0.1$ mmHg, we obtain $\Delta T = 10$ deg after complete recombination. The direct effect of this temperature rise is hardly significant, but the temperature gradient thus

produced may be important [80]. This thermal effect, which increases with $[I_2]/[M]$, is revealed by a decrease of the observed rate constant during the recombination, compensating thereby the true increase of the constant as $[I_2]/[M]$ is raised. To explain the last finding, the rapid reaction $I + I + I_2 \rightarrow I_2' + I_2$ was postulated. When this and the process $I + I + M \rightarrow I_2 + M$ are taken into account, the kinetic law changes:

$$\frac{d[I_2]}{dt} = k_M[I]^2[M] + k_{I_2}[I_2][I]^2 = k_{init}[I]^2[M] , \quad (5)$$

$$k_{init} = k_M + k_{I_2}[I_2]/[M] , \quad (6)$$

where k_M and k_{I_2} are the true termolecular constants for the third bodies M and I_2 respectively and k_{init} is the effective rate constant determined experimentally in the initial stage of the recombination. Eqn. (6) shows that this constant does indeed vary linearly with $[I_2]/[M]$ and the fact that the straight lines in Fig. 3 are parallel confirms satisfactorily that the slope is related solely to the effectiveness of the I_2 molecule as third body and is independent of the nature of the inert gas M. The slope of the straight lines in Fig. 3 corresponds to $k_{I_2} \simeq 8.5 \times 10^{17}$ cm^6 mole^{-2} s^{-1} at room temperature, which is approximately 260 times higher than k_{Ar} (by a factor of 650 according to the data of Bunker and Davidson [127]). Evidently such high effectiveness of I_2 cannot be explained solely by an increase of the kinetic collision cross-section. However, as early as 1932, Rollefson and Eyring [151] predicted theoretically the possibility of the existence of relatively stable triatomic halogen molecules. The hypothesis of the formation of an I_3 molecule of this kind in the recombination of iodine atoms explains satisfactorily the anomalously high effectiveness of I_2 as the third body M. According to Semenov's estimate [108], the above experimental results correspond to $\Delta E \simeq -6$ kcal mole^{-1} as the energy of formation of I_3 in the reaction $I + I_2 \rightleftharpoons I_3$; Bunker and Davidson [17] quote for the same reaction $\Delta H^\circ = -5.3$ kcal mole^{-1} and $\Delta S^\circ = -20$ e.u.¶.

The rate constant k_{I_2} falls with temperature much faster than those for less effective third bodies (Table 6): at 1300°K the ratio k_{I_2}/k_{Ar} no longer exceeds 30. [133] This fact is in good agreement with the general tendency towards an increase of the negative temperature coefficient with increase of the effectiveness of recombination described in Section II, subsection 3.

For the recombination of Br atoms, it has also been reliably established that the species $M = Br_2$ is distinguished by enhanced effectiveness, although not to the same extent (Tables 7 and 8); an even smaller relative effect is observed [45,152] for $M = Cl_2$ in the reaction $Cl + Cl + M \rightarrow$ product and, finally, there exist only qualitative data indicating that in the recombination of F atoms molecular fluorine is somewhat more effective than argon [153].

The deviation of the rate constant from Eqn. (6) at low values of $[I_2]/[M]$ (Fig. 3), observed by Christie and coworkers [121,149], probably demonstrated for the first time a breakdown of the equilibrium distribution in the recombination of atoms. Generalising the various experimental data, Christie [150] concluded that the deviations from linearity may be attributed to the retardation of the vibrational deactivation of the excited molecule I_2' (formed in the recombination) as the concentration of I_2 diminishes. Although it is known that iodine molecules are initially formed at high vibrational levels, it is nevertheless always postulated that, of the two possible processes

$$I + I + M \rightarrow I_2' + M , \quad (a)$$

$$I_2' + M \rightarrow I_2 + M , \quad (b)$$

the rate-determining stage is the recombination (a), i.e. it is assumed that process (b) is fairly rapid. This assumption is justified if various gases have the same effectiveness in the two processes. If, however, molecular iodine is much more effective (by a factor of 10^4 and more) than an inert gas in the deactivation of I_2', then process (b) proceeds mainly in the following way even at very low values of $[I_2]/[M]$: $I_2' + I_2 > 2I_2$ ($v < 3$); when the contribution of $M = I_2$ to the overall rate of recombination (a) is negligibly small, then process (b) may become the rate-determining stage under the condition $k_b[I_2'][I_2] < k_M[I_2][M]$. Thus a deviation from linearity occurs when $([I_2]/[M])_{dev} = k_M[I_2]/k_b[I_2']$ and, under the initial experimental conditions, $([I_2]/[M])_{dev}$ should be proportional to k_M, as found experimentally (Fig. 3).

Table 7. Rate constants for the recombination of bromine and chlorine atoms close to room temperature.

Third body M	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.	Third body M	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.
$Br + Br + M \rightarrow Br_2 + M$			$Cl + Cl + M \rightarrow Cl_2 + M$		
Ar	2.4	77	He	3.0	152
	3.73	128	Ar	4.0	152
	2.7	154		4.25	45,46
	2.0	155	Cl_2	27	152
Br_2	49	154		0.3**	157
	48*	156		20.4	45,46
	260	155	O_2	7.9***	158
Cl_2	15*	156			
CO_2	9.8	77			
	7.8	128			
O_2	5.8	77			
	7.9	128			
H_2	4.0	77			
He	1.4	77			
N_2	4.5	77			
CH_4	6.5	77			

*The results quoted were obtained from a study of the photochemical reaction $Br_2 + Cl_2 \rightarrow$ product by comparing the effectiveness of Br_2 and Cl_2 with that of CO_2, using for the latter the result of Rabinowitch and Wood [77] (the direct determination was difficult in view of the heterogeneity of the thermal reaction).

**This result deviates markedly from the data of other workers; possibly, the method used here may yield relatively unreliable results in the presence of excited species [45].

***Measured at 229°K.

However, Nikitin [164,165] believes that for the recombination reactions under conditions of flash photolysis this interpretation is incorrect; according to his estimate, in this case (recombination of iodine) the disequilibrium arises due to the retardation of the transition between the excited and ground electronic states of I_2. In the formation of the system $I_2'-I_2$ there arise electronic levels strongly differing from those for two isolated I_2 molecules

¶Here the situation differs from that which obtains in the recombination of H atoms (see p. 597), since the diatomic product molecule is the chemically active third body. It would be interesting to carry out experiments designed to investigate the effectiveness of free halogen atoms as the third body M.

and there is a high probability of non-adiabatic transitions in the region where the energy levels of the complex I_2'–I_2 come very close together. In the interaction of I_2 with an inert gas atom one cannot expect a pronounced change in the position of the electronic levels; this accounts for the large difference between the effectiveness of the relaxation of I_2' on collision with M = I_2 and inert gas atoms.

Table 8. Rate constants for the recombination of halogen atoms at high temperatures.

Third body, M	T, °K	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.	Third body M	T, °K	$10^{-15}k$, cm^6 mole^{-2} s^{-1}	Refs.
	$I + I + M \rightarrow I_2 + M$				$Br + Br + M \rightarrow Br_2 + M$		
He	1300	0.25	133	He	1700	0.32	161
Ar	1300	0.45	133	Ar	1770	0.29	162
	1460	0.36	134		1600	0.33	81
O_2	1300	0.53	133		1700	0.40	161
N_2	1300	0.71	133	HBr	1600	0.39	163
	1460	0.35	134	Br_2	1600	2.6	81
I_2	1300	13.5	133		1600	3	163
					1770	0.73	162
	$Cl + Cl + M \rightarrow Cl_2 + M$				$F + F + M \rightarrow F_2 + M$		
Ar	1600	2.5	159	Ar	1400	0.007	153
	2100	0.17	160				

The constants for the midpoint of the temperature range of the measurements are quoted in the table.

It is noteworthy that the very high effectiveness is observed also in other cases where there is a possibility of a chemical bond: for example, with M = NO in the recombination reactions of halogen atoms (Table 4).

6. Effect of the Third Body in the Recombination of Alkyl Radicals

Since alkyl radicals are fairly complex species, in their recombination there is a relatively high probability of their stabilisation as a result of internal energy redistribution; nevertheless at low pressures the role of deactivation in collisions with a third body increases, leading to significant deviations towards a third-order process. The kinetic mechanism of such reactions is usually expressed in terms of the energy transfer mechanism (ET); then the general equations show that the effect of the third body begins to operate at higher pressures the lower its deactivating capacity. Furthermore, this effect becomes more pronounced with increase in temperature due to the decreased life-time of the complex R_2^*, which demonstrates the significant role which it may play in high-temperature pyrolytic processes.

Numerous experiments [166–174] have now yielded a fairly large number of quantitative data for the simplest process of this type—the recombination of methyl radicals:

$$CH_3 + CH_3 \underset{k_B}{\overset{k_A}{\rightleftharpoons}} C_2H_6^*,$$

$$C_2H_6^* + M \xrightarrow{k_C} C_2H_6 + M,$$

whence the rate of accumulation of ethane is:

$$\frac{d[C_2H_6]}{dt} = \frac{k_A k_C}{k_B + k_C[M]}[CH_3]^2[M]. \quad (7)$$

Under the condition $k_C[M] \ll k_B$, a third-order process is realised:

$$\frac{d[C_2H_6]}{dt} = \frac{k_A k_C}{k_B}[CH_3]^2[M] = k_{eff}[CH_3]^2[M] \quad (8)$$

Ingold and Lossing [166] measured mass-spectrometrically the rate of recombination of methyl radicals produced by the thermal decomposition of dimethylmercury and found that the rate has a negative temperature coefficient, without observing at the same time deviations from a second-order process as the helium pressure changed from 18.5 to 4.8 mmHg; this contradicts both the observed negative temperature coefficient and the low deactivating capacity expected for helium. Indeed, as was to be expected, repetition of the observations [167] revealed a linear variation with [He]. Although the negative temperature coefficient of the rate (according to Ingold and Lossing, $E = -2.2$ kcal mole^{-1}) is satisfactorily consistent with the known general properties of three-body recombination reactions, this phenomenon in the recombination of CH_3 radicals can be explained in another way not involving a third-order process [175].

The effect of the third body in this reaction was studied by Kistiakowsky and Roberts [168] and almost simultaneously by Dodd and Steacie [169] in experiments on the photolysis of acetone. These experiments showed that at temperatures in the range 150–250°C the deviations become significant at pressures of about 10 mmHg, which agrees well with the theoretical prediction of Marcus [172] concerning the existence of a transition region near 5 mmHg. According to Dodd and Steacie [169], the rate of spontaneous dissociation of $C_2H_6^*$ at 250°C is not greater than 6×10^7 s^{-1} (lifetime $\geq 1.6 \times 10^{-8}$ s) and increases with increasing temperature, and for the effectiveness of various third bodies in the deactivation of $C_2H_6^*$ these workers found the following values (relative to acetone): Ar(< 0.03), CO_2 (0.03), C_4F_{10} (0.2), $CF_3.C_6F_{11}$ (0.3), C_6H_6 (1.0), and acetone (1.0) at a temperature near 250°C. The absolute values of the effective third-order rate constants are then much higher than for the recombination of atoms.

Among the later investigations, the experiments of Toby and Weiss [173] on the photolysis of azomethane yielded important results. Azomethane proved to be a deactivating agent less effective by a factor of approximately three than acetone, which made it possible to extend the range of investigation of the effect of the third body to higher pressures. Carbon dioxide and sulphur hexafluoride were also investigated as third bodies, and their effectiveness in relation to azomethane proved to be 0.04 and 0.24 respectively.

Numerous experimental data on the recombination of CH_3 radicals in the transition region were analysed by Kondrat'ev [176]. This analysis led to the most reliable values of the kinetic characteristics of the process.

When the reactions of ethyl and more complex radicals are examined, the situation becomes somewhat more complicated. Qualitatively it is clear that the effect of the third body can operate here at even lower pressures; furthermore, the recombination is accompanied by disproportionation reactions, which complicate the composition of the products.

In experiments on the photolysis of diethylmercury, Bradley et al. [177] investigated the kinetics of the interaction of ethyl radicals and the composition of the products; the effect of the third body becomes clearly apparent at low pressures of M = Ne. However, the authors' interpretation of the experimental data in this region is incompatible

with the energy transfer mechanism. The authors' treatment is based on the postulate that the three-body recombination of C_2H_5 radicals is an independent reaction which takes place simultaneously with bimolecular recombination and disproportionation. Then the composition of the products is a linear function of pressure of the following form:

$$\frac{[\text{butane}]}{[\text{ethane}]} = \frac{1}{R} + \frac{k_{tr}}{k_r + k_d} \cdot \frac{1+R}{R}[M]. \quad (9)$$

where k_r and k_d are the rate constants for the bimolecular recombination and disproportionation reactions, k_{tr} is the three-body recombination rate constant, and $R = k_d/k_r$, which is equal to the ratio [ethane]/[butane] in the absence of the termolecular process. Extrapolation using Eqn. (9) to [M] = 0 yields R and then

$$\frac{k_{tr}}{k_r + k_d}.$$

However, the initial postulate of the separate occurrence of bimolecular and termolecular recombination of radicals gives rise to objections. It leads to the conclusion that at fairly high pressures three-body recombination will completely "suppress" bimolecular recombination, while experiments in fact show that the third-order law is fulfilled only at extremely low pressures. It is most likely that, as in simpler cases, these reactions are part of the same process, the order of which may change with pressure:

$$C_5H_5 + C_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_4H_{10}^* ,$$

$$C_4H_{10}^* + M \xrightarrow{k_2} C_4H_{10} + M ,$$

$$C_2H_5 + C_2H_5 \xrightarrow{k_3} C_2H_6 + C_2H_4$$

and the ratio of the product concentrations can also be expressed in terms of the relation

$$\frac{[\text{butane}]}{[\text{ethane}]} = \frac{k_1 k_2}{k_3} \frac{[M]}{k_{-1} + k_2[M]} ,$$

which is probably the true one. This relation is close to linearity only when $[M] \ll k_{-1}/k_2$; on the other hand, extrapolation to [M] = 0 when experimental points relatively far from this value are available may lead to considerable errors. When $[M] \to 0$, we have [butane]/[ethane] $\to k_1k_2[M]/k_{-1}k_3 \to 0$ provided that all the important elementary stages are incorporated in the mechanism quoted above.

It is remarkable that at very much higher pressures, when the ET mechanism gives rise to a second-order process, there is a possibility in principle of the simultaneous occurrence of three-body recombination, but solely by an RMC mechanism, i.e. with a different rate constant. In other words, we are dealing with the possible occurrence of a second transition (in the sense of a change in reaction order) pressure range. Unfortunately so far there are no data on the kinetics of radical recombination under conditions where this effect might be expected to occur.

There is extremely little information about the role of third bodies in the reactions of more complex radicals. However, theoretically for each case of this kind it is possible to predict a pressure range where the kinetic order of the recombination process should change [197].

III. INTERPRETATION OF EXPERIMENTAL DATA

Many theoretical papers on the problem of the three-body recombination of atoms have now been published. These studies are concerned both with the discussion of the general dynamics of the interaction of three atoms in the course of recombination and with the analysis of the possible two-stage process mechanisms from the standpoint of the classical and quantum mechanics and statistical physics. Modern theories of atomic recombination have been reviewed [165,203]. Here we shall consider only the possibility of the interpretation of the kinetics of three-body recombination on the basis of the simplest theoretical concepts—the kinetic collision theory and the activated complex method.

1. The Collision Theory

As for other elementary gas-phase reactions, the first attempt at the interpretation of the experimental data on three-body recombination involved the use of the Arrhenius formula (1). Before the discovery and systematic investigation of the negative temperature dependence, it was usually assumed that $E = 0$ in this formula, in the belief that the addition of free atoms or more complex paramagnetic species with unpaired spins does not require activation energy. The problem thus reduced to the calculation of the pre-exponential factor in formula (1), which is identifiable with the number of triple collisions z (possibly with an accuracy to within the steric factor $s \leq 1$, so that $A = sz$). According to Bodenstein's earliest estimate [2],

$$\frac{\tau_{12}}{\tau_\lambda} \simeq \frac{d}{\lambda} , \quad (10)$$

where τ_{12} is the duration of the ordinary (two-body) collision, τ_λ the time taken for the particle to traverse its free path, λ the mean free path, and d the diameter of the molecule. However, the fraction of the total time during which the molecule formed collides is approximately equal to the ratio of the number of three-body collisions to the total number of collisions. At atmospheric pressure it amounts to 1/1000; nevertheless Rabinowitch's experiments [75-79] showed that three-body recombination takes place more effectively.

Tolman [3] based his interpretation on the calculation of the average lifetime of the pair formed in the two-body collision when the particles approach one another to a distance not greater than δ. Then the number of elastic collisions of all the particles in an ideal gas can be calculated from Eqn. (2) if the steric factors are neglected.

Other workers proposed different versions of the calculation of the number of three-body collisions, differing mainly in the model adopted: for example, according to Herzfeld [11], the same formula is obtained but δ is treated as the average diameter of the colliding particles; according to Syrkin [178], a three-body collision occurs when all the particles are within a sphere of radius r and the formula differs somewhat from Eqn. (2). Thus all the formulae contain an undetermined parameter which characterises in one way or another the effective region of operation of intermolecular forces. In Tolman's equation (2) this parameter (δ) is defined as the maximum distance between particles 1 and 2 and 1 and 3.

It should be noted that, in the recombination of atoms in collisions with not unduly effective inert gas species even the above simplest formula gives rise to fairly good agreement with the experimental rate constants when a reasonable value of δ is chosen [108,179]. This applies of course only to the absolute value of the constant and agreement is observed only close to room temperature.

Over a wider range, Eqn. (2) is naturally inconsistent with experiment, since it does not constitute a general expression for the rate constant; this is evident if only from the fact that it predicts an increase of the rate constant with temperature as $\sqrt{T}$†. Furthermore, the interpretation of the higher effectiveness of certain third bodies (for example, benzene or a number of other hydrocarbons) on the basis of formula (2) alone would require anomalously high kinetic diameters [180]. Rabinowitch [15] gave a detailed interpretation of his own experiments and those which he carried out together with Wood [76-79] on the recombination of atoms (A + A → product), using the simple collision theory and thus avoiding the difficulties associated with the indeterminacy of the kinetic diameter of the excited molecule $d_{A_2^*}$ in Steiner's treatment [6]. When the two possible recombination mechanisms were taken into account, i.e. (A + A) + M → product and (A + M) + A → product, the total number of three-body collisions leading to recombination was obtained:

$$z = 4\sqrt{2}\,\pi d_{AM}^2 d_{AA}^2 \frac{RT}{m_A}\sqrt{\frac{m_A + m_M}{m_M}}\,N_A^2 N_M (2\tau_{AA} + \tau_{AM})\beta \quad , \quad (11)$$

where τ_{AA} and τ_{AM} are the lifetimes of the corresponding complexes and β is the effectiveness (the "steric factor")‡. Assuming that the experimental rate constant is equal to the number of collisions determined in this way, Rabinowitch calculated from the experimental data the value of $(2\tau_{AA} + \tau_{AM})\beta$. In Table 9 these values are quoted together with later results for A = I; they are somewhat too high, but in general they express correctly the tendency for the given quantity to increase on going to more complex third bodies.

This simple analysis of the recombination process in three-body collisions clearly shows that the high effectiveness of the latter (relative to Bodenstein's initial estimate) depends not so much on the diameter as on the large difference between the distance over which the interaction begins and the distance of closest approach of the particles. Rabinowitch's explanation of the much higher values of τ calculated from experiments with benzene and pentanes, based on "sticky" collisions between the atom and M, is more likely than the possibility of anomalously large cross-sections of the vibrational deactivation of A_2^* by these molecules (ET mechanism).

In the more general form, when account is taken of all possible mechanisms of the termolecular reaction A + B + C → product and the steady-state concentrations of the binary complexes AB, BC, and CA are calculated initially, the model of an elastic spherical collision leads to the following formula for the experimental rate constant [181]:

$$k = s_C z_{AB.C} z_{AB} \tau_{AB} e^{-E_C/RT} + s_A z_{BC.A} z_{BC} \tau_{BC} e^{-E_A/RT} + s_B z_{CA.B} z_{CA} \tau_{CA} e^{-E_B/RT} \quad , \quad (12)$$

Here z_{AB}, $z_{AB.C}$, etc. are the numbers of two-body collisions between the initial particles and between the binary complex and the third particle, τ_{ab} etc. are the lifetimes of the corresponding binary complexes, which are equal to the reciprocals of their decomposition rate constants, and s are steric factors. Incidentally, even this simple treatment shows that, in general, with a rigid model the steric factors for trimolecular reactions should be lower than for bimolecular reactions [182]. Indeed, Eqn. (12) shows that $s_C = s_{AB} s_{AB.C}$ if AB etc. are species actually produced in the process, the formation of which is characterised by a particular steric factor in each case.

Table 9. Experimental values of $10^{13}(2\tau_{AA} + \tau_{AM})\beta$ (seconds).

A	Third body M										Refs.
	He	H_2	Ar	N_2	O_2	CH_4	CO_2	C_5H_{12}	neo-C_5H_{12}	C_6H_6	
Br	0.64	1.2	2.0	3.2	4.5	3.4	6.9				15
I	1.2	1.7	5.0	7.3	12.5	9.6	20.0			84	15
I			3.0					36	32		125

Then $s_{AB.C}$ is the steric factor of the AB + C collision under the condition that AB has in fact formed, i.e. it expresses the conventional probability of the configuration AB...C. Since, from their nature, both s_{AB} and $s_{AB.C}$ are less than unity, it is clear that s_C is less than s_{AB}. If the effective activation energies E_A, E_B, and E_C are low, the steric factors, which are themselves functions of temperature, may have a marked influence on the temperature variation of the rate constant [182,183].

The explanation of the properties of three-body recombinations based on the simple kinetic model involving collisions of structureless particles is of course primitive and constitutes only a first approximation. However, in many simple systems it leads to reliable estimates and helps in extracting useful information from experimental data.

However, we may mention here one difficulty which is common to all three-body recombination theories and which has still not been completely overcome–the problem of the so called "statistical factor". Let us consider as an example the thoroughly investigated recombination of iodine atoms. It is known [184] that two I atoms in the ground electronic state $^2P_{3/2}$ may interact with formation of molecules in the states $^1\Sigma_g^+$, $^1\Pi_u$, and $^3\Pi_{2u,1u}$ whose potential energy curves have minima. The assumption that recombination can give rise only to the ground molecular state $^1\Sigma$ would imply the introduction of a statistical factor of 1/16 in the expression for the rate constant; allowance for other electronic states increases this factor. According to Rabinowitch [15], the interaction of recombining atoms begins at very long distances, for which the energy differences between the curves are very small, so that the perturbing effect of the third body may ultimately lead to a transition from the unstable to a stable curve and then in general any collision of two atoms in the presence of an approaching third particle may be effective for stabilisation and all statistical limitations should be removed. Probably this is an overstatement, but so far there exists no single view concerning this problem and various workers make different allowances for the statistical effect.

†Strictly speaking in a real gas the temperature variation of z according to Eqn. (2) is less pronounced because the diameters vary in accordance with Sutherland's formula:

$$d^2 = d_\infty^2\left(1 + \frac{C}{T}\right) \quad .$$

‡In a more general derivation account must of course be taken of the fact that $\beta \neq$ const for the two types of collisions, i.e. the corresponding factor should be replaced by $2\tau_{AA}\beta_1 + \tau_{AM}\beta_2$. The experiments of Christie et al. [120] showed that in the recombination of iodine $\beta_1 < \beta_2$ (the best values are $\beta_1 = 0.04$ and $\beta_2 = 0.7$).

2. Three-body Recombination of Particles and the Theory of Equilibrium Reaction Rates. Application of the Surface Potential Function. Certain Modifications of the Collision Theory and Analysis of the Trajectories

The determination of the rate constant for an elementary chemical process by methods of the transition state theory (TST) requires detailed information about the interaction between the reacting particles. This interaction is usually represented by a potential energy surface [185].

Both the general methods of construction and the properties of potential surfaces are well known as are the solutions for many specific problems within the framework of TST; [9,186] therefore we shall confine ourselves here to certain general features characteristic of the class of reactions with which we are dealing.

It has been shown [9] that in many cases the state of a three-atom system having minimum potential energy is colinear—all three atoms are located on a single straight line (we may note that in systems with an inert third atom there is also a possibility that other configurations are effective in stabilising the molecule formed). For a colinear system, the construction of a potential energy surface is particularly convenient, and the process may be readily interpreted. Fig. 4 presents such surfaces, describing the combination of atoms A + B + C → AB + C in two cases: when the atoms B and C interact to a considerable degree and when they almost do not interact at all.

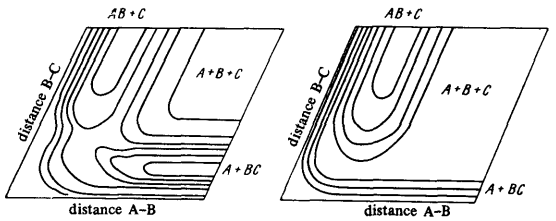


Figure 4. Potential energy surfaces for three-body recombination reactions: *a*) atoms B and C interact chemically; *b*) atoms B and C scarcely interact.

The flat "plateau" in the upper right-hand corner corresponds to the completely dissociated state; if the two atoms form a bond, then a deep "valley" is obtained in the figure, which is parallel to the corresponding coordinate axis when the distance from the third body is very large. Let us consider the first case. If the representative point rolls from the plateau straight into the AB + C valley, then transverse motions, i.e. vibrations, can return it to the plateau and the reaction will not occur. A stable molecule is formed only when the point rolls into the AB + C valley at an appropriate angle, i.e. with a sufficient store of translational and vibrational energy, and crosses the ridge into the product valley; then the translational energy is transformed into vibrational energy. If B and C interact fairly strongly, then the valley parallel to the abscissa axis is deeper and the ridge separating it from the product valley is relatively low, which leads to high effectiveness of C as the third body. It is precisely this case that is realised, for example, in the recombination H + H + H → product (cf. Section II, subsection 1). On the other hand, if the third atom is inert (Fig. 4*b*), the A + BC valley is shallow, the plateau is very wide, and for the reaction to occur the point must reach the region with curved equipotential lines (pathway 1): otherwise the point will be "reflected" from the lower edge of the valley (pathway 2). This imposes more severe limitations on the angle at which the point would leave the plateau, significantly reducing thereby the probability of the reaction. Gershinowitz [187] constructed the exact potential energy surface for the particular case of the H + H + He collision; the probability of the reaction was indeed found to be relatively low. A similar study was also made by Rabinowitch [15].

Eyring et al. [54] calculated the rate constants for the recombination of three hydrogen atoms by TST methods:

$$k = \gamma \frac{g^{\neq}}{g_i} \cdot \frac{[2\pi(m_1+m_2+m_3)\,kTh^{-2}]^{3/2}\prod_{j=1}^{3}(1-e^{-h\nu_j/kT})^{-1}}{(2\pi m_1 kTh^{-2})^{3/2}(2\pi m_2 kTh^{-2})^{3/2}(2\pi m_3 kTh^{-2})^{3/2}} \cdot \frac{8\pi^2 \mathcal{J}^{\neq} kT}{h^2 \sigma^{\neq}} H\bar{v} \cdot \quad (13)$$

In this formula the superscript ≠ denotes quantities referring to the activated complex, γ is the transmission coefficient, g the electronic degeneracy, $\mathcal{J}^{\neq}$ the moment of inertia, ν_j the vibration frequency, $\sigma^{\neq}$ the symmetry number, and $\bar{v} = (kT/2\pi\mu)^{1/2}$ the average velocity with which the point intersects the symmetry axis of the corresponding potential energy surface [9,186]. The factor H constitutes the vibrational component of the partition function of the activated complex, which is responsible for the energy distribution in the latter leading to reaction. Eqn. (13) follows from the more general formula derivable from TST for the rate constant of any trimolecular reaction [8]:

$$k = \gamma \frac{kT}{h} \frac{Q_{(A\ldots B\ldots C)^{\neq}}}{Q_A Q_B Q_C} e^{-E_0/RT} \quad (14)$$

where $Q_{(A\ldots B\ldots C)^{\neq}}$, Q_A, Q_B, and Q_C are the partition functions of the activated complex and the total partition functions of the initial species and E_0 is the zero-point activation energy.

Eyring et al. [54] constructed the potential energy surface on the assumption that in the H–H interaction the Coulombic integral amounts to 14% of the total bond energy § and is independent of the distance. This assumption is permissible, since in calculations of this kind only a relatively small region of the configurational space near the activated state is important (incidentally, this is why analogous assumptions are possible also for certain other parameters). Several additional assumptions concerning the geometry and frequencies of the activated complex permitted the complete calculation of the rate constant, which proved to be 3.1×10^{15}. Eyring et al. [54] also considered the possibility of a different configuration of the activated H...H...H complex—in the form of an equilateral triangle. Then the rate of formation of H_2 proved to be less; nevertheless the correction for the possible non-linear configuration may bring still closer together the theoretical and experimental values.

The application of TST methods makes it particularly convenient to consider the problem of the pre-exponential factor associated with the rate constant as expressed by the Arrhenius formula (1) or obtained directly from formula (14). The point is that, for a wide class of reactions with low activation energies, it is in fact the variation of the pre-exponential factor (or more correctly the steric factor) that is responsible for the temperature variation of the rate constant at fairly high temperatures. This effect

§The possibility of making such estimates has already been discussed [108] (Appendix II).

of the pre-exponential factor may be very large. For example [182], in the general case of a trimolecular reaction (between complex species) the pre-exponential factor in Eqn. (14) varies with temperature as $\varphi(T)/T^5$, where $\varphi(T)$ denotes the contribution of the vibrational partition functions; thus if the vibration frequencies are high, the pre-exponential factor decreases with temperature in proportion to $1/T^5$.

The method developed by Stepukhovich and co-workers [188-192] for bimolecular reactions permits the calculation of the pre-exponential and steric factors provided that the geometry and the frequencies of the activated complexes are known (or postulated), without the necessity of knowing the activation energy. This method is applicable also to trimolecular reactions. Since the number of three-body collisions varies with temperature as $\sqrt{T}$, one can write according to Eqn. (2).

$$E_{exp} = E_0 + \frac{1}{2}RT \ , \qquad (15)$$

$$E_{exp} = E_0 + RT^2 \frac{d \ln A^{\neq}}{dT} \ , \qquad (16)$$

where $A^{\neq}$ is the pre-exponential factor in Eqn. (14); then comparison of this equation with the formula $k = sze^{-E/RT}$ yields the following expression for the steric factor:

$$s = \gamma \frac{kT}{h} \frac{1}{z} \frac{Q_{(A\ldots B\ldots C)^{\neq}}}{Q_A Q_B Q_C} \exp\left\{\frac{1}{2} + T\frac{d}{dT} \ln \frac{Q_{(A\ldots B\ldots C)^{\neq}}}{Q_A Q_B Q_C}\right\} \ . \qquad (17)$$

Stepukhovich and Umanskii [182] applied this method and Eqn. (17) in the approximate calculation of pre-exponential and steric factors and the rate constants for the three-body recombination of halogen atoms in collisions with inert gas atoms on the basis of the hypothesis of a triangular configuration of the activated complex. It was assumed that the bond between the halogen atom and the inert gas atom is of the van der Waals type and that the energy of this bond is approximated by the 12-6 Lennard-Jones potential [193,194]:

$$\varepsilon(r) = 4\varepsilon_0 \left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^{6}\right] \ , \qquad (18)$$

where ϵ_0 is the depth of the potential well and σ_0 the distance over which the potential becomes zero (attraction and repulsion forces are equal). In order to estimate σ_0 and ϵ_0 for halogen atoms, values taken from the viscosity data for the nearest inert gas were used, the interaction parameters being calculated according to the following rules [193]:

$$\sigma_0^{12} = \frac{1}{2}(\sigma_0^1 + \sigma_0^2); \ \varepsilon_0^{12} = (\varepsilon_0^1 \varepsilon_0^2)^{\frac{1}{2}}. \qquad (19)$$

Assuming that the position of the inert gas atom in the complex corresponds to the lowest potential energy of the system, it is possible to determine the characteristic vibration frequencies of the weak van der Waals bonds:

$$\nu = \frac{1}{2\pi}\sqrt{\left(\frac{\partial^2 \varepsilon}{\partial r^2}\right)_{r_0}/\mu} = \frac{3 \cdot 2^{1/3}}{\pi \sigma_0}\sqrt{\frac{\varepsilon_0}{\mu}} \ , \qquad (20)$$

where $r_0 = 2^{1/6}\,\sigma_0$ is the equilibrium interatomic distance.

The steric factors calculated by Eqn. (17) for the reactions 2I + M → product and 2Br + M → product proved to be similar and of the order of 10^{-3} at room temperature, i.e. indeed lower than for bimolecular reactions between atoms. This was in fact to be expected on the basis of of what has been said in Section II, subsection 2. Furthermore, the steric factors were found to increase approximately linearly with temperature, which is contrary to their behaviour in bimolecular reactions. From the standpoint of thermodynamics, such variation indicates that the entropy of activation increases with temperature, i.e. the configurational disorder of the activated complex increases to a greater extent than the disorder of the initial state. Within the framework of the concept of two stages in trimolecular reactions, this implies that the second stage, in which the activated complex is formed from a large number of species and breaks down like a complex species, is rate-determining. The higher is the temperature, the more rapid is the breakdown of the complex. An increase of temperature has the same effect as in monomolecular reactions, although the latter have a positive entropy of activation. The classical pre-exponential factor $A = sz$ increases with temperature together with the steric factor.

We shall now examine the contradictions to which Semenov drew attention [108] using as an example the reaction $Br_2 + M \rightleftharpoons 2Br + M$. It consists in the fact that the equilibrium constant for this process calculated from the ratio of the rate constants for the forward and reverse stages is consistent with the experimental value only under the condition that the steric factor for the dissociation reaction is 10^2, which is unlikely on physical grounds. Indeed, per molecule $k_{rec} \simeq 10^{-32}$ and for binary collisions $z_2 \simeq 10^{-10}$, so that we should have

$$K = \frac{(Br)^2}{(Br_2)} = \frac{s_2 z_2 e^{-Q/RT}}{k_{rec}} \simeq s_2 \cdot 10^{22} e^{-Q/RT} \ , \qquad (21)$$

where Q is the heat (however, in this expression it is assumed that $E_{rec} \simeq 0$, so that $E_{diss} = Q$). At the same time, the equilibrium constant is well known from independent data:

$$K = \frac{(Br)^2}{(Br_2)} \simeq 10^{24} e^{-Q/RT} \ . \qquad (22)$$

The above contradiction can be simply and naturally resolved in the light of the concept of steric factors. The equilibrium constant must be written in the form

$$K = 10^{24} e^{-Q/RT} = \frac{k_{diss}}{k_{rec}} = \frac{s_2 z_2}{s_3 z_3} \frac{e^{-E_s/RT}}{e^{-E_s/RT}} = \frac{s_2 z_2}{s_3 z_3} e^{-Q/RT} \ . \qquad (23)$$

Assuming that z_2 and z_3 are 10^{-10} and 10^{-32} respectively, we obtain for the ratio of the steric factors corresponding to dissociation and recombination $s_2/s_3 \simeq 10^2$, which can be accounted for by the above calculations, showing that $s_3 \simeq 10^{-3}$. The point is that at moderate temperatures the steric and energy factors approximately cancel out¶:

$$\frac{1}{s_3} \simeq e^{-E_s/RT} \ ,$$

and because of this the rate constant is indeed of the same order of magnitude under these conditions as the classical (Tolman) number of collisions [Eqn. (2)]. This fact, already mentioned in section III, subsection 1, can now be fully understood†.

The method described was also used [183], with a somewhat modified model of the activated complex, to interpret the trimolecular homogeneous chain termination reaction $H + O_2 + M \rightarrow HO_2 + M$ in the chain hydrogen combustion process [108,109,118]. The rate constant calculated for this reaction with M = Ar agrees very well with the experimental data of Clyne and Thrush [113] (Table 5). We may

¶For the recombination of halogen atoms in collisions with inert gas atoms, $E_0 = 2$–3 kcal mole^{-1}.

†Keck [195] showed by a statistical procedure that the rate constant for the recombination process at low temperatures must be close to the classical number of three-body collisions.

note that this calculation allows some improvement in the solution of the problem of the temperature variation of the upper explosion limit, which is regulated by the competition between this reaction and the chain-branching reaction $H + O_2 \rightarrow OH + O$.

Umanskii and Stepukhovich [196] calculated the kinetic characteristics of certain other reactions of the type $A + BC + M \rightarrow ABC + M$. An analogous approach may be employed to interpret the effect of the third body in the recombination of radicals at low pressures, where the rate is determined by the "pure" third-order constant. Umanskii and Stepukhovich [196,197] suggested that in the second stages of radical recombination by ET and RMC mechanisms the same activation complex is formed. Then the three-body recombination rate constants (at low pressures) are

$$k^{ET} = A^{\neq}\left(\frac{E^*}{RT}\right)^{m-1}\frac{1}{(m-1)!}\ , \qquad (24)$$

$$k^{RMC} = A^{\neq}\exp\left(\frac{\Delta E}{RT}\right)\ , \qquad (25)$$

the expressions involving the same pre-exponential factor $A^{\neq}$ defined by the TST formulae. E^* is the energy distributed among m internal degrees of freedom in the first stage of the ET mechanism and ΔE the energy of formation of the radical-molecular complex.

It is qualitatively clear that the energy transfer mechanism is more likely in the recombination of complex radicals, since it postulates the formation of an intermediate compound with a larger number of internal degrees of freedom and consequently with a longer lifetime (at least in the case of simple third bodies).

Here the concept of the "loose" activated complex was employed [194,198,199]. It is now generally accepted that in bimolecular radical recombination reactions a complex of this kind is in fact involved. Nevertheless in the early studies [15] it was shown that, whereas the number of two-body collisions of relatively simple particles may be fairly well estimated on the basis of rigid molecular models, it is evident that no three-body collisions can involve absolutely rigid molecules. This applies to an even greater extent to complex polyatomic species‡.

On the basis of these considerations, the third-rate order rate constant for the symmetrical recombination of certain alkyl radicals with straight-chain [200] and branched-chain [200] structures and the rate constants for unsymmetrical recombination [197] were calculated. In the latter case it was found that, if in the reaction $R' + R'' + M \rightarrow$ product, the recombining radicals differ markedly in the degree of their complexity, the rate constant may greatly exceed the geometrical mean of the constants for the symmetrical recombination reactions $R' + R' + M \rightarrow$ product and $R'' + R'' + M \rightarrow$ product. The pre-exponential factors for all these reactions proved to be very similar. The steric factor was found to be lower than for atomic recombination due to increase in steric hindrance. Generalising the results of the above discussion of steric factors for three-body recombination reactions involving various species, one may conclude that the following characteristic features obtain:

Recombination of atoms: $s \simeq 10^{-3};\ \frac{ds}{dT} > 0$,

Recombination of atoms with simple molecules: $s \simeq 10^{-3} - 10^{-4};\ \frac{ds}{dT} \simeq 0$,

Recombination of complex radicals: $s \leqslant 10^{-5};\ \frac{ds}{dT} < 0$.

‡The considerations adduced above concerning the relation between the steric factors for trimolecular and bimolecular reactions do not of course refer to the free activated complex model.

The knowledge of the calculated third-order rate constants permit the prediction of the pressure ranges where the order of the reaction changes provided that the experimental second-order rate constants describing the recombination at high pressures [197] are known. The characteristic transition pressure is higher the higher the temperature and the simpler the recombining radicals and the third body.

Examination of the elementary step characteristic of TST, with the aid of the potential energy surface was subsequently applied also in combination with various simplified interaction models whereby the dynamics of three-body collisions may be described mathematically. We may note, for example, the idealised theory of atomic recombination proposed by Jepsen and Hirschfelder [201]. In this theory the calculation of the rate of recombination of atoms in a colinear three-body collision requires the determination of the individual collision trajectories in order to find the fraction of activated complexes decomposing into recombination products. These authors examined an idealised interaction potential for three atoms located on a single straight line in the form

$$V = v(r_{12}) + v(r_{23})\ , \qquad (26)$$

the potential $v(r)$ being approximated by the rectangular potential well model. The potential energy surface corresponding to this model is shown in Fig. 5*a* in skewed coordinates (the angle between the axes is 60°, since the masses of all three atoms are assumed to be identical).

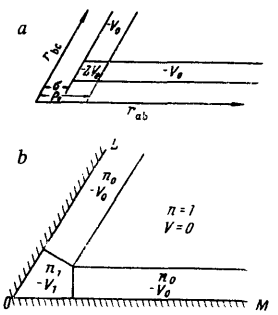


Figure 5. Potential energy surface in the idealised theory [201].

The surface consists of a plateau in the upper right-hand corner (dissociated state), two "trenches" with sheer walls parallel to the coordinate axes (two possible associated states), and a "well" in the lower left-hand corner of the diagram (activated complex or a metastable triatomic molecule). However, in order to facilitate the calculations, a somewhat different surface was employed (Fig. 5*b*) and for the sake of generality the depth of the well V_1 was assumed to be arbitrary. The motion of the representative point with a specified energy E over such a surface exhibits complete analogy with geometrical optics if a refractive index $n = [(E - V)/E]^{1/2}$ is assigned to each part of the surface. This motion is characterised by a linear trajectory which undergoes reflection and refraction at the discontinuities in the potential. It is limited by the internal region of the angle *LOM* in Fig. 6*a* ("the region of motion"), and the trajectories can be studied particularly

conveniently when this region is expanded on the kaleidoscope principle (Fig. 6*b*). The task thus reduces to the determination of the flux of representative points per unit time across the DB_0E line which ensures recombination, i.e. the corresponding trajectories no longer re-emerge from the region of bound states.

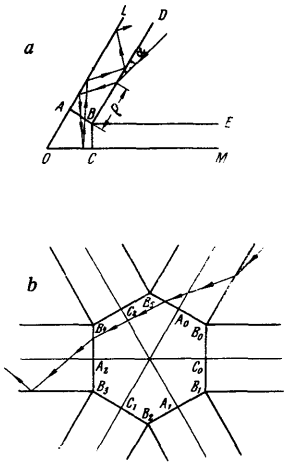


Figure 6. Idealised theory[201]. Trajectory of the representative point: *a*) in the "region of motion"; *b*) in the expanded form.

The aim of any treatment of this kind reduces to finding a formula for the frequency of the effective three-body collisions where only the masses and diameters of the reacting species are included as parameters (we may recall that simple kinetic formulae for the number of three-body collisions contain an undefined parameter characterising the region of operation of intermolecular forces). In his discussion of the contribution of essentially simultaneous three-body collisions to the overall rate of recombination, Smith[202] holds the same view. For a symmetrical description of the motion of three particles in a six-dimensional space, we must construct three three-dimensional cylinders representing the pair interactions between atoms (a "cut off" potential of pair interaction is considered). These cylinders intersect in the region S near the origin of coordinates where all three species interact simultaneously. In those parts where there is no interaction the trajectory is linear and it can enter the region S either directly ("pure" three-body collision) or indirectly, passing first through one of the cylinders and forming a diatomic complex before collision with a third particle. The determination of an effective collision cross-section requires the determination of a geometrical section through the region S. Smith[202] gives an approximate estimate of this section for the case where two of the three reacting atoms are identical. Comparison of the results of the calculations with the experimental data of Christie et al.[121] for the reaction 2I + M → product (Table 4) showed that at 293°K the effectiveness of the simultaneous three-body collisions in the recombination is of the order of 10^{-2}–10^{-3} (1/44 for M = Xe and 1/720 for M = He), the effectiveness being greater the closer is the mass of the third body to that of the recombining atom.

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