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Negative Temperature Coefficient in Chemical Reactions

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A systematic analysis of reactions whose rate decreases with increase of temperature is presented. The possibility of a negative temperature coefficient in the elementary reactions is examined from the standpoint of the transition state theory and of collision theory. The mechanisms of complex reactions in which the temperature dependence of the rate is anomalous are discussed, and possible reasons for the anomaly are examined.
The bibliography contains 175 references.

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I. INTRODUCTION

Temperature is one of the most important factors affecting the rate of chemical reactions. The temperature range of chemical reactions in nature is very great: from a few tens of degrees Kelvin in interstellar clouds to thousands of degrees in flames, electrical discharges, etc. We need means of calculating the rates of processes at temperatures where experimental measurements are difficult or impossible. One usually assumes that if the rate constant measured at room temperature is very high (equivalent to 10% or more of the collision frequency) the activation energy is close to zero, and the rate of the reaction is almost independent of temperature. However, often this assumption is an oversimplification, and in many cases it is simply not true[1]. This can have serious consequences when attempts are made to extrapolate experimental results over a wide temperature range.

For most reactions the rate increases with temperature according to the Arrhenius equation

$$k=A\exp(-E_a/RT), \qquad (1)$$

where k is the rate constant, A is the pre-exponential factor, and E_a is the experimentally determined activation energy. However, there are many reactions whose rate decreases with increase of temperature, in obvious contradiction of the Arrhenius equation. There have been no attempts so far to discuss systematically the reactions which have a negative temperature coefficient (NTC) and to analyse the causes of the phenomenon, yet the need for such a review is urgent, both from the theoretical and from the practical point of view. Thus the rate of a reaction with a NTC could decrease very considerably on raising the temperature. A process which is predominant at moderate temperatures may be replaced (partially or fully) by competing processes with normal temperature coefficients. Conversely, a decrease in temperature should cause greater selectivity towards these reactions, and this may be important both under laboratory and under industrial conditions.

The NTC phenomenon is of interest also in astrophysics and in the physics and chemistry of the upper atmosphere, because the rate of reaction in those environments could increase by many orders of magnitude when the temperature

is lowered by hundreds of degrees[2]. Evidently, allowance for these anomalous temperature effects is needed, for example, in models of processes in interstellar clouds, of the reactions involved in the destruction of ozone in the stratosphere, etc.

Reactions with NTC are of interest also in chemical reaction theory, since many of their features are incompatible with classical chemical kinetics (collision theory and transition state theory). Therefore an analysis of these reactions could be important as a test of the theory of elementary chemical reactions, of exact or semi-empirical methods of calculating the dynamics of molecular interactions, etc.

Lastly, we note that in chemical kinetics a knowledge of the formal parameters of the rate equation (for example, the order with respect to each of the reactants) is very important in establishing the mechanism of the reaction. The detection of a NTC and the study of its origin can give valuable information on the reaction mechanism. However, it is important to remember that the NTC phenomenon could be due to the reaction itself (i.e. to its mechanism) or it could be merely a manifestation of "external" factors (an increase in the concentration of reactants caused by a decrease in temperature of the solution, the temperature dependence of the physicochemical properties of the solvent, etc.). These topics also will be discussed in this review.

A NTC was first reported for the termolecular reaction $2NO + O_2 \rightarrow 2NO_2$: together with a few similar reactions; this was treated as a rare exception, especially since the temperature coefficient was small in absolute value. However, mainly as a result of the development of sensitive new methods for monitoring the kinetics of fast reactions and of various methods for generating active species[3], the number of gas-phase reactions in which the temperature dependence of the rate is anomalous has increased in recent years. The number of reactions of this type discovered in the liquid phase and studied by traditional methods has also increased. This review will be concerned mainly with studies of the NTC published during the last 10 years, but we shall also discuss some of the older work to give the reader a more balanced view of the problem, since there are no suitable bibliographies.

II. THEORETICAL VIEWS ON THE NATURE OF THE NEGATIVE TEMPERATURE COEFFICIENT IN SIMPLE REACTIONS

1. Formal Methods of Describing the Temperature Dependence of the Rate of Chemical Reactions

In 1889 Arrhenius proposed an empirical equation to describe the temperature dependence of the rate constant of chemical reactions [Eqn.(1)]. The equation had an enormous success and became one of the fundamental equations of physical chemistry, for at least two reasons. Firstly, the vast majority of experimental data could successfully be fitted to a straight line in the Arrhenius coordinates ($\ln k$, $1/T$). As recently at the 1950's it was stated that "there are no data on unimolecular or bimolecular reactions which cannot be described by the Arrhenius equation within likely experimental error[4]". Secondly, the development of the theory of absolute reaction rates (the "activated complex" or "transition state" theory)[5] has given a clear physical meaning to the empirical parameters A and E_a.

Most of the early kinetic measurements were confined to a narrow range of temperature, for which the parameters (A and E_a) of Eqn.(1) can be treated as temperature-independent. It was difficult to encompass a wider temperature range because the conventional kinetic methods could not be used to measure rates differing by more than two orders of magnitude. For example, it was recently assumed[6] that the minimum error in the determination of the activation energy for the addition of atoms and radicals to alkenes, alkynes, and arenes in the gas phase was 4–8 kJ mole^{-1}, with a corresponding error in A between 0.6 and 1.2 litre mole^{-1} s^{-1} at 350 K. (The method of calculating mean values and standard errors of the rate constants and of their temperature dependence are discussed in Ref.7.) In many cases the reaction kinetics could be described by Eqn.(1) only because of the low precision of the determination of the rate constants and of the relatively narrow temperature range.

Improved techniques in experimental kinetics led to more precise values of the rate constants over a wider temperature range (by up to an order of magnitude). In some cases Eqn. (1) was found to apply over the extended temperature range. The "record" in this respect can be claimed by the reaction of hydrogen atoms with ethane, which obeys the Arrhenius relationship between 330 and 1350 K.[8] However, in many other reactions the Arrhenius equation was not applicable, especially in some gas-phase exchange reactions and in dissociation and recombination reactions[9]. Indeed, it has been suggested[9] that improvements in experimental techniques and theoretical developments will force us to consider not why some Arrhenius plots are curved but the very opposite problem: why so many experimental Arrhenius plots are found to be rectilinear.

The experimentally observed failure (or near-failure) of Arrhenius equation to describe various types of reaction may be due to the following factors.

1. In reactions with low or vanishingly small activation energies (or, in general, for $E_a \ll RT$) the temperature dependence of the rate constant is mainly (or even wholly) determined by the temperature dependence of the pre-exponential term A, whereas in reactions with a high activation energy the dependence of A on temperature is almost totally masked by the exponential term in the Arrhenius equation. As a result the formal application of Eqn.(1) gives a curvilinear plot, and the E_a value determined over a limited range of temperature cannot be identified with the true activation energy[10].

2) The parameter A in Eqn.(1) is not constant over a wide range of temperature, introducing a curvature into the plot of $\ln k$ against $1/T$ for any activation energy. This problem is reviewed in detail for reactions in the gas phase in Ref.9, and more generally in Ref.11, which discusses the temperature dependence of the "experimental" activation energy.

3) The Arrhenius equation assumes that the temperature of the system is uniquely defined and can be measured during the reaction. This assumption is valid if the translational and rotational degrees of freedom of the molecules are in equilibrium (or nearly so), i.e. if T is the thermodynamic equilibrium temperature. In real systems this condition is not always met, especially in the reactions taking place at high temperatures behind the front of a shock wave, in an electric arc, etc. At low temperatures deviations from the equilibrium distribution are found in fast reactions, for example in some reactions between ions and neutral molecules[12]. In these cases the rate of the process is a function of the quantum states and of the velocities of the reacting particles, and a special approach is needed[13].

In a wider range of reactions the formal application of Eqn.(1) leads to negative values of the activation energy E_a, from −1 to −40 kJ mole^{-1} or more. The statistical interpretation of the activation energy as the difference between the average energies of the activated and of the non-reacting molecules[14] formally allows the activation energy to be

negative. However, it is almost inconceivable that the activated molecules could contain less energy than the non-reacting molecules, since the activation process consists in raising the energy of a particle with respect to its normal state[15]. For this reason many workers have stated (in different ways) that a negative activation energy is physically meaningless, at least in the case of an elementary bimolecular reaction[1,2,15–19]. It is therefore preferable to use the concept of a NTC than to attempt to define a negative activation energy.

The failure of the Arrhenius equation to describe an increasing number of systems has stimulated a search for other mathematical relationships between the rate constant and the temperature of reactions. The best known is the three-parameter equation[20]

$$k = AT^n \exp(-E_a/RT) \qquad (2)$$

or

$$\ln k = A' + n \ln T - E_a/RT, \qquad (2a)$$

The three-parameter equation is theoretically justified[11] (the collision theory giving $n = 1/2$ and the transition state theory giving $n = 1$), but its application requires very precise measurements of the rate constants over a wide temperature range[7].

A simplified form of Eqn.(2) is often used for reactions with small, zero, or "negative" values of the activation energy:

$$k = A(T/T_0)^n, \qquad (3)$$

where T_0 is an arbitrary fixed temperature (for example, 298 K). In reactions with a NTC the parameter n is negative in Eqns.(2) and (3). In many systems a linear plot of $\ln k$ against $\ln T$ was obtained by Eqn.(3) over a wide range of temperature (up to 500 K), whereas in Arrhenius coordinates the plot was not linear[2].

A four-parameter $k(T)$ dependence has also been proposed[21] ($k = A \cdot \exp(-B/T) + C(T/T_0)^n$), as well as a polynomial in powers of temperature[11]. However, these equations have not been widely used, partly because of their excessive formality and partly because of the difficulties encountered in determining their parameters exactly and interpreting them physically.

Some workers have used an alternative presentation of their results: for example, by Eqns.(1) and (3) simultaneously. Often the same experimental data are described equally well by different types of equation. As an example we may quote a series of gas-phase reactions involving the t-butyl cation, which were shown[22] to obey Eqn.(3) with $n = -3$ between 190 and 570 K. In order to establish the extent to which the validity of Eqn.(3) excludes Eqn.(1), i.e. the existence of an activation energy, the authors[22] re-calculated their results by Eqn.(2a) for different assumed values of E_a, and for each E_a they chose the value of n which gave the best agreement with experiment. For $E_a > 8$ kJ mole^{-1} agreement could not be obtained with any combination of the parameters, but for $E_a = 8$ kJ mole^{-1} agreement was obtained with $n = -6$. This means that if these reactions have an activation energy it must be small. The choice of the correct equation for the temperature dependence of the rate constant is relatively unimportant for interpolation of experimental data within the experimental temperature range, but it becomes important if the data have to be extrapolated over a wider range of temperature.

2. The Negative Temperature Coefficient in the Transition State Theory

The theory of the transition state was developed for bimolecular gas-phase reactions[5]. Various mechanism are possible for the elementary act of bimolecular reactions (rebound, direct dislodgment, stripping, or pick-up)[23,24]. In the transiton state theory only a rebound mechanism of the A + BC → [A...B...C]$^{\neq}$ → AB + C type is usually considered. Let us examine the possibility of a NTC in a reaction of this type.

We should note first of all that a NTC is unusual in an elementary bimolecular reaction[25]. Most bimolecular processes have a significant activation energy, i.e. the temperature dependence of the reaction rate is determined by the exponential term in the canonical equation of the transition state theory:

$$k = \kappa \frac{k_B T}{h} \left(\frac{Q^{\neq}}{Q_A Q_B} \right) e^{-\frac{E_0}{RT}}, \qquad (4)$$

where κ is the transmission coefficient of the activated complex through the energy barrier E_0, k_B is Boltzmann's constant, h is Planck's constant, and $Q^{\neq}$, Q_A, and Q_B are the full partition functions for the activated complex and the initial reactants. If $E_0 \gg RT$ the temperature dependence of the pre-exponential term can be ignored. In the opposite limit ($E_0 \ll RT$) the temperature dependence of the reaction is determined by the ratio of the partition functions. In intermediate cases ($E_0 \cong RT$) both terms make a contribution, and a more complex temperature dependence of the reaction rate can be expected.

In the transition state method any inaccuracy in the choice of the activation barrier has a much stronger effect on the calculated rate constants than the uncertainty in the geometric parameters of the activated complex, which are used to calculate the partition functions. Therefore the transition state method is used only to calculate the pre-exponential factor in the Arrhenius equation[24]. Let us consider the cases in which a NTC can be expected, and its likely magnitude.

Obviously, a NTC in a bimolecular reaction can be expected only through the temperature dependence of the pre-exponential term in Eqn.(4), which is determined by the ratio of partition functions on the assumption that $\kappa = 1$. Usually the contribution from nuclear and electronic terms can be ignored, and the translational, rotational, and vibrational partition functions per degree of freedom can be expressed by the equations[5]

$$q_t = (2\pi m k_B T)^{1/2}/h, q_r = (8\pi^2 I k_B T/\sigma h^2)^{1/2},$$

and

$$q_v = [1 - \exp(-h\nu/k_B T)]^{-1}$$

It follows from these formulae that $q_t \propto T^{1/2}$ and $q_r \propto T^{1/2}$ always, whereas $q_v \propto T^0$, i.e. it is independent of temperature, for high-frequency vibrations and low temperatures ($h\nu \gg k_B T$), and $q_v \propto T$ for low-frequency vibrations and (or) high temperatures ($h\nu \ll k_B T$). Thus the result depends both on the vibration frequency and on the temperature[26]. For example, at 80 K $q_v \cong 1$ for practically all the frequencies of molecular vibrations, whereas at 300 K $q_v = 1.0000005$ for $\nu = 3000$ cm^{-1}, 1.008 for $\nu = 1000$ cm^{-1}, and 1.097 for $\nu = 500$ cm^{-1}, so that the error caused by assuming $q_v \cong 1$ is greater than 10% only for frequencies lower than 500 cm^{-1}. In molecules of moderate complexity the number of low-frequency vibrations is small, and therefore the q_v value begins to deviate significantly from 1 only at high temperatures, where the condition $k_B T \ll h\nu$ is not satisfied.

The ratio $Q^{\neq}/Q_A Q_B$ has been determined[27], together with the temperature dependence of the pre-exponential, for some bimolecular reactions with different configurations of the reactants in the activated complex. It was assumed in the calculations that the formation of the activated complex is

accompanied by the loss of three translational degrees of freedom in one of the reactants and by the appearance of new vibrational degrees of freedom, including one in the direction of the reaction coordinate. This low-frequency vibration is responsible for the appearance of the factor k_BT/h in formula (4). It is also assumed that the reactants and the activated complex can rotate as a single entity: for example, in the reaction between an atom and a linear molecule with a linear activated complex two rotational degrees of freedom (each) from the reactants and the complex cancel.

Table 1. Temperature dependence of the pre-exponential factor A for different types of bimolecular reaction.

No.	Reactants and activated complex*	A	$A(T)$	
			$h\nu \gg k_BT$	$h\nu \ll k_BT$
1	A + A → (AK)$_{lin}$	$(k_BT/h)(q_t^2/q_t^3)$	$A \sim T^{1/2}$	$A \sim T^{1/2}$
2	A + M$_{lin}$ → (AK)$_{lin}$	$(k_BT/h)(q_V^2/q_t^3)$	$A \sim T^{-1/2}$	$A \sim T^{3/2}$
3	A + M$_{lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)(q_Vq_r/q_t^3)$	$A \sim T^0$	$A \sim T^1$
4	A + M$_{non\text{-}lin}$ → (AK)$_{lin}$	$(k_BT/h)(q_V^3/q_t^3q_r)$	$A \sim T^{-1}$	$A \sim T^2$
5	A + M$_{non\text{-}lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)(q_V^2/q_t^3)$	$A \sim T^{-1/2}$	$A \sim T^{3/2}$
6	M$_{lin}$ + M$_{lin}$ → (AK)$_{lin}$	$(k_BT/h)(q_V^4/q_t^3q_r^2)$	$A \sim T^{-3/2}$	$A \sim T^{5/2}$
7	M$_{lin}$ + M$_{lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)(q_V^3/q_t^3q_r)$	$A \sim T^{-1}$	$A \sim T^2$
8	M$_{lin}$ + M$_{non\text{-}lin}$ → (AK)$_{lin}$	$(k_BT/h)(q_V^5/q_t^3q_r^3)$	$A \sim T^{-2}$	$A \sim T^3$
9	M$_{lin}$ + M$_{non\text{-}lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)(q_V^4/q_t^3q_r^2)$	$A \sim T^{-3/2}$	$A \sim T^{5/2}$
10	M$_{non\text{-}lin}$ + M$_{non\text{-}lin}$ → (AK)$_{lin}$	$(k_BT/h)(q_V^6/q_t^3q_r^4)$	$A \sim T^{-5/2}$	$A \sim T^{7/2}$
11	M$_{non\text{-}lin}$ + M$_{non\text{-}lin}$ → (AK)$_{non\text{-}lin}$	$(k_BT/h)(q_V^5/q_t^3q_r^3)$	$A \sim T^{-2}$	$A \sim T^3$

*Symbols. A is an atom, M$_{lin}$ and M$_{non\text{-}lin}$ are linear or non-linear molecules, AK is the activated complex.

The results of the calculation and estimates of possible temperature dependences of the pre-exponential are given in Table 1. We note that an inverse temperature dependence of the pre-exponential is theoretically possible, and that the effect is most marked for reactions at moderately high temperatures involving complex molecules giving a non-linear activated complex without low-frequency vibrations, i.e. for $h\nu \gg k_BT$. Under these conditions the exponent in Eqns.(2) and (3) becomes† $n = -2$. If Eqn.(3) is used to describe the temperature dependence of the reaction rate the negative values of n obtained according to Table 1 are easily converted into "negative activation energies" by the formula $E_a = nRT$.

Thus according to the transition state theory the magnitude of the NTC should increase as the temperature increases. The maximum possible NTC at 300 K ($n = -2$) corresponds to $E_a = -5$ kJ mole^{-1}, and therefore the presence of even a small activation barrier can fully compensate the inverse temperature dependence of the pre-exponential. Hence according to transition state theory a NTC can be expected for bimolecular reactions with a small (or zero) activation energy (for example, reactions involving free radicals). From the standpoint of the transition state theory the NTC phenomenon has been analysed for the addition of OH$^\cdot$ radicals to unsaturated compounds[28,29] as well as the addition of oxygen atoms[1] and other atoms and radicals[6], and for the reaction of NO with BrO$^\cdot$ [30] and with $CH_3OO^\cdot$.[31]

† Case 10 in Table 1, which gives $n = -2.5$, is hardly likely to be realisable in practice.

The formulae in Table 1 give only an approximate estimate of the pre-exponential because of the incorrectly assumed equality of the partition functions of the reactants and of the activated complex[32]. The change in the vibrational partition functions accompanying the formation of the activated complex was allowed for in an analysis[32] of the temperature dependence of the steric factor in the expression $A = Pz$, where A is the pre-exponential terms P is the steric factor, and z is the frequency factor: it was found that for simple unimolecular reactions the parameter P is only weakly temperature-dependent. For example, in the decomposition of ethane P increases approximately 10-fold when the temperature is increased from 300 to 400 K, but the effect is completely masked by the increase of 2^{10} in the Boltzmann factor.

For bimolecular reactions the dependence of the steric factor on temperature was found to be

$$\mathrm{d}\ln P/\mathrm{d}T = -3{,}5/T - (h^2c^2/k_B^2T^3) \times \times \sum \{\nu_i^2 \exp(h\nu_i/k_BT)/[\exp(h\nu_i/k_BT) - 1]^2\} , \quad (5)$$

where ν_i are the vibration frequencies, and terms in the summation appear with the "plus" or "minus" sign according to whether they refer to the reactants or to the activated complex. Thus a negative temperature coefficient of the steric factor is a characteristic feature of bimolecular reactions. In replacement reactions at $T > 273$ K the second term in formula (5) can be ignored, so that $\mathrm{d}\ln P/\mathrm{d}T = -3.5/T$, i.e. $P \propto T^{-3.5}$. The frequency factor varies with temperature according to the law $z \propto T^{1/2}$, and therefore in this type of reaction we expect $A \propto T^{-3}$.

When analysing the temperature dependence of $Q^{\neq}/Q_AQ_B$ we must also allow for possible internal rotations in the reactants and in the activated complex. Several gas-phase reactions between ions and neutral molecules have been examined from this standpoint[2,22,26,33,34]. In the expression for the ratio of the full partition functions only the q_V values corresponding to vibrational degrees of freedom unchanged by the transition from the reactants to the activated complex were retained. However, the initial molecules may have internal rotational degrees of freedom (for example, the rotation of methyl groups). The formation of the activated complex converts some of the internal rotations of the reactants into torsional vibrations of the complex, which contribute an additional term to the temperature dependence of the pre-exponential.

The following expression has been obtained[26] for the temperature dependence of the rate constant:

$$k = CT \frac{(T_t^{\neq})^{3/2}(T_r^{\neq})^{j/2}}{\prod_i (T_t)_i^{3/2}(T_r)_i^{j/2}} T_{\text{int.rot.}}^{\Delta r/2} \exp(-E_0/RT) , \quad (6)$$

where C includes the temperature-independent terms, Δr is the total number of new internal rotations, i.e. the difference between the number of new internal rotational degrees of freedom in the activated complex and the number of frozen internal rotational degrees of freedom in the reactants, $j = 0$ for atom reactions, $j = 2$ for linear molecules, and $j = 3$ for non-linear molecules, and the subscript to T indicate the origin of the various temperature terms. It is assumed (to simplify the problem) that the torsional vibrations of the activated complex produced by the suppression of the internal rotations have a fairly high frequency and do not contribute significantly to the temperature dependence of the rate constant: for this reason Eqn.(6) does not include explicitly a term for this vibration. For the opposite assumption each low-frequency torsional vibration would contribute a temperature-dependent term, and in the limit of $\nu \to 0$ we would obtain the $q_V \propto T$ dependence.

The temperature dependences of the pre-exponential factor calculated with the above assumptions for bimolecular reactions of atoms and molecules with different configurations of the reactants and of the activated complex are given in Table 2. Unlike the data in Table 1, those in Table 2 show that the absolute value of the NTC depends on the complexity of the reacting molecules. Thus the maximum NTC (for negative Δr) will be observed when the largest number of internal rotations in the reactant molecules is suppressed without forming new internal rotations in the activated complex. This can be expected in rigid activated complexes: in "loose" complexes the reactants retain their rotational degrees of freedom and the temperature dependence of the pre-exponential is weak. The parameter Δr can be calculated from experimental data. Thus the temperature dependence $k \propto T^{-3}$ mentioned above for the reaction of the t-butyl ion with isopentane[22] can be compared with the equation $k \propto T^{(\Delta r - 4)/2}$ (last line in Table 2), giving $(\Delta r - 4)/2 = -3$, and $\Delta r = -2$, which corresponds to the suppression of only two internal degrees of freedom in the activated complex. At the same time if a rigid activated complex is formed in the same system up to six internal rotational degrees of freedom can be frozen, and in general the model can be used to interpret experimental data without difficulty[22].

Table 2. Temperature dependence of the pre-exponential factor for bimolecular reactions allowing for the loss of internal rotations in the activated complex.

No.	Reactants and activated complex*	$A(T)$
1	$A + A \rightarrow (AK)_{lin}$	$A \sim T^{1/2}$
2	$A + M_{lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-1)/2}$
3	$A + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{\Delta r/2}$
4	$A + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-2)/2}$
5	$A + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-1)/2}$
6	$M_{lin} + M_{lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-3)/2}$
7	$M_{lin} + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-2)/2}$
8	$M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-4)/2}$
9	$M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-3)/2}$
10	$M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$A \sim T^{(\Delta r-5)/2}$
11	$M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$A \sim T^{(\Delta r-4)/2}$

*Symbols as in the footnote to Table 1.

Let us now examine termolecular reactions in terms of the transition state method. These reactions include the recombination of atoms and simple radicals. The NTC phenomenon was observed in the recombination of halogen atoms[35–40], in the reactions $H^{\cdot} + O_2 + M \rightarrow HO_2^{\cdot} + M$ [41] and $OH^{\cdot} + NO_2 + M \rightarrow HNO_3 + M$ (where M is any third body able to take up the excess energy),[42] and also in some processes accompanied by light emission in which electronically excited particles are first formed[43]. Some reactions involving NO have also been classified as termolecular[44,45]. Lastly, the termolecular mechanism probably applies to some reactions involving ions, for example $N^+ + N_2 + He \rightarrow N_3^+ + He$;[26] many of these reactions have a high NTC (see Refs. 46–48 for experimental data on their kinetics).

In termolecular reactions the total number of participating atoms is usually small, internal molecular rotations are usually absent, and the temperature dependence of the pre-exponential factor can be calculated as in Table 1. From the formulae thus obtained (Table 3) we note that the transition state theory predicts the possibility of a NTC for any termolecular reaction. There is no energy barrier to the recombination of atoms, and therefore according to the theory we can expect a NTC for these reactions in the form of Eqn. (3), with $n = -1$ or $n = -1/2$.

Table 3. Temperature dependence of the pre-exponential factor in termolecular reactions.

No.	Reactants and activated complex*	A	$A(T)$	
			$h\nu \gg k_BT$	$h\nu \ll k_BT$
1	$A + A + A \rightarrow (AK)_{lin}$	$(k_BT/h)(q_t^2q_v^3/q_t^6)$	$A \sim T^{-1}$	$A \sim T^{2}$
2	$A + A + A \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_r^3q_v^3/q_t^6)$	$A \sim T^{-1/2}$	$A \sim T^{3/2}$
3	$A + A + M_{lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^5/q_t^6)$	$A \sim T^{-2}$	$A \sim T^{3}$
4	$A + A + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_rq_v^4/q_t^6)$	$A \sim T^{-3/2}$	$A \sim T^{5/2}$
5	$A + M_{lin} + M_{lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^7/q_t^6q_r^2)$	$A \sim T^{-3}$	$A \sim T^{4}$
6	$A + M_{lin} + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_v^6/q_t^6q_r)$	$A \sim T^{-5/2}$	$A \sim T^{7/2}$
7	$M_{lin} + M_{lin} + M_{lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^9/q_t^6q_r^4)$	$A \sim T^{-4}$	$A \sim T^{5}$
8	$M_{lin} + M_{lin} + M_{lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_B/Th)(q_v^8/q_t^6q_r^3)$	$A \sim T^{-5/2}$	$A \sim T^{7/2}$
9	$M_{lin} + M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^5/q_t^{10}q_r^5)$	$A \sim T^{-9/2}$	$A \sim T^{9/2}$
10	$M_{lin} + M_{lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_v^9/q_t^6q_r^4)$	$A \sim T^{-4}$	$A \sim T^{5}$
11	$M_{non\text{-}lin} + M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{lin}$	$(k_BT/h)(q_v^{12}/q_t^6q_r^7)$	$A \sim T^{-11/2}$	$A \sim T^{13/2}$
12	$M_{non\text{-}lin} + M_{non\text{-}lin} + M_{non\text{-}lin} \rightarrow (AK)_{non\text{-}lin}$	$(k_BT/h)(q_v^{11}/q_t^6q_r^6)$	$A \sim T^{-5}$	$A \sim T^{6}$

*Symbols as in the footnote to Table 1.

A stronger temperature dependence should be observed for reactions involving complex molecules. The maximum value ($n = -11/2$) of the NTC is found in case 11 of Table 3 for a zero activation energy and no low-frequency vibrations ($q_V \propto T^0$, i.e. it is independent of temperature). However, if a reaction of this type has a small positive activation energy the rate constant will go through a maximum[5,49]. The condition for a maximum in the function $T^n \exp(-E_0/RT)$ gives $T_{max} = -E_0/nR$. The greater the activation energy for a given n, the higher the temperatures at which a NTC will be observed. For example, for $n = -5$ and $E_0 = 8$ kJ mole^{-1} the NTC will be found at $T > 200$ K. In the presence of low-frequency vibrations, when q_V increases with temperature, the NTC effect may be compensated by the contribution from the vibrational partition functions. Thus we note from Table 3 that the q_V terms appear in the numerators of the formulae for the pre-exponential factor raised to a high power, so that the positive temperature dependence will increase steeply with temperature, as shown in Table 3 by the second limiting value (when $h\nu \ll k_BT$ and $q_V \propto T$).

We can allow for the low-frequency vibrations as follows[5,49]. Consider, for example, the reaction of three linear molecules with a non-linear activated complex (case 8 of Table 3, which can be realised by the reaction between NO and O_2). For this reaction Eqn. (4) becomes

$$k = \varkappa C T^{-7/2} \left\{ \prod_{j=1}^{11} [1 - \exp(-h\nu_j/k_BT)]^{-1} \Big/ \prod_{i=1}^{3} [1 - \exp(-h\nu_i/k_BT)]^{-1} \right\} \times \exp(-E_0/RT), \quad (7)$$

where the term C includes all the temperature-independent factors, the subscripts i denote the reactants, and j denotes the activated complex, in which 1 of 12 vibrational degrees

of freedom is converted into the reaction coordinate. Eqn. (7) can be re-written

$$\frac{d}{d(1/T)} \ln \{k\Pi [1-\exp(-h\nu_i/k_B T)]^{-1} T^{7/2} / \Pi [1-\exp(-h\nu_j/k_B T)]^{-1}\} = -E_0/R \quad (8)$$

Thus a plot of the polynomial

$$\ln k + \ln \Pi [1-\exp(-h\nu_i/k_B T)]^{-1} - \ln \Pi [1-\exp(-h\nu_j/k_B T)]^{-1} + {}^7/_2 \ln T$$

against reciprocal temperature should give a straight line of slope $-E_0/R$. This approach allows us to calculate the "true" activation energy from the experimental dependence of the rate constant on temperature[49,50]. The calculation assumes a knowledge of all the vibration frequencies in the initial molecules and in the activated complex.

In termolecular reactions involving complex molecules we can allow for the internal rotations of non-linear activated complexes as was done for bimolecular reactions. For example, in case 8 of Table 3 the addition of one free rotation to the activated complex converts the $T^{-7/2}$ term into T^{-3} in formula (8). If the initial molecules are diatomic the frequencies are high enough to make the corresponding q_V values independent of temperature, leading to a simplified form[49] of Eqn.(8):

$$\frac{d}{d(1/T)} \left\{ \ln k + 3 \ln T - \ln \prod_{j=1}^{\bar{r}} [1-\exp(-h\nu_j/k_B T)]^{-1} \right\} = -E_0/R \ .$$

Thus in the framework of the transition state method the conditions for the appearance of a NTC in simple bimolecular and termolecular reactions are the following: a small or zero activation energy (the NTC can be expected mainly in fast reactions[51]), the absence of low-frequency molecular vibrations, which produce compensation of the NTC for $h\nu \ll k_B T$, and the suppression of the internal rotations of the reactant molecules without forming new internal rotational degrees of freedom in the activated complex. More detailed discussions of problems in the activated complex theory are given in Refs.52–68.

The requirements on the activation energy must be examined specifically, because the conventional expression for the rate constant does not successfully predict the temperature dependence of the rate of reactions with a small or zero activation energy[55,56]. This has been demonstrated, for example, by analysing more than 60 elementary reactions in the gas-phase photochlorination of various compounds[54]. Several workers have pointed out[58] the shortcomings of the Rice–Ramsperger–Kassel (RRK) theory, which uses a model with a fixed activated complex to calculate the partition functions of the transition state in elementary reactions of the radical recombination type[59,60]. The limitations of the standard transition state theory when applied to reactions with a low or zero activation energy stimulated the development of new methods of calculation in which the position of the activated complex on the reaction coordinate is chosen near the maximum in the free energy rather than in the potential energy[55,57], or by using empirical parameters[61,62].

We should also note that the transition state theory and its corollaries are very sensitive to the assumed structure of the activated complex, especially in the case of low-frequency vibrations[9,30]. In many cases the experimental data can be described satisfactorily (including the appearance of a NTC) by postulating a set of "reasonable" parameters for the activated complex, but in other cases the observed inverse dependence of the reaction rate on temperature can only be explained by the transition state theory by ascribing unrealistic properties to the activated complex (for example, chemical bonds stronger than those of the initial molecules[1,67]). In these cases it is always assumed that the transmission coefficient in formula (4) depends on temperature[9,68].

Great care is needed[17,44] in applying the transition state theory to termolecular reactions, since most of the formally "termolecular" reactions take place by a complex mechanism rather than in a single step. Hence many of the dependences listed in Table 3 have only a theoretical significance.

3. The Negative Temperature Coefficient in the Collision Theory

Consider the temperature dependence of the rate constant of a reaction in terms of the classical collision theory[11]:

$$k = Pz \exp(-E_0/RT) \ . \quad (9)$$

This expression allows only for the translational degrees of freedom, and the molecules are treated as hard spheres. Formula (9) shows that the classical collision theory is incompatible with the NTC phenomenon, since both the energy term and the collision factor ($z \propto T^{1/2}$) increase with temperature. The steric factor P is usually assumed to be independent of temperature. For fast reactions with small or zero E_0 values the rate is determines by the pre-exponential factor $A = Pz$. If $A \propto T^n$, where n is a small positive number, the rate constant given by the simple collision theory will vary with temperature like the transport coefficients of the system, which are usually proportional to $T^{1/2}$ (viscosity, thermal conductivity) or to $T^{3/2}$ (diffusion)[69].

The development of theoretical and of experimental methods for studying fast bimolecular reactions resulted in the insertion into the formula of a reaction cross-section which is a function of the energy of the reactants[70]. In this case the temperature dependence of the rate constant is a function not only of the temperature dependences of the frequency factor z and of the Boltzmann factor $\exp(-E_0/RT)$, but also of the dependence of the reaction cross-section on the energy of the particles, which is related to temperature. If the energy of the molecules has its equilibrium distribution, the expression for the rate constant is[71]

$$k = (\pi\mu)^{-1/2} (2/k_B T)^{3/2} \int_0^\infty \sigma(E) E \cdot \exp(-E/k_B T) \, dE \ , \quad (10)$$

where μ is the reduced mass of the two reacting molecules, E is the relative translational energy, $\sigma(E)$ is the energy-dependent reaction cross-section, i.e. the probability of a collision between two particles having the relative energy of translational motion resulting in reaction. The parameter σ is sometimes called the "excitation function": its dimensions are cm^2 $molecule^{-1}$. Eqn.(10) implies that the reaction cross-section is unaffected by the internal states of molecules.

By introducing the function $\sigma(E)$ into the collision theory it became possible to describe formally many experimental data on the kinetics of elementary reactions[72]. In reactions with a barrier $E_0 \gg RT$ the Maxwell–Boltzmann distribution "selects" for the reaction only those molecules for which the reaction cross-sections correspond to the energies of the reacting pairs near the barrier ($E \cong E_0$). In this case the number of collisions between particles with $E \gg E_0$ is negligibly small, i.e. the reaction is confined to the "tail" of the energy distribution of the molecules, and the effect of the $\sigma(E)$ function can be ignored as in the classical collision theory.

In reactions with a small or zero threshold energy E_0 the exact form of the $\sigma(E)$ dependence becomes important. In principle these dependences can be determined both theoretically and experimentally. The former method relies either on quantum-chemical calculations or on the method of classical trajectories[23,70,72], in which the classical equations of motion are integrated numerically for given interaction potentials and initial conditions.

Important advances have been made in recent years in the theoretical calculation of reaction rates by analysing the trajectories of motion of reacting species. The calculations assumed a model interaction potential: this implies constructing the potential energy surface and solving the dynamic problem of the motion of the reacting particles on this surface (for example, by using classical mechanics). In these calculations the rate constants are obtained directly from the parameters of the intermolecular interactions, and they can be used to calculate $\sigma(E)$. Calculations by the classical trajectories method have given important results (in particular, on the dependence of the reaction cross-section on the energy of the reactants), but their description of the system is at best semi-quantitative because they often rely on arbitrary initial potentials[24].

As an example of this type of calculation we shall examine the reaction $D^{\cdot} + I_2 \rightarrow DI + I^{\cdot}$.[73] The calculations suggest that the vast majority of the collisions between deuterium atoms and iodine molecules cause a transition through the col of the potential energy surface, but only 30% of the collisions lead to reaction. In the remaining collisions the heavy iodine atoms are unable to move apart even by a distance of ~0.1 Å, and the deuterium atom passing through the saddle point of the potential surface rapdily reaches the far steep side, loses energy, and "slips" back into the region of the reactants. This phenomenon is characteristic of reactions between light atoms and heavy molecules: it is due to the fact that the relative velocity of the approaching deuterium and iodine atoms is much greater than the velocity with which the two atoms move apart in the iodine molecule. It is possible that, as the velocity of approach of the reactants increases, a steadily smaller proportion of the light atoms is able to negotiate the bend in the potential surface after passing through the saddle point, and this effect could be responsible for the appearance of a NTC of the reaction rate.

Calculations of the classical trajectories for elementary bimolecular reactions between particles of similar mass indicated that even in these reactions the cross-section can fall as the energy of the colliding particles increases[74]. However, the rate of decrease of the function $\sigma(E)$ is insufficient to account for a NTC of the rate constant, because the decrease in $\sigma(E)$ with temperature is masked by the positive temperature dependence of the collision frequency[67]. On the basis of these calculations[74] it was concluded that a NTC is unlikely to be found in an elementary bimolecular reaction between neutral molecules. However, a NTC has been observed experimentally in this type of reaction[75–78]. In other reactions (for example, the reaction of ions with neutral molecules) the possibility of the function $\sigma(E)$ decreasing fast enough with increase of E to cause a NTC of the reaction rate cannot be excluded. Further calculations with more precise interaction potentials are needed to reach unambiguous conclusions.

The second approach to formulating the function $\sigma(E)$ is to determine it experimentally, either from molecular beam experiments[70] or by a reverse transformation of kinetic data for the rate constant[75]. Methods of calculating rate constants from a given function $\sigma(E)$ are discussed in Ref.71.

Experimental or calculated data on the function $\sigma(E)$ for specific reactions are still scarce, and we usually need to rely on a defined model. Let us analyse some models from the standpoint of the possible existence of a NTC in the corresponding reaction.

Model 1. We assume that $\sigma(E)$ is a delta-function:

$$\sigma(E)=\sigma_0 \quad \text{for} \quad E=E_0,$$
$$\sigma(E)=0 \quad \text{for} \quad E \gtrless E_0,$$

i.e. that the reaction can take place only at the reactant energy E_0.[1] In this case we obtain from Eqn.(10)

$$k=(\pi\mu)^{-1/2}(2/k_B T)^{3/2}\sigma_0 E_0 \exp(-E_0/k_B T),$$

and if the activation barrier is small the temperature dependence is determined by the term $T^{-3/2}$. This model is not likely to apply to a real system because it is difficult to see how a reaction could be confined to a single value of the energy of the reactants (or even to a narrow band).

Model 2. Expressing the function $\sigma(E)$ as[11,72]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C \quad \text{for} \quad E \geqslant E_0,$$

where $C = \pi(r_A + r_B)^2$, and r_A and r_B are the effective radii of the molecules, leads to the following expression for the rate constant:

$$k = 2(r_A + r_B)^2(2\pi k_B T/\mu)^{1/2}(1 + E_0/k_B T)\exp(-E_0/k_B T).$$

If the probability of the reaction is independent of the excess energy of the reactants above the threshold value we have $k \propto T^{1/2}$ for $E_0 \ll k_B T$, and for $E_0 \gg k_B T$ the temperature dependence of k is determined by the term $T^{-1}\exp(-E_0/k_B T)$, and stays positive because of the rapid increase of the Boltzmann factor with temperature.

Model 3. This is a more realistic model, in which the reaction cross-section depends on the energy of the reactants. One of the simplest of these models assumes that the reaction between the reactants (represented as hard spheres) takes place when the relative energy of the particles along the collision line exceeds the threshold value E_0, and that the reaction cross-section increases to a limiting value of $C = \pi(r_A + r_B)^2$ as the energy increases above the threshold[9,24,72,77]:

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C(1-E_0/E) \quad \text{for} \quad E \geqslant E_0.$$

It is assumed that the barrier is surmounted only by virtue of the relative energy of translational motion, and that the reaction probability is independent of the way in which the vibrational energy is distributed in the molecules. In this case Eqn.(10) becomes

$$k=2(r_A+r_B)^2(2\pi k_B T/\mu)^{1/2}\exp(-E_0/k_B T),$$

giving the classical formula of the collision theory. This is formally analogous to an Arrhenius with an activation energy $E_a = E_0 + RT/2$. This model gives a poor description of processes with energies near the threshold, or with very large energies[9].

So far we have examined models in which the reaction cross-section increases with the energy of the reacting molecules, or stays constant. Experiments with crossed molecular beams have shown that in many reactions $\sigma(E)$ increases from zero at some threshold energy E_0 and rapidly reaches a maximum before falling again. Obviously, a decrease in the probability of reaction as the energy of the molecules increases can lead to a NTC. Let us examine the models of the reaction cross-section which allow for the possibility of a decrease of $\sigma(E)$ with increase of E.

Model 4. In reactions with a small or zero activation energy the dependence of the cross-section on energy takes the simple form[11,72,75]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=CE^n \quad \text{for} \quad E \geqslant E_0,$$

where C = const. This type of dependence is found, for example, in reactions of molecules with ions, where in most cases $n = -0.5$ ("Langevin cross-section", which never

leads to a non-equilibrium distribution of the molecular velocities[80]). In general this model gives a complex expression for the rate constant and the experimental activation energy E_a.[72] For integral and half-integral values of n the expressions become simpler and can be formulated analytically or tabulated in the usual way. If the reaction has no threshold energy ($E_0 = 0$ and $\sigma(E) = CE^n$) we have $E_a = 0$ for $n = -0.5$ and $E_a < 0$ for $n < -0.5$, i.e. we have a NTC.[75] The steeper the decrease of $\sigma(E)$ with temperature, the greater is the NTC. For example, for $n = -1.25$ a $k \propto T^{-0.17}$ dependence was found[75], and for $n = -1.5$ the dependence was $k \propto T^{-1}$. Plots of E_a against temperature for different values of n are given in Ref.72.

Model 5. The cross-sections of many reactions between neutral molecules can be fitted to the function[11,72]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C(E-E_0)^n\cdot\exp[-m(E-E_0)] \quad \text{for} \quad E\geqslant E_0,$$

where C = const, and m, $n > 0$. The presence of an exponential term ensures that as the energy E increases, the function $\sigma(E)$ goes through a maximum at $E = E_0 + n/m$, and then decreases again at a rate determined by the parameter m. In general the dependences of k and E_a on temperature are also complex, and therefore we shall limit the discussion to a few special cases. Thus for $m = n = 0$ the model reduces to model 2. If $m = 0$ the function $\sigma(E)$ can only increase with E, and in this case a NTC is not observed. If $m \neq 0$, E_a is always negative at high enough temperatures, and for $m \gg 0$ the function $\sigma(E)$ approaches the delta-function of model 1. Under these conditions $E_a = E_0 - 3RT/2$. Lastly, if the threshold energy is high enough ($E_0 \gg RT$) we have $E_a \cong E_0 + RT(n - 1/2)$, and only a positive and weakly temperature dependent activation energy can be expected. In the opposite limit, when the threshold energy is zero, $\sigma(E) = CE^n\cdot\exp(-mE)$, and the activation energy is always finite and temperature-dependent: $E_a = RT(n + 1/2) - m(n + 2)(RT)^2/(1 + mRT)$. If $mRT \gg 1$ a NTC is observed: $E_a = -3RT/2$.

Model 6. This model is similar to model 5, and is used to describe reactions between hard spherical molecules: in contrast to model 3, we put $\sigma(E) \to 0$ for $E \to \infty$:[11,72]

$$\sigma(E)=0 \quad \text{for} \quad E<E_0,$$
$$\sigma(E)=C[(E-E_0)^n/E]\exp[-m(E-E_0)] \quad \text{for} \quad E\geqslant E_0$$

where C = const. Model 3 is therefore a special case of model 6, for $n = 1$ and $m = 0$.

The general expression for the rate constant is very complex in this model, and the activation energy is $E_a = E_0 + RT(n - 1/2) - m(n + 1)(RT)^2/(1 + mRT)$, so that the observed activation energy can be both positive and negative.

All these models can lead to unexpected results, incompatible with the classical collision theory. For example, in model 6 with $m = 0$ and $n \gg 1$ at high temperatures the activation energy can be much higher than the threshold energy, so that E_a becomes temperature-dependent. For $m \neq 0$, when the function $\sigma(E)$ goes through a maximum, the activation energy at high temperatures is always negative. This form of the function is especially important in reactions with a low threshold energy E_0, because in this case the NTC phenomenon is observable even at intermediate temperatures. For reactions with $E_0 = 0$ model 6 gives $\sigma(E) = CE^{n-1}\cdot\exp(-mE)$, which is essentially the same as the corresponding expression for model 5. The compatibility of model 6 with the Arrhenius equation and the reality of the various n values are discussed in Ref.79.

In the last three models the reaction probability decreases as the energy increases. This is because both the translational and the internal energy of the colliding particles contribute to the reaction[2,81]. For example, the probability of the reaction K + HCl → KCl + H decreases almost 2-fold for a one-quantum increase in the rotational angular momentum with J = 1–4.[82]

The physical significance of the form of the function $\sigma(E)$ in models 4–6 can be inferred from the relationship between the absolute value of the threshold energy E_0 and the activation energy of the reaction. By inserting into the equation $E_a = RT^2(\mathrm{d}\ln k/dT)$, which follows from Eqn.(1), the value of k given by Eqn.(10) we find that the activation energy of the reaction is the difference between the average energy of the collisions leading to reaction and the average energy of all the collisions between pairs in the system[14,75]: $E_a = \bar{E}_{\text{reac}} - \bar{E}$. As we have already pointed out, in most bimolecular reactions with a large threshold energy E_0 a very small fraction of all the molecules (those in a "tail" of the energy distribution) is able to react, and we can only observe the rising branch of the $\sigma(E)$ function. Under these conditions $\bar{E}_{\text{reac}} > \bar{E}$, and the activation energy is positive. On the falling branch of the $\sigma(E)$ function (for a small or zero threshold energy) it is possible to find $\bar{E}_{\text{react}} < \bar{E}$, which formally corresponds to a negative activation energy. The physical significance of this observation is that the rate of reaction is higher for molecules whose energy is less than the average thermal energy of the molecules in the system. Increasing the temperature lowers the concentration of those molecules, and therefore it lowers the reaction rate. These effects are most marked at high temperatures.

The falling branch of the $\sigma(E)$ function is usually obtained in fast reactions (for example, in the recombination of free radicals). An interesting phenomenon is sometimes observed: a formally negative activation energy, indicating that the activation energy for the reverse process (the unimolecular decomposition into radicals) is lower than the spectroscopic dissociation energy D_0, since $D_0 = E_{\text{diss}} - E_{\text{reac}}$.[14,81,83] Expressing the temperature dependence of the recombination rate constant by the empirical relationship (3) gives $E_{\text{diss}} = D_0 - nRT$. Both phenomena (the NTC for the recombination reaction and the decrease in E_a for the reverse (dissociation) reaction) are usually observed at low pressures, and they denote the participation of the internal degrees of freedom of the molecules in the reaction. Thus the analysis of recombination reactions with a NTC relies on the theories of unimolecular decomposition for the reverse dissociation reactions: the relationship between the two processes and the development of a unified theory are specially examined in Ref.84. An analysis of the NTC in terms of the temperature dependence of the reaction cross-section has been reported[75] for the reaction between ClO˙ and BrO˙ radicals.

The analysis of termolecular reactions by the collision theory involves some fundamental difficulties. The first is that in the simplest form of the theory the reacting molecules are treated as hard spheres: in these circumstances the concept of a termolecular reaction is meaningless, since the probability of simultaneous contact between three hard spherical molecules is zero[44]. We therefore need to define more precisely what is meant by a three-body collision. For example, we could define a distance δ within which molecules are treated as colliding. The problem then becomes to calculate the probability of finding three molecules at distances not greater than δ. Alternatively we could introduce the time τ, defined as the duration of the binary collision (the life time of the quasi-molecule), and equate it (to a first approximation) to one vibration period, i.e. 10^{-13} s. The calculated frequencies of ternary collisions are 2 or 3 orders of magnitude lower than those of binary collisions[49,85,86].

This is why elementary reactions are almost invariably bimolecular: the only exceptions are the reactions which can only take place by a termolecular mechanism (for example, atom recombination reactions). As the number of participating atoms increases, the reaction adopts an "indirect" termolecular mechanism, with preliminary formation of a binary complex, and can no longer be considered to be elementary[87]. For example, instead of the reaction A + BCD + E → ABCD + E we have a two-step process, A + BCD → (ABCD)* followed by (ABCD)* + E → ABCD + E or (ABCD)* + E → AE + BCD, etc. (see theoretical analysis in Section III).

It has long been known that the simplest termolecular reactions in the gas phase (atom recombination reactions) have a NTC. This is inconsistent with the simple gas-kinetic theory of termolecular collisions, which gives[87] $k \propto T^{1/2}$. The classical collision theory is similarly unable to account for the absolute rate of these reactions, which are anomalously slow.

In the framework of the elementary termolecular mechanism the NTC phenomenon can be explained by postulating a reaction cross-section dependent on the energy of the reactants. It is usually assumed that the reaction is barrier-less, and that the function $\sigma(E)$ decreases as the temperature increases. "Head-on" collisions between three particles are very rare, and nearly all the collisions have an angular momentum, which increases with temperature. As a result, more energy is needed for the close approach, since some energy is dissipated in surmounting the rotational barrier. This lowers the effectiveness of the collisions and the probability of reaction at higher temperatures[81].

As in the case of bimolecular recombination reactions, which are associated with the reverse unimolecular dissociation reactions, termolecular reactions of the A + B + C → D + E type can be associated with the reverse bimolecular reactions D + E → A + B + C. This allows us to use one of the above models for bimolecular processes in the description of termolecular reactions, and hence to calculate their rate constants. Thus if we use model 5 for the cross-section of the bimolecular reaction we obtain four types of temperature dependence for the rate constant of the termolecular reaction[88]. The observed activation energy can be strongly temperature-dependent, and it can be either positive or negative depending on the threshold energy E_0 and on the parameters m and n of the model. For example, for $E_0 = 0$ and $0 < n \leq 1$ the rate constant has a maximum at $T = 0$ and falls monotonically to zero as the temperature rises. On the other hand if $n > 1$ with $E_0 = 0$, or if $n > 0$ with $E_0 > 0$, we have $k = 0$ at $T = 0$, after which the rate constant increases to a maximum before beginning to fall back again as the temperature is increased. In every case we can expect a NTC at high temperatures, since $k \propto T^{-3}$. The main weakness of this analysis of the possibility of a NTC in various bi- and termolecular reactions is the lack of a theoretical method of predicting reliably the form of the $\sigma(E)$ function for specific reactions.

In liquid-phase reactions the molecules react in a "cage" of solvent rather than by free collisions, as in the gas phase[89], and a "third body" is not needed to make possible a recombination reaction: the solvent can always act as the third body. For this reason it is impossible to lower the reaction cross-section in a solvent by raising the temperature.

In solutions bimolecular reactions with small activation energies are limited by diffusion, and therefore have a positive temperature coefficient of velocity. Thus, in the gas phase the recombination of perfluorinated ethyl, propyl, and butyl radicals at 297–457 K has a NTC,[90] whereas the recombination of ethyl radicals in liquid ethane at 94–154 K has a positive activation energy $E_a = +3.3$ kJ mole^{-1}, consistent with the activation energy for diffusion[91].

Termolecular processes are possible in solutions, since the solvent molecules in the "wall" of the cage can act as reactants. If the process is diffusion-limited it cannot have a NTC. On the other hand if the rate of the reaction is much lower than the rate of diffusion as a result of a large negative entropy of activation, and if the activation energy is close to zero, a NTC becomes possible, and we can use the transition state theory to express the temperature dependence of the rate constant.

Thus both the transition state theory and the collision theory predict the possibility of a NTC in elementary reaction under specified conditions. Most chemical reactions take place in a succession of steps, each of which (in theory) could have a positive or a negative temperature coefficient. The overall temperature coefficient of such reactions is discussed in the next Chapter of this review.

III. NEGATIVE TEMPERATURE COEFFICIENT IN COMPLEX MULTI-STEP REACTIONS

1. Negative Temperature Coefficient in Reactions Involving an Intermediate

The formation of an intermediate compound (complex) can lead to a NTC for the overall reaction. As in the definition of the concept of a termolecular collision we must define more precisely what is meant by a complex. It is usually assumed that if the reacting particles experience attractive forces and the energy of the reaction is not very great the reactants will form a "long-lived" intermediate compound. Direct experiments with molecular beams have shown that this does not always happen, and that reaction can take place by a direct mechanism[92]. We shall adopt as a formal criterion for the formation of a complex the ability of the reactants to remain at a mutual distance corresponding to a normal chemical bond for the duration of several rotation periods (i.e. for times of more than 10^{-12} s).[92]

In solutions the reactant molecules experience ~10^2 collisions in the solvent cage at each encounter, and therefore any encounter of a pair of reactants can be formally treated as a weak complex, A + B ⇌ AB.[85,89] For this equilibrium the rates of the forward and the reverse process and the equilibrium constant are, respectively, $w_1 = A_e[A][B]$, $w_{-1} = (1/\tau)[AB]$, and $K = A_e\tau$, where A_e is the encounter frequency and τ is the life time of the molecules in the cage.

We shall begin our analysis of the possibility of a NTC in reactions with an intermediate complex by considering the fast and reversible formation of a complex by the scheme

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB \xrightarrow{k_p} P \quad , \qquad (I)$$

where $k_1 \gg k_p$ and $k_{-1} \gg k_p$. This type of system is often found in solutions. For example, molecular donor–acceptor complexes in solution are formed almost without activation energy at rates close to the diffusion rate. However, the rapid conversion of the complex into the product can be prevented by a large negative entropy of activation even if the activation energy of this step is small: such an entropy may arise from the need to transfer the molecular complex from a state of relatively free motion to the more rigid configuration of the activated complex during the conversion of AB into the product P. We may quote as an example the diene synthesis reaction of tetracyanoethylene with 9,10-dimethylanthracene, for which a NTC has been observed in various solvents[93].

Fast and reversible complex formation is possible also in gas-phase reactions at high enough pressures if the complex is in thermodynamic equilibrium with the initial substances. We may assume that under these conditions the termolecular complex formation reaction (in which the function of the third body is to dispose of the excess energy of the complex and to stabilise it) is kinetically of the second order (k_1 corresponds to k_1^∞ in the high-pressure limit), and the monomolecular decomposition reactions of the complex by two paths are in the first-order region (k_p corresponds to k_p^∞, and k_{-1} corresponds to k_{-1}^∞).

For [B] ≫ [A] the rate of reaction (I) is given by the expression

$$d[P]/dt = k_p[AB] = k_pK[A][B]/(1 + K[B]) = k_p\alpha[A] , \quad (11)$$

where $K = k_1/k_{-1} = K_0 \cdot \exp(-\Delta H/RT)$ is the equilibrium constant, and $\alpha = K[B]/(1 + K[B])$ is the extent to which component A is bound in the complex. The temperature dependence of the reaction rate is a complex function, determined by the activation energy E_p (positive), the enthalpy of complex formation ΔH (negative), and the concentration of the reactant B. It follows from Eqn.(11) that for $K[B] \gg 1$ (strong binding, $\alpha = 1$) $d[P]/dt = k_p[A]$, and for $K[B] \ll 1$ (weak binding, $\alpha = K[B]$) $d[P]/dt = k_pK[A][B]$. For strong binding the activation energy $E_a = E_p$ is positive; for weak binding $E_a = E_p + \Delta H$, so that the observed activation energy can be either positive (for $E_p > |\Delta H|$) or negative (for $E_p < |\Delta H|$). In the latter case the initial rate of reaction or the effective rate constant, depending on [B], will increase with temperature initially, go through a maximum at the temperature

$$T_{max} = \frac{-\Delta H}{R[\ln(-\Delta H/E_p - 1) - \ln(K_0[B])]} ,$$

and decrease at still higher temperatures. Similar results are obtained for the formation of intermediates of more complex composition (for example, AB_2): under these conditions the absolute value of the NTC may be higher than for the 1 : 1 complexes, since the enthalpy of formation is usually higher in the larger complexes[94].

In many fast gas-phase reactions we find three competing processes: decomposition of the complex into the initial substances, decomposition into the reaction products, and stabilisation of the vibrationally excited complex by collision with a third particle[2,52]:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AB)^* \begin{cases} \xrightarrow{k_p} P \\ \xrightarrow[k_m]{M} AB \end{cases} . \quad (II)$$

The stationary state condition gives

$$[(AB)^*] = k_1[A][B]/(k_{-1} + k_p + k_m[M]) .$$

The expression for the reaction rate is

$$d[A]/dt = -d[B]/dt = k_1[A][B] - k_{-1}[(AB)^*] = k_1(k_p + k_m[M])[A][B]/(k_{-1} + k_p + k_M[M]) .$$

The experimentally determined rate constant of the bimolecular reaction is a complex function of the temperature and pressure of the system:

$$k_{exper} = k_1(k_p + k_m[M])/(k_{-1} + k_p + k_m[M]) . \quad (12)$$

Let us examine some special cases of scheme (II).

1) For low pressures and short life-times of the complex we have $k_m[M] \ll k_p$, and scheme (II) becomes $A + B \rightleftharpoons (AB)^* \rightarrow P$. It follows from Eqn.(12) that under these conditions $k_{exper} = k_1k_p/(k_{-1} + k_p)$, i.e. the rate constant is independent of pressure. If the predominant reaction path is the decomposition of the complex into products ($k_p \gg k_{-1}$) we have $k_{exper} = k_1$ and we observe the "forward" reaction. The possibility of a NTC for these reactions has already been discussed. This case is met, in practice, when the activation energy barrier opposing the conversion of the complex into the product is small.

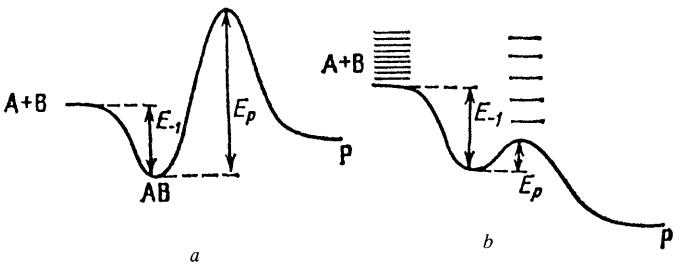


Figure 1. Energy profile of the reaction A + B ⇌ AB → P for zero vibrational level and different relative values of E_{-1} and E_p.

In the opposite limit ($k_p \ll k_{-1}$) we have $k_{exper} = k_1k_p/k_{-1}$. Since the activation barrier to the formation of the complex is usually small or zero, the temperature dependence of k_{exper} will be determined by the relative values of E_p and E_{-1}. For the temperature coefficient to be negative the energy of the activated complex for the k_p step should be lower than the energy level of the reactants ($E_p < E_{-1}$, see Fig.1). At first sight the condition $E_p < E_{-1}$ is incompatible with the condition $k_p < k_{-1}$. However, the density of energy levels for the k_{-1} reaction is much greater than the density of levels for the forward reaction (k_p) for equal internal energies (Fig.1*b*), i.e. the entropy factor strongly favours the reverse reaction and thus compensates the energy factor of the forward reaction[52,95,96]. Therefore the condition $k_p < k_{-1}$ can be satisfied even if $E_p < E_{-1}$.

In the general case ($k_p \cong k_{-1}$) the activation energy of the reaction is determined by the equation[2,97]

$$E_a = E_1 + (E_p - E_{-1})k_{-1}/(k_{-1} + k_p) ,$$

and if $E_1 \cong 0$ and $E_{-1} > E_p$ we find $E_a < 0$. This equation for E_a also shows that the absolute value of the NTC should increase with temperature, since the ratio $k_{-1}/(k_{-1} + k_p)$ increases with temperature.

Both the decomposition paths of the complex are unimolecular processes, with rate constants k_{-1} and k_p, and they can be analysed by standard methods (for example, the RRK theory[2,58,96]). The pre-exponential factors for the k_p and k_{-1} steps were calculated[67,98], and it was shown that if these factors (A_{-1} and A_p) are similar, $k_p \gg k_{-1}$, i.e. the forward reaction takes place. In order to observe the NTC associated with the reversibility of the complex formation we must satisfy the condition $A_{-1} \gg A_p$, which has been shown theoretically to be easily possible in real systems[98].

2) At high enough pressures the rate of deactivation of the complex is much greater than the rate of conversion into products ($k_m[M] \gg k_p$), i.e. scheme (II) is converted into the scheme $A + B \rightleftharpoons (AB)^* \xrightarrow{M} AB$. In this case it follows from Eqn.(12) that $k_{exper} = k_1k_m[M]/(k_{-1} + k_m[M])$; the main reaction is the association of the initial molecules A and B

into the product AB (a stable complex or molecule[28,58,99]). Stabilisation of the transition complex (AB)* usually takes place through collision with a third body, but radiative stabilisation has also been reported[58,100]. If $k_m[M] \gg k_{-1}$, we have $k_{exper} = k_1$, and we observe the "forward" reaction; if $k_m[M] \ll k_{-1}$, $k_{exper} = k_1 k_m[M]/k_{-1}$. The possibility of a NTC in these cases was discussed above.

In the general case ($k_m[M] \cong k_{-1}$) we can assume that the rate constants of the bimolecular processes k_1 and k_m are not very different from the frequency factors, and weakly dependent on temperature. Under these conditions the temperature dependence of k_{exper} will be determined by the temperature dependence of the function $1/k_{-1}$. Some workers have used the RRK theory to describe the constant k_{-1} qualitatively[2,58]: for small molecules at moderately high temperatures this gives $k_{-1} \propto T^{s-1}$, where s is the number of oscillators. Thus for small molecules $k_{exper} \propto T^{1-s}$, and if $s > 1$ this gives a NTC.[2]

Other bimolecular reaction mechanisms with formation of an intermediate complex are also possible. For example, the product may be formed from the stabilised (rather than from the excited) complex by the scheme[2] $A + B \rightleftharpoons (AB)^* \xrightarrow{M} AB \xrightarrow{C} P$. This scheme also can produce a NTC. Thus, if $[C] \ll [M]$ and $[AB] \ll [A]$ we have $k_{exper} = k_p K[M]$, whence $E_a = E_p + \Delta H$, and a NTC is observed when $E_p < |\Delta H|$, where ΔH is the enthalpy of the process $A + B \rightleftharpoons (AB)^*$.

The NTC has been attributed to the reversible formation of an intermediate complex in reactions involving atoms of oxygen and other elements of Group VI,[66,68,101,102] in the interaction between BrO· radicals[103], in the gas-phase reaction of mercury with ammonia and with hydrogen iodide[104], in proton transfer reactions of ion–molecule processes[105], and in the reactions $HO_2^{\cdot} + NO \rightarrow OH^{\cdot} + NO_2$,[106] $CH_3O_2^{\cdot} + HO_2^{\cdot} \rightarrow CH_3OOH + O_2$,[107] and $OH^{\cdot} + C_6H_5CH_3 \rightarrow$ products[108].

More complex schemes, involving several complexes[2,34], have also been used to explain experimental results.

The participation of two types of complex is postulated in many gas-phase organic reactions[33,96,109]. For example, it has been shown by the ion cyclotron resonance method that typical nucleophilic substitution reactions can be acclerated by up to 20 orders of magnitude by transition from an aqueous solution to the gas phase: this is explained by the large change in the energy profile of the reaction on changing from strongly solvated to totally non-solvated particles[109] (Fig.2). In the gas phase the approaching particles form the ($OH^- \cdot CH_3Br$) complex, which is converted into the product (with a small activation barrier) through the intermediate complex $CH_3OH \cdot Br^-$. We see from Fig.2 that under these conditions the energy profile is similar to that of Fig.1*b*. Obviously, in the gas phase the reaction should be fast, with a NTC. In an aqueous solution the reaction is slow because of the high energy barrier resulting from the difference in solvation between the reactants and the activated complex and because of the need to break down the solvation shell of the transition state. The solvation also hinders the attractive forces between the reactants and the formation of the complex.

The kinetics of a reaction in the gas phase with stepwise solvation of the reactants by one, two, etc. water molecules are discussed in Ref.109. Solvation by only two water molecules is sufficient to raise the energy barrier opposing the conversion of the complex to the level of the initial substances, or even higher (Fig.2). Thus solvation suppresses the reaction, and the NTC is replaced by a positive temperature coefficient.

In the gas phase these reactions show an effect analogous to the Polanyi–Semenov rule. A study of 22 reactions of the type of $R_1^+ + R_2H \rightarrow R_2^+ + R_1H$ (whose energy profile is shown in Fig.1*b*) has shown that the rate increases with the exothermicity of the process[33]. This effect is due to the lowering of the activation barrier in the more exothermic reactions. An even more interesting correlation is that between the parameters k and n of the equation $k = At^n$: it was found that for a fixed temperature these parameters are linearly related in a series of reactions. Therefore the slower reactions of this type have a higher NTC, and they are more strongly retarded by an increase of temperature[33].

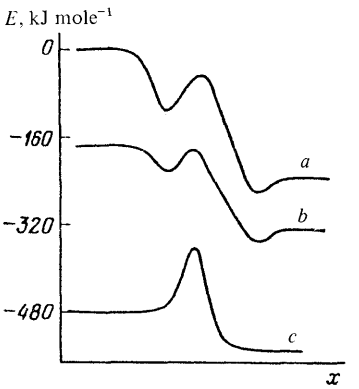


Figure 2. Energy profile of the reaction $OH^- + CH_3Br \rightarrow CH_3OH + Br^-$ for non-solvated reactants (*a*), and reactants solvated with two water molecules (*b*) or in an aqueous solution (*c*); x is the reaction coordinate.

The presence of two types of intermediate complex, mutually in equilibrium, has been suggested also for several liquid-phase reactions (for example, addition to multiple bonds[94,110]). These reactions show a NTC if the barrier to the conversion of the complex into the product is lower than the enthalpy of complex formation. The NTC phenomenon has been observed also in the gas-phase addition of hydrogen chloride to propene: in this case it was due to the reversible formation of the $(HCl)_2$ dimer and its subsequent reaction with the $C_3H_6 \cdot HCl$ complex[111].

The intermediate compound is not necessarily a complex. For example, in the scheme

$$P \xleftarrow{k_1} A \overset{K}{\rightleftarrows} B \xrightarrow{k_2} P \qquad \text{(III)}$$

A and B are isomers mutually in equilibrium, having different reactivities or different solvations. If the equilibrium is established rapidly the observed activation energy is given by the expression

$$E_a = E_1 - \frac{K}{1+K}\Delta H + \frac{Kk_2/k_1}{1+Kk_2/k_1}(\Delta H - E_1 + E_2), \qquad (13)$$

where ΔH and K are the enthalpy and the equilibrium constant for the $A \rightleftharpoons B$ process, and E_1 and E_2 are the activation energies for the conversion of A and B into the product[11]. If $|\Delta H| > |E_1 - E_2|$, for $\Delta H > 0$ and a low enough temperature ($K \ll 1$) we have $E_a = E_1$, whereas at high temperatures ($K \gg 1$) $E_a = E_2$. In either case the NTC is not observed. However, for $\Delta H < 0$ the Arrhenius dependence of the reaction rate can have several extrema, giving a NTC in some temperature ranges. Similar effects may be found in enzyme reactions when all the forms of the enzyme are present in equilibrium. Plots of the change in activation energy with temperature are shown in Ref.11.

If only one of the species reacts in scheme (III) Eqn.(13) reduces to the simpler expression $E_a = E_1 - K\Delta H/(1 + K)$ for $Kk_2/k_1 \ll 1$, or to the expression $E_a = E_2 + \Delta H/(1 + K)$ for $Kk_2/k_1 \gg 1$. In both cases a NTC can arise for certain ratios of the parameters E_1, E_2, and ΔH.

Various theories have been proposed to explain the NTC in termolecular reactions with formation of an intermediate complex (for example, the recombination of atoms and simple radicals)[81]. Most workers adopt a mechanism involving a third molecule M as well as the intermediate complex[112] (the Radical-Molecular Complex (RMC) or Intermediate Complex (IC) mechanism). If both the reactants R_1 and R_2 can form a complex with M the recombination scheme $R_1 + R_2 \rightarrow R_1R_2$ can be written, in general, as a system of many elementary steps[60,113]:

$$\begin{array}{ll} R_1 + M \rightleftarrows R_1M^* & R_2 + M \rightleftarrows R_2M^* \\ R_1M^* + M \rightleftarrows R_1M + M & R_2M^* + M \rightleftarrows R_2M + M \\ R_1M^* + R_2 \rightleftarrows R_1R_2 + M & R_2M^* + R_1 \rightleftarrows R_1R_2 + M \\ R_1M + R_2 \rightleftarrows R_1R_2 + M & R_2M + R_1 \rightleftarrows R_1R_2 + M \text{ etc.} \end{array}$$

A large number of kinetic equations is needed to describe the system fully in the general case, but far fewer equations are sufficient if $R_1 = R_2$. Even greater simplification is achieved if the equilibrium $R + M \rightleftharpoons RM$ can be assumed: in this case the recombination is third-order at low pressures and second-order at high pressures[113].

The simplified recombination scheme gives $k_{rec} = A \cdot \exp(\Delta E/RT)$ at low temperatures and $k_{rec} = A \cdot \exp[(\Delta E - RT)/RT]$ at high temperatures, where ΔE is the bond energy in the RM complex[113]. Since $\Delta E > 0$ always, we observe a NTC increasing in magnitude with the strength of the complex. For example, in the recombination of iodine atoms[44] E_a is found to vary from −5.9 kJ mole^{-1} for M = He to −22.3 kJ mole^{-1} for $M = I_2$. The complex RM is weak if M is an inert gas atom, but it can be quite strong and comparable to that in a chemical compound (for example, I—NO and I—NO_2).

Many recombination reactions have been studied over a wide range of temperature and pressure for a variety of "third molecules" (M). Heavy and complex "inert" molecules like SF_6 were found to be the most effective in recombination reactions, the NTC of the reaction increasing with the effectiveness of M. Even gases like He, Ar, and N_2 are not fully inert in practice, and they always form an RM complex[114] as well as RM_n clusters (at higher pressures[60]).

Mechanisms including the formation of an intermediate complex do not always satisfactorily describe experimental data. Thus the magnitude of the NTC is often inconsistent with the energy of the R—M bond. For example, in the reaction $I^\cdot + I^\cdot + He \rightarrow I_2 + He$ an I—He bond several times stronger than expected from the van der Waals forces had to be postulated[115]. Problems are met also in attempting to explain the temperature dependence of the activation energy of these reactions. There is no doubt that at least one more mechanism is possible for the recombination:

$$\begin{array}{l} R_1 + R_2 \rightleftarrows R_1R_2^* \\ R_1R_2^* + M \rightleftarrows R_1R_2 + M \end{array} .$$

This mechanism (Energy Transfer, or ET mechanism) competes with the formation of an intermediate complex, and it can be predominant (for example, in the NO + Cl → NOCl [116] and NO + O → NO_2 reactions[117]). This mechanism also gives a NTC, as was found above for scheme (II) with $k_m[M] \gg k_p$. In the ET mechanism the temperature dependence of the reaction rate is determined by the expression AT^n, and the observed activation energy varies with temperature ($E_a = nRT$), whereas in the intermediate complex mechanism the parameter E_a is almost independent of temperature.

The relative contribution of the two mechanisms depends on the temperature; it is difficult to extract quantitative information on the force of the R—M interaction from the temperature dependence of the recombination rate constant alone, and additional data on the dependence of k_{rec} on pressure, nature of M, etc. are needed[60]. The contribution of each mechanism depends on a number of factors: the strength of the R—M and R—R* interactions, the relative concentration of particles, and their size and complexity[87]. In the recombination of halogen atoms with M = Ar, Xe the intermediate complex mechanism is dominant at low temperatures, and the ET mechanism at high temperatures, but with M = He the latter mechanism is always predominant[114,118].

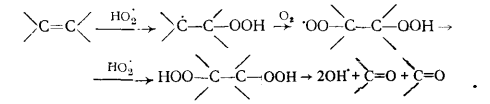
The contribution from each mechanism is harder to predict when M is a complex molecule (HCl, HBr, SO_2).[118] Keeping all other conditions the same, the relative importance of the two mechanisms is a complicated function of pressure, since clusters of M can take part in the reaction[60]. For example, in the reaction $Br^\cdot + Br^\cdot + He \rightarrow Br_2 + He$ the contribution from the ET mechanism is 40% at $p < 150$ bar and almost zero at $p > 400$ bar. In the presence of other M molecules the intermediate complex mechanism is predominant at all pressures[119]. The same is true of other reactions involving free radicals, for example $HO_2^\cdot + HO_2^\cdot \xrightarrow{M} H_2O_2 + O_2$ (M = NH_3, H_2O).[80,97,120]

2. Negative Temperature Coefficient in Gas-phase Hydrocarbon Oxidation Reactions

The oxidation of hydrocarbons is a branching chain process whose rate is a function of temperature. In most cases an increase in temperature causes a large increase in rate[121]. However, some exceptions to this rule are known. In the oxidation diagrams (in T, p coordinates) of some reactions a region in which the reaction rate decreases with increase of temperature is found above the cold flame region, i.e. a NTC is present. This NTC region lies between the low-temperature and the high-temperature oxidation region[122]. It has been suggested that the cold flame is a suppressed chain explosion which has failed to develop because of the passage of the system into the NTC zone[123].

The NTC phenomenon is observed even in the oxidation of ethane, but is more marked with the higher hydrocarbons. Thus in the oxidation of propane the reaction rate increases to a maximum in the region of 300–350 °C before falling steeply to zero when the temperature is increased to 450 °C. The reaction re-starts at 475 °C, and becomes explosive[123]. So far a NTC has been reported for the gas-phase oxidation of alkanes, alkenes, aromatic hydrocarbons, and ketones. The phenomenon is discussed in many monographs and reviews[122–126], many experimental studies have been made of it, but so far the mechanism of the NTC is not entirely clear.

Some of the early workers attributed the NTC to the presence of two parallel reactions[123], or to reactor wall effects[127]. The hypothesis of two different chain breaking mechanisms with very different activation energies was tested by kinetic calculations[128]. In the most widely used hypotheses an increase of temperature lowers the probability of chain propagation because of the presence of a competing reaction[123]. According to one of these hypotheses the NTC is due to the reaction $HO_2^\cdot + HO_2^\cdot \rightarrow H_2O_2 + O_2$, which suppresses the chain-branching reaction[124]



However, this hypothesis has been shown to be incorrect by the kinetic isotope effect method[129]. According to other interpretations a branching reaction of the type of

$(CH_3)_2CHOO^{\cdot} + C_3H_8 \rightarrow (CH_3)_2CHOOH \rightarrow CH_3CHO + OH^{\cdot} + CH_3^{\cdot}$ is replaced by a chain propagation reaction at higher temperatures[130].

It has also been suggested that in the oxidation of hydrocarbons one of the intermediate products (the aldehyde) loses its ability to cause chain branching at high temperatures[123]. The kinetics of the formation of the main intermediates and products (including free radicals) in the NTC region have been studied in detail by advanced measurement techniques[131], including continuous monitoring in a cold trap by ESR.[132,133] In the NTC region the maximum concentration of free radicals (like the reaction rate) was found to go through a maximum. However, at short times, when the branching reactions can be ignored, the concentration of free radicals in the same region increases with temperature, indicating a relationship between the NTC and the branching reactions. Thus a study of the kinetics of the high-temprature oxidation of ethane has shown that the branching steps are associated with the accumulation of intermediate products of the reaction, whereas in the initial stages a non-branching chain process is taking place[134]. The experiments also showed that in the NTC region and at even higher temperatures there was no qualitative difference in the composition of the oxidation products and only a slight quantitative difference[128]. Yet, the chain length must decrease in the NTC region, since the active radicals which propagate the chain ($H^{\cdot}$, $RO^{\cdot}$) are replaced by less active radicals as a result of the reactions between active particles and intermediate products of the HCHO and CH_3CHO type[135]. Thus the NTC in these reactions arises from a decrease in the effectiveness of chain branching at high temperatures.

3. Other Reactions

NTC have been observed also in other reactions of various types: in some cases the origin of the NTC is clear, but in other cases detailed studies of the mechanism of the process are needed to account for the effect. Thus a NTC will always be found in parallel reactions ($B \overset{k_1}{\leftarrow} A \overset{k_2}{\rightarrow} C$) if the temperature dependence of the yield of the substance formed with the lower activation energy is measured. At any instant the relationship $[B]/[C] = [B]_{\infty}/[C]_{\infty} = k_1/k_2$ applies[136]. If $E_2 > E_1$ the relative yield of the product B decreases as the temperature increases. This behaviour has been observed, for example, in the radical decomposition of azo compounds in solution[137]. It was found that an increase in temperature lowers the fractional number of radicals which recombine in the solvent cage. For azoethane in iso-octane solution this fraction (f) is 0.852 at −80 °C, 0.670 at 0 °C, and 0.539 at +85 °C. The quantity $F = f/(1 - f)$ corresponds to the ratio of the probabilities of the radicals recombining in the cage or emerging from it. In Arrhenius ($\lg F$, $1/T$) coordinates a straight line is obtained, giving an effective activation energy $E_a = E_{cage} - E_{diff}$ which is independent of the nature of the solvent and varies from −5.5 to −11.8 kJ mole^{-1} for different azo compounds.

The presence of parallel reactions can also account for the decreased rate of sulphochlorination of paraffins by the scheme $RH + SO_2 + Cl_2 \rightarrow RSO_2Cl + HCl$ when the temperature is raised, as a result of the increased rate of the direct chlorination $RH + Cl_2 \rightarrow RCl + HCl$.[138] An increase in temperature also lowers the rate of liquid-phase sulpho-oxidation of paraffins[139]. In this case the mechanism is similar to the development of a NTC in the gas-phase oxidation of hydrocarbons. The main product, the sulphonic acid RSO_3H, is formed by the gradual accumulation of persulphonic acid in the chain reaction

$$R^{\cdot} + SO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RSO_2^{\cdot} \xrightarrow{O_2} RSO_2O_2^{\cdot} \xrightarrow{RH} RSO_2O_2H\ ,$$

followed by degenerate branching by the scheme $RSO_2O_2H \rightarrow RSO_3^{\cdot} + OH^{\cdot}$, $RSO_3^{\cdot} + RH \rightarrow RSO_3H + R^{\cdot}$. On raising the temperature we make the formation of the $RSO_2^{\cdot}$ radical less probable: this lowers the equilibrium concentration of persulphonic acid and favours side reactions. For $R = CH_3$ the ratio of the constants k_1/k_{-1} is 200 at 25 °C, 40 at 65 °C, and 1 at 150 °C.[140]

Another example of NTC in a liquid-phase chain reaction is the oxidation of β-ionone by atmospheric oxygen[141]: for a constant rate of initiation the chain length and the reaction rate decrease with increase of temperature. In this case the NTC phenomenon is associated with a change in the chain breaking mechanism, quadratic chain breaking being replaced by linear chain breaking as the temperature is raised.

A decrease in the reaction rate with increase of temperature has been observed also in the iodination of silver films[142], the bromination of 2-chloro-3-t-butyl- and 3-carbomethoxyphenanthrene in CCl_4 solution[143], the oxidation of alkaline-earth metal vapours in NO_2, Cl_2, and Br_2 atmospheres at high temperatures[144], and in the reactions of solvated electrons in irradiated melts of alkali metal halides[145].

IV. NEGATIVE TEMPERATURE COEFFICIENT DUE TO THE EFFECT OF THE MEDIUM

So far we have examined reactions in which the NTC phenomenon arises from the properties of the reacting system. In many cases a NTC may be induced by "external" causes, independent of the mechanism of the reaction. We shall discuss some cases of the development of a NTC under the stimulus of external conditions.

1. Volume Expansion of the Solvent

Reactions in solution usually take place at constant pressure, and the volume of the solution and the concentration of the reactants can vary with temperature. The thermal volume change of liquids is determined by the coefficient of volume expansion[146]

$$\alpha_t' = (1/V)(dV/dt)\ (K^{-1}), \qquad (14)$$

where V is the volume and t is the temperature (°C). Putting $V = V_0$ for $t = t_0$ and changing to absolute temperatures we obtain, after integration of Eqn.(14),

$$V = V_0 \exp[\alpha_t'(T - T_0)]\ . \qquad (15)$$

The contribution (E') to the observed activation energy due to the volume expansion of the solution if the corresponding changes in the concentration of reactants are not allowed for in the kinetic measurements can be calculated. If the rate of the reaction is described by the equation $w = k[A]^n$ the contribution E' due only to the change in [A] caused by the change in volume (i.e. for k = const) is given by the expression

$$E' = RT^2(d\ln w/dT) = RT^2 n(d\ln[A]/dT). \qquad (16)$$

If m is the number of moles of A, $[A] = m/V$, and according to Eqn.(15) we have $[A] = m/V_0 \exp[\alpha_t'(T - T_0)$. Inserting this expression into (16) gives

$$E' = -RT^2 n\alpha_t'\ . \qquad (17)$$

For a third-order reaction ($n = 3$) we obtain $E' = 2.14 \times 10^3 \alpha_t'$ kJ mole^{-1} at 293 K. Using tabulated data[146] for α_t' we

arrive at the following values of E' for typical solvents by formulae (17):

Solvent	H_2O	$(CH_3)_2CO$	C_6H_6	CH_3OH	$CHCl_3$	$(C_2H_5)_2O$	Petroleum ether
$10^3\alpha_t'$ (K^{-1})	0.21	1.49	1.24	1.26	1.27	1.66	2.25
E', kJ $mole^{-1}$	−0.45	−3.20	−2.66	−2.70	−2.72	−3.55	−4.85

Thus even in solvent with a large value of α_t' the contribution of E' to the observed activation energy is small (within experimental error limits). A negative temperature coefficient could be observed only in reactions with a very small or zero "true" activation energy, but these reactions are diffusion-limited in solutions.

2. Changes in the Physicochemical Characteristics of the Solvent

In reactions involving ions or molecules with a dipole moment the rate is very dependent on parameters such as the dielectric constant of the medium, the ionic strength of the solution, the pH, etc. The contribution to the experimental activation energy from terms arising from the temperature dependence of the properties of the medium (i) is given by the equation[110]

$$E' = -R\sum_j \frac{\partial \ln k_{exper}}{\partial i_j} \cdot \frac{\partial i_j}{\partial (1/T)} \quad . \qquad (18)$$

If the change in the property i and the corresponding change in k_{exper} caused by the change in temperature are such that the two factors in the summation of Eqn.(18) have the same sign, a NTC can be observed if the contribution E' is greater in absolute value than the true (isoparametric) activation energy. The calculation assumes a knowledge of the temperature dependence of the properties of the medium and of the effect of these properties on the reaction rate.

Detailed studies of the dependence of the rate constant of many reactions on the dielectric constant of the medium ε have been reported. If only ε is taken as the parameter i Eqn.(18) can be re-written[147]

$$E' = -R\frac{\partial \ln k_{exper}}{\partial \varepsilon} \cdot \frac{\partial \varepsilon}{\partial (1/T)} \quad . \qquad (19)$$

If the reactants are two ions of the same sign, or two dipolar molecules whose dipole moments are smaller than that of the transition state, the rate of the reaction increases with ε, whereas ε itself usually increases with decrease of temperature. If both tendencies are well developed we can expect a NTC even in reactions with a high isodielectric energy of activation.

Since the dependence of the reaction rate on ε is usually expressed in $\ln k$, $1/\varepsilon$ coordinates in both theoretical and experimental work, and the dependence of ε on temperature is given as $\varepsilon = \varepsilon_0 \exp(-LT)$ or $L = -\partial \ln \varepsilon/\partial T$,[148] it is convenient to insert these relationships into Eqn.(19). Since

$$\frac{\partial \ln k}{\partial \varepsilon} = -\frac{1}{\varepsilon^2}\frac{\partial \ln k}{\partial (1/\varepsilon)} \text{ and } \frac{\partial \varepsilon}{\partial (1/T)} = -\varepsilon T^2 \frac{\partial \ln \varepsilon}{\partial T},$$

we obtain

$$E' = R\frac{\partial \ln k}{\partial (1/\varepsilon)} \cdot \frac{\partial \ln \varepsilon}{\partial T} \cdot \frac{T^2}{\varepsilon} = -R\frac{\partial \ln k}{\partial (1/\varepsilon)}\frac{L}{\varepsilon}T^2 \quad . \qquad (20)$$

Let us calculate possible values of E'. For ionic reactions the point-charge model gives[89]

$$\partial \ln k/\partial(1/\varepsilon) = z_A z_B e^2/r_{AB}k_B T \quad ,$$

where z_A and z_B are the charges on the ions, e is the electronic charge, and r_{AB} is the distance between the charges. If $z_A = z_B$, and $r_{AB} = 3$ Å, we find $\partial \ln k/\partial(1/\varepsilon) = 185$, which agrees in order of magnitude with the value calculated[89] for the reactions of the mono-anions of dibasic acids with OH^- ions. A similar value is obtained from the Kirkwood model for the reactions of dipolar molecules. The second factor in Eqn.(20) can be calculated from tabulated values of L, which for the majority of solvents lie in the range from 10^{-3} to 10^{-2} K^{-1}.[148] It is evident from Eqn.(20) that under otherwise identical conditions the contribution E' will be a maximum when the ratio L/ε is a maximum. This ratio for a number of solvents is tabulated below:

H_2O	CCl_4	$CHCl_3$	CH_3OH	$C_2H_4Cl_2$	$(CH_3)_2CO$	$(C_2H_5)_2O$	n-C_6H_{14}
0.058	0.40	0.78	0.19	0.52	0.23	1.18	0.44 .

Inserting (for a reaction in $(C_2H_5)_2O$) the values $L/\varepsilon = 1.18$ and $\partial \ln k/\partial(1/\varepsilon) = 185$ into Eqn.(20) we obtain $E' = -140$ kJ $mole^{-1}$ at 300 K.

This calculation shows that in some solvents the increase in rate on lowering the temperature caused by an increase in ε can be so large as to mask the decrease in rate due to the Arrhenius factor, and it can thus produce a NTC, whereas in aqueous solutions (where L/ε is small) a NTC is much less likely. This theoretical prediction[149] was experimentally confirmed in the oxidation of naphthoquinone derivatives by potassium periodate in aqueous-alcoholic solutions[147]. At pH 6.3 it was found that $E_a = -8.2 \pm 0.9$ kJ $mole^{-1}$, whereas the isodielectric activation energy is 80 ± 2 kJ $mole^{-1}$: this corresponds to a contribution $E' = -88$ kJ $mole^{-1}$.

A similar correction to the observed activation energy can be calculated for the change in other parameters of the medium. For example, if we identify the parameter i with the pH we can use the Brønsted relation[110] $\partial \ln k/\partial(\text{pH}) = \alpha$. Since changes in pH can cause large changes in reaction rate (in either sense) the observed activation energy may be higher of lower than the true activation energy by several tens of kJ $mole^{-1}$. The temperature dependence of the influence of the properties of the medium on the kinetics of reactions in the liquid phase is discussed in Ref.150.

3. Freezing of the Solvent

If reactants in a solvent (which can also take part in the reaction as one of the reactants) are mutually miscible in the solid as well as in the liquid phase, i.e. if they form a continuous series of solid solutions, the region of existence of the liquid phase at temperatures below the melting point of the solvent can be very small. Therefore a decrease in temperature in these systems rapidly suppresses the reaction because of the freezing of the solution. On the other hand if the reactants are not accommodated in the crystal lattice of the solidifying solvent and the system forms a simple eutectic system the region of existence of the liquid phase can extend for several tens of degrees below the melting point of the pure solvent before the freezing point of the eutectic is reached. In this case when the temperature is lowered the pure solvent freezes first and the effective local concentration of the reactant in the liquid phase increases, with a corresponding increase in reaction rate in keeping with the law of mass action. Under certain conditions this contribution may exceed the Arrhenius dependence in absolute value and give rise to a NTC.[151]

By comparing experimental data on the reaction rate in frozen solutions with calculations by the Arrhenius equation for the same temperature we find that the acceleration can be as high as several orders of magnitude. The following theoretical equation has been proposed for the rate constant:

$$k = \frac{T_0 - T}{\Delta}\exp(-E_a/RT) \quad ,$$

where T_0 is the freezing point of the solvent and Δ is its cryoscopic constant[110]. The maximum rate is found at the temperature $T_{max} = [E_a^2/4R^2 + E_aT_0/R]^{1/2} - E_a/2R$. Experimental data for many systems agree satisfactorily with these equations[110].

4. Other Mechanisms

An unusual phenomenon, consisting in a large increase in the reaction rate following the rapid cooling of a solid matrix, has recently been reported. For example, an equimolar mixture of methylcyclohexane and chlorine in which free radicals are photolytically generated reacts explosively when the frozen system is cooled further[152]. The velocity of propagation of the reaction front under these conditions is ~1 m s^{-1}. According to the authors[152], internal stresses in the sample are mainly responsible for this phenomenon. Active centres can be generated in various ways in these systems. Thus if a chlorine–butyl chloride, chlorine–methylcyclohexane, or hydrogen bromide–ethylene system frozen at 77 K is exposed to γ radiation from ^{60}Co and then slowly cooled to 4.2 K no changes are observed. However, if the system is cooled rapidly a "flash" reaction is observed, preceded by mechanical disintegration of the sample. These observations suggest that the thermal mechanism does not play a major role, and that the reaction may be propagated by a self-exciting process[153–155].

An increase in temperature can suppress many heterogeneous catalytic reactions if the heat of adsorption is greater in absolute value than the activation energy of the step leading to formation of the product[156]. In biocatalytic reactions a similar reversible retardation can be produced by the reversible denaturing of the enzyme over a limited temperature range. Under these conditions we expect a bell-shaped temperature dependence of the reaction rate, characterised by an optimum temperature for the reaction[157,158].

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In conclusion we should stress that the discovery of a negative temperature coefficient in a particular system can tell us a great deal about the mechanism of the reaction. First of all we must establish whether the NTC is caused by "external" conditions or whether it is inherent in the reaction system. In the former case the appropriate external factors can be isolated by an analysis of the experimental data, and the isoparametric kinetic characteristics of the reacting system itself can be identified. In the latter case a more detailed study of the reaction kinetics over a wide range of parameters is needed (mainly, a range of temperature). It is equally important to establish the possibility of various reversible processes in the system, and if necessary to obtain their thermodynamic characteristics by independent methods.

While this review was being written several reports of NTC in new systems and of more detailed studies of known NTC were published. For gas-phase processes the following studies should be noted: the recombination of $HO_2^{\cdot}$ radicals at low pressures[159], the reactions of $OH^{\cdot}$ and $O^{\cdot}$ at temperatures typical of the upper layers of the atmosphere[160], the reactions of allyl radicals with each other and with NO over a wide range of temperature[161], etc. The NTC phenomenon has been studied in several gas-phase radical reactions: $OH^{\cdot} + HNO_3 \rightarrow$ products[162,163], $NH_2^{\cdot} + O_2 \rightarrow NH_2O_2^{\cdot}$,[164] $OH^{\cdot} + SO_2 \rightarrow HOSO_2^{\cdot}$,[165] and $Cl^{\cdot} + ClONO_2 \rightarrow Cl_2 + NO_3^{\cdot}$;[166] in this type of process the highest NTC was reported for the reaction $OH^{\cdot} + C_3H_6 \rightarrow C_3H_6OH$, in which the bimolecular rate constant decreases 15-fold as the temperature is raised from 255 to 458 K, corresponding to the equation $k = AT^{-4.4}$.[167]

Activation energies $E_{obs} = -3.2$ and -7.1 kJ $mole^{-1}$ were obtained for trimethylethylene and tetramethylethylene respectively in studies of the addition of diphenylcarbene to olefins. The results were attributed to the formation of an intermediate complex which isomerises into the cyclopropane derivative[168].

A much larger NTC was observed for the bromination of hept-1-ene,[169] and for the chlorination[170] and bromination[171] of styrene in non-polar solvents. Thus in the bromination of heptene the temperature dependence of the reaction rate is bell-shaped, with $E_{obs} = -60$ kJ $mole^{-1}$ in the range 240 to 270 K. The negative temperature coefficient in these reactions is ascribed to the participation of molecular complexes in the dark radical generation step. The NTC phenomenon in the hydrochlorination of unsaturated compounds is discussed in a recent review[172]. Model calculations of the kinetics of reactions involving molecular complexes and showing a NTC are given in Ref.173.

The relationship between the changes in physicochemical properties of the medium and the NTC has been studied in detail for the oxidation of the phosphate esters of hydroquinone by potassium periodate in aqueous-ethanolic solutions[174]. A NTC has been observed also in the solid-phase oxidation of hydrazobenzene by a stable nitroxyl radical at 238–258 K.[175]

REFERENCES

1. D.D.Davis, R.E.Huie, and J.T.Herron, J.Chem.Phys., 1973, **59**, 628.
2. M.Meot-Ner, in "Gas Phase Ion Chemistry" (Edited by M.T.Bowers), Acad.Press, New York, 1979, Vol.1, p.197.
3. F.Kaufman, J.Phys.Chem., 1979, **83**, 1.
4. S.Veilas, "Khimicheskay Kinetika i Raschety Promyshlennykh Reaktorov" (Chemical Kinetics and Calculations for Industrial Reactors), Izd.Khimiya, Moscow, 1967, p.30.
5. S.Glasstone, K.J.Laidler, and H.Eyring, "Theory of Rate Processes" (Translated into Russian), Inostr. Lit., Moscow, 1948, p.135.
6. J.A.Kerr and M.J.Parsonage, "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds", Butterworths, London, 1972, p.9.
7. R.J.Cvetanović, D.L.Singleton, and G.Paraskevopoulos, J.Phys.Chem., 1979, **83**, 50.
8. P.Camillery, R.M.Marshall, and J.H.Purnell, J.Chem. Soc., Faraday Trans.I, 1974, **70**, 1434.
9. W.C.Gardiner, Acc.Chem.Res., 1977, **10**, 326.
10. H.Labhart, Chem.Phys.Letters, 1967, **1**, 263.
11. B.Hayman-Perlmutter, Progr.Inorg.Chem., 1976, **20**, 229.
12. K.Koura, J.Chem.Phys., 1981, **74**, 6743.
13. J.C.Light, J.Ross, and K.E.Shuler, in "Kinetic Processes in Gases and Plasmas", Acad.Press, New York–London, 1969, p.281.
14. S.W.Benson, "Thermochemical Kinetics" (Translated into Russian), Izd.Mir, Moscow, 1971, p.29.
15. A.D.Stepukhovich, Zhur.Fiz.Khim., 1958, **32**, 2415.
16. M.S.Zahniser and F.Kaufman, J.Chem.Phys., 1977, **66**, 3673.
17. O.K.Rice, J.Chem.Phys., 1936, **4**, 53.
18. P.P.Bemand, M.A.A.Clyne, and R.T.Watson, J.Chem. Soc., Faraday Trans.II, 1974, **70**, 564.

19. R.Lesclaux, Khe Van Pham, P.Dezauzier, and J.C.Soulignac, Chem.Phys.Letters, 1975, **35**, 493.
20. V.I.Shimulis and A.N.Lukashik, Zhur.Fiz.Khim., 1980, **54**, 3075 [Russ.J.Phys.Chem., 1980(12)].
21. R.M.Stimpfle, R.A.Perry, and C.J.Howard, J.Chem. Phys., 1979, **71**, 5183.
22. J.J.Solomon, M.Meot-Ner, and F.H.Field, J.Amer. Chem.Soc., 1974, **96**, 3727.
23. E.E.Nikitin, Uspekhi Khim., 1969, **38**, 1153 [Russ. Chem.Rev., 1969(7)].
24. V.N.Kondrat'ev, E.E.Nikitin, A.I.Reznikov, and S.Ya.Usmanskii, "Termicheskie Bimolekulyarnye Reaktsii v Gazakh" (Thermal Bimolecular Reactions in Gases), Izd.Nauka, Moscow, 1976, pp.3, 140.
25. D.L.Singleton, S.Furuyama, R.J.Cvetanović, and R.S.Irwin, J.Chem.Phys., 1975, **63**, 1003.
26. M.Meot-Ner, J.J.Solomon, F.H.Field, and H.Gershinowitz, J.Phys.Chem., 1974, **78**, 1773.
27. A.A.Frost and R.G.Pearson, "Kinetics and Mechanism", John Wiley, New York, 1953, p.92.
28. R.Atkinson, R.A.Perry, and J.N.Pitts, J.Chem.Phys., 1977, **66**, 1197.
29. R.Atkinson and J.N.Pitts, J.Chem.Phys., 1975, **63**, 3591.
30. R.T.Watson and S.P.Sander, J.Phys.Chem., 1979, **83**, 2936.
31. R.Simonaitis and J.Heicklen, J.Phys.Chem., 1981, **85**, 2946.
32. A.D.Stepukhovich, Uspekhi Khim., 1956, **25**, 263.
33. M.Meot-Ner and F.H.Field, J.Amer.Chem.Soc., 1978, **100**, 1356.
34. M.Meot-Ner and F.H.Field, J.Chem.Phys., 1976, **64**, 277.
35. R.E.Antrim, G.Burns, and J.K.K.Ip, Canad.J. Chem., 1977, **55**, 749.
36. R.K.Boyd and G.Burns, J.Phys.Chem., 1979, **83**, 88.
37. A.J.Stace, J.Chem.Soc., Faraday Trans.II, 1979, **75**, 1657.
38. B.P.Dymov, G.A.Skorobogatov, V.E.Khomenko, and S.A.Shchukarev, Zhur.Obshch.Khim., 1977, **47**, 848.
39. A.P.Genich, G.B.Manelis, and Yu.P.Myagkov, Dokl. Akad.Nauk SSSR, 1977, **235**, 1082.
40. T.C.Clark and M.A.A.Clyne, Chem.Comm., 1966, 287.
41. A.M.Arustamyan, I.K.Shakhnazaryan, A.G.Piliposyan, and A.B.Nalbandyan, Arm.Khim.Zhur., 1978, **31**, 3.
42. K.Erler, D.Field, and R.Zellner, Z.Elektrochem., 1977, **81**, 22.
43. T.Carrington and D.Garvin, in "Excited Species in Chemical Kinetics" (Translated into Russian), Izd. Mir, Moscow, 1973, Ch.3.
44. R.P.Wayne, Comprehensive Chem.Kinetics, 1969, **2**, 189.
45. J.R.Gilbert and J.H.Thomas, Comprehensive Chem. Kinetics, 1972, **6**, 139.
46. D.L.Baulch, D.D.Drysdale, J.Duxbury, and S.J.Grant, "Evaluated Kinetic Data for High Temperature Reactions", Butterworths, London–Boston, 1976, Vol.3.
47. V.N.Kondrat'ev, "Konstanty Skorosti Gazofaznykh Reaktsii" (Rate Constants of Gas-phase Reactions), Izd.Nauka, Moscow, 1971.
48. D.L.Baulch, R.A.Cox, R.F.Hampson, J.A.Kerr, J.Troe, and R.T.Watson, J.Phys.Chem.Ref.Data, 1980, **9**, 295.
49. H.Gershinovitz and H.Eyring, J.Amer.Chem.Soc., 1935, **57**, 985.
50. J.D.Greig and P.G.Hall, Trans.Faraday Soc., 1967, **63**, 655.
51. B.Veyret and R.Lesclaux, J.Phys.Chem., 1981, **85**, 1918.
52. D.M.Golden, J.Phys.Chem., 1979, **83**, 108.
53. V.A.Ulitskii and A.D.Stepukhovich, Zhur.Fiz.Khim., 1963, **37**, 689 [Russ.J.Phys.Chem., 1963(3)].
54. H.S.Johnston and P.Goldfinger, J.Chem.Phys., 1962, **37**, 700.
55. C.Anastasi and I.M.Smith, J.Chem.Soc., Faraday Trans.II, 1978, **74**, 1056.
56. G.E.Bullock and R.Cooper, J.Phys.Chem., 1972, **76**, 1931.
57. C.Anastasi and I.M.Smith, J.Chem.Soc., Faraday Trans.II, 1976, **72**, 1459.
58. D.R.Bates, J.Chem.Phys., 1979, **71**, 2318.
59. I.S.Zaslonko and V.N.Smirnov, Kinetika i Kataliz, 1979, **20**, 575.
60. J.Troe, Ann.Rev.Phys.Chem., 1978, **29**, 223.
61. W.H.Wong and R.A.Marcus, J.Chem.Phys., 1971, **55**, 5625.
62. M.Quack and J.Troe, Z.Elektrochem., 1977, **81**, 329.
63. W.H.Miller, J.Chem.Phys., 1976, **65**, 2216.
64. N.C.Blais, D.G.Truhlar, and B.C.Garrett, J.Phys. Chem., 1981, **85**, 1094.
65. R.A.Marcus, J.Chem.Education, 1968, **45**, 356.
66. D.L.Singleton and R.J.Cvetanović, J.Amer.Chem. Soc., 1976, **98**, 6812.
67. M.T.Leu and W.B.De More, J.Phys.Chem., 1978, **82**, 2049.
68. R.Atkinson and R.J.Cvetanović, J.Chem.Phys., 1972, **56**, 432.
69. F.T.Smith, in "Kinetic Processes in Gases and Plasmas", Academic Press, New York–London, 1969, p.257.
70. E.S.Filatov, V.A.Lebedev, and A.N.Nesmeyanov, Khim.Vys.Energii, 1977, **11**, 291.
71. L.S.Polak and A.V.Khachoyan, Khim.Vys.Energii, 1981, **15**, 26.
72. R.L.Le Roy, J.Phys.Chem., 1969, **73**, 4338.
73. V.P.Dmitriev and A.M.Evseev, Zhur.Fiz.Khim., 1976, **50**, 541 [Russ.J.Phys.Chem., 1976(2)].
74. R.L.Jaffe, "On the Possibility of Negative Activation Energies in Bimolecular Reactions", NASA-TM-78 509, A-7537; Chem.Abs., 1978, **90**, 77 106.
75. A.Menon and N.Sathyamurthy, J.Phys.Chem., 1981, **85**, 1021.
76. M.T.Leu, Chem.Phys.Letters, 1979, **61**, 275.
77. J.W.Hepburn, D.Klimek, K.Liu, R.G.Macdonald, F.J.Northrup, and J.C.Polanyi, J.Chem.Phys., 1981, **74**, 6226.
78. S.P.Sander and R.T.Watson, J.Phys.Chem., 1981, **84**, 2960.
79. Yu.V.Pervushin, Zhur.Fiz.Khim., 1977, **51**, 1682 [Russ.J.Phys.Chem., 1977(7)].
80. R.-R.Lii, M.C.Sauer, and S.Gordon, J.Phys.Chem., 1981, **85**, 2833.
81. H.O.Pritchard, Acc.Chem.Res., 1976, **9**, 99.
82. H.H.Dispert, M.W.Geis, and P.R.Brooks, J.Chem. Phys., 1979, **70**, 5317.
83. J.E.Hardy, W.C.Gardiner, and A.Burcat, Internat.J. Chem.Kinetics, 1978, **10**, 503.
84. D.Gutkowicz-Krusin, J.Chem.Phys., 1977, **67**, 2830.
85. A.W.Adamson, "A Textbook of Physical Chemistry", Academic Press, New York–San Franciso–London, 1979, pp.543, 612.
86. E.N.Eremin, "Osnovy Khimicheskoi Kinetiki" (Foundations of Chemical Kinetics), Izd.Vysshaya Shkola, Moscow, 1976, Ch.6.
87. F.T.Smith, in "Kinetic Processes in Gases and Plasmas", Academic Press, New York–London, 1969, p.321.

88. R.E.Mickens, Letters Nuovo Cimento, 1974, **11**, 187.
89. S.G.Entelis and R.P.Tiger, "Kinetika Reaktsii v Zhidkoi Faze. Kolichestvennyi Uchet Vliyaniya Sredy" (Kinetics of Liquid-phase Reactions. Quantitative Allowance for the Effect of the Medium), Izd.Khimiya, Moscow, 1973.
90. G.A.Skorobogatov, V.G.Seleznev, and O.N.Slesar', Dokl.Akad.Nauk SSSR, 1976, **231**, 1407.
91. R.W.Fessenden and R.H.Schuler, J.Chem.Phys., 1963, **39**, 2147.
92. R.Wolfgang, Acc.Chem.Res., 1970, **3**(2), 48.
93. V.D.Kiselev and J.G.Miller, J.Amer.Chem.Soc., 1975, **97**, 4036.
94. G.B.Sergeev, Yu.A.Serguchev, and V.V.Smirnov, Uspekhi Khim., 1973, **42**, 1560 [Russ.Chem.Rev., 1973(9)].
95. R.D.Cates, M.T.Bowers, and W.T.Huntress, J.Phys. Chem., 1981, **85**, 313.
96. J.I.Brauman and J.M.Jasinski, J.Amer.Chem.Soc., 1980, **102**, 2906.
97. R.-R.Lii, R.A.Gorse, M.C.Sauer, and S.Gordon, J.Phys.Chem., 1979, **83**, 1803.
98. R.S.Lewis and R.T.Watson, J.Phys.Chem., 1980, **84**, 3495.
99. G.A.Skorobogatov and O.N.Slesar', Vestnik Leningrad. Univ., 1979, No.4(1), p.39.
100. R.W.Gross and N.Cohen, J.Chem.Phys., 1968, **48**, 2582.
101. J.Connor, A.Van Roodselaar, R.W.Fair, and O.P.Strausz, J.Amer.Chem.Soc., 1971, **93**, 560.
102. N.Cohen and J.Heicklen, Comprehensive Chem. Kinetics, 1972, **6**, 123.
103. S.P.Sander and R.T.Watson, J.Phys.Chem., 1981, **85**, 4000.
104. A.Jeannotte, E.H.Appelman, F.Schreiner, and B.M.Abraham, J.Phys.Chem., 1978, **82**, 2353.
105. M.Meot-Ner, E.P.Hunter, and F.H.Field, J.Amer. Chem.Soc., 1977, **99**, 5576.
106. C.J.Howard, J.Chem.Phys., 1979, **71**, 2352.
107. R.A.Cox and G.S.Tyndall, Chem.Phys.Letters, 1979, **65**, 359.
108. F.P.Tully, A.R.Ravishankara, R.L.Thompson, J.M.Nicpvich, R.C.Shah, and N.M.Kreuter, J.Phys. Chem., 1981, **85**, 2262.
109. D.K.Bohme and G.I.Mackay, J.Amer.Chem.Soc., 1981, **103**, 978.
110. G.B.Sergeev and V.A.Batyuk, "Kriokhimiya" (Cryochemistry), Izd.Khimiya, Moscow, 1978.
111. M.J.Haugh and P.R.Dalton, J.Amer.Chem.Soc., 1975, **97**, 5674.
112. H.Hippler, K.Luther, and J.Troe, Z.Elektrochem., 1974, **78**, 178.
113. G.Porter, Discuss.Faraday Soc., 1962(33), 198.
114. N.Snider, Canad.J.Chem., 1979, **57**, 1167.
115. H.W.Chang and G.Burns, J.Chem.Phys., 1976, **64**, 349.
116. J.H.Lee, J.V.Michael, W.A.Payne, and L.J.Stief, J.Chem.Phys., 1978, **68**, 5410.
117. J.V.Michael and W.A.Payne, J.Chem.Phys., 1976, **65**, 4830.
118. H.W.Chang and G.Burns, J.Chem.Phys., 1975, **62**, 2426.
119. H.Hippler, K.Luther, V.Schubert, and J.Troe, J.Photochem., 1978, **9**, 143.
120. R.-R.Lii, R.A.Gorse, M.C.Sauer, and S.Gordon, J.Phys.Chem., 1980, **84**, 813.
121. V.V.Azatyan, Kinetika i Kataliz, 1977, **18**, 282.
122. V.N.Kondrat'ev and E.E.Nikitin, "Kinetika i Mekhanizm Gazofaznykh Reaktsii" (Kinetics and Mechanism of Gas-phase Reactions), Izd.Nauka, Moscow, 1974.
123. V.Ya.Shtern, "Mekhanizm Okisleniya Uglevodorodov v Gazovoi Faze" (Oxidation Mechanism of Hydrocarbons in the Gas Phase), Izd.Akad.Nauk SSSR, Moscow, 1960, pp.81, 342.
124. V.N.Kondratiev, Comprehensive Chem.Kinetics, 1969, **2**, 81.
125. A.B.Nalbandyan and A.A.Mantashyan, "Elementarnye Protsessy v Medlennykh Gazofaznykh Reaktsiyakh" (Elementary Processes in Slow Gas-phase Reactions), Izd.Akad.Nauk ArmSSR, Erevan, 1975, Ch.6.
126. N.N.Semenov, "O Nekotorykh Problemakh Khimicheskoi Kinetike i Reaktsionnoi Sposobnosti" (Some Problems in Chemical Kinetics and Reactivity), Izd.Akad.Nauk SSSR, Moscow, 1958, p.573.
127. R.O.King, S.Sandler, and R.Strom, Nature, 1957, **180**, 335.
128. R.I.Moshkina, S.S.Polyak, I.F.Masterovoi, and A.B.Nalbandyan, Kinetika i Kataliz, 1975, **16**, 1377.
129. R.I.Moshkina, S.S.Polyak, N.A.Sokolova, and A.B.Nalbandyan, Dokl.Akad.Nauk SSSR, 1976, **227**, 1401.
130. R.Y.Hoddad and D.E.Hoare, J.Chem.Soc., Faraday Trans.I, 1979, **75**, 2798.
131. E.A.Poladyan and A.A.Mantashyan, Arm.Khim.Zhur., 1980, **33**, 529.
132. G.A.Sachyan, G.Sh.Alaverdyan, and A.B.Nalbandyan, Dokl.Akad.Nauk SSSR, 1972, **204**, 883.
133. A.A.Mantashyan, G.L.Grigoryan, and A.S.Saakyan, Dokl.Akad.Nauk SSSR, 1972, **204**, 1392.
134. M.Cathonnet and H.James, J.Chim.phys., 1977, **74**(2), 156.
135. E.A.Poladyan and A.A.Mantashyan, Arm.Khim.Zhur., 1975, **28**, 949.
136. N.M.Emanuel' and D.G.Knorre, "Kurs Khimicheskoi Kinetiki" (Textbook of Chemical Kinetics), Izd. Vysshaya Shkola, Moscow, 1974, p.191.
137. A.P.Stefani, G.F.Thrower, and C.F.Jordan, J.Phys.Chem., 1969, **73**, 1257.
138. F.Azinger, "Khimiya i Tekhnologiya Parafinovykh Uglevodorodov" (Chemistry and Technology of Paraffin Hydrocarbons), Gostoptekhizdat, Moscow, 1959, Ch.5.
139. V.V.Nesterovskii and M.V.Ermolaev, "Radiatsionnoe Okislenie i Sul'fookislenie Parafinovykh Uglevodorodov), TsNIITEneftekhim, Moscow, 1974, p.60.
140. A.Good and J.C.J.Thynne, J.Appl.Chem., 1968, **18**, 229.
141. N.M.Evteeva and A.B.Gagarina, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 2715.
142. M.Shiojiri, Y.Hasegawa, K.Konishi, and Y.Tsujikura, J.Appl.Chem., 1973, **44**, 3370.
143. R.Bolton, Comprehensive Chem.Kinetics, 1973, **9**, 1.
144. O.E.Kashireninov, G.B.Manelis, and L.F.Repka, Zhur.Fiz.Khim., 1982, **56**, 1030 [Russ.J.Phys.Chem., 1982(4)].
145. T.N.Zhukova, I.E.Makarov, and A.K.Pikaev, Dokl. Akad.Nauk SSSR, 1981, **261**, 409.
146. "Spravochnik Khimika" (Chemist's Handbook), Izd.Khimiya, Leningrad, 1971, Vol.1, p.566.
147. G.B.Sergeev, V.A.Batyuk, T.N.Saprykina, B.M.Sergeev, and N.R.Konstantinova, Dokl.Akad. Nauk SSSR, 1978, **242**, 1122.
148. E.T.Denisov, "Kinetika Gomogennykh Khimicheskikh Reaktsii" (Kinetics of Homogeneous Chemical Reactions), Izd.Vysshaya Shkola, Moscow, 1978, p.97.

149. G.V.Sergeev, V.A.Batyuk, and B.M.Sergeev, Dokl. Akad.Nauk SSSR, 1975, **224**, 387.
150. T.N.Mandrugina, Thesis, Moscow, 1982.
151. R.E.Pincock and T.E.Kiovsky, J.Amer.Chem.Soc., 1966, **88**, 51.
152. V.A.Benderskii, E.Ya.Misochko, A.A.Ovchinnikov, and P.G.Filippov, Zhur.Eksper.Teor.Fiz.Pis'ma, 1980, **32**, 429.
153. A.M.Zanin, D.P.Kiryukhin, V.V.Barelko, I.M.Barkalov, and V.I.Gol'danskii, Dokl.Akad.Nauk SSSR, 1981, **260**, 1397.
154. V.V.Barelko, I.M.Barkalov, D.A.Vaganov, A.M.Zanin, and D.P.Kiryukhin, Dokl.Akad.Nauk SSSR, 1982, **264**, 99.
155. A.M.Zanin, D.P.Kiryukhin, V.V.Barelko, I.M.Barkalov, and V.I.Gol'danskii, Khim.Fiz., 1982, **1**. 265.
156. S.L.Kiperman, "Osnovy Khimicheskoi Kinetiki v Geterogennom Katalize" (Foundations of Chemical Kinetics in Heterogeneous Catalysis), Izd.Khimiya, Moscow, 1979, p.51.
157. F.M.Huennekens and B.Chance, in "Techniques of Organic Chemistry", Wiley Interscience, New York–London 1963, Vol.8, Pt.2, pp.1231, 1292.
158. I.V.Berezin and A.A.Klesov, "Prakticheskii Kurs Khimicheskoi i Fermentativnoi Kinetiki" (Practical Course of Chemical and Enzyme Kinetics), Izd. Moskov.Univ., 1976, p.250.
159. B.A.Thrush and G.S.Tundall, Chem.Phys.Letters, 1982, **92**, 232.
160. L.F.Keyser, J.Phys.Chem., 1982, **86**, 3439.
161. J.M.Tulloch, M.T.Macpherson, C.A.Morgan, and M.J.Philling, J.Phys.Chem., 1982, **86**, 3812.
162. A.R.Ravishankara, F.L.Eisele, and P.H.Wine, J.Phys.Chem., 1982, **86**, 1854.
163. J.J.Margitan and R.T.Watson, J.Phys.Chem., 1982, **86**, 3819.
164. W.Hack, O.Horie, and H.G.Wagner, J.Phys.Chem., 1982, **86**, 765.
165. M.T.-Leu, J.Phys.Chem., 1982, **86**, 4558.
166. J.J.Margitan, J.Phys.Chem., 1983, **87**, 674.
167. R.H.Smith, J.Phys.Chem., 1983, **87**, 1596.
168. N.J.Turro, G.F.Lehr, J.A.Butcher, R.A.Moss, and W.Guo, J.Amer.Chem.Soc., 1982, **104**, 1754.
169. G.B.Sergeev, V.V.Smirnov, M.I.Shilina, and E.A.Popov, Kinetika i Kataliz, 1982, **23**, 322.
170. G.B.Sergeev, A.Kh.Khairi, V.V.Smirnov, I.N.Chizhova, and F.Z.Badaev, Kinetika i Kataliz, 1982, **23**, 547.
171. G.B.Sergeev, V.V.Smirnov, and E.A.Popov, Kinetika i Kataliz, 1982, **23**, 542.
172. G.B.Sergeev, V.V.Smirnov, and T.N.Rostovshchikova, Uspekhi Khim., 1983, **52**, 455 [Russ.Chem.Rev., 1983(3)].
173. I.A.Leenson, "Tezisy Dokladov Vtorogo Vsesoyuznogo Soveshchaniya po Khimii Nizkikh Temperatur" (Abstracts of Papers Presented to the Second All-Union Congress on Low-temperature Chemistry), Izd.Moskov.Univ., 1982, p.90.
174. G.B.Sergeev, V.A.Batyuk, and T.N.Mandrugina, Kinetika i Kataliz, 1983, **24**, 1305.
175. G.B.Sergeev, V.A.Batyuk, and T.I.Boronina, Kinetika i Kataliz, 1983, **24**, 283.

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