RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

November 1978

Translated from *Uspekhi Khimii*, 47, 1905-1932 (1978)

U.D.C. 541.121/123

Theory of Chemical Reactivity

S.Beran, P.Carsky, P.Hobza, J.Pancir, R.Polak, Z.Slanina, and R.Zahradnik

This critical review deals with the present state of the theory of chemical reactivity, based on the methods of quantum chemistry and statistical thermodynamics. Reactions in the gaseous phase and in solution are examined. The static and dynamic theories of reaction rates are analysed. Catalytic reactions are discussed briefly. The bibliography contains 272 references.

CONTENTS

I. Introduction 1025
II. General problems of the theory of chemical reactivity 1026
1. Stationary points of potential energy surfaces 1026
2. Energy in the Hartree-Fock method and exact (non-relativistic) energy; the problem of allowing for correlation energy 1026
3. Calculation of thermodynamic functions in statistical thermodynamics 1028
III. Equilibrium and kinetics of reactions 1029
1. Classification of chemical reactions 1029
2. Equilibrium in the gaseous phase 1029
3. Kinetics of reactions in the gaseous phase 1030
4. Equilibrium in solution: solvation energy 1033
5. Kinetics of reactions in solution 1034
6. Catalytic reactions 1034

I. INTRODUCTION

The calculation of equilibrium constants and rates, based on the methods of quantum chemistry and statistical thermodynamics, is one of the most important problems of theoretical chemistry and hence is of considerable significance not only for the development of chemistry but also for its various practical applications.

For the solution of many problems in experimental chemistry it is sufficient to know the relative values of the equilibrium constants and rates in series of structurally related compounds. Nevertheless, the absolute values of these quantities for reactions taking place under different conditions is of considerable interest for present-day theoretical chemistry. Although this problem has already been solved in principle for some time, considerable difficulties are encountered in applying the theory to specific problems. In the theory of reactivity there are many problems, the solution of which requires new ideas. These ideas need not always be completely new; in some cases, the modification of old methods may lead to considerable progress. An example is provided by collision theory (in chemical reactions), the development of which has led in the last 15 years to the formulation of the present dynamic theory of reactivity.

The elementary quantum-chemical theory of reactivity, which reduced chiefly to the construction of correlations for experimental data, reached its greatest development in the nineteen-fifties [1-8] and was for the most part complete by the nineteen-sixties [4]. Even now, however, this theory is useful for chemists. In the nineteen-seventies, the development of the static theory of reactivity is taking place in the following directions [9]: a) calculations of the absolute values of equilibrium constants and rates; b) the study of the structure of the potential energy surfaces of reacting species; and c) calculations of solvation energies (this last is extremely important, since 95% of chemical reactions take place in solution).

In the second half of the nineteen-sixties, considerable efforts were directed to the study and development of the principle of the conservation of orbital symmetry, [9] which met with considerable response in organic and then inorganic chemistry. In this field, important results were obtained, which made it possible to estimate qualitatively the relative values of activation barriers and hence the possibility of a given type of reaction.

In the first part of the present review, problems at present common to the entire theory of chemical reactivity are discussed. In the second part, various theoretical studies in the field of reactivity are examined, An attempt has been made to cover completely work on the calculation of the absolute values of equilibrium constants or rates. Very little work of this kind has been published up to the present. Since the present review emphasises quantitative work, almost no attention is paid to methods for the qualitative study of reaction kinetics, except for adiabatic reactions taking place in the electronic ground state. Most attention is paid to the theory of the equilibrium and kinetics of reactions, and to various types of reaction between reagents. Some catalytic reactions are also included in the review.

II. GENERAL PROBLEMS OF THE THEORY OF CHEMICAL REACTIVITY

1. Stationary Points of Potential Energy Surfaces

Points on the potential energy surface at which the first derivatives with respect to the coordinates of all the atoms are equal to zero are called stationary points [10]. Stationary points are of particular importance in the theory of chemical reactivity. For the subsequent treatment it is convenient to divide these into three groups, on the basis of the properties of the matrix of the second derivatives of the energy with respect to the coordinates, that is the matrix of force constants. If all the eigenvalues of this matrix are positive, the point is a local minimum and corresponds to a stable conformation of the molecule. If only one eigenvalue of the force constant matrix is negative, the point is called a saddle point and corresponds to an activated complex in the sense of the theory of absolute reaction rates (see Part III). If more than one eigenvalue of the force constant matrix is negative, the corresponding stationary point is of no interest for the theory of chemical reactivity. For the description of equilibria it is necessary to consider only points of the first type, and for the description of the kinetics of processes, the points of the first and second types should be known. The determination of these points until recently presented considerable difficulties, which in practice could not be overcome for molecules containing five or more atoms.

The development of computer techniques and optimisation methods in recent years has led to the development of new algorithms for finding local minima. The method of successive optimisation of the coordinates [10], which has a low efficiency, has been replaced by more effective methods [11-25]. The rate of convergence of the calculation depends on the energy characteristics used to define the stationary points. Methods based only on energy values, in particular the simplex method [14,15], require considerable machine time; on the other hand, methods based on the use of second derivatives (of the energy with respect to the coordinates) also have a low efficiency, since the values of the second derivatives are calculated numerically from the values of the first derivatives, and this increases considerably the time required for the calculations [11-13,20,26].

The most effective methods are those which use only the first derivatives of the energy. The simplest of these, the linearly converging method of steepest descent, is less effective [20] than the quadratically converging methods of variable metrics. The Fletcher–Powell algorithm [27] has been used by Bloemer and Bruner [21], and this algorithm and those of Broyden [28], Goldfarb [29], and Hoshino [30] have been used by Pancíř [26]. The most effective method has been found to be that of Murtagh and Sargent [31], used by a number of authors [16,19,23,26]. By carrying out the optimisation of the geometry and the SCF procedure in a single iteration cycle in the CNDO/2, INDO, and MINDO/2 approximations, the time required for complete optimisation of the geometry has been decreased considerably [19].

In all cases, the determination of the stationary points of the potential energy surface is based on some initial approximation. The choice of this approximation presents no difficulty for finding local minima, since in this case the information on the structure of the molecule is usually sufficient. In the case of saddle points, the situation is more complicated (see Part III for the method for finding these points). Moreover, in the determination of saddle points it is impossible in the general case to employ methods based on the use of only the values of the energy or its first derivatives. Gardient methods are applicable only for symmetrical molecules, and then only when the eigenvector belonging to the negative eigenvalue satisfies definite symmetry conditions [16]. The calculation of the matrix of the second derivatives of the energy, which complicates the determination of stationary points, is necessary in the case of saddle points: the analysis of the eigenvalues of the force constant matrix is the only method for determining the type of stationary point, and in addition the eigenvectors give information on the direction of the reaction coordinate (see Refs. 26 and 32 for more details). Unfortunately, the time required for the optimisation of the geometry when the force constant matrix obtained by semi-empirical methods of the CNDO type are used is more than ten times the time required for the solution of this problem by the method of variable metrics [26].

2. Energy in the Hartree–Fock Method and Exact (Non-relativistic) Energy: the Problem of Allowing for Correlation Energy

Most quantum-chemical calculations are carried out in the SCF approximation. It is therefore important to know the extent to which SCF methods are suitable for the study of chemical reactivity. For this purpose, qualitative results obtained in this field, chiefly by non-empirical methods, are examined below.

One unsatisfactory feature of the SCF method is that the probability density (the combined distribution of the coordinates) of two electrons in this approximation is equal to the product of one-electron functions. This means that the motion of the electrons is regarded as taking place independently, so that no allowance is made for electron correlation. The difference between the energy obtained by exact solution and the energy from the SCF solution is called the correlation energy. The energy of the exact solution is understood to be the lowest non-relativistic energy in the Born–Oppenheimer approximation, and the energy of the SCF solution the lowest energy possible within the framework of the SCF method.

From the viewpoint of chemical reactivity, the chief disadvantage of the SCF approximation is the incorrect description of a large part of the dissociation region of the system. A classical example is the potential energy curve for the hydrogen molecule (Fig. 1). In this case it is possible to describe the dissociation correctly [33] if allowance is made for the interaction of the ground state with the doubly excited state $(1\sigma_u)^2$. In the case of the molecules C_2 and N_2, however, the correct description of the dissociation requires the use of four or ten configurations [34] respectively. Thus the solution of a problem of this type must be carried out by the method of configuration interaction or some other method taking account of correlation energy. The same unsatisfactory features of the SCF method appear in the study of activated complexes.

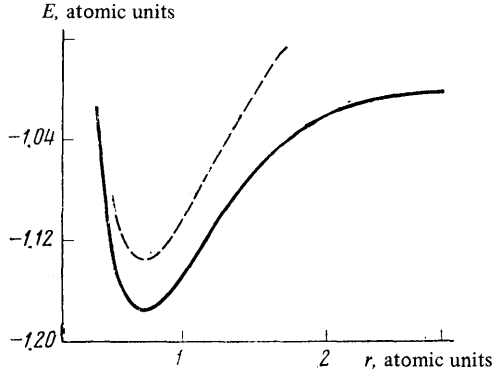
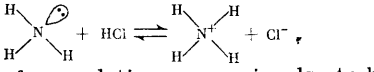


Figure 1. Potential energy curves [33] (in atomic units) for the H_2 molecule. Continuous line—exact solution, broken line—SCF approximation.

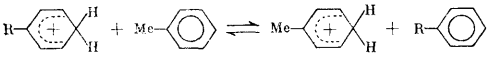
In the general case, the use of the SCF approximation to construct energy surfaces with "chemical accuracy" is fairly limited. For one type of reaction, however, the SCF approximation is satisfactory [35]. These are exothermic reactions, which, according to Polanyi [36], correspond to a potential energy surface without any barriers or activation energy. The problem of the activated complex thus diappears in this case. Moreover, for ion–molecular reactions of the type $Li^+ + H_2 \rightarrow H^+ + LiH$ the structure of the potential energy surface is determined chiefly by ion–quadrupole and ion–induced dipole interactions, which can readily be taken into account in the SCF approximation [37].

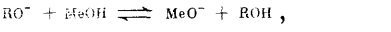
In the case of chemical equilibria, it is possible to limit the treatment to the study of fairly small regions around the minima of the energy surfaces. It has been established empirically [38,39] that the enthalpy of a reaction depends little on the correlation energy if all the reagents are systems with closed electron levels. The enthalpies of reactions, however, are not determined with an accuracy which would make it possible to carry out reliable statistical-thermodynamic calculations of the equilibrium constants. For the correlation energy to be preserved in a reaction, certain conditions must be fulfilled [40], namely: a) the number of electron pairs† should not change, and b) the relative arrangement of neighbouring electron pairs should also be preserved approximately‡.

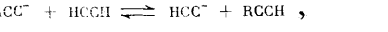
In reactions involving molecules with filled orbitals, the first condition is often satisfied, but the second less frequently. In other words, for the preservation of correlation energy, not only in-pair interactions (in-pair correlation energy), but also between-pair interactions (between-pair correlation energy), are important. An elementary example of a reaction in which both of these conditions are fulfilled is the following [42]:

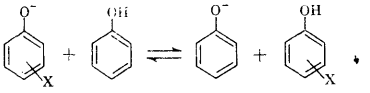

(1)

Preservation of correlation energy is also to be expected in so-called isodesmic reactions. This term was introduced by Pople and coworkers [43] for reactions in which the number of bonds of a definite formal type is preserved, but the relative arrangement of the bonds is changed. Condition (a) is always fulfilled for these reactions. Condition (b) may be fulfilled to different extents; for example, it is fulfilled to a sufficient extent in the following cases [44,45]:


(2)


(3)

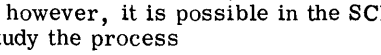

(4)


(5)

The enthalpy of a reaction can often be determined indirectly; for example, for the reaction


(6)

none of the above conditions is fulfilled, Since NaCl is an ionic compound, however, it is possible in the SCF approximation to study the process


(7)

†To keep the subsequent discussion simple, an exact definition of electron pair will not be given.

‡For example, for internal rotation in ethane. In this case the potential energy curves obtained by the SCF and PC methods are very similar [41].

for which both conditions are fulfilled, Since the correlation energies of Na, Cl, and $Na^+ + Cl^-$ are well known, this method[46] can be used to find the exact value of the enthalpy of reaction (6). Thermochemical cycles are used similarly to study so-called bond separation reactions[43]. These are isodesmic processes of the type

$$X{-}Y{-}Z + Y \rightarrow X{-}Y + Z{-}Y, \quad (8)$$

or, for example,

$$CH_3CHO + CH_4 \rightarrow C_2H_6 + H_2CO, \quad (9)$$

which are not of interest in themselves, but which can be used to obtain useful results.

A description of methods for the direct calculation of correlation energy is beyond the scope of the present review. Only a few brief points will therefore be made. Mention may be made first of the simplest method[47], in which a constant empirical value of the correlation energy is associated with each bond, and the total correlation energy is calculated as the sum of the individual contributions (just as dipole moments, heats of formation, etc. are estimated empirically in chemistry). This method can hardly give sufficiently accurate values of the correlation energy, since it does not take account of in-pair interaction. Of semi-empirical methods, mention may be made of that based on the many-electron theory of Sinanoğlu[50], in which allowance is made for the effective paired correlation energy (the EPCE method[48,49]), and the method proposed by Lie and Clementi[51], in which Wigner's equation[52] is used. The results which have been published do not yet make it possible to discuss the possibilities of these methods more fully. The results obtained by the present authors[53] for the complex $(H_2)_2$ show that the EPCE method may give useful information for the description of van der Waals interaction. An advantage of both of the above methods is their relative simplicity, but an unsatisfactory feature is the incorrect description of the dissociation limits in most cases.

Many versions of non-empirical methods exist. In some of these, however, allowance is made only for in-pair correlation energy (calculations based on the theory of geminals), or else the part played by correlation energy is overestimated, and it is usually difficult to estimate the error (the approximation of independent electron pairs, IEP [40]); other methods require a large expenditure of machine time (PC SCF methods) with allowance for a large number of configurations. A modified IEP approximation[54,55] or simple versions of the configuration interaction method[56,57] are therefore usually employed.

To conclude this section, brief mention may be made of semi-empirical SCF calculations of the CNDO and INDO types. Among those who use these methods, there is the widespread opinion that correlation effects can be taken into account by empirical parameters, so that there is no need to consider the estimation of the correlation energy. In fact, the empirical parameters are chosen in such a way that the bond energy of the molecule is reproduced for the equilibrium geometry. These semi-empirical methods, however, are based on non-empirical versions of the SCF method and therefore should exhibit all the weaknesses of this approximation, for example the incorrect description of the dissociation limits. It may be assumed, however, that the study of energy surfaces by semi-empirical methods is meaningful and that studies in this field are required, since these surfaces may give at least useful "semi-quantitative" information.

3. Calculation of Thermodynamic Functions in Statistical Thermodynamics

The quantitative estimation of the equilibrium constants and rates of chemical reactions is based on statistical thermodynamics. For the great majority of processes taking place in the gaseous phase at temperatures not exceeding 1000 K, involving normal molecules, radicals, or ions (in contrast to van der Waals complexes), the equilibrium constants (or rates) are determined chiefly by the value of ΔH_0° (or $\Delta H_0^{\neq}$). The calculation of the enthalpy change is of course a quantum-chemical problem. Thus the problem of improving the rigid rotator–harmonic oscillator (RR–HO) approximation is not the primary problem, although from the physical viewpoint it is a crude approximation. Thus the principal and very difficult problem is the calculation of the enthalpy changes by the methods of quantum chemistry. The value obtained corresponds to 0 K and does not take account of zero-point vibrational energy.

The calculation of the vibrational partition function (since it is desired to avoid the use of experimental data) can be carried out by the methods developed by Wilson and coworkers[58] and El'yashevich[59]; the zero-point energy is of course again determined. The complete partition functions can be used to calculate the values of the thermodynamic functions at any temperature. The relationships between the thermodynamic functions and the partition functions, and methods for calculating the partition functions from spectroscopic data, has been described in textbooks and monographs[60–63]. In the general case, an appreciable contribution to the total partition function is made by the translational, rotational, and in a number of cases vibrational partition functions. Analysis of the structure of the vibrational partition function shows that with increase in the temperature and decrease in the frequency of the normal vibrations, the magnitude of the contribution from the vibrational partition function increases. At temperatures not exceeding 1000 K, for systems in which there are no vibrational modes having frequencies (wavenumbers) smaller than 100 cm^{-1}, the contribution of the vibrational partition function is small. This is a favourable feature, since the purely theoretical calculation of the fequencies of the normal vibrations not only is tedious and requires considerable skill, but also is accompanied by extremely large errors.

Analysis of the literature shows that if the experimental values of ΔH_0° are used, the calculation based on the spectroscopic data and the partition functions in the rigid rotator–harmonic oscillator approximation leads to extremely reliable equilibrium constants; the error often does not exceed ±10%. The results of calculations for 33 reactions in the gaseous phase and for reactions between solids and gases have been published[64]. The error in the determination of $\lg K_p$ using the results of theoretical calculations of partition functions based on semi-empirical methods (CNDO/2, INDO, MINDO/2) has been studied[65,66]. The error introduced by the rotational partition function is independent of temperature, whereas the error due to the vibrational partition function increases with increase in temperature (by 2–3 orders of magnitude on going from 100 K to 2000 K).

In the general case, the results of the most reliable recent calculations of ΔH_0° (or $\Delta H_0^{\neq}$) indicate that the calculated values of the rotational and vibrational partition functions (based on semi-empirical quantum-chemical methods) are satisfactory. Nevertheless, it is appropriate

to discuss the possibilities provided by various approximations which represent improvements on the RR–HO approximation[67].

Statistical thermodynamics provides general equations for calculating partition functions in the non-rigid rotator–anharmonic oscillator NR–ANO approximation[68]. The rotational–vibrational spectra have been studied to the extent required for the NR–ANO approximation for only a small number of molecules, however. Nevertheless, for this group of molecules it is possible to reach definite conclusions regarding the relationships between the thermodynamic functions calculated in the two approximations. For example, for the entropy of water at 1000 K, Godnev[69] gives the following data: RR–HO approximation, $S^0_{1000} = 55.52$ cal.mole^{-1} K^{-1}; NR–ANO approximation, $S^0_{1000} = 55.598$ cal. mole^{-1} K^{-1}. The calculations show that allowance for the anharmonicity and non-rigidity of the molecule introduces small corrections to the value of the logarithm of the equilibrium constant[65,70].

At the present time, for most molecules, calculations of the thermodynamic functions based on experimental data or on the methods of quantum chemistry are possible in practice only in the RR–HO approximation. Comparison of the results of calculations carried out in the RR–HO and NR–ANO approximations show that the RR–HO approximation is fully applicable, at least for rigid molecules.

It would be extremely attractive to be able to determine the molecular data appearing in the partition functions from an analysis of the potential energy surfaces. It is not very simple, however, to use the results of quantum-chemical calculations to solve problems in molecular spectroscopy. For the construction of the rotational–vibrational Hamiltonian it would be most convenient to have an analytical expression describing the potential energy surface. Even if this problem were solved, however, it is impossible to find a general analytical solution of the corresponding eigenvalue problem, and this makes the exact calculation of the partition functions impossible. With the exception of the simplest systems, energy surfaces at present cannot be represented in analytical form.

The methods of quantum chemistry can be used to find the first derivatives of the total energy, and this makes it possible to carry out the approximate calculation of the second derivatives at the stationary points (see Part II). If however it is desired to take account, albeit partly, of anharmonicity and rotational–vibrational interaction in the calculation of the thermodynamic functions, it is necessary for this purpose to find the values of the derivatives of third and fourth orders. Except for the case of diatomic molecules, the possibilities provided by present-day quantum chemistry for the solution of this problem are extremely limited[67]. At least a partial solution to this problem was proposed by Simons and coworkers[71], who introduced a new type of anharmonic potential. The results obtained up to the present indicate that it is possible to take account of anharmonicity and non-rigidity without complicating appreciably the quantum-chemical calculations, compared with the harmonic approximation.

In conclusion it may be noted again that the errors introduced into the equilibrium constant K_p in the calculation of the entropy term in the RR–HO approximation are at present much smaller than the errors in the calculation of ΔH°_0. It is therefore necessary to pay particular attention to the development of reliable methods for estimating the enthalpy term.

III. EQUILIBRIUM AND KINETICS OF REACTIONS

1. Classification of Chemical Reactions

Not only from a formal viewpoint, but also from physical considerations, it is convenient to divide reacting systems into two groups: equilibrium and kinetic. A more detailed classification of chemical processes can be carried out according to the states of aggregation of the reactants and reaction products. There are three types of homogeneous processes: reactions in the gaseous (1), liquid (2), and solid (3) phases. In addition, reactions may be heterogeneous, that is they may take place at the interface between two phases: liquid and gas (4), liquid and solid (5), and gas and solid (6).

The subsequent treatment deals chiefly with homogeneous reactions taking place in the gaseous and liquid phases, and processes of the fourth and sixth types are discussed briefly.

2. Equilibrium in the Gaseous Phase

Calculations of the equilibrium constants of reactions in gases are of considerable importance for the development of the theory of reactivity. The quantum-chemical analysis of equilibria in the gaseous phase is facilitated by two features: firstly, these processes can be sufficiently effectively studied by the methods of chemical thermodynamics, and secondly, the intermediate results of quantum-chemical calculations for many reactions can be compared with experimental data (molecular geometry, frequencies of the normal vibrations, electronic spectra, barriers to internal rotation, heats of formation, and enthalpies of reactions).

Although the basic scheme for calculating K_p in the gaseous phase is clear, its application to problems of chemical reactivity is still extremely limited. Various gaseous equilibria have been studied[72–83] on the basis of theoretical calculations of K_p with different potential functions (empirical functions, or functions found from the solution of the Schrödinger equation). Except for the case of diatomic molecules, the partition functions in the RR–HO approximation were used in all cases (see Section II.3).

In the determination of equilibrium constants by theoretical methods, the enthalpy of reaction is the most complicated characteristic to calculate. The rotational and vibrational partition functions have little influence on the accuracy of the calculation of K_p. It can be shown that an error of 3 kcal mole^{-1}, allowed in the determination of the enthalpy at low temperatures, leads to an error in the equilibrium constant which is greater by two orders of magnitude. The versions of the MO methods available at present can hardly give enthalpy values even with this clearly inadequate accuracy of ±3 kcal mole^{-1}. In 1970, the semi-empirical MINDO/2 method aroused great expectations, but it was found in the general case that this method also does not make it possible to calculate ΔH°_f with the required accuracy[84].

Nevertheless, there are a large number of reactions for which the NDO approximation can be used to carry out sufficiently accurate calculations of equilibrium constants. These calculations can be carried out directly only by the MINDO/2 method, since the CNDO/2 and INDO methods require modification[83]. (Examples can be found

in papers [81,83] on the dimerisation of the radicals CH_3, NH_2, HCO, and NF_2.) In many cases the error of the determination of the enthalpy of reaction is so great that it makes it impossible to estimate equilibrium constants reliably by semi-empirical methods. At present there is no semi-empirical method which is sufficiently general and could be used to find the enthalpies of reactions with the required accuracy. The recently published MINDO/3 method [85] has not yet been thoroughly tested.

Some positive results have been obtained by semi-empirical methods. The dimerisation of NF_2 represents an equilibrium involving the isomerisation of the reagent; this feature is encountered fairly frequently, but does not usually attract attention. Tetrafluorohydrazine exists in *trans*- and *gauche*-forms

$$2NF_2^{\cdot} \rightleftarrows \textit{trans}\text{-}N_2F_4 \qquad (10)$$

$$\Vert\Vert$$

$$2NF_2^{\cdot} \rightleftarrows \textit{gauche}\text{-}N_2F_4 \,. \qquad (11)$$

The values of ΔH_0° for reactions (10) and (11) were obtained by the CNDO method [83] with modified values of the parameters; for this purpose, a number of N and F compounds having known properties were used. The optimised molecular geometries and calculated frequencies of the normal vibrations were used to calculate ΔH_T°, ΔS_T^0, and the equilibrium constants of reactions (10) and (11). In the calculation of the entropy term, the existence of two optical isomers [86] of the *gauche*-form of N_2F_4 was taken into account. The values of ΔH°, ΔS^0, and K_p for the equilibrium $2NF_2^{\cdot} \rightleftharpoons N_2F_4$ were calculated from Eqns. (12)–(14), in which the index "i" refers to reactions (10) and (11) [88,89]

$$K_p = \sum_{i=1}^{n} K_p^i, \qquad (12)$$

$$\Delta H^0 = \sum_{i=1}^{n} \frac{K_p^i}{K_p} \Delta H_i^0, \qquad (13)$$

$$\Delta S^0 = \sum_{i=1}^{n} \frac{K_p^i}{K_p} \left(\Delta S_i^0 + R \ln \frac{K_p}{K_p^i} \right). \qquad (14)$$

The values obtained show fairly good agreement with the experimental data.

The study of the carbon systems C_n in the vapour over graphite is of both theoretical and experimental interest. The geometry has been determined experimentally only for C_2 and C_3; for $n > 3$, a linear arrangement of the carbon atoms was first assumed [73], and for these systems the values of ΔH_0° were calculated by the simple MO method (as far as C_{17}). Later, it was established theoretically that rings are more stable than linear forms [90,91]. The study of the potential energy surfaces of several of these systems has shown, however, that the species C_n have a more complex geometric structure at the stationary points. As an illustration, Fig. 2 gives the geometry of the singlet ground state of C_4 at different stationary points of the surface. Of the seven stationary points, three are minima; the linear form corresponds to a saddle point. The thermodynamic characteristics of the reaction $4C(\text{graphite}) \rightleftharpoons C_4(\text{gas})$ have been published [74,92].

To conclude this section, mention may be made of a systematic study [66] of the applicability of the CNDO/2, INDO, and MINDO/2 methods in the calculation of the entropy term of equilibria. It was shown that the replacement of the experimental molecular data by quantities determined by the methods of statistical thermodynamics introduces into the value of $\lg K_p$ (at temperatures below 1000 K) an error not exceeding 0.5%. This feature provides an optimistic estimate of the possibilities provided by semi-empirical methods for the calculation of K_p in the gaseous phase.

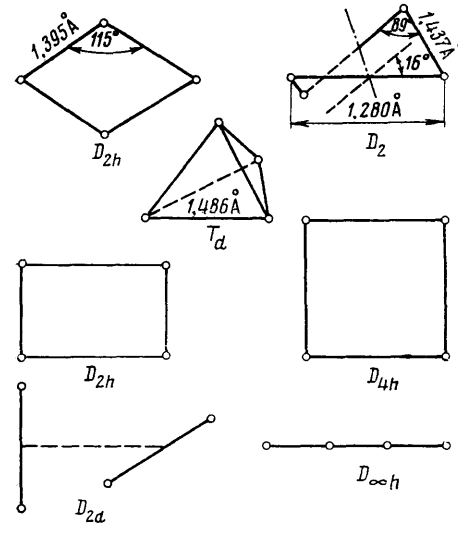


Figure 2. Configurations of the nuclei of the C_4 molecule corresponding to stationary points situated on its energy surface. For configurations in which the energy is a minimum, their symmetry groups and geometric parameters are indicated.

3. Kinetics of Reactions in the Gaseous Phase

a) Static approximation

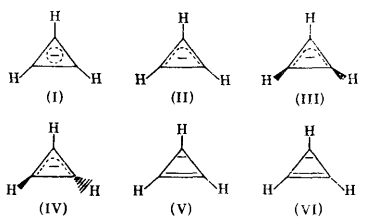
Static methods for studying chemical reactivity are based on the theory of absolute reaction rates, formulated by Eyring in the nineteen-thirties. In contrast to the case of "dynamic" methods, it is assumed that the velocity of the reacting species is so low that in the course of the reaction, energy transfer between different degrees of freedom can take place. The reaction trajectory, and hence the dependence of the geometry of the reacting species on the time measured from the start of the reaction, is replaced by the reaction coordinate, defined as the "energetically most favourable" path by which it is possible to go from the starting materials to the reaction products as a result of a continuous change in the geometry of the molecules. The change from reaction trajectory to reaction coordinate is extremely significant. The positions of the points on the reaction trajectory depend on the initial conditions—the geometries and momenta of the reacting species. Since these quantities are usually unknown (more accurately, they should be regarded as random quantities), it is necessary, in the calculation by dynamic methods, to carry out a large number of calculations for different initial conditions and to treat these results statistically. The reaction coordinate is independent of the choice of initial state of the system,

and as a rule, only one reaction coordinate can be constructed for a given reaction. Thus the use of static methods leads to considerable economy in the calculations. It is necessary, however, to take account of the assumption that the reaction takes place sufficiently slowly. From this viewpoint, the extent to which the static or dynamic approximation corresponds to the conditions for the problem being studied can be estimated.

As already noted, the description of the reaction mechanism by static methods is independent of the initial conditions (the relative arrangement of the atoms and the momentum). Moreover, if various purely quantum-chemical effects, for example the tunnel effect, are neglected, it is sufficient, for the calculation of the rate constant, to know only the properties of the reacting species and the system situated on the reaction coordinate and exhibiting the highest energy. This system is called the activated complex; the difference between the energy of this complex and the energy of the original molecules is called the activation energy. If the treatment is restricted to qualitative or comparative conclusions, it is possible to estimate the reactivity of molecules by studying the properties of the starting materials. This can be done by methods using the theory of reactivity indices [7,93,94], the theory of frontier orbitals [4,96], and a whole series of methods based on perturbation theory [95,97-101]. Finally, it is possible to make qualitative estimates of the nature of a reaction without any calculations, merely on the basis of symmetry considerations, as for example in the simple version of the Woodward–Hoffman theory [9,102]. All these methods are static methods. The present review, however, will deal chiefly with methods which can be used (in principle at least) to carry out exact calculations of rate constants. These methods are based directly on the theory of absolute reaction rates.

Although accurate data on the structures of the molecules of the reacting substances are often available, there is almost no information on the structure of the activated complex. The determination of the geometry of the activated complex or of all possible activated complexes in the case where a given reaction can take place by several mechanisms is therefore a fundamental problem of the theory of absolute reaction rates. In the case of unimolecular reactions for symmetrial molecules, the study of activated complexes reduces to an analysis of the stationary points of the potential energy surfaces. This analysis can be carried out using programmes for the automatic optimisation of the geometry (see Part II).

An example is provided by the calculation of the possible structures of the excited singlet state of the cyclopropenyl anion [103]. In this case the programme for optimising the geometry gave the completely symmetrical structure (I) and also structures (II)–(VI) having a lower symmetry. System (VI) is a stable isomer; structures (III)–(V) are activated complexes. Structures (I) and (II) are neither stable isomers nor activated complexes.



An analogous problem was examined by Dewar and coworkers [104-106] and Komornicki and McIver [107], who did not, however, analyse the nature of the stationary points. If even qualitative information on the structure of the activated complex is available, the correct structure of the activated complex can be obtained by optimising the geometry [108].

In most cases, there is of course no reliable information on the structure of the activated complex. If however a definite structure is taken as a basis, it is always possible that there exists another activated complex, which may correspond to a lower activated energy. In the general case, it is in practice impossible to carry out a rigorous analysis of the energy as a function of all the internal coordinates of the molecule. It may be noted that for a complete description of one of the simplest reactions of the type $AB + C \rightleftharpoons A + BC$, involving only three particles, it is necessary to take account of three internal coordinates, so that in this case it is necessary to study a surface in four-dimensional space. The problem can often be simplified by assuming that only one or two internal coordinates of the molecule (bond lengths, valency angles, or twisting angles) change in the course of the reaction, while all the other coordinates remain constant. This method has been used in many cases [109-118].

This method has two important disadvantages. Firstly, it is assumed that only a small number of coordinates change in the course of the reaction. This assumption is never fully justified in practice, and it introduces an error which cannot be calculated, even approximately. Moreover, for many reactions it is impossible to describe a mechanism involving changes in only two coordinates. Secondly, when certain coordinates are distinguished, a subjective factor is introduced into the calculation; a definite reaction mechanism, not necessarily correct, is assumed a priori.

The first of these unsatisfactory features was eliminated soon after the development of methods for the automatic optimisation of the geometry. When these methods are used, allowance is made for the fact that the activated complexes correspond to points situated on the reaction coordinates; it is assumed that in the course of the reaction the system is unstable with respect to one of the internal coordinates, the so-called critical coordinate, which may be, for example, a bond length in the case of addition or dissociation, a valency angle in isomerisation, or a torsional angle in the study of barriers to rotation. A series of calculations is then carried out, in which the critical coordinate is varied in definite steps, and the other coordinates are optimised.

This technique was used by Dewar [114-116] and McIver and Komornicki [117]. The method is undoubtedly more convenient than the methods mentioned earlier, since the multi-dimensional problem is reduced to a one-dimensional problem, and involves essentially modelling of the most favourable reaction path. The coordinate of the forward reaction determined in this way usually differs from the coordinate of the back reaction, however, and neither of them passes through the point corresponding to the activated complex [117]. This "chemical hysteresis" naturally does not agree with experiment. A more significant unsatisfactory feature is the arbitrary nature of the choice of critical coordinate. In most cases this choice is based on intuition, and the chemical hysteresis may increase considerably if the choice of critical coordinate is not successful. Moreover, many reactions cannot be described satisfactorily in terms of one critical coordinate.

These unsatisfactory features were eliminated in a study [32] based on the classical idea that the reaction coordinate is described by a point which changes along a

path passing through one of the troughs of the potential energy surface. The method of calculation is analogous to that in which the critical coordinate is used. The reaction coordinate is approximated successively by a series of points x_k. It is first assumed that these points are equally separated from one another. The first approximation of the $(\mu + 1)$th point $x'_{\mu+1}$ is determined from the μth point and the direction of the gradient. The position of the $(\mu + 1)$th point is then refined until the conditions formulated in the work cited[32] are fulfilled. If c_{ik} is the ith component of the kth eigenvector, E_k the kth eigenvalue of the force constant matrix, g'_j the jth component of the gradient at the μth point, and n the number of the eigenvector parallel to the gradient, the correction r_i to the ith coordinate of the point $x'_{\mu+1}$ is given by the equation:

$$r_i = -\sum_{k \neq n} E_k^{-1} c_{ik} S_k, \qquad (15)$$

where $S_k = \sum_j c_{jk} g'_j$. This method makes it possible in principle to calculate all reaction coordinates and to obtain all activated complexes; the method does not exhibit chemical hysteresis.

b) Dynamic approximation

Chemical reactions represent the sum of a whole series of elementary processes taking place between atoms and molecules, as a result of which the molecules of the reagents interact with one another for a period of time, forming so-called "collision complexes", activated complexes, or transition states. If the lifetime of this system is sufficiently long ($\tau > 10^{-12}$ s), the interaction of the particles may lead to energy exchange between separate degrees of freedom. In this case the subsequent course of the elementary reactions depends chiefly on the properties of the "collision complex", and the process can be described within the framework of the theory of absolute reaction rates. In those cases where $\tau < 10^{-12}$ s, the course of the elementary process depends on the initial state of the system, and its description requires non-stationary methods. It is to be expected that "collision complexes" having a long lifetime will be more probable for systems having a large number of degrees of freedom than for systems having a small number of degrees of freedom.

The study of the dynamics of elementary chemical reactions is almost always based on the Born–Oppenheimer approximation. This problem therefore essentially breaks down into two independent problems: a) solution of the electronic Schrödinger equation and determination of the potential energy functions, which depend on the coordinates of the nuclei; and b) determination of the dynamic behaviour of the nuclei in the known potential field.

The solution of the first problem belongs to the field of quantum chemistry. The calculation of the potential energy surfaces raises a number of specific problems. The calculation must be carried out with sufficient accuracy, and the potential energy surface should provide a correct quantitative description of all possible modes of dissociation of the system, and for this it is necessary that the total energy of the system be sufficiently well determined for all internuclear distances.

At present, calculations of the ab initio type having the required accuracy can be carried out only for relatively small systems[118] (where the number of electrons does not exceed 40), and potential energy surfaces (for the ground state or the most important lower electronic excited states) have been found only for some of the simplest systems[119–127]. Considerable attention is now being paid to the problem of constructing model potentials in analytical form[128–133].

For complex systems, calculation of the potential energy surfaces is possible only by semi-empirical or empirical methods. The use of these methods is particularly attractive in those cases where it is possible to determine the potential in analytical form. The potential energy surfaces are most frequently calculated by the LEPS method (London–Eyring–Polanyi–Sato)[134–136]; the DCM method (diatomic complexes in molecules)[137,138], proposed more than ten years ago[139], has recently been used successfully.

The study of the dependence of the dynamics of a chemical reaction on the initial conditions and the form of the potential surface is a problem in the field of the quantum theory of scattering. In the stationary theory of scattering, the wavefunction $\psi(r)$ of a system of reacting particles is determined by solving the equation

$$\psi(r) = \varphi(r) - \int G(r, r') \cdot V(r') \cdot \psi(r')\, dr' \qquad (16)$$

(the Lippman–Schwinger equation[140]), where $V(r')$ is the potential energy of the interaction, $\varphi(r)$ the wavefunction of the system of independent particles, and $G(r, r')$ the corresponding Green's function. For the case of elastic scattering, when the internal structure of the reacting particles remains unchanged, the Green's function can usually be found, so that the calculation of the scattering process presents no fundamental difficulty. The situation is more complicated for inelastic collisions. In this case the calculation can generally be carried out only after a number of crude approximations. The results obtained in this field have been summarised in a number of monographs[140,141] and reviews[142,143]. (The quantum theory of scattering has also been used to study various elementary chemical reactions[144–155].)

The scattering problem, even in the case of three particles, at present does not have an exact solution. One possible way of overcoming this difficulty is to replace the quantum-chemical description of the motion of the particles by the classical description. In this case, however, it must be borne in mind that certain quantum-mechanical phenomena have no analogy in classical mechanics, for example the tunnel effect or zero-point vibrational energy. From general considerations it may be concluded that the agreement between the results obtained by the two methods should improve with increase in the kinetic energy and mass of the interacting particles, and depends on the nature of the potential surface.

The classical reaction trajectories can be found by solving Hamilton's equations of motion

$$\frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt}, \qquad \frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}. \qquad (17)$$

where q_i represents the generalised coordinates of the reacting particles, p_i the generalised momenta, and H is Hamilton's function, which in the case of purely conservative forces has the significance of the total energy of the system. These equations form a system of first order differential equations, which (for given initial conditions) can be solved by standard methods of numerical integration. The initial conditions are naturally determined by the positions of the particles and their velocities. The

vibrational and rotational states of the particles are also taken into account in the initial conditions. The values of the coordinates and momenta obtained from the solution of the system of equations (17) can be used to determine firstly the nature of the reaction and secondly the state of the reaction products. In order to use these calculations to interpret experimental data, it is necessary to find a sufficiently large number of trajectories, corresponding to different initial conditions and modelling the real conditions statistically. A detailed analysis of the problem of the collision of three particles was carried out by Karplus and coworkers [156].

The application of the method of classical trajectories to systems having a large number of particles presents no fundamental difficulties [157] if the reaction takes place under adiabatic conditions. A number of processes take place under non-adiabatic conditions, however. Typical reactions of this kind are, for example, reactions involving the transfer of charge or of electronic energy, or spin-forbidden reactions. In the case of non-adiabatic reactions, the important regions are those in which several potential surfaces are situated fairly close to one another; this leads to considerable interaction between different states. Examples of this type of interaction are non-adiabatic electron–nuclear interactions or spin–orbital coupling. Considerable attention has been and is being paid to the calculation of these effects and the probabilities of transitions between different surfaces [158-160]; from these studies it is possible to modify the method of classical trajectories in such a way that it can be used to carry out calculations for non-adiabatic reactions [161].

The method of classical trajectories is used to solve the following problems:

a) for the theoretical estimation of various experimentally observable quantities [162-164]: the total reaction cross-section (or reaction rate constant), angular distributions and energy distributions of the products, etc.;

b) to study the influence of the nature of the potential surface and the states of the reagents on the reaction cross-section [165-169];

c) for comparison with the results of calculations by other methods [170-177] (in quantum mechanics, theory of absolute reaction rates).

Finally, the method of classical trajectories has been successfully used to study a number of reactions [162-164, 178-203].

4. Equilibrium in Solution; Solvation Energy

The properties of molecules in the gaseous phase often differ from the properties in the liquid phase. This difference is due to the interaction between the molecules of the solute and solvent. Depending on the nature of the medium, it is convenient to distinguish two types of interaction—specific and non-specific [204]. In non-specific solvation, no allowance is made for the specific characteristic features of the molecules of the solvent, which is regarded as a uniform and isotropic medium, characterised by various macroscopic constants, such as the dielectric constant or refractive index, Within the framework of this model, the energy of solvation is defined by the following equation, derived by Born [205]:

$$\Delta G = -\frac{q^2}{2r_0}\left(\frac{1}{\varepsilon} - 1\right), \qquad (18)$$

where ϵ is the dielectric constant of the solvent, q the charge of the ion, and r_0 the radius of the ion. The theory of the continuous model of a solvent was developed in more detail by Onsager [206] and Kirkwood [207]. These methods, however, make it possible to estimate only the magnitude of the solvation energy. Recently, several methods have been proposed [208-212], based on specific allowance for solvent effects directly in the Hamiltonian. These methods make it possible to take account of the influence of the solvent on those properties of the molecule which can be studied by quantum-mechanical methods. The disadvantages of the continuous model of a liquid have been discussed in detail [204].

In specific solvation, allowance is made for the specific characteristic features of the molecules of the solute and solvent. Interactions of this type are studied using models consisting of the molecules of the solute and an ordered set of solvent molecules. These systems are regarded as supermolecules, and studied by the methods of quantum chemistry. In practice, this procedure involves a number of difficulties: 1) the arrangement of the solvent molecules relative to the solute molecule is not known; 2) an appropriate potential has to be chosen for calculating the energy of interaction; and 3) usually, only the primary§ solvation shell is taken into account. These difficulties can be considered in more detail.

1. The determination of the structure of the primary or secondary solvation shells is very difficult. The experimental data can be used to estimate in a number of cases [213] only the number of solvent molecules in the primary solvation shell. This problem is unlikely to be solved for polyatomic molecules in the near future. The only possibility remaining is to model the solvation shell theoretically. In principle, this can be done by three methods: a) by using the Monte Carlo method to determine the most stable structures consisting of a given number of solvent molecules; b) to optimise, by a standard method, the structure of the entire solvation shell consisting of a given number of solvent molecules; and c) to study not the entire solvation shell, but only the part interacting most strongly with the solute molecule. All three methods have advantages and disadvantages. The Monte Carlo method is most appropriate, but even for small solute molecules the use of this method involves a considerable expenditure of machine time, even on modern fast computers. The second method can give valuable information on solvation for the expenditure of much less machine time. The third method can also be used for large molecules, but it must be borne in mind that this method can be used only to study some properties of the solvated molecule, for example the spectra or the conformation.

2. In the selection of the interaction potential, the entire structure of the molecules of the solute and solvent must first be taken into account. For the calculation of the energy of interaction it is possible to use all available methods—empirical, semi-empirical, and non-empirical. Brief mention may be made of some of the most promising methods.

Ab initio methods have been used to study the structures of various models of solvation layers. Mention may be made first of all of the work of Clementi and coworkers [214], who studied the hydration of various ions (Li^+, Na^+, K^+, F^-, and Cl^-). Here, the potential was determined by calculations of the Hartree–Fock type, after which the Monte Carlo method was used. It is very difficult to compare theoretical calculations of solvation energies with

§The primary solvation shell consists of those solvent molecules which interact directly with the solute molecule.

experimental data. The calculated enthalpies of the complexes of the ions with 1, 2, 3, etc. water molecules show fairly good agreement, however, with mass-spectrometric data[215,216]. One method for the direct confirmation of calculations of solvation energies is by comparing the theoretical and experimental radial distribution functions. Best agreement in the case of water was obtained in a study[217] using a two-particle potential, defined in the Hartree–Fock approximation with allowance for correlation energy. For ion–H_2O complexes, unfortunately, there are no published experimental estimates of the corresponding partition functions.

The method of Clementi and coworkers[214] is fairly well founded from the physical viewpoint, but as a consequence it is used at present only for the study of the hydration of ions and small molecules. In the case of polyatomic systems, it is practically impossible to study the supermolecule either in the Hartree–Fock approximation or by the Monte Carlo method.

In a study of the hydration of the Li^+ ion, Kollman and Kuntz[218] estimated the total energy of the complexes $Li^+ + nH_2O$ ($n = 2$, 4, 6) from the $Li^+...OH_2$, $Li^+...(OH_2)...(OH_2)$, and $OH_2...OH_2$ potentials. In this way, the authors cited were able to avoid the need to examine the complex as a whole. The electrostatic model (see below) was used to take account of the H_2O molecules in the secondary and tertiary hydration shells. It was shown that the central ion influences the arrangement of the molecules in the tertiary hydration shell. The use of two-particle and three-particle potentials for a definite geometry of the solvation shell is at present the only available method for calculating the solvation energy of polyatomic systems. Complete allowance for the entire solvation shell and solvate molecule is extremely complicated, and the calculations have been carried out only for small systems.

Pullman and coworkers[219] developed a method in which only part of the solvation shell is studied. This method is based on the determination of the most stable complexes containing a small number of solvent molecules. Various properties of the solvated molecules, such as the conformation or the spectra, can be interpreted using a complex of this type. An example is provided by the results of studies of the conformations of the histamine mono- and dications by the PCILO method (see below)[220]. The isolated molecule exists in only one conformation—*gauche* in the case of the monocation and *trans* in the case of the dication. From ab initio calculations it was found that in aqueous solution the monocation can exist in both the *gauche* and *trans* forms; in the case of the dication, the *gauche*-isomer may accompany the *trans*-isomer. These results agree with experiment.

Semi-empirical methods have been used to calculate the solvation energies of ions and simple systems. In most cases the solvation layer and the central ion were regarded as a supermolecule. Good results were obtained for the hydration of ions (ion–polar molecule interaction[221-224]). The study of solvation in non-polar systems at a semi-empirical level is unlikely to succeed. It has recently been shown that the results obtained in the study of the conformation of molecules and the interactions between molecules using the semi-empirical PCILO method show good agreement with the results of calculations by ab initio methods[225]. The PCILO method is apparently the most promising method for the study of the influence of the solvent on the properties of solvated molecules.

In conclusion, brief mention may be made of a simple method for estimating the energy of interaction for polar or charged systems, based on the electrostatic approximation[226]. From the wavefunctions of two systems it is possible to estimate the energy of their electrostatic interaction and to determine their relative arrangement, corresponding to the potential energy minimum. The positions in a molecule most favourable for electrophilic attack by a point particle carrying a positive charge are often of interest. From the wavefunction (non-empirical or semi-empirical) of the corresponding molecule, the electrostatic potential at the point r_i can readily be determined from the equation:

$$V(r_i) = -\sum_{q,s} P_{qs} \cdot \int \frac{\chi_q(1)\,\chi_s(1)}{r_{i1}}\, d\tau_1 + \sum_{\alpha} \frac{Z_\alpha}{r_{\alpha i}}, \qquad (19)$$

where $\chi_q(1)$ and $\chi_s(1)$ are the AO; P_{rs} is the element of the density matrix corresponding to these AO; Z_α the charge of the nucleus of the atom α; and $r_{\alpha i}$ and r_{i1} represent respectively the distances from the point r_i to the nucleus α and to the electron. By connecting points at which the values of the potential are equal, it is possible to obtain isopotential surfaces, which give a clear description of the possible directions of electrophilic attack.

3. Kollman and Kuntz[218] used the SCF method (ab initio) to study the hydration of the Li^+ ion. It was shown that the tetrahedral structure of the primary hydration shell is energetically most favourable, and that the hydration energy is 107 kcal mole^{-1}. The energy of the interaction of the Li^+ ion with the water molecules of the secondary and even the tertiary hydration shells is fairly high: in the first case it is equal to 80 kcal mole^{-1}, and in the second case it amounts to almost 20% of the total hydration energy (the experimental value is 228 kcal mole^{-1}). Here it must be borne in mind that the energy of the interaction of the Li^+ ion with water is unusually high. In the case of the hydration (or solvation) of neutral molecules, it is to be expected that allowance for only the primary or secondary hydration (solvation) shells will not introduce a large error into the calculation of the energy of hydration (or solvation).

5. Kinetics of Reactions in Solution

The calculation of the rate constants of reactions in solution is an extremely complex problem[227-230]. The development of the theory of chemical reactions in the gaseous phase[231] will obviously facilitate the successful solution of this complex problem. In general, however, the methods of studying reactions in the gaseous phase can hardly be applied directly to the study of reactions in solution. It is only in the case of relatively weak interactions between the molecules of the reactants and the activated complex on the one hand and the solvent on the other hand that these methods can lead to correct semi-quantitative results.

6. Catalytic Reactions

The methods of quantum chemistry used in catalysis can be divided into two groups[232]. The first group consists of the methods of solid state physics[233-244]. For catalysis, information on the states of the electrons on the catalyst surface (surface states) are most important, since their symmetry and energy can give information on the course of the adsorption. The bulk and surface states can be studied without particular difficulty in the case of the ideal

lattice of a semi-infinite crystal. Unfortunately, deviations from the ideal lattice (for example in the surface layer) and the presence of defects and chemisorbed molecules introduce considerable difficulties.

The second group consists of various methods in the quantum chemistry of molecules. The most promising methods for the solution of problems in catalysis are those which take account of all the valency electrons (semi-empirical methods of the CNDO and EHM type). The methods of this group can be used to study small systems comparatively easily, so that the catalyst is usually modelled by a system consisting of several atoms. The quality of the theoretical study of a catalytic process depends on the reliability of the quantum-chemical approximation and on the model of the catalytic reaction used.

Chemical reactions in the presence of a catalyst usually take place in several stages, the first of which is the interaction of the molecules of the original reagents with the catalyst (the formation of an adsorbate–catalyst complex, A–C). This first stage has been studied by many workers in different systems. Mention may be made of several studies [245-258] of the adsorption chiefly of diatomic molecules on the surfaces of transition metals and oxides. The authors cited obtained a model of the solid state by considering a part of a crystal consisting of several tens of atoms (three-dimensional model) or a part of the surface of the crystal (two-dimensional model), or considered only one metal atom (or one molecule of the oxide). Most calculations have been carried out by the simplest version of the EHM.

Several procedures can be used in the study of a catalytic reaction by the methods of quantum chemistry. The most fully developed of these involves the calculation of the potential energy surface for the system consisting of the atoms of the adsorbate and catalyst. Because of the complexity of the calculations, however, this approach can be used only for the simplest reactions [258-260]. For the study of systems of chemical interest, it is possible to use a simpler method involving the calculation of the electronic structure, geometry, total energy, and various other physical characteristics of A–C systems for assumed intermediate products and possible activated complexes [261,262]. The reliability of the information on the catalytic process obtained in this way depends to a considerable extent on the choice of the model for the reaction, that is on the assumptions regarding the intermediate products or activated complexes. The third and most economic method is based on the calculation of the electronic structure of the complex A–C. The reactivity of this complex is estimated using quantum-chemical indices of reactivity [263] or orbital symmetry conservation rules [264-267].

From the foregoing it follows that in the study of a catalytic reaction by the methods of quantum chemistry, the description of the catalyst presents the greatest difficulty. A model of the catalyst, taking account of its surface or bulk properties, should consist of a large number of atoms, and this complicates the calculation considerably. Moreover, in these models, allowance is made for crystal lattice defects. Another no less important problem concerns the quality of the quantum-chemical approximation. Non-empirical methods are in practice inapplicable to the solution of problems of catalysis, because of the complexity of the systems. Even without considering the problem of the parametrisation of semi-empirical methods for transition metals, the use of these methods to study the reactivity of systems containing a model of the catalyst with a large number of atoms still lies beyond the computing facilities of most laboratories. Thus at present the reactivity of a complex A–C can in most cases be studied only by means of the EHM, which suffers from a fairly large number of disadvantages. Even this method, however, can be used to study the potential energy surface or any cross-section of this surface only for the simplest catalytic reactions.

Thus the problems associated with taking explicit account of the catalyst are related to the specific features of the methods of quantum chemistry and difficulties of computation. In this connection, in the study of a catalytic reaction, the catalyst is taken into account implicitly as a perturbation of the adsorbate. The reactivity of this adsorbate can be studied by standard methods of quantum chemistry.

The results of the theoretical analysis and the experimental data, discussed in more detail elsewhere [232,268], indicate that the interaction of an adsorbate with a catalyst is accompanied by the transfer of electron density from a bonding MO of the adsorbate to a vacant MO of the catalyst, and also from a filled MO of the catalyst to an antibonding MO of the adsorbate. The degree of electron density transfer is determined by the electronic structure of the adsorbate and catalyst. When the transfer of charge is approximately the same in both directions, the state of the adsorbate is analogous to the excited state of the isolated molecule, or the superposition of several excited states. In charge transfer, the frontier orbitals of the interacting systems usually play the most important roles, so that it may be assumed that the state of the adsorbate corresponds to the first excited state. An example is provided by the interaction of a two-electron adsorbate (for example H_2) and a two-electron catalyst (this model can be used to study the interaction of the frontier orbitals of a many-electron adsorbate and a many-electron catalyst) (Fig. 3*a*). If φ^A represents a filled MO and φ^B a vacant MO of the adsorbate, and ψ^B and ψ^A represent filled and vacant MO of the catalyst respectively (the superscripts A and B characterise the symmetry of the MO), the MO of the complex A–C has the form:

$$\begin{aligned}\Phi_1^A &= c_1^A\varphi^A + c_2^A\psi^A,\\ \Phi_2^B &= c_1^B\psi^B + c_2^B\varphi^B,\\ \Phi_3^A &= c_1^A\psi^A - c_2^A\varphi^A,\\ \Phi_4^B &= c_1^B\varphi^B - c_2^B\psi^B.\end{aligned} \qquad (20)$$

$(c_2^A)^2$ then provides a measure of the transfer of electron density from the adsorbate to the catalyst (from the MO φ^A to the MO ψ^A), and $(c_2^B)^2$ the transfer of electron density from the catalyst to the adsorbate (from the MO ψ^B to the MO φ^B). The difference $(c_2^A)^2 - (c_2^B)^2$ characterises the charge on the adsorbate, and the smaller of the squares of these coefficients gives the degree of excitation of the adsorbate. If one of the coefficients is much greater than the other (see Figs. 3*b* and 3*c*), charge transfer takes place in only one direction. In extreme cases, when $c_1^A \simeq 1/\sqrt{2}$, $c_2^A \simeq 1/\sqrt{2}$ and $c_1^B \simeq 1$, $c_2^B = 0$, a radical-cation is formed, and when $c_1^B \simeq c_2^B \simeq 1/\sqrt{2}$ and $c_1^A \simeq 1$, $c_2^A \simeq 0$, a radical-anion is formed.

It may thus be expected that the reactivity and various other physical properties of the adsorbate in the complex A–C corresponds qualitatively to the properties of radical-ions or an excited state of the adsorbate. Here, the following points should be borne in mind:

a) only "part" of the electron density is transferred from the metal atom to the ligand;

b) the donor and acceptor powers of the adsorbate with respect to the metal atom are usually different, so that quantitatively, the decrease in the population of the bonding MO is different from the increase in the population of the antibonding MO;

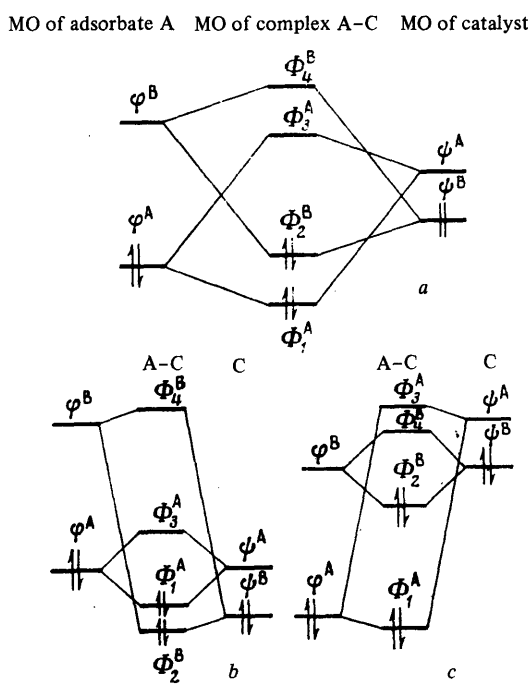


Figure 3. Interaction of the molecular orbitals of the adsorbate (A) and catalyst (C): *a*) for the formation of a partly excited state of the adsorbate ($c_2^A \simeq c_2^B$); *b*) for localisation of the positive charge on the adsorbate ($c_2^A \gg c_2^B$); *c*) for localisation of the negative charge on the adsorbate ($c_2^B \gg c_2^A$).

c) charge transfer takes place not only from the highest filled MO, but also from other orbitals, Moreover, there may be changes in the population of other vacant MO (although the frontier orbitals probably play the chief role in this process);

d) in this model, no allowance is made for the specific characteristic features of the catalyst surface.

The potential at the catalyst surface, which may lead to appreciable changes in the electronic structure of the adsorbate, is of considerable importance in heterogeneous catalytic processes. A strong electrostatic field may lead to appreciable decrease in the strength of the bonds of the adsorbate[269,270]. Moreover, allowance must be made for the fact that the magnetic moments of the atoms of the catalyst also influence the course of the reaction.

Comparison of catalytic and non-catalytic reactions.

Catalytic reactions	Non-catalytic reactions
Reactions catalysed by electron-acceptor systems (for example metal oxides)	Reactions of radical-cations and reactions taking place in the source of a mass spectrometer (cationic mass spectrometry)
Reactions catalysed by electron-donor systems (for example alkali metals)	Reactions of radical-anions and reactions taking place in the source of a mass spectrometer (anionic mass spectrometry) (Ref.271)
Reactions catalysed by systems in which the back-donation mechanism occurs (transition metal atoms and ions)	Reactions of electronically excited particles (photochemistry)
Reactions influencing the catalyst surface; the action of its force field	Reactions in an external electric or magnetic field

The mechanism of the effect of the catalyst on the adsorbate described above have analogies in other fields of chemistry (see Table). The analysis of catalytic reactions can therefore be facilitated by studying these processes, involving radical-ions (radical reactions,

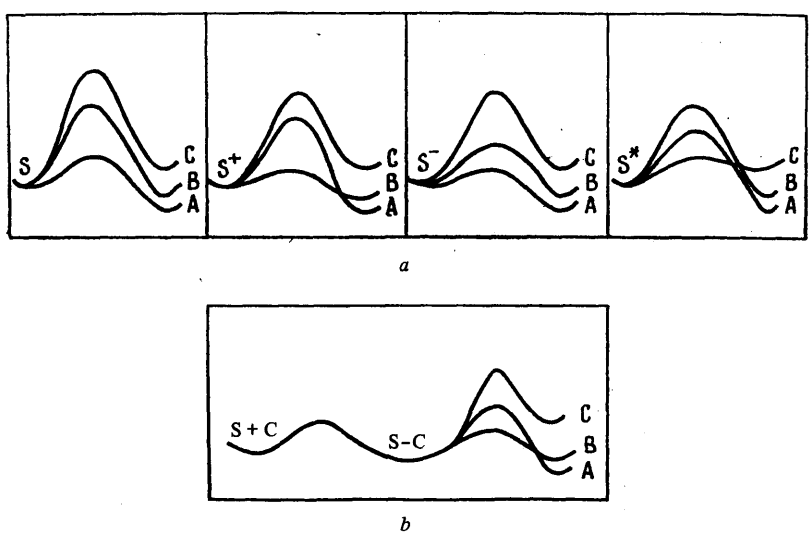


Figure 4. Section of the energy surface: *a*) for the molecule of a hypothetical substance S, for the radical-cation S^+, for the radical-anion S^-, and for the excited state S*; *b*) for the catalytic reaction.

cation and anion mass spectrometry) and molecules in excited electronic states. In the theoretical study of catalytic processes, the state of the adsorbate in the A–C complex can be modelled either by an appropriate radical-ion or by an excited electronic state[232], depending on the nature of the catalyst. This procedure makes it possible to use more fully developed quantum-chemical methods than in the case where explicit account is taken of the catalyst. The quality of the results naturally depends on the extent to which the model corresponds to the actual state of the adsorbate interacting with the catalyst.

The similarity between catalytic processes on the one hand and radical or photochemical reactions on the other makes it possible to determine beforehand the appropriate type of catalyst for carrying out the reaction. Fig. 4*a* gives the cross-sections of the potential energy surface of a molecule of a hypothetical substance S, its ions S^+ and S^-, and its excited state S^*. It is assumed that the transformation of the substance S can take place according to the following scheme:

$$S \rightarrow \begin{cases} A \\ B \\ C \end{cases}.$$

It is assumed that analogous processes are possible for other forms of the adsorbate. Comparison of the activation energies (see Fig. 4) shows that the decomposition of the substance S (S^+, S^-, or S^*) gives the products A for S and S^-, B for S^+, and C for S^*. If it is desired to use a catalyst to obtain, for example, product B, it is necessary to use a catalyst with strong electron-acceptor properties. The cross-sections of the corresponding surface for the S–C complex for a catalyst of this type are shown in Fig. 4*b*. If on the other hand the products of the catalytic transformation of the substance S are known, it is possible to determine, from the known reactivity of the radical-ions and excited states of the adsorbate, how the catalyst influences the adsorbate.

REFERENCES

1. R. D. Brown, Quart. Rev., 6, 63 (1952).
2. R. Daudel, R. Lefebvre, and C. Moser, Quantum Chemistry, Intersci., New York, 1959.
3. N. D. Sokolov, Uspekhi Khim., 32, 967 (1963) [Russ. Chem. Rev., No. 8 (1963)].
4. R. Zahradnik, Aspects de la chimie quantique contemporaine. Colloques Internat. du CNRS organisé par R. Daudel et A. Pullman, Menton, 1970.
5. M. Simonetta, Topics in Current Chemistry, 42, 1 (1973).
6. M. J. S. Dewar, Adv. Chem. Phys., 8, 65 (1965).
7. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists" (Translated into Russian), Mir, Moscow, 1965.
8. M. V. Bazilevskii, "Metod Molekulyarnykh Orbit i Reaktsionnaya Sposobnost' Organicheskikh Molekul" (The Molecular Orbital Method and the Reactivity of Organic Molecules), Izd. Khimiya, 1969.
9. R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry" (Translated into Russian), Izd. Mir, Moscow, 1971.
10. M. S. Gordon and J. A. Pople, J. Chem. Phys., 49, 4643 (1968).
11. P. Pulay, Mol. Phys., 17, 197 (1969).
12. P. Pulay, Mol. Phys., 18, 473 (1970).
13. P. Pulay, Mol. Phys., 21, 329 (1971).
14. M. J. S. Dewar and W. W. Schoeller, J. Amer. Chem. Soc., 93, 1481 (1971).
15. N. Bodor and M. J. S. Dewar, J. Amer. Chem. Soc., 93, 6685 (1971).
16. J. W. McIver, Jr. and A. Komornicki, Chem. Phys. Letters, 10, 303 (1971).
17. A. Dargelos, D. Liotard, and M. Chaillet, Tetrahedron, 28, 5595 (1972).
18. G. A. Shchembalov and Yu. A. Ustynyuk, Theor. Chim. Acta, 24, 389 (1972).
19. J. Pancíř, Theor. Chim. Acta, 29, 21 (1973).
20. P. Pulay and F. Török, Mol. Phys., 25, 1153 (1973).
21. W. L. Bloemer and B. L. Bruner, J. Chem. Phys., 58, 3735 (1973).
22. J. D. Pulfer and M. A. Whitehead, Canad. J. Chem., 51, 2220 (1973).
23. M. Grimmer and D. Heidrich, Z. Chem., 13, 356 (1973).
24. M. Grimmer, Dissertation, Leipzig (1975).
25. H. Huber, P. Carsky, and H. Zahradnik, Theor. Chim. Acta, in the press (1976).
26. J. Pancíř, Coll. Czech. Chem. Communs, 40, 2726 (1975).
27. R. Fletcher and M. J. D. Powell, Comput. J., 6, 163 (1963).
28. C. G. Broyden, J. Inst. Math. Appl., 6, 222 (1970).
29. D. Goldfarb, Math. Comput., 24, 23 (1970).
30. S. Hoshino, J. Inst. Math. Appl., 10, 394 (1972).
31. B. A. Murtagh and R. W. H. Sargent, Comput. J., 13, 185 (1970).
32. J. Pancíř, Coll. Czech. Chem. Communs, 40, 1112 (1975).
33. C. A. Coulson and E. T. Stewart, in The Chemistry of Alkanes, edited by S. Patai, Intersci., New York, 1964.
34. G. C. Lie and E. Clementi, J. Chem. Phys., 60, 1288 (1974).
35. P. K. Pearson, W. J. Hunt, C. F. Bender, and H. F. Schaefer III, J. Chem. Phys., 58, 5358 (1973).
36. J. C. Polanyi, Accounts Chem. Res., 5, 161 (1972).
37. H. F. Schaefer III, The Electronic Structure of Atoms and Molecules. A Survey of Rigorous Quantum Mechanical Results, Addison-Wesley, Reading, 1972, 226.
38. L. C. Snyder, J. Chem. Phys., 46, 3602 (1967).
39. L. C. Snyder and H. Basch, J. Amer. Chem. Soc., 91, 2189 (1969).
40. W. Kutzelnigg, Fortschr. Chem. Forsch., 41, 31 (1973).
41. See Ref. 37, Chapter V.
42. E. Clementi and J. N. Gayles, J. Chem. Phys., 47, 3837 (1967).
43. W. J. Hehre, D. Ditchfield, L. Radom, and J. A. Pople, J. Amer. Chem. Soc., 92, 4796 (1970).
44. W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, J. Amer. Chem. Soc., 96, 7162 (1974).
45. L. Radom, Chem. Communs, 403 (1974).
46. R. L. Matcha, J. Chem. Phys., 48, 335 (1968).
47. J. B. Moffat, J. Mol. Struct., 15, 325 (1973).
48. H. Ö. Pamuk, Theor. Chim. Acta, 28, 85 (1972).
49. O. Sinanoğlu and H. Ö. Pamuk, J. Amer. Chem. Soc., 95, 5435 (1973).
50. O. Sinanoğlu, Adv. Chem. Phys., 6, 315 (1964).
51. G. C. Lie and E. Clementi, J. Chem. Phys., 60, 1275 (1974).

52. E. Wigner, Phys. Rev., 46, 1002 (1934).
53. P. Carsky, P. Hobza, and R. Zahradnik, Theor. Chim. Acta, in the press (1976).
54. W. Meyer, J. Chem. Phys., 58, 1017 (1973).
55. R. Ahlrichs, H. Lischka, V. Staemmler, and W. Kutzelnigg, 62, 1225 (1975).
56. W. Meyer, Int. J. Quant. Chem., 5S, 341 (1971).
57. P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine, in Computational Methods for Large Molecules and Localized States in Solids (edited by F. Herman, A. D. McLean, and R. K. Nesbet), Plenum Press, New York, 1973.
58. E. B. Wilson, Jr., J. Chem. Phys., 7, 1047 (1939).
59. M. A. El'yashevich, Dokl. Akad. Nauk SSSR, 28, 604 (1940).
60. S. Glasstone, Theoretical Chemistry, D. Van Nostrand Comp., New York, 1947.
61. F. C. Andrews, Equilibrium Statistical Mechanics, Wiley, New York, 1963.
62. G. J. Janz, Thermodynamic Properties of Organic Compounds, Acad. Press, New York, 1967.
63. N. B. Colthup, L. H. Daly, and S. E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Acad. Press, New York, 1964.
64. Z. Slanina and R. Zahradnik, Coll. Czech. Chem. Communs, 39, 729 (1974).
65. Z. Slanina, Candidate's Thesis, Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovakian Academy of Sciences, Prague, 1974.
66. Z. Slanina, P. Beråk, and R. Zahradnik, Coll. Czech. Chem. Communs, in the press (1976).
67. M. Gelus and W. Kutzelnigg, Theor. Chim. Acta, 28, 103 (1973).
68. H. W. Woolley, J. Res. Nat. Bur. Stand., 56, 105 (1956).
69. I. N. Godnev, "Vychislenie Termodinamicheskikh Funktsii po Molekulyarnym Dannym" (The Calculation of Thermodynamic Functions from Molecular Data), GITTL, Moscow, 1956.
70. J. Bron and M. Wolfsberg, J. Chem. Phys., 57, 2862 (1972).
71. G. Simons and J. M. Finlan, Phys. Rev. Letters, 33, 131 (1974).
72. J. Berkowitz, J. Chem. Phys., 29, 1386 (1958).
73. K. S. Pitzer and E. Clementi, J. Amer. Chem. Soc., 81, 4477 (1959).
74. Z. Slanina and R. Zahradnik, in preparation for publication.
75. M. E. Schwartz and L. J. Schaad, J. Chem. Phys., 47, 5325 (1967).
76. P. Čársky, Z. Slanina, and R. Zahradnik, unpublished data (1975); R. Ahlrichs, Theor. Chim. Acta, 39, 149 (1975).
77. P. Kollman, C. F. Bender, and S. Rothenberg, J. Amer. Chem. Soc., 94, 8016 (1972).
78. D. Booth and J. N. Murrell, Mol. Phys., 24, 1117 (1972).
79. R. Kostoff, R. D. Levine, and R. B. Bernstein, Mol. Phys., 27, 981 (1974).
80. C. Braun and H. Leidecker, J. Chem. Phys., 61, 3104 (1974).
81. R. Zahradnik, Z. Slanina, and P. Čársky, Coll. Czech. Chem. Communs, 39, 63 (1974).
82. Z. Slanina, P. Hobza, and R. Zahradnik, Coll. Czech. Chem. Communs, 39, 218 (1974).
83. Z. Slanina, J. Schlanger, and R. Zahradnik, Coll. Czech. Chem. Communs, 41, 1864 (1976).
84. Bodor N., M. J. S. Dewar, A. Harger, and E. Haselbach, J. Amer. Chem. Soc., 92, 3854 (1970).
85. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc., 97, 1285 (1975).
86. C. B. Colburn, F. A. Johnson, and C. Haney, J. Chem. Phys., 43, 4526 (1965).
87. Z. Slanina, Coll. Czech. Chem. Communs, 40, 1997 (1975).
88. F. A. Johnson and C. B. Colburn, J. Amer. Chem. Soc., 83, 3043 (1961).
89. G. von Ellenrieder, E. Castellano, and H. J. Schumacher, Z. phys. Chem. (Frankfurt), 55, 144 (1967).
90. S. J. Strickler and K. S. Pitzer, Molecular Orbitals in Chemistry, Physics, and Biology (edited by B. Pullman and P.-O. Löwdin), Acad. Press, New York, 1964.
91. R. Hoffmann, Tetrahedron, 22, 521 (1966).
92. J. Dronart, R. P. Burns, G. De Maria, and M. G. Inghram, J. Chem. Phys., 31, 1131 (1959).
93. L. Pauling and G. W. Wheland, J. Chem. Phys., 1, 362 (1933).
94. C. A. Coulson, Disc. Faraday Soc., 2, 9 (1947).
95. R. G. Pearson, Acc. Chem. Res., 4, 152 (1971).
96. K. Fukui, T. Yonezawa, and H. Shingu, J. Chem. Phys., 20, 722 (1952).
97. R. G. Pearson, J. Amer. Chem. Soc., 94, 7287 (1972).
98. L. Salem, J. Amer. Chem. Soc., 90, 543, 553 (1968).
99. A. Devaquet and L. Salem, J. Amer. Chem. Soc., 91, 3793 (1969).
100. N. D. Epiotis, J. Amer. Chem. Soc., 94, 1924, 1935, 1941, 1946 (1972).
101. J. Pancíř and J. Kopecký, Coll. Czech. Chem., Communs, 39, 3608 (1974).
102. M. C. Caserio, J. Chem. Educ., 48, 782 (1971).
103. J. Pancíř and R. Zahradnik, in preparation for publication.
104. A. Brown, M. J. S. Dewar, and W. W. Schoeller, J. Amer. Chem. Soc., 92, 5516 (1970).
105. M. J. S. Dewar, Fortschr. chem. Forsch., 23, 15 (1971).
106. M. J. S. Dewar and R. C. Haddon, J. Amer. Chem. Soc., 95, 5836 (1973).
107. A. Komornicki and J. W. McIver, Jr., J. Amer. Chem. Soc., 95, 4512 (1973).
108. G. H. Schmid and G. M. Hallman, J. Mol. Struct., 18, 489 (1973).
109. R. Hoffmann, J. Chem. Phys., 39, 1397 (1963).
110. M. S. Gordon, J. Amer. Chem. Soc., 91, 3122 (1969).
111. A. Devaquet and L. Salem, Canad. J. Chem., 49, 977 (1971).
112. D. M. Hayes and K. Morokuma, Chem. Phys. Letters, 12, 539 (1972).
113. J. A. Altmann, J. G. Csizmadia, and K. Yates, J. Amer. Chem. Soc., 96, 4196 (1974).
114. M. J. S. Dewar and S. Kirchner, J. Amer. Chem. Soc., 93, 4290, 4291 (1971).
115. M. J. S. Dewar and M. C. Kohn, J. Amer. Chem. Soc., 94, 2704 (1972).
116. N. Bodor, M. J. S. Dewar, and J. S. Wasson, J. Amer. Chem. Soc., 94, 9095 (1972).
117. J. W. McIver, Jr. and A. Komornicki, J. Amer. Chem. Soc., 94, 2625 (1972).
118. M. Krauss, Ann. Rev. Phys. Chem., 21, 39 (1970).
119. Ch. F. Bender, P. K. Pearson, S. V. O'Neil, and H. F. Schaefer III, J. Chem. Phys., 56, 4626 (1972).
120. C. W. Wilson, Jr. and W. A. Goddard III, J. Chem. Phys., 56, 3913 (1972).

121. R. D. Poshusta and D. F. Zetik, J. Chem. Phys., 58, 118 (1973).
122. S. V. O'Neil, P. K. Pearson, H. F. Schaefer III, and Ch. F. Bender, J. Chem. Phys., 58, 1126 (1973).
123. B. Liu, J. Chem. Phys., 58, 1925 (1973).
124. W. Kutzelnigg, V. Staemmler, and C. Hoheisel, Chem. Phys., 1, 27 (1973).
125. G. G. Balint-Kurti, Mol. Phys., 25, 393 (1973).
126. C. W. Wilson, Jr., R. Kapral, and G. Burns, Phys. Letters, 24, 488 (1974).
127. D. H. Liskow, Ch. F. Bender, and H. F. Schaefer III, J. Chem. Phys., 61, 2507 (1974).
128. F. T. Wall and R. N. Porter, J. Chem. Phys., 36, 3256 (1962).
129. I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, J. Chem. Phys., 48, 2700 (1968).
130. L. M. Raff, L. Stivers, R. N. Porter, D. L. Thompson, and L. B. Sims, J. Chem. Phys., 52, 3449 (1970).
131. D. L. Bunker and M. D. Pattengill, J. Chem. Phys., 53, 3041 (1970).
132. P. J. Kuntz, Chem. Phys. Letters, 16, 581 (1972).
133. T. Valenchich and D. L. Bunker, J. Chem. Phys., 61, 21 (1974).
134. H. Eyring and M. Polanyi, Z. phys. Chem. (Leipzig), B12, 279 (1931).
135. S. Sato, J. Chem. Phys., 23, 592, 2465 (1955).
136. P. J. Kuntz, E. M. Nemeth, J. C. Polanyi, S. D. Rosner, and C. E. Young, J. Chem. Phys., 44, 1168 (1966).
137. P. J. Kuntz and A. C. Roach, J. Chem. Soc., Faraday Transactions II, 68, 259 (1972).
138. J. C. Tully, J. Chem. Phys., 58, 1396 (1973).
139. F. O. Ellison, J. Amer. Chem. Soc., 85, 3540 (1963).
140. R. D. Levine, Quantum Mechanics of Molecular Rate Processes, Univ. Press, Oxford, 1969.
141. E. E. Nikitin, "Teoriya Elementarnykh Atomno-molekulyarnykh Protsessov v Gazakh" (The Theory of Elementary Atomic-Molecular Processes in Gases), Izd. Khimiya, Moscow, 1970.
142. J. Ross, Proc. Internat. School of Physics "Enrico Fermi", Course XLIV, edited by Ch. Schlier, Acad. Press, New York, 1970, p. 392.
143. M. Karplus, Proc. Internat. School of Physics "Enrico Fermi", Course XLIV, edited by Ch. Schlier, Acad. Press, New York, 1970, p. 407.
144. R. P. Saxon and J. C. Light, J. Chem. Phys., 56, 3874, 3885 (1972).
145. D. A. Micha, J. Chem. Phys., 57, 2184 (1972).
146. P. McGuire and D. A. Micha, Mol. Phys., 25, 1335 (1973).
147. C. G. Miller, J. Chem. Phys., 59, 267 (1973).
148. D. G. Truhlar, A. Kuppermann, and J. T. Adams, J. Chem. Phys., 59, 395 (1973).
149. G. Wolken, Jr. and M. Karplus, J. Chem. Phys., 60, 351 (1974).
150. W. G. Cooper, N. S. Evers, and D. J. Kouri, Mol. Phys., 27, 707 (1974).
151. M. Baer, Mol. Phys., 27, 1429 (1974).
152. P. McGuire, Chem. Phys., 4, 249 (1974).
153. B. H. Choi and K. T. Tang, J. Chem. Phys., 61, 5147 (1974).
154. M. Baer, J. Chem. Phys., 62, 305 (1975).
155. J. N. L. Connor, W. Jakubetz, and J. Manz, Mol. Phys., 29, 347 (1975).
156. M. Karplus, R. N. Porter, and R. D. Sharma, J. Chem. Phys., 43, 3259 (1965).
157. A. Rahman and F. H. Stillinger, J. Chem. Phys., 55, 336 (1971).
158. E. E. Nikitin, Chemische Elementarprocesse, edited by H. Hartmann, Springer, Berlin, 1968, S. 43.
159. B. R. Johnson and R. D. Levine, Chem. Phys. Letters, 13, 168 (1972).
160. J. C. Tully, J. Chem. Phys., 59, 5122 (1973).
161. J. C. Tully and R. K. Preston, J. Chem. Phys., 55, 562 (1971).
162. L. Bunker, Methods Comput. Phys., 10, 287 (1971).
163. P. J. Kuntz, The Physics of Electronic and Atomic Collisions, edited by T. R. Govers and F. J. DeHeer, North Holland Publ. Co., Amsterdam, 1972, p. 427.
164. J. C. Tully, Berichte der Bunsen Gesellschaft für physikalische Chemie (Berichtshelf Ion-Molekül Reaktionen, Berlin), 77, 557 (1973).
165. F. T. Wall and R. N. Porter, J. Chem. Phys., 39, 3112 (1963).
166. J. C. Polanyi and W. H. Wong, J. Chem. Phys., 51, 1439 (1969).
167. M. H. Mok and J. C. Polanyi, J. Chem. Phys., 51, 1451 (1969).
168. A. G. Clarke and G. Burns, J. Chem. Phys., 58, 1908 (1973).
169. S. F. Wu, B. R. Johnson, and R. D. Levine, Mol. Phys., 25, 839 (1973).
170. P. Pechukas and F. J. McLafferty, J. Chem. Phys., 58, 1622 (1973).
171. G. C. Schatz, J. M. Bowman, and A. Kuppermann, J. Chem. Phys., 58, 4023 (1973).
172. J. J. Tyson, R. P. Saxon, and J. C. Light, J. Chem. Phys., 59, 363 (1973).
173. J. M. Bowman and A. Kuppermann, J. Chem. Phys., 59, 6524 (1973).
174. J. W. Duff and D. G. Truhlar, Chem. Phys., 4, 1 (1974).
175. S. D. Augustin and W. H. Miller, Chem. Phys. Letters, 28, 149 (1974).
176. G. W. Koeppl, J. Chem. Phys., 60, 1684 (1974).
177. M. Baer, U. Halavee, and A. Persky, J. Chem. Phys., 61, 5122 (1974).
178. G. H. Kwei, B. P. Boffardi, and S. F. Sun, J. Chem. Phys., 58, 1722 (1973).
179. R. L. Wilkins, J. Chem. Phys., 58, 2326 (1973).
180. R. N. Porter, L. B. Sims, D. L. Thompson, and L. M. Raff, J. Chem. Phys., 58, 2855 (1973).
181. R. L. Wilkins, J. Chem. Phys., 58, 3038 (1973).
182. W. H. Wong and G. Burns, J. Chem. Phys., 58, 4459 (1973).
183. J. M. White, J. Chem. Phys., 58, 4482 (1973).
184. T. Valenchich and D. L. Bunker, Chem. Phys. Letters, 20, 50 (1973).
185. I. W. M. Smith and P. M. Wood, Mol. Phys., 25, 441 (1973).
186. R. L. Wilkins, J. Chem. Phys., 59, 698 (1973).
187. R. K. Preston and R. J. Cross, Jr., J. Chem. Phys., 59, 3616 (1973).
188. D. R. McLaughlin and D. L. Thompson, J. Chem. Phys., 59, 4393 (1973).
189. R. A. LaBudde, P. H. Kuntz, R. B. Bernstein, and R. D. Levine, J. Chem. Phys., 59, 6286 (1973).
190. P. J. Kuntz and A. C. Roach, J. Chem. Phys., 59, 6299 (1973).
191. S. Chapman and R. J. Suplinskas, J. Chem. Phys., 60, 248 (1974).
192. S. Chapman and R. K. Preston, J. Chem. Phys., 60, 650 (1974).
193. J. R. Krenos, R. K. Preston, R. Wolfgang, and J. C. Tully, J. Chem. Phys., 60, 1634 (1974).
194. J. D. McDonald, J. Chem. Phys., 60, 1634 (1974).
195. D. L. Thompson, J. Chem. Phys., 60, 4557 (1974).
196. J. M. White and D. L. Thompson, J. Chem. Phys., 61, 719 (1974).

197. N. C. Blais and D. G. Truhlar, J. Chem. Phys., 61, 4186 (1974).
198. R. L. Wilkins, Mol. Phys., 28, 21 (1974).
199. U. Havemann, L. Zülicke, E. E. Nikitin, and A. A. Zembekov, Chem. Phys. Letters, 25, 487 (1974).
200. B. Garetz, M. Rubinson, and J. I. Steinfeld, Chem. Phys. Letters, 28, 120 (1974).
201. G. E. Zahr, R. K. Preston, and W. H. Miller, J. Chem. Phys., 62, 1127 (1975).
202. J. C. Whitehead, Mol. Phys., 29, 177 (1975).
203. R. L. Wilkins, Mol. Phys., 29, 555 (1975).
204. Z. Kecki, Adv. Mol. Relaxation Processes, 5, 137 (1973).
205. M. Born, Z. Phys., 1, 45 (1920).
206. L. Onsager, J. Amer. Chem. Soc., 58, 1486 (1936).
207. J. G. Kirkwood and F. M. Westheimer, J. Chem. Phys., 6, 506 (1938).
208. G. Klopman, Chem. Phys. Letters, 1, 200 (1967).
209. H. A. Germer, Jr., Theor. Chim. Acta, 34, 145 (1974).
210. J. Hylton, R. E. Christoffersen, and G. Hall, Chem. Phys. Letters, 26, 501 (1974).
211. O. Tapia and O. Goscinski, Mol. Phys., in the press.
212. O. Tapia, E. Poulain, and F. Sussman, Chem. Phys. Letters, 33, 65 (1975).
213. H. G. Hertz, Angew. Chem., Internat. Edit., 9, 124 (1970).
214. H. Kistenmacher, H. Popkie, and E. Clementi, J. Chem. Phys., 61, 799 (1974).
215. I. Dzidic and P. Kebarle, J. Phys. Chem., 74, 1466 (1970).
216. M. Arshadi, R. Yamdagni, and P. Kebarle, J. Phys. Chem., 74, 1475 (1970).
217. H. Kistenmacher, H. Popkie, E. Clementi, and R. O. Watts, J. Chem. Phys., 60, 4455 (1974).
218. P. A. Kollman and I. D. Kuntz, J. Amer. Chem. Soc., 96, 4766 (1974).
219. A. Pullman and B. Pullman, Quart. Rev. Biophys., 7, 505 (1974).
220. B. Pullman and J. Port, Mol. Pharmacol., 10, 360 (1974).
221. P. Hobza and R. Zahradnik, Coll. Czech. Chem. Communs, 40, 809 (1975).
222. P. Russegger, H. Lischka, and P. Schuster, Theor. Chim. Acta, 24, 191 (1972).
223. R. E. Burton and J. Daly, Trans. Faraday Soc., 67, 1219 (1971).
224. B. M. Rode, M. Breuss, and M. P. Schuster, Chem. Phys. Letters, 32, 34 (1975).
225. B. Pullman, The World of Quantum Chemistry, edited by R. Daudel and B. Pullman, D. Reidel Publ. Co., Dordrecht-Holland, 1974, p. 61.
226. R. Bonaccorsi, A. Pullman, E. Acrocco, and J. Tomasi, Theor. Chim. Acta, 24, 51 (1972).
227. P. Cremaschi, A. Gamba, and M. Simonetta, Theor. Chim. Acta, 24, 237 (1972).
228. P. Cremaschi and M. Simonetta, Theor. Chim. Acta, 37, 341 (1975).
229. A. C. Hopkinson and I. G. Csizmadia, Theor. Chim. Acta, 31, 83 (1973).
230. B. M. Rode and H. Preuss, Theor. Chim. Acta, 35, 369 (1974).
231. S. Yamabe, S. Kato, H. Fujimoto, and K. Fukui, Theor. Chim. Acta, 30, 327 (1973).
232. R. Zahradnik and S. Beran, in the press.
233. F. F. Vol'kenshtein, Zhur. Fiz. Khim., 21, 1317 (1947); 26, 1462 (1952).
234. J. Koutecky, Dokl. Akad. Nauk SSSR, 101, 119 (1955); Angew. Chem., 76, 365 (1964).
235. T. B. Grimley, Adv. in Catal., 12, 1 (1960).
236. V. L. Bonch-Bruevich, Zhur. Fiz. Khim., 25, 1033 (1951); 27, 622 (1953).
237. B. J. Thorpe, Surface Sci., 33, 306 (1972).
238. K. F. Wojciechowski, Proc. Phys. Soc., 87, 583 (1966).
239. D. M. News, Phys. Rev., 178, 1123 (1969).
240. M. I. Molotskii, Kinetika i Kataliz, 13, 435 (1972).
241. V. I. Oshcherov, Dokl. Akad. Nauk SSSR, 135, 1168 (1960).
242. J. W. Gadzuk, Surface Sci., 6, 133 (1967).
243. M. Tomášek, Surface Sci., 4, 471 (1966).
244. S. G. Davison and A. T. Amos, J. Chem. Phys., 43, 2223 (1966).
245. A. J. Bennett, B. McCaroll, and R. P. Messemer, Surface Sci., 24, 191 (1971).
246. G. Blyholder and C. A. Coulson, Trans. Faraday Soc., 63, 1782 (1967).
247. G. Blyholder, Chem. Communs, 625 (1973).
248. N. N. Bulgakov and Yu. A. Borisov, Kinetika i Kataliz, 7, 608 (1966).
249. N. N. Bulgakov and Yu. A. Borisov, Izv. Akad. Nauk SSSR, Ser. Khim., 23 (1972).
250. H. Dunken and H. H. Dunken, Z. Chem., 6, 233 (1966).
251. H. H. Dunken, H.-C. Fritsche, P. Kadura, L. D. Kühne, H. Müller, and Ch. Opitz, Z. Chem., 12, 433 (1972).
252. S. G. Gagarin, Yu. A. Kolbanovskii, and L. S. Polak, Teor. Eksper. Khim., 8, 216 (1972).
253. Yu. A. Kruglyak and K. B. Yatsimirskii, Teor.
253. Yu. A. Kruglyak and K. B. Yatsimirskii, Teor. Eksper. Khim., 5, 308 (1969).
254. J. C. Robertson and C. W. Wilmsen, J. Vac. Sci. Technol., 9, 901 (1972).
255. V. A. Zasukha and L. M. Roev, Kinetika i Kataliz, 15, 1005 (1974).
256. Yu. S. Mardashev and L. M. Roev, Dokl. Akad. Nauk SSSR, 18, 35 (1974).
257. T. Toya, J. Res. Inst. Catalysis, Hokkaido Univ., 6, 308 (1958).
258. A. Sherman and H. Eyring, J. Amer. Chem. Soc., 54, 2661 (1932).
259. I. I. Zakharov and V. D. Sutula, Kinetika i Kataliz, 10, 631 (1969).
260. I. I. Zakharov, V. V. Pozumentshchikov, and V. D. Sutula, Kinetika i Kataliz, 14, 694 (1973).
261. S. G. Gagarin and I. A. Lygina, Kinetika i Kataliz, 15, 224 (1974).
262. H. Kölbel and K. D. Tillmetz, J. Catal., 34, 307 (1974).
263. N. D. Chuvylkin, G. M. Zhidomirov, and V. V. Kazanskii, Kinetika i Kataliz, 14, 943 (1973); 14, 1579 (1973); 16, 92 (1975).
264. W. Th. A. M. van der Lugt, Tetrahedron Letters, 2281 (1970).
265. F. D. Mango and J. H. Schachtschneider, J. Amer. Chem. Soc., 93, 1123 (1971).
266. G. S. Lewandos and R. Pettit, J. Amer. Chem. Soc., 93, 7087 (1971).
267. R. Pearson, Acc. Chem. Res., 4, 152 (1971).
268. R. Ugo, Proc. V Int. Congr. Catal., Miami Beach, 1972, B-19 (1973).
269. G. B. Backay and N. S. Hush, Theor. Chim. Acta, 32, 311 (1974).

270. V. V. Lobanov, M. M. Aleksankin, and Yu. A. Kruglyak, Preprint, Institute of technical Physics, Academy of Sciences of the Ukrainian SSR, 74–15E, Kiev, 1974.
271. In Advances in Mass Spectrometry, v. 6, A. R. West, ed., Applied Science Publ. Barking, Essex, 1974, p. 259–335.
272. N. D. Chuvylkin, G. M. Zhidomirov, and V. B. Kazanskii, "II Sovetsko-frantsuzskoe Soveshchanie po Katalizu" (Proceedings of the Second Soviet–French Conference on Electrochemistry), Kiev, 1974.

Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovakian Academy of Sciences