Russian Chemical Reviews

October 1987



Translated from *Uspekhi Khimii*, **56**, 1593-1638 (1987)

U.D.C. 541.1

Modern Chemical Physics. Aims and Pathways to Progress

A.L.Buchachenko

CONTENTS

I. Chemical physics in modern chemistry 907
II. Structure of matter 908
1. Isolated species 908
2. Small assemblies 909
3. Large assemblies 910
III. Molecular dynamics and molecular organisation 914
1. Molecular dynamics 914
2. Molecular organisation 916
IV. Energy dynamics 918
1. Energy dynamics in gases 918
2. Migration of energy in clusters 922
3. Energy dynamics in liquids 923
4. Energy relaxation in solids 924
V. Reaction dynamics 925
1. Potential energy surfaces and theories of reaction dynamics 925
2. Energetics in reaction dynamics 929
3. Chemical kinetics and reaction mechanisms 931
VI. Spin dynamics 932
VII. Conclusion 933

I. CHEMICAL PHYSICS IN MODERN CHEMISTRY

Modern chemistry has become a high risk science. Progress in engineering and technology requires from chemistry the creation of new substances and materials with extreme and frequently contradictory and at first sight incompatible properties, the development of economical efficient technologies based on new non-traditional principles, the creation of new means for the control and diagnostics of processes and materials, and the development of new principles of chemical energetics. Under these conditions, scientific research along traditional lines of trial and error has become very

refined, laborious, and expensive and the risk of unsuccessful research, the risk of invalid trials, and the risk of errors have increased. The more complex the problem, the greater the risk of failure and of fruitless expenditure of labour, materials, and time.

The degree of risk can be reduced only on the basis of a profound knowledge of the physics of chemical processes, the theory of structure, molecular organisation, the functioning and transformation of chemical systems, and a profound analysis of the predictions following from such knowledge and understanding, i.e. on the basis of the principles constituting chemical physics. The level of this science and its state determine the horizons of chemical materials science, chemical synthesis, chemical technology and power generation, chemical diagnostics, and environmental chemistry. Naturally, each of these fields develops as a result of its intrinsic internal potential frequently entirely without being based (or not knowingly based) on chemical physics, but the increase of the complexity of chemical problems, which can be seen objectively to arise from scientific and technical progress, inevitably makes it necessary to resort to chemical physics, its corollaries and predictions, and its growing predictive power.

The aim of this article is to analyse the concerns of modern chemical physics, its present level, its aims, its ability to reduce the risks discussed above, and its growing points and prospects.

II. STRUCTURE OF MATTER

The atomic-molecular and electronic structures of chemical species and substances constitute the classical problem of chemical physics. Structure is the first, key element in the series structure–property–function. The determination of relations in this series is a problem of fundamental importance; its solution makes it possible to predict on the basis of the structure of the substance its function and purpose and its likely usefulness and applications.

Traditionally chemical physics has been concerned with the direct problem—the determination of structure and then the investigation of properties, which resulted in the determination of the field in which the given substance can be used and can function. However, the converse problem has become increasingly acute in modern chemistry—the creation of chemical structures with a specified atomic-molecular architecture in order to ensure specified properties and functions of these structures. This is important in the creation of purpose-designed drugs, semiconducting materials with specified conducting properties, alloys with specified corrosion resistance, ceramic materials with definite thermal and mechanical stabilities, optical glasses with specified electrochromism, etc.—the generality of this problem is universal.

This Section deals with the level and style in which modern chemical physics solves structural problems and the characteristics, trends, methods, and means used in such solutions. They are different for structures with different scales and levels of organisation and we shall therefore immediately introduce the following classification: isolated species (atom, molecule, ion, and radical), small assemblies (van der Waals molecule, complex, macromolecule, micelle, cluster), and large assemblies (crystal, liquid, amorphous body, membrane, etc.).

1. Isolated Species

The determination of the structural-chemical and structural-physical parameters of isolated species is the traditional task of chemical physics; these parameters characterise the electron shell and nuclear skeleton of the species (the angles and distances between atoms and bonds, the frequencies and amplitudes of vibrations, internal rotations, inversions, and conformational transitions, the energies and symmetries of the electronic, vibrational, and rotational states, ionisation potentials, electron affinities and bond energies, the polarisability tensor, the magnetic and electrical dipole moments, the charge and spin distributions, the dipole moments of electronic transitions, the oscillator strengths, the electron delocalisation frequencies, the energies of quadrupole and electron-nucleus magnetic interactions, etc.). They are required for calculations on the thermodynamics of gases and plasma, for the calculation of the composition of species and their state, for the prediction of properties, stability, and conditions governing the existence and the reactions of chemical systems (especially at high and ultrahigh temperatures). They are needed in chemical energetics (emissive power of high-temperature gases under non-equilibrium conditions, the functioning of gas lasers, etc.).

Three new features have imparted a modern "aspect" to this traditional task of chemical physics: intense efforts to attain highly excited states, the endeavour to characterise "exotic" species, and finally, the very high (sometimes close to the limit) metrological accuracy.

The very marked tendency to specify the structural and spectroscopic characteristics of excited states—just as complete as for the ground state—has arisen for a number of reasons. Firstly, this is associated with the search for new laser systems and the choice of species (emitters) suitable for generation. For this purpose, one needs knowledge of the spectroscopy of the species which is as complete as possible—the energy and symmetry of the excited levels, the radiative lifetimes, the probabilities of the radiative and nonradiative transitions, etc.

Secondly, it is needed as an analytical means for the identification and recognition of excited species in processes induced by electron impact, photo-excitation, and powerful collisions (the chemistry and optics of the atmosphere, space chemistry and plasma, high-temperature chemistry, combustion and explosion, shock waves, etc.).

Thirdly, the properties of excited states and their potential energy surfaces are needed for the prediction of reaction pathways, for the prediction of orbital symmetry-dependent prohibitions, for the assessment of the adiabatic nature of reactions and calculations on the chemical dynamics of elementary processes, for the analysis of ways of transforming chemical energy and procedures for the chemical pumping of the reaction products. An enormous amount of work has already been carried out on the characteristics of the excited state of atoms and diatomic and triatomic molecules and radicals and this "energy programme" in chemical physics has been extended increasingly to polyatomic molecules and radicals; the principal research techniques are laser and microwave spectroscopy in different versions and combinations. The "energy programme" in chemical physics is characterised most strikingly by the enormous range of the states of atoms investigated—from hot, Rydberg atoms to ultracold atoms.

When the valence electron is excited to high orbitals with large values of the principal quantum number n (n reaches values of several tens up to 100) and is remote from the nucleus, its energy levels are described by the familiar simple Rydberg formula and such excited atoms are referred to as Rydberg atoms. The energy transitions between levels with high values of n correspond to millimetre waves; the energy of the levels is altered by an external electric field, which can even induce the ionisation of the Rydberg atoms; one method for their detection is based on this phenomenon.

The properties and energetics of Rydberg atoms have been investigated quite widely and in fair detail. For example, even the isotopic shifts in the energy of the atoms, caused by the magnetic electron–nucleus interaction, have been measured. Thus the difference between the energies of the ^{86}Sr (nuclear spin $I = 0$) and ^{87}Sr ($I = 9/2$) isotopes and its dependence on n have been measured for the Sr ($5sns$) atoms. The difference ΔE is 0.4 GHz for $n = 35$, 0.9 GHz for $n = 50$, and 1.7 GHz for $n = 70$; in the limit at $n \to \infty$, ΔE tends to 2.8 GHz—the energy of the hyperfine interaction of the 5s electron with the ^{87}Sr nucleus.

One of the remarkable properties of Rydberg atoms is as follows. In a resonator with a very high Q-factor, the photon emitted by a Rydberg atom is retained for a fairly long time, so that it can be recaptured by the same atom. Hence arises the possibility of constructing a single-atom laser, in which a two-level atom interacts with a single-frequency electromagnetic field, which is accompanied by the absorption and emission of the same photon by the same atom. A system which will make it possible to test experimentally the postulates and predictions of quantum electrodynamics is being created at the present time. From this point, chemical physics is at the junction with atomic physics and quantum electrodynamics.

The preparation of ultracold atoms is based on the alteration of the velocity of an atom following the absorption of an optical quantum (laser cooling of atoms). If the atoms and laser photons are tuned in such a way that the absorption takes place in the low-frequency wing of the absorption line, then the resonance absorption by the atom moving towards the photons shifts to the centre of the line and intensifies by virtue of the Doppler shift, whereas for atoms moving in the same direction as the stream of photons the Doppler effect displaces the resonance from the centre of the line and decreases the absorption. As a result the atoms experience a retarding force directed along the stream of photons. If the atoms are now placed in opposed laser beams directed along three orthogonal axes, it is possible to ensure a comprehensive retardation of the atoms. In such a laser field, the movement of the atoms is retarded with a velocity decay time of $\sim 10^{-4}$ s as if they were in an optically viscous medium, which is referred to as "optical treacle". Thus Na atoms can be cooled to 2.4×10^{-4} K and in principle there is a possibility of cooling down to 10^{-6}–10^{-10} K.

Ultracold atoms, virtually lacking kinetic energy, are of interest in precision spectroscopy and in the probing of atom–atom and atom–surface potentials. They also lead to a unique possibility of an experimental test of the fundamental postulates of quantum mechanics, in particular of Bose condensation. Here again, chemical physics adjoins quantum physics.

The second feature of modern structural chemical physics involves a sharp and bold expansion of the assortment of species investigated, including the chemical bonds between the atoms of the elements of almost the entire Periodic System in various combinations, many of which were not so long ago regarded as exotic: Si_2H_2, AsH_2, AsN, CrO^+, PH, ZrO, BeTi, LiPd, Cd_2, CsH, BI, SeO^+, PCl^+, NaCr, HCr, ScLi, SrBr, Si_3, Si_2C, SeS, Li_3, MgC_2, CrN^+, CrC^+, muonium and muonium-containing molecules, ions, and radicals, etc.—the list of such species is becoming ever longer. The distances and angles between atoms, the vibration frequencies, the energies of the ground and excited states, the Coriolis constants, the spin-rotational and spin–spin interactions, potentials, etc. have been measured for them. These trends have been stimulated by the search for new laser systems, the research into the spectroscopic detection of high-energy processes in plasma, in flames, in interstellar space, and in the atmospheres of the stars and planets, and also the search for ways of synthesising new substances and materials. Earlier such exotic molecules were detected predominantly in space, whilst nowadays they are obtained and investigated in wide assortment under laboratory conditions.

The third feature is the extremely high metrological level of the structural information and its exact quantitative description, i.e. the high level of what can be designated in English by the simple word quantification (the corresponding Russian term "kolichestvennost'" is unusual and is hardly likely to be adopted in our language). Thus the hyperfine interaction energy in the Cs atom in the ground $^2S_{1/2}$ state is 9192 631 784 ± 31 Hz and has been measured with an accuracy of 1 part in 10^9. Furthermore, the dependence of this quantity a on the inert gas pressure p has been measured; the change amounts to approximately 10^{-6} of α. For He and Ne, $da/dp = +874$ and 450.2 Hz GPa^{-1}, while for Ar we have $da/dp = -146.7$ Hz GPa^{-1}, which means that the collisions of the Cs atom with He and Ne "clamp" the unpaired Cs electron to the nucleus and intensify the electron–nucleus interaction, while collisions with Ar move the electron away from the Cs nucleus and diminish this energy (probably as a result of the mutual "adhesion" of the Cs and Ar atoms and the partial, approximately 10^{-6}, electron transfer from Cs to Ar). In the excited state $^2P_{1/2}$, the hyperfine interaction energy is 1168 MHz, while in the $^2P_{3/2}$ state it is only 200 MHz. The latter values were obtained with coherent laser excitation of the D_1 and D_2 lines of the Cs atoms and from the observed quantum beats in the transitions between the levels of the hyperfine structure.

The molecular constants of MgO, PbO, and N_2O_3 have been measured with a high degree of accuracy for all the isotopic forms of these molecules and the quadrupole and magnetic interaction tensors and the spin-rotational coupling constants have been determined. The molecular constants for all the isotopic forms of O_2 [including the constants of the magnetic spin-Hamiltonian and among these the constant for the hyperfine interaction with the ^{17}O nucleus: $a(^{17}O) = -54.758$ MHz] have been determined. Measurements have been made with a high degree of accuracy for the hyperfine interactions (both isotropic and anisotropic) of the radical-cation $Cr(CO)_4^+$ with the ^{53}Cr and ^{13}C nuclei and on their basis it was concluded that the above radical-cation has the T_d symmetry and that the unpaired electron is localised in the pure σ orbital. These are only a few instances demonstrating how the high metrological level of the structural information ensures the reliability and non-ambiguity of the conclusions concerning the chemical structure of the species.

The high degree of "quantification" of structural chemical physics reflects, on the one hand, the high metrological level of the modern physical research methods—magnetic resonance in its different versions, Mössbauer, microwave, laser, X-ray, and photoelectron spectroscopy, mass spectrometry, and their numerous "hybrid" combinations. On the other hand, it is of practical value for quantum magnetometry with its frequency standards—it ensures the "raising" of the accuracy and reliability of quantum chemistry as well as the improvement of its computational methods and schemes.

2. Small Assemblies

Small assemblies occupy a position intermediate between individual molecules and continuous systems constituting a phase (liquid, crystal, amorphous glass, etc.). They represent a bridge between the individual molecules and their infinitely large assembly, where intermolecular interactions arise and the characteristics of matter are manifested.

Depending on the character and strength of the intermolecular interactions in the substance, either the properties and features of individual molecules are retained or they are completely lost.

In chemical physics there is an old problem which has now got, as it were, a new lease of life by virtue of advances in the study of the structure and properties of small assemblies. This is the problem of how the hierarchy based on composition (ranging from an individual molecule to a substance) is related to the hierarchy based on properties and functions in a given series, for which quantitative compositions are the qualitative features of a substance (or a phase) manifested, and for what number of individual species does the combined assembly of the latter become a substance and does this occur gradually or is there a "critical" threshold mass.

Van Der Waals Molecules and Complexes. The term van der Waals molecules is given to weakly bound complexes of atoms, radicals, or molecules which exist by virtue of intermolecular attraction. They are observed in rarefied molecular beams, gas streams expanding at ultrasonic velocities, in solid inert gas matrices, and in liquids, and are investigated by laser and microwave spectroscopic methods. An enormous number of such species are known: He_2, Xe_2, $(H_2)_2$, Hd.Ar, $(HF)_2$, Hg.He, $C_6H_6.CH_4$, ICl.Ne, HF.CO, $(N_2O)_2$, $(CO_2)_2$, $(SF_6)_2$, $OCS.CH_4$, Mg.Ca, H_2S.Ar, C_2H_4.Ar, C_2H_4. .NO, CO.He, HCl.Xe, $(C_2H_2)_2$, etc. The completeness, reliability, and "quantification" of the structural information for such molecules and complexes is not inferior to that for isolated species. For van der Waals molecules, measurements are made of the symmetry and geometry (on the basis of the rotational spectra and moments of inertia), the quadrupole and spin–spin interaction constants, the rotational g-factors, the magnetic susceptibility and its anisotropy, the dipole and quadrupole moments, the vibration frequencies, the dissociation energies, the lifetimes, etc.

Thus $HCl.C_2H_4$ and $HCl.C_2H_2$ have the T-form: the axis of HCl passes through the centre of the partner molecule and is perpendicular to its axis. The distance from the Cl atom (it is the more remote) to the centre of the partner molecule is 3.724 and 3.699 Å for C_2H_4 and C_2H_2 respectively. In the van der Waals molecules $HCl.C_3H_6$ and $HCl.C_6H_6$, the HCl axis is perpendicular to the planes of the cyclopropane and benzene molecules and coincides with the C_{3v} and C_{6v} symmetry axes of these molecules. The distances from the remote Cl atom to the C_3H_6 and C_6H_6 planes are 3.567 and 3.629 Å. The molecules Kr.HCl and Kr.DCl are linear and their dissociation energies are 179 and 200 cm^{-1}, i.e. even a negligible isotope effect in the dissociation energies is readily measurable. The partner molecules CO and HF are organised into a linear complex with $C_{\infty v}$ symmetry, in which the H atom is "stuck" to the C atom; the dipole moment of the complex, measured on the basis of the Stark effect in the ground vibrational state for the rotational transition $J = 1 \to 2$, amounts to 2.352 D. The complex of N_2 with HF is linear, i.e. N(1)–N(2).HF; for this complex, the components of the quadrupole interaction tensor involving both ^{14}N nuclei have been measured and it has been found that the addition of the HF molecule induces a shift of electron density from N(1) to N(2), amounting to 0.03 of an electron.

In the NaK molecules, the partners are held together by long-range van der Waals forces and the two electronic states differing in spin ($^1\Sigma^+$ and $^3\Sigma^+$) are therefore energetically equivalent with a dissociation energy $D_e = 203.1$ cm^{-1} and an interatomic distance of 5.457 Å. For $NaLi(X^1\Sigma^+)$, we have $D_e = 6850$ cm^{-1} and in the excited state ($B^1\Pi$) the corresponding value is $D_e = 1758$ cm^{-1}. In the LiLi, LiNa, LiK, LiRb, and LiCs series, the vibration frequency decreases linearly from 350 to 180 cm^{-1} as a function of $m^{1/2}$, where m is the reduced mass of these van der Waals molecules (these results have been obtained in molecular beams using the laser-induced fluorescence of these molecules).

The dynamics of the van der Waals molecules, namely the lifetime in the ground state, the lifetimes in the excited and dissociative states, the distribution of the energy among the fragments after dissociation, etc., has been studied in detail. Thus the $He.I_2$ molecule exists for ~100 ps, while the lifetime of H_2.Ar is three times longer; in both cases τ decreases with increase of the excess energy. The energetics and "energy problems" of the van der Waals molecules are examined in greater detail in Section IV.

In a liquid, the shifts of the lines in the electronic absorption spectra and their dependence on the polarisability of the solvents are believed to indicate the presence of van der Waals molecules. Thus the combination of the partner molecules in the species C_6H_6.He, C_6H_6.Ar, $C_6H_6.CH_4$, CH_4.toluene, CH_4.aniline, Ar.toluene, etc. has been identified.

The question arises why there is so much interest in the van der Waals molecules and why they are needed. The van der Waals molecules are the most reliable and the richest source of information about the intermolecular atom–atom pair potentials—their form and parameters; by virtue of these molecules, intermolecular potentials have now entered the age of high spectroscopic accuracy. Furthermore, a reduced potential has been found for inert gas atom pairs which is universal for these pairs and describes the interaction of the atoms with an accuracy better than to within 1%. One of the important questions is whether this universality is a common property of any pairs of atoms or whether it applies only to pairs of inert gas atoms and this question still awaits an answer.

Intermolecular potentials are reference quantities in problems of molecular dynamics in liquids, glasses, and macromolecules, in problems of chemical dynamics (calculation of the trajectories traversed by the reacting systems on the potential energy surface), in problems concerning intermolecular energy transfer and energy relaxation (in this case the efficiency of the transfer or relaxation is determined by the Fourier component of the potential and the frequency of the energy transition).

Interatomic and intramolecular potentials are responsible for the molecular organisation of crystals and large molecules, the packing of molecules in liquids, glasses, etc. A high accuracy of the potentials over all distances is required for such purposes and potentials of different interactions are needed: atom–atom, atom–non-spherical molecule, molecule–molecule, molecule–ion, etc.

The formation of van der Waals molecules is manifested in the macroscopic properties of gases—it alters the form of the pVT diagrams, the second virial coefficient, and the viscosity. These molecules induce the condensation of gases, crystallisation, and apparently other phase transitions. They are important at the critical points of the substances, where they determine the density fluctuations and the correlation radius. All these problems are within the sphere of the concerns of modern chemical physics.

The question arises whether van der Waals molecules play any significant role in chemical reactions. At first sight, the answer should be negative, because the bond energy between the partner species is low, frequently less than kT, so that collisions with extraneous molecules induce the decomposition of the van der Waals molecules. However, the angular distribution of the reaction products in molecular beams indicates unambiguously that many reactions are preceded by the formation of an intermediate complex, whose lifetime is longer or comparable to its rotation period (≳1 ps) and is much longer than the duration of the collision of the

reactants. Such reactions include Cs + RbCl → CsCl + Rb, Cl + I_2 → ICl + I, D + H_2 → DH + H, etc. The intermediate complexes in these reactions can be regarded as van der Waals molecules, because they can hardly involve any specific interactions other than the van der Waals interactions (for example in D.H_2, in the reaction D + H_2 → DH + H). In chemical dynamics, it is assumed that such reactions proceed via a statistical complex (see Section V). Van der Waals molecules and complexes are two concepts between which it is not possible to draw a boundary in the general case. There exist, however, two approximate criteria for their differentiation—the energy and structural criteria. A complex is assumed to be a species in which the bond energy between the partners exceeds kT and can reach considerable values; if, on the other hand, the bond energy is less than or comparable to kT, such a complex is regarded as a van der Waals molecule. Furthermore, in the van der Waals molecule the interactions between the partner species are universal and non-localised; on the other hand, in the complex the interactions between the partner species are specific and localised and one can rigorously specify and demonstrate the mutual orientation of the partner species, the atoms or atomic groups through which they are bound, and the electronic orbitals which they place at the disposal of one another on "contact". For other complexes (such as complexes of metal ions with organic and inorganic ligands included within the sphere of interest of inorganic and coordination chemistry), the solution of the problem of the organisation of the partner species has long been known. For weakly bound complexes in solutions and in gases, this problem has also been solved successfully by microwave and laser spectroscopy and magnetic resonance. For example, the characteristic features of the complex formation reactions of organic radicals and molecular oxygen with organic ligands, based on the magnetic properties of the complexes and their manifestations in magnetic resonance (EPR and NMR), have been found and the structure and dynamics of these complexes have been established.

Complex formation is an old, classical problem of chemical physics and two features impart to it its modern aspect: firstly, the high level of "quantification", characteristic, as mentioned above, of the entire chemical physics; secondly, definite structural characteristics of the organisation of the partner species—how they are oriented, which orbitals participate in complex formation, and what is the topography of the complex. Behind structural problems, there is another, more important functional problem—how does complex formation modify the electronic shells of the partner species and how does it alter their reactivities? Here chemical physics endeavours to achieve a major aim—to employ complex formation as a chemical principle for the control of the reactivity of species, to establish the general internal relations between structure and reactivity, and to extend them to the predictive level.

Particular attention is paid in modern chemical physics to complexes of excited molecules—excimers and exciplexes. Their characteristic feature is that the bonding in them is achieved only in the excited electronic state of one of the partner species; in the ground, unexcited state, there is no bonding and this state is dissociative. The interest in these complexes is partly associated with the investigation of the pathways leading to energy relaxation, but interest is mainly concentrated on excimer lasers in which the generation threshold is reduced as a result of the emptying of the lowest level (because it is dissociative) and a high generation power is attained.

Clusters. This term combines a wide set of species containing from several atoms or molecules to several tens or hundreds of atoms or molecules, for example $(H_2O)_n$, Cu_n, Na_n, Na_n^+, Ag_n, $(OCS)_n$, Cu_n^+, $(NH_3)_n$, Bi_n, $(CO_2)_n$, $(H_2)_n$, K_n, Mg_n, Pt_n, Al_n, $(H_2O)_n(NH_3)_mH^+$, He_n, $(N_2)_n(NO^+)$, Hg_n^+, K_n, Xe_n, In_n, $Cu_nBe_m^+$ $Pt_{38}(CO)_{44}$, etc. where n and m vary from several units to 1–2 tens and for certain clusters up to several tens and even hundreds. Clusters can be atomic, molecular (comprising atoms and molecules), and mixed—atomic-molecular, neutral, or charged. They are obtained and investigated in gases (for example, in streams expanding at ultrasonic velocities), in zeolite channels (the In_8 cluster has been obtained in this way), and in solid matrices (for example, in solid argon or xenon). Fig.1 illustrates the composition of the gas clusters formed by iodine in a helium–neon mixture; the great structural variety of these species is clearly seen. They differ in composition, properties, and in the nature of the forces retaining the species within the cluster.

Clusters are comparatively new species in chemistry and their appearance is due to advances in organoelemental and organometallic chemistry in the first place and also in chemical physics (for atomic and molecular clusters). An enormous number of studies are now being devoted to the methods of synthesis of clusters and their properties and structure. Their role in the physics of condensation, evaporation, and crystallisation, where they are precursors of a new phase, a kind of "protophase", has been clearly recognised. However, the greatest interest is associated with the chemistry of these species, their reactivity, their catalytic "potentials", and their direct use in chemical materials science.

The concerns of chemical physics are concentrated on the structure and properties of these species, their spectroscopy, energetics, dynamics, stability, and conditions governing their existence. The level of "quantification" is in this instance no worse than for individual species. For example, it is known that the Cu_3 cluster is a triangular Jahn–Teller molecule with a pseudorotation barrier of 111 cm^{-1}, which is only slightly less than the energy of the zero-point vibrations (118 cm^{-1}), and a symmetrical vibration frequency of 269.5 cm^{-1}. The electronic states of this cluster, the frequencies and intensities of their electronic transitions, their geometry, etc. are known. It has been demonstrated by time-of-flight mass spectrometry that the Xe_n clusters have a preferentially eicosahedral structure with stability maxima corresponding to certain coordination numbers under the conditions of maximum close packing (the "magic" numbers n = 13, 19, 55, 147).

However, the main, fundamental problem (with which we began this Section on small assemblies) concerns the question how the properties of individual species evolve on combination of the latter into the properties of a substance—the properties of a new phase. This is a problem of evolution of quantity into quality and is being vigorously developed in terms of two aspects—the structural-physical and purely chemical aspects.

In the structural-physical aspect, one establishes the dependence on the structure of the cluster of its physical parameters and properties: the symmetry and type of lattice the interatomic distances, the vibration frequencies and amplitudes, the bond energies, the ionisation potentials, the Debye temperatures, the heat capacities, and the dielectric constants, and, for metallic clusters, also the Fermi levels, the spin and charge densities and their distribution within the bulk of the cluster, the electrical resistance, magnetisation, etc.

Here are a few examples illustrating the level attained in the solution of the structural "cluster" problems. Among the charged molecular hydrogen clusters $(H_2)_n^+$, obtained by the photoionisation of the neutral clusters $(H_2)_n$, only the odd ions H_{2n-1}^+ have been detected but not the even ions. On the basis of experiments and calculations, it has been

concluded that the odd clusters contain at the centre the skeleton of the triangular ion H_3^+ surrounded by hydrogen molecules. The adiabatic ionisation potentials of the water molecule, its dimer, and ice vary in the sequence 12.6, 11.1, and 8.8 eV, i.e. the change in potential on dimerisation is ~40% of its total change in the transition from an isolated molecule to a substance (ice). This is also valid for the vertical potential and means that the greatest changes in properties occur in the association of the first two–three molecules. On the other hand, the ionisation potential of the Na_n clusters diminishes slowly with increase of n and its fall is accompanied by oscillations; the even members of the series have a higher ionisation potential than the odd members, but even for the Na_{14} cluster the ionisation potential is still greater (appreciably greater—by a factor of 1.5) than electron work function of metallic sodium. In the Ag_n clusters, the characteristics of the transition from molecular properties to metallic properties are manifested already for $n = 6$ (they are observed in the electronic spectra from the excitation of the surface plasmons characteristic of the metallic state), while for $n = 10–15$ the cluster becomes purely metallic.

The Fe_{15} cluster has an average magnetic moment of 2.2 μ_B per atom, while in the metal this quantity is 2.7 μ_B. Theoretical estimates yield the following distribution of the magnetic moment with respect to the bulk of the cluster: 1.1 μ_B for the central atom, 2.7 μ_B for each of the first eight neighbours, and 2.8 μ_B for each of the six neighbours of the second "rank". The electrons are also distributed non-uniformly: the central atom of the cluster has 1.27 electrons more than the surface atoms. In terms of a number of properties (the structure of the electronic spectrum, magnetism), the Fe_{15} cluster is already fairly close to metallic iron, although certain differences from the metal are observed even for the Fe_n clusters with $n > 15$).

The Cr_{15} cluster has a magnetic moment (in contrast to the metal which is anti-ferromagnetic) and the distribution with respect to its bulk is as follows: -0.7 μ_B for the central atom, +4.1 μ_B for the first neighbours, and -3.4 μ_B for the second neighbours. In metallic chromium the magnetic moment of each atom is 0.7 μ_B, i.e. the magnetic state of the central atom in Cr_{15} is the same as in the metal, while the overall magnetic moment of the cluster is determined by the magnetism of the surface atoms (the non-equality of the magnetic moments of the first and second spheres).

The structural-physical studies embrace all types of clusters—atomic, molecular, purely metallic, and organometallic, whose nucleus consists of the metal atoms and the surround is made up of organic groups. The clusters in biomolecules (for example in nitrogenase and ferrodoxin), where they are responsible for the functioning of these biomolecules, merit special attention.

We shall now discuss the chemical behaviour of the clusters (we recall that this will be done in connection with the evolution of quantity into quality). The idea of the "chemical" approach will be illustrated in relation to the proton transfer reaction. In the $(HA)B_n$ cluster, the acid molecule HA is combined with n molecules of the base B. The proton transfer from HA to B via the reaction $(HA)B \rightarrow A^-(H^+B_n)$ is detected from the appearance of the anion A^-. The question is whether this reaction depends on n and whether there is a threshold value of n at which it begins. Experiments of this type have been performed with the aid of laser spectroscopy. In the α-naphthol (HA) clusters with ammonia (B), HA is excited to the singlet state S_1. In the ground state α-naphthol is a weak acid with $pK_\alpha = 9.4$, while in the excited S_1 state it is a strong acid with $pK_a = 0.5$. The proton transfer in the $(HA^*)B_n$ cluster does not occur for $n = 1–3$ (the A^- anion is not formed). The proton is transferred only in the clusters with $n \geq 4$. In the case of β-naphthol, whose $pK_a = 2.8$ in the excited S_1 state, the same reaction occurs only in clusters with $n \geq 10$. In the $(HA).(H_2O)_n$ clusters with α-naphthol in the S_1 state, proton transfer is detected only for $n \geq 20$. Thus the question whether the cluster acquires the properties of a "phase" has a clear-cut answer, but it is not as yet general. In the examples quoted above,

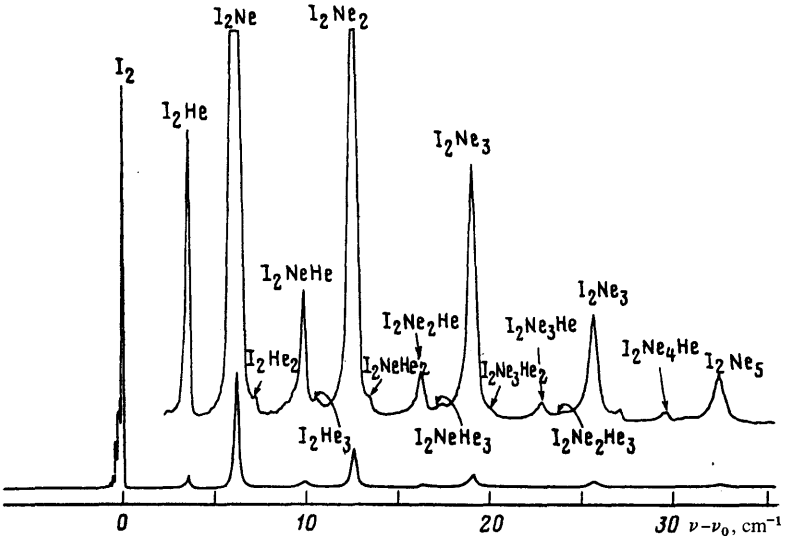


Figure 1. The fluorescence excitation spectrum of a stream of iodine vapour in a helium–neon mixture expanding at an ultrasonic velocity; the assignments of the lines to clusters having different compositions are illustrated; $\nu_0 = 17982$ cm^{-1}

the threshold value of n depends on the strength of the acid and base—the stronger the acid and base, the sooner does the cluster exhibit the features of a "phase".

For the same purpose, extensive studies have been made of the ion–molecule reactions in the clusters $(H_2O)_nH^+$, $(NH_3)_nH^+$, $(CH_3OH)_nH^+$, $(CH_3COCH_3)_nH^+$, and $(CH_3X)_n^+$ (X = F, Cl, Br, or I), and also in the mixed clusters $(CH_3X)_n^+ \cdot (CO)_m$, $(CH_3X)_n^+(N_2)_m$, $(CH_3COCH_3)_n^+(CH_3OCH_3)_m$, etc. The aim of these studies was to find the characteristic features of the ion–molecule reactions (radical, nucleophilic, electrophilic) in such small assemblies, to create bridges between these reactions in gases and liquids, and to establish how the characteristics of the gas-phase reactions are transformed into those of liquid-phase processes and what is the size of the cluster when the latter begins to simulate the liquid or solid phase.

The answers to these questions are of special interest for catalysis—both homogeneous and heterogeneous. This is a problem of molecular organisation—how the atoms must be "arranged" on the surface of the catalyst and what should be their number in the cluster in order to ensure the activation of specified molecules and the catalysis of definite, selective reactions. For example, the catalytic activity of metallic gas-phase Nb_x clusters in the dehydrogenation of benzene has a threshold character: it is manifested for $x \geq 4$ and reaches a maximum for $x = 5$, 6, and 11, but it is found to be low for $x = 8$ and 10. The Nb_8 and Nb_{10} clusters also exhibit a low activity in the reactions with H_2 and N_2 and are distinguished among other clusters by their high ionisation potentials.

It is known that molecular hydrogen dissociates when it is adsorbed on metallic nickel and cobalt. However, calculations have shown that there is no dissociation in the interaction of nickel and cobalt atoms or of Ni_3 and Co_3 in the linear configuration with hydrogen. However, the Ni_3 and Co_3 triangular clusters as well as the Ni_{13} cluster do ensure dissociation. Thus the triatomic cluster with C_{3v} symmetry is the smallest, "threshold" structural element ensuring, for example, the catalysis of hydrogenation.

The problem of the evolution of quantity into quality has not so far had a general solution—neither in the structural-physical nor in the chemical aspect, but ways leading to the solution have already been found and progress on these lines constitutes one of the most important fields of chemical physics.

Special mention should be made of the chemical physics of metallic clusters in connection with the wide prospects for the application of these clusters in materials science and their use in optoelectronics and microelectronics (light filters, radiation receivers, solar batteries, composite materials, amorphous metals, new types of ferrites, etc.). [Isolated macromolecules must also be included among small assemblies. The concerns of chemical physics include the statistics of macro-molecules, internal rotation barriers, stereochemistry, optical isomerisms, the shape of macromolecules and the relative contributions of chaos and order to their organisation (coils, helices, linear chains, etc.), the interaction of macromolecules (the permeability and intertwining of coils, crystallisation, complex formation, and binding of macromolecules, including their binding to solid surfaces) "phase" transitions in isolated macromolecules (of the helix–coil type), etc. The aim of the studies of the structure and dynamics of macromolecules is to understand the principles governing the organisation of such macromolecules in block polymers, in blends, and in composite materials and to develop methods of controlling such organisation. These problems are important for ensuring the elasticity and strength of polymeric materials, for their rheology, and for the creation of new materials; here chemical physics adjoins the molecular physics of macromolecules.

3. Large Assemblies

The study of the structures of liquids and solids—amorphous and crystalline, individual components, and solutions—is the traditional task of chemical physics. The theories of liquids and solids (classical, semiclassical and quantum theories, statistical and dynamical theories), the short- and long-range order, the dynamics and the phonon spectra of crystals, the distribution function, and the computer simulation of structure and dynamics is a far from complete list of the traditional problems. The same problems are formulated in the study of disperse systems—suspensions, porous bodies, emulsions, aerosols, etc.

However, gradually the emphasis is shifting towards less traditional problems, among which most attention is being devoted to the structure of molecularly organised systems and the structure of defects and defective bodies. Thin films, adsorption layers, interfaces, liquid crystal formations, clathrates, "whiskers", monolayer and two-layer membranes, micelles, layer structures, intercalates, and Langmuir–Blodgett films—are examples of non-ideally organised structures (in contrast to crystals with their ideal organisation). The structure of these systems, their thermodynamics, the determination of the conditions governing their existence and their stability, and their behaviour in various external fields (electrical, mechanical, magnetic, and acoustic) are being investigated with the aim of deducing the principles governing the molecular organisation of such systems, the development of methods for controlling their organisation, and the prediction of the varied and useful functions of these systems.

Another modern aspect of structural chemical physics is the increasing interest in defects: impurity centres, dislocations, vacancies, molecular cavities, and local heterogeneities. New methods in chemical physics—high-resolution magnetic resonance, the annihilation of the positron and positronium, and the chemistry of muonium—are used together with traditional structural methods to analyse the defects, their nature, the structure and crystallographic environment in the vicinity of the defects, and the symmetry and amplitude of the distortions. Like isolated species, the defects are characterised by a high level of "quantification". For example, the irradiation-induced defect in zinc acetate is the radical $\dot{C}H_2CO_2(Zn)$, in which the CH_2 group executes complete rotations (jumps) around the CH_2–CO_2 bond with a barrier of 18.4 kJ mol^{-1}, while the torsional vibrations take place with an energy of 6.7 kJ mol^{-1}. This level of accuracy is typical also for the characteristics of other crystal defects.

The detection of structural heterogeneities and local cluster formation is very important for materials science; methods are being developed for non-disruptive detection. Thus the localisation of residual Si–H bonds of the cluster type has been observed in amorphous silicon (the importance of this material is generally known) by NMR. Atomic aggregates corresponding to Fe_n clusters with $n \cong 45$, in which the spin "ferromagnetic" correlation is retained at temperatures exceeding the macroscopic Curie temperature by 80 K, have been found in metallic iron from low-angle neutron scattering, i.e. the local Curie temperature is much higher than the average Curie temperature.

There is a growing interest in two extremes–completely ideal defect-free structures and highly defective structures; the latter is associated with the unusual effects and the unusual behaviour of substances under the conditions of shear deformation under pressure. In particular data are available concerning the appearance of strong paramagnetism in deformed diamagnetic metals and there has been a claim (which requires

confirmation) that ferromagnetism appears in highly defective NaCl.

Structural chemical physics has self-evident aims: it "operates" on materials science—a large and most timely field of modern engineering, and is concerned with the development of principles governing the organisation of matter into specified structures and the principles used in controlling structure in order to create new generation materials with a predicted functional purpose. The strategy based on the transition from structure to properties and functions is the most reliable in modern materials science, on the basis of which considerable advances have already been achieved: new surfactants have been obtained for the large-scale removal of petroleum pollution from the surface of the sea and superconducting ceramics, organic metals, ferromagnetics, etc., have been created.

---o0o---

The structure of individual chemical species and their assemblies—large and small—belongs to the set of classical problems of chemical physics. While modern chemical physics is still concerned with the solution of this problem, nevertheless most attention (priority) is given to dynamic problems, which can be grouped to a first approximation into "four types of dynamics":

1) molecular dynamics, i.e. the dynamics of the movement and displacement of species;

2) the energy dynamics, characterising the time evolution of the energy in isolated molecules and their assemblies (migration, transformation, and relaxation of energy);

3) chemical dynamics, i.e. the development of the chemical interaction of species as a function of time (including chemical kinetics as a diagnostic method for the mechanisms of chemical reactions);

4) spin dynamics, i.e. the dynamics of the population and evolution of the spin states of the reacting species.

III. MOLECULAR DYNAMICS AND MOLECULAR ORGANISATION

The important position of molecular dynamics and chemical physics is due to the following factors. Firstly, molecular movements ensure the time modulation of intermolecular potentials, i.e. they create perturbed, random ("white") or correlated noise. The Fourier spectrum of this noise determines the energy dynamics of the molecules (energy transfer and quenching of excited states, energy pumping, and relaxation). Molecular movements modulate also the magnetic interactions and they are therefore responsible for the spin dynamics and magnetic relaxation.

Secondly, molecular dynamics ensures contact between the reacting species and their appropriate mutual orientation, namely their suitable "micro-organisation" in the transition state of the reaction—not noly for diffusion controlled reactions (this is self-evident and even trivial) but also for reactions occurring under kinetic conditions (especially in solids-see Section V).

Thirdly, molecular dynamics constitutes a pathway to molecular organisation; it is not fortuitous that both concepts are considered here together in a single Section. One cannot say that molecular organisation is a function of molecular dynamics alone, that only dynamics organises structures. Molecular organisation is determined primarily by thermodynamics and its laws. However, among molecularly organised systems (including biomolecules), non-equilibrium systems occupy a major place (they are in fact as a rule of greatest interest) and their formation, stability, and, what is still more important, their functioning are determined by molecular dynamics. Finally, the most important factor is that the dynamics of translational, rotational, and orientational movements of the structural elements of substances and materials (electrical and magnetic dipoles, electrons, ions, and molecular fragments) determines the properties of materials—mechanical strengths, elasticity and plasticity, rheology, electrical conductivity, magnetism, dielectric strength, etc.

1. Molecular Dynamics

The theoretical methods used in the analysis of molecular dynamics are just as varied as the experimental methods. The task of the theory is to find ways for the correct description of diffusion, to establish a relation between the "microscopic" dynamics and the transport macroproperties of the medium, and ultimately to impart a predictive power to the theory. A number of approaches have been developed for the solution of this problem. The self-diffusion coefficient D is expressed in terms of the autocorrelation velocity function $z(t) = \langle u_x(t).u_x(0)\rangle$, where u_x is the x component of the velocity of the selected species; in its turn, the function $z(t)$ is related to the radial distribution function and the frequencies of the harmonic oscillations of the given species in the medium. Its detailed behaviour is investigated by the computational methods of molecular dynamics based on the synthesis of the trajectories in the movement of the species by the numerical integration of the classical equations of motion. The validity of the approximations in the selection of the parameters and the function $z(t)$ is estimated by comparing the theoretical and experimental values of D. For low densities of the medium, $z(t)$ decreases as $t^{-3/2}$, while for high densities its behaviour is complex, oscillatory, and analytical predictions are difficult.

The dynamics of a Brownian particle (i.e. a large and heavy particle placed in a medium comprising small and light particles) constitutes a traditional problem. Such a particle does not respond to individual impacts by the molecules in the medium and its dynamics is controlled by the random fluctuations of the forces acting on its surface. The equation of motion has the classical form of Newton's second law:

$$mu = F[t, u(t')] \ ,$$

where the velocity u and the force F at time t depends also on the velocity $u(t')$ in the preceding instant t'. Depending on whether there is a correlation between the past and the present (i.e. a correlation between t' and t) and its form, the solutions assume different forms. The search for these solutions at different correlation levels and comparison of their predictions with the experimental reality constitute in essence the subject with which the theory is concerned.

If the characteristic time of the fluctuations F is short compared with the velocity decay time, then F depends solely on $u(t)$ and there is no correlation between the past and the present. This situation is described by the familiar simple Langevin equation in which the force and the coefficient of friction are calculated. This problem is again solved at different approximation levels for the autocorrelation velocity function and the force, for the distribution of the initial velocity u_0, etc. In one of the approximations (u is small and the liquid is incompressible), one finds, in particular, the familiar Stokes–Einstein relation. For high velocities, the characteristic velocity decay time is $\sim 10^{-13}$ s, i.e. is of the same order of magnitude as the time taken by a sound wave to traverse the intermolecular distance. The Stokes

approximation then fails and account must be taken of the elastic properties of the medium and the high-frequency spectrum of the elastic vibrations: this is the familiar Zwanzig–Bixon approximation.

The simple Langevin equation predicts an exponential decrease of the autocorrelation velocity function, which is not correct. This means that one cannot neglect the correlation between t and t'. The equation taking into account the correlation between the past and the present is known as the generalised Langevin equation, which includes the correlation time function—the memory function. It takes into account the fact that the species considered creates in the course of its movement a perturbation at time t', which extends in time and at the instant t returns to its source. The choice of the memory function, its various approximations, and the solutions of the generalised Langevin equation employing these functions constitutes one of the developing theoretical fields.

Another field is concerned with the development of the kinetic theory in which the probability density in the phase space of the coordinates and velocities and its time evolution are calculated. This density takes into account the correlation between the velocity and momentum. In the case of frequent but weak "soft" collisions, the movement of the species is described by the familiar Fokker–Planck equation, whose solutions are obtained and analysed at different approximation levels and subject to different initial conditions. In the case of infrequent and strong collisions with a large transfer of momentum, the movement is described by the Boltzmann equation (if it is assumed that there is no correlation with respect to the coordinates and velocities between the Brownian particles and the particles constituting the medium) or by the Enskog equation is a spatial correlation is retained.

The simple Langevin equation and the Fokker–Planck equation describe the behaviour of large particles for which the fluctuating driving force arises from the frequent and weak impacts by the species in the medium. The Boltzmann–Enskog equations describe the second limiting situation of the rare and strong binary collisions without any correlation between them. In a real situation, the theory cannot ignore the dynamic correlation between the collisions and in this sense the generalised Langevin equation with its memory function corresponds most adequately to reality. However, the difficulty is that the memory effects and the correlation between the past and the present are taken into account semiempirically with selected memory functions. The *ab initio* derivation of these functions from first principles is a difficult and unsolved part of the many-body problem. The task if theoretical molecular dynamics therefore remains the creation of bridges between the dynamics of an individual collision and the long-period dynamic behaviour of the species.

At the level of the theoretical approaches examined, solutions are being obtained to the problem of the Brownian movement with different dimensions—one-dimensional, two-dimensional, and three-dimensional—for the description of the behaviour of species in narrow channels and porous media, on surfaces within thin films and membranes, and in liquids and solids. Many studies have been devoted to the dynamics of pairs and to the calculation of the probability of their reaction or annihilation; this problem is particularly timely for radical pairs—neutral and charged, with and without allowance for spin evolution, with and without allowance for the acceptance and decomposition of radicals, with unrestricted diffusion and with diffusion limited by a closed volume with absorbing or reflecting walls. The solutions are used in photochemistry and in the chemical physics of magnetic-spin effects.

The generalised Langevin equation is solved in different versions, with different memory functions, and there exist classical and quantum solutions. The dynamic problems are solved for different intermolecular potentials and the effects of the anisotropy of the potential, the contribution of attraction and repulsion, and the role of short-range and long-range parts of the potential, its Coulombic and exchange branches, are analysed. Many problems are associated with the collective dynamics of crystal lattices, networks, liquid crystals, and membranes and with the dynamic behaviour of quasi-particles—phonons, solitons, magnons, plasmons, and excitons. Theoretical problems of molecular dynamics are frequently at the junction with the problems of contiguous fields of physics—the theory of elasticity and relaxation, plastic deformation, thermal conductivity, and rheology.

The scope of the experimental research into molecular dynamics is almost limitless; it refers to the transport of molecules in liquids, the transport of atoms in metals and alloys, the drift of electrons and ions in semiconductors and liquid and solid electrolytes, and diffusion in porous, microheterogeneous, and molecularly organised systems (micelles, clusters, adsorption layers, membranes, and Langmuir–Blodgett films). Studies on the dynamics of phase formation, especially in the early stages of this process under precritica conditions and at the critical points, and the dynamics of aggregation, coagulation, and cluster formation occupy an important place.

An independent field of study is associated with the dynamics of macromolecules—synthetic and biological: the conformational dynamics of neutral molecules and polyelectrolytes, the kinetics of helix–coil transitions, the "breathing" of macromolecular coils, the dynamics of the entanglement and disentanglement of coils, the untwisting of helices and of binding to substrates, the local dynamics of segments and the "macrodiffusion" of large molecules, etc. All these questions refer directly to polymer materials science, to the problems of the physics and mechanics of polymeric materials, and, for biomolecules, to the problems of their functioning (the synthesis of proteins, DNA, RNA, enzyme catalysis, muscle contraction, the permeability of membranes, bioenergetics, and immunological recognition).

Surface diffusion constitutes an important branch of dynamics associated with the problems of the growth and perfection of crystals, epitaxial layers, and films and with the problems of adsorption and heterogeneous catalysis. Appriciable advances in this field have been ensured by ion-field microscopy of surfaces whereby one can observe single atoms and follow events involving them. Thus the diffusion coefficient of Ba on tungsten changes by several orders of magnitude on different planes and the activation energies for diffusion on the (110), (111), and (112) planes differ sharply: 5.0, 11.5, and 17.5 kcal mol^{-1} respectively. On the face-centred lattice of rhodium, the atoms of the latter on the (111) plane migrate already at 55 K, while on the (110) plane they begin to move only at 300 K. The activation energies for diffusion also differ greatly: $\varepsilon(111) = 3.6$, $\varepsilon(311) = 12.4$, $\varepsilon(110) = 13.9$, and $\varepsilon(100) = 20.2$ kcal mol^{-1}. Under these conditions, the entire difference between the rates is determined by the energetics, the contribution of the entropy component being constant. On corrugated surfaces [of the (110), (311), and (331) types], the diffusion is directed strictly along definite channels—the potential energy ravines. The properties of the self-diffusion of platinum and tungsten are the same.

On the surface of body-centred lattices, new features appear in diffusion; in particular, along certain planes [for example, Rh (111)], the diffusional behaviour of a pair of atoms differs from the behaviour of a single atom, i.e. a

correlated movement appears and gives rise to new problems concerning the ratio of the individual and collective movements and their contribution to diffusion. The W, Re, and Ir atoms on the W(211) surface move in pairs; the Pt_2, Pt_3, and Pt_4 clusters (which are linear) move on the W(110) plane via jumps of single atoms with retention of correlations in pairs and clusters.

Surface two-dimensional dynamics is an actively developing field in chemical physics. It refers not only to solid surfaces but also to monomolecular films on liquids (lateral diffusion), to membranes, and other two-dimensional systems. Here the main interest concerns the problem how the characteristics of two-dimensional dynamics are related to the atomic structure of the planes, to the molecular organisation of the two-dimensional systems, and to their thermodynamics and structure.

Excellent physical methods are used to investigate molecular dynamics: Rayleigh and Raman light scattering, acoustic and magnetic relaxation, the annihilation of positrons and positronium, coherent and non-coherent scattering of cold neutrons, laser picosecond and femtosecond spectroscopic methods, and also mathematical methods for the modelling of molecular dynamics. Laser picosecond holography merits special attention. The idea of this method involves the optical generation of a short-lived holographic lattice in a liquid or solid and subsequent observation of the dynamics of the "dissipation" of this lattice. The holographic lattice is created by passing through the liquid or crystal two picosecond pulses, coinciding in time, which cross in the specimen at an angle θ. Their interference creates in the specimen a holographic lattice with a constant $d = \lambda/2\sin(\theta/2)$, where λ is the wavelength of the laser emission generating the lattice. The principle governing the appearance of the holographic lattice involves the formation of electronically excited states, the excitation of intramolecular vibrations, and the generation of acoustic waves (phonons). Regardless of its specific cause, the holographic lattice constitutes a spatial-periodic change in the refractive index. Such a lattice "dissipates" after a time owing to molecular diffusion, the energy relaxation, or the decay of waves, while the dynamics of the dissipation can be detected by means of a delayed laser probe beam, which is diffracted by the holographic lattice. The intensity of the diffraction as a function of the delay of the probe beam yields the kinetics of the dissipation of the lattice on a picosecond scale. The characteristic dissipation times can be obtained from the time variation and the spatial scale of the dynamic processes responsible for the dissipation of the holographic lattice and the spatial averaging of the refractive index can be obtained from the frequency dependence (because d depends on λ).

The transport of excited molecules, their energy relaxation, the energy transfer (the transfer times and distances), the generation and detection of coherent acoustic phonons in crystals, and the rate at which they spread along different crystallographic axes are investigated in this way and the same procedure is used to observe the vibrational overtones and to measure the elastic and photoelastic constants of crystals. The method can be used for the non-disruptive monitoring of optical materials (including fibres) and for the analysis of the dynamics of membranes, liquid crystals, and amorphous bodies.

2. Molecular Organisation

Continued interest in molecularly organised systems has become a new feature of modern chemical physics. Molecular and supermolecular organisation of *ensembles* of species is an important principle governing the regulation of chemical processes and constituting a major resource in chemical technology and materials science. So far, this principle has been developed and adopted to only a slight extent, but its potential is exceptionally great and there are grounds for the claim that in the future "organised" chemistry will occupy a leading place in technology and materials science.

Studies on these lines are so wide in scope that it is impossible to analyse them fully. Even a cursory listing of selected examples gives an idea about the scale of such research at all levels—from molecular to macroscopic and supermolecular. The organisation of molecules into complexes, their incorporation in clathrates and micelles, immobilisation, the creation of organised systems simulating biochemical systems (biomimetic systems), the molecular organisation of active centres in metalloenzymes (nitrogenase, ferredoxin), clusters, intercalates, and layer structures—this is only a limited series of examples of organisation at the molecular level. The conformational organisation of macromolecules (helix, coil, extended chain, and their combinations) determine their packing in polymeric materials and specify the physicomechanical properties of fibres, block and regular copolymers, and blended compositions: the problem is how is this achieved, what is the form of the bridges between organisation and properties, and how their interrelation should be controlled.

Conformational dynamics, complex formation, and molecular organisation of polyelectrolytes, which have opened up major prospects for the creation of a new generation of immunogens and vaccines, in which it is possible to bypass even the genetic control of the immune response occupy a special place, i.e. it is possible to ensure that only B-lymphocytes are active, bypassing the T-lymphocytes responsible for the genetic prohibition of immunogenesis.

Phase organisation and phase transitions are traditional physicochemical problems which are still far from being solved. For example, it is known that there is a short-range order in the structure of simple liquids, in the organisation of which atomic configurations with odd (fifth) order symmetry elements predominate, while in a crystal lattice no matter how small, there should be symmetry elements with even orders only; there is virtually no understanding of the liquid–crystal transition with a rearrangement of the symmetry.

The answers to the following questions are of fundamental importance for the creation of materials with a regulated structure, with a specified combination of elastic and plastic properties, etc.: how to predict the fusion curve, the pVT diagram, and the thermodynamics of the phase transition from the intermolecular potentials; what is the microscopic mechanism of crystallisation, which factors control crystallisation, supercooling, and glass formation, what are the mechanisms of first- and second-order phase transitions and their relation with the short- and long-range order potentials; what are the contributions of the individual and collective molecular dynamics to phase transitions, and how is phase microheterogeneity created and how does it develop.

For example, the structure and organisation (both molecular and spin, magnetic organisation) of solid oxygen have attracted much attention. The existence of several phases in solid O_2 has been established experimentally and the reasons for their stability and magnetic properties have been determined: the orientationally disordered paramagnetic γ-phase; the antiferromagnetic β-phase with long-range orientational order and molecular axes parallel to the C_3 screw axis; the antiferromagnetic, monoclinic α-phase with two mirror magnetic sublattices. Theoretical analysis of the lattices with allowance for the magnetic component of the

potential and the Heisenberg exchange spin–spin attraction predicted new stable phases with unusual magnetic properties. The importance of these studies does not lie merely in the prediction of new magnetic phases in solid O_2; it is much more important that the principles of molecular and spin organisation, which ensure specified magnetic properties, have been deduced in relation to this example. These principles are also important for the creation of organoferromagnetic materials, organic semiconductors, metals, and superconductors, ferromagnetic alloys, glasses, and various ceramics (including superconducting ceramics).

The phases and phase transitions in two-diemensional systems, especially in adsorbed layers, are even more varied. The ways in which the species on the surface are organised, the reorganisation of the two-dimensional structure to form a three-dimensional structure and conversely, the order–disorder transitions (fusion–crystallisation), the decomposition into domains and clusters, the dynamics of the surface migration of the domains, and the correspondence or lack of it between the organisation of the adsorption layers and the structure of the lattice of the solid (commensurate and non-commensurate phases) are important in this instance.

Many physical methods, including the diffraction of slow electrons and optical generation of the second harmonic are used to investigate the organisation and dynamics of a two-dimensional lattice gas and phase states and transitions. For example, it has been established on the basis of electron diffraction that hydrogen adsorbed on the Ni(111) plane forms an ordered two-dimensional phase for coverages of 0.3–0.5 and at a temperature below 250 K; for other coverages and for $T > 250$ K the adsorbed layer is disordered and non-organised.

The interest in two-dimensional organisation is targeted towards adsorption and adsorbents and heterogeneous catalysis and catalysts; but there is also another aim—the creation of surface layers with unusual properties by incorporating atoms in the upper layers of the lattice. For example, when a gold layer on silicon is bombarded with Ar^+ ions (100 keV), a mixed Au/Si layer is created and the intermettallic compound Au_3Si is formed. This is a non-equilibrium metastable phase which does not exist under equilibrium conditions. When titanium and zirconium phosphates are bombarded with Ar^+ ions, the surface layers are depleted in oxygen and phosphorus atoms, which are driven to the lower "levels" of the lattice.

The questions which fall within the range of concerns of chemical physics are how atoms are dislodged as a result of impact by an ion, how the electron shells are shaken in this process and how energy and momentum are lost, what are the secondary reactions of the hot atoms and electrons of the target, and how the atomic layers of the lattice are reorganised. The organisation and reorganisation of the surface layers of solids by ionic implantation of plasma and laser "microsurgical" methods constitute a promising pathway to the modification of the surface and the imparting of unusual mechanical, anticorrosion, magnetic, electrochemical, electrophysical, and photosensitive properties, which constitutes the principal stimulus of the research into this branch of chemical physics.

Numerous chemical and physicochemical processes occur at interfaces and the atomic-molecular organisation of the latter is associated with their functioning. The optical generation of the second harmonic is known to occur in non-centrosymmetric crystals, but the second-order optical non-linearity arises also at the boundary between two centrosymmetric media if a symmetry gap occurs in the interface. Since the thickness of the interface is much smaller than the optical wavelength, the dipoles induced at the interface form a polarised layer generating the second harmonic. This method is sensitive to the structure of the interfaces and ordered monolayers, to their dynamics with a small time resolution, to surface reconstruction, and to phase transitions. For example, Langmuir–Blodgett layers, their "evaporation" (liquid–gas-like two-dimensional state transition), and their "fusion" (two-dimensional "liquid"– two-dimensional "solid" transition) have been investigated by this method. The anisotropy of the polarisation tensor has been measured for a monolayer of pentadecanoic acid on water and it has been shown that, for low coverages, the molecules are inclined to the water surface at an angle of 30° while with increase of coverage they "straighten out" and in the limit lie along the normal to the surface.

The monolayers of docosanoic acid on aluminium and carbon form a two-dimensional hexagonal lattice, in which the molecules are perpendicular to the surface of the support and, when the number of monolayers increases to 7, the molecules are inclined and the hexagonal lattice is transformed into an orthorhombic lattice, whereupon one can observe the evolution of the phase transition. The phase transitions in biological membranes and their relation with the cooperative rotational movements of the hydrocarbon chains, the electrical double layers on electrode surfaces, etc. can be investigated in this same way. The first attempts have been made to create monolayers which are two-dimensional ferromagnetics.

Molecular and supermolecular organisation is a characteristic property of biochemical processes (the synthesis of proteins and nucleic acids, photosynthesis, ion transport, enzyme catalysis, immunological responses, electron transport, phosphorylation, etc.). Enzymes bind and orient reagents, organising the elementary chemical steps and ensuring a high stereoselectivity, as well as selectivity with respect to the reagent, the type of reaction, its localisation, temperature, pH, etc. Not only the elementary steps but whole sequences of reactions are organised in biochemical processes. The selectivity and productivity of biochemical processes reach a level which is only rarely attained in the usual chemistry (for example, polymerisation on immobilised catalysts) precisely by virtue of the high degree of organisation.

This situation is recognised with increasing clarity and there has been a sharp growth of interest in organised systems and their "chemical" functioning in recent years. The characteristics of chemical reactions in liquid crystals, layers, membranes, micelles, clathrates, clusters, etc. are being widely investigated. Organised catalytic systems are being constructed in accordance with the principles of enzyme catalysis and biomimetic processes simulating the operation of biosystems are being developed.

The self-organising systems in which the molecular organisation is induced by the chemical reaction are especially attractive. For example, the colourless molecule of a spiropyran dye with a long hydrocarbon "tail" is transformed photochemically into the merocyanine dipolar coloured form with separated charges, the molecules combining into micelles only in this form. The pohtochemical reaction functions in this instance as a trigger which "switches on" micelle formation.

The reaction can also "switch on" phase transitions (for example, the crystallisation of a solvent on nuclei—the molecules of the reaction product). This principle of the chemical trigger makes it possible, in particular, to increase by many orders of magnitude the sensitivity of the photodetecting systems (for example, in photography). An example of a "natural" chemical trigger is provided by the photoisomerisation of rhodopsin, which induces conformational transformations in the protein opsin, and the latter initiates a cascade of enzymic reactions, which ultimately lead to the generation

of a membrane potential and the visual reception of light in the retina of the eye.

The most striking examples of supermolecular organisation have been observed in chemical reactions and crystals. For molecules organised into a crystal, their intrinsic reactivity, which is controlled by the structure of the electron shell, proved to be much less significant for the reaction than the mode of packing—the arrangement of the molecules in the crystal. The mode of reaction is determined by the intermolecular distances in the crystal, the mutual orientation of the molecules, and the spatial symmetry of the crystal. There are a number of examples of the unique selectivity and topological directionality of the reactions in crystals, which are atypical for the usual reactions in liquids or melts. Many organic substances have several (sometimes up to 10–12) crystal-chemical modifications. In fact, one can speak of the creation of a new branch of chemistry—the crystal-engineering chemistry, whose task is to construct crystals programmed for a specified type of chemistry.

Just as striking examples exist in heterogeneous reactions. Thus the Fe(111) plane is 430 times more effective in the synthesis of ammonia from H_2 and N_2 than the (110) plane and is 13 times more active than the (111) plane. On the Pt(111) plane, hexane is converted into benzene, while on the (100) plane cyclic and branched saturated hydrocarbons are formed from hexane. The molecular organisation of crystals or lattice atoms on the surface does indeed "write the script" of the chemical reaction in this instance.

IV. ENERGY DYNAMICS

In terms of the scale of research, energy dynamics occupies a leading place in chemical physics and such research has two major aims. The first aim is to create the theoretical foundations for and to develop the principles of selective, "non-statistical" chemistry ensuring a directed activity and specified reactions of the molecules (plasma-chemical activation, laser "surgery" of the molecules, energy stimulation of reactivity). The second aim is to search for ways of storing energy in the internal degree of freedom of molecules (electronic, vibrational, and rotational) in order to create new lasers, including lasers with solar pumping.

Energy dynamics includes a wide range of problems: selective population of rotational, vibrational, and electronic states, the exchange and transfer of energy between various states within the molecule and intermolecular exchange, and the relaxation of internal energy to kinetic and lattice energy. Here these problems will be considered briefly in terms of the following logical arrangement: the energy dynamics in gases and on the gas–solid surface, where it is possible to differentiate the individual contacts between species and to identify more reliably the physical interactions responsible for the fate of the energy; this is followed by the energy dynamics in van der Waals molecules and clusters as intermediate structures in which many-species interactions are switched on; finally, we have the energy dynamics in large assemblies—in liquids and solids.

1. Energy Dynamics in Gases

This is the most thoroughly developed and most vigorously developing field; the main cause of interest in it is the comparatively small number of contacts between energy-rich species (particularly at low pressures), their long lifetime, and hence good conditions for the storage, control, and utilisation of energy.

The exchange of the electronic energy (E) of excited atoms for the vibrational (V), rotational (R), and translational (T) energy of the molecules is a fundamental process in the energy dynamics of plasma, interstellar lasers, and many chemical gas-phase processes. The energy exchange via different channels ($E-V$, $E-R$, $E-T$) and different mechanisms, the time scale of the exchange, and the cross-sections of the channels depend on a multiplicity of causes, the most important of which is the mechanism of the exchange and the topology of the potential energy surface of the initial and final states of the system of interacting partners.

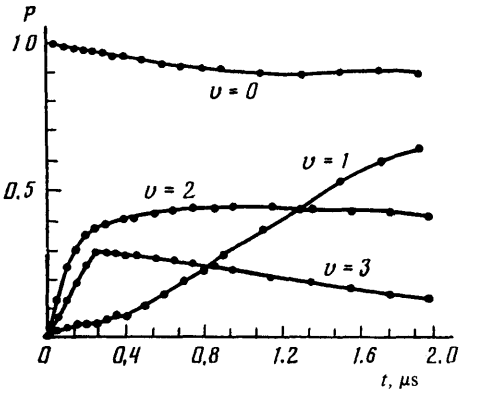


Figure 2. Dynamics of the population P of the vibrational states of the hydrogen molecule for $J = 1$ after the laser pumping of Na atoms (in relative units); 570 K, $p_{H_2} = 1$ bar, duration of laser pulse 0.2 μs.

The $E-V$ exchange can proceed via a direct "physical" mechanism without the rupture of chemical bonds or via "chemical" mechanisms. Thus the $Na(^2P_{1/2})$ atom, with a cross-section almost identical with the gas-kinetic cross-section, transfers its electronic energy to the vibrational-rotational levels of the H_2, N_2, CO, NO, O_2, I_2, C_2H_4, etc. molecules. These processes are investigated by laser spectroscopy: the pulse from one laser pumps the Na atoms (for example, in a mixture of sodium vapour and hydrogen) and the probing pulses of the second laser, with a variable time arrest, probe the populations of the vibrational-rotational states of the H_2 molecules and their time evolution. The $Na(^2P_{1/2})$ atom pumps the vibrational state of H_2 with $v = 1$, 2, 3 (populations of 13, 61, and 26% respectively) in accordance with complex kinetics, which depend on v, an example of which is illustrated in Fig. 2. It constitutes a complex interplay of processes involving electronic-vibrational exchange between Na and H_2 and the migration of the V-energy via the vibrational reservoir of the H_2 molecules. The rotational distribution for different v depends also on the rotational quantum number J (Fig. 3), the states with odd J being populated to a greater extent than those with even J. In the $E-V$ exchange between $Na(^2P_{1/2})$, on the one hand, and N_2, CO, and NO, on the other, the high vibrational states up to $v = 3-5$ (in the interaction with N_2 and CO) and up to 7 (in the interaction with NO) are populated. The CO states with $v_{max} = 5$ are populated in the $Hg(^3P_1)$ + CO process.

It was assumed that the $E-V$ exchange in the A + BC system proceeds via the ionic state $A^+ \ldots (BC)^-$ and that the ionic energy level intersects the energy levels of the initial and final states, the points of intersection ensuring the resonance energy transfer. However, *ab initio* calculations of the potential energy surfaces (PES) for Na + H_2, Na + N_2, and Na + CO have shown that this mechanism does not operate. The non-adiabatic transitions (the $E-V$ exchange) occur in the region of the intersection of the ground ($^2A_1$) and excited ($^2B_1$) PES in the C_{2v} configuration for Na*H_2 and Na*N_2 (Na is attached at right angles in the middle of the H_2 and N_2 bond) and in the $C_{\infty v}$ configuration for Na*CO (linear configuration). In this region the molecules are in the extended phase and after decomposition of the complex remain vibrationally excited.

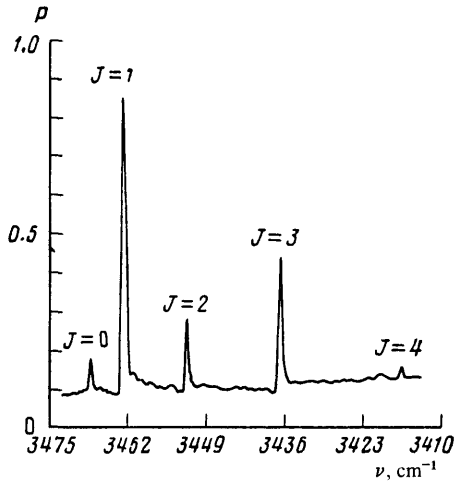


Figure 3. The spectrum of the rotational states of the hydrogen molecule for the $v = 3$ level after the laser pumping of Na atoms; delay time 0.5 μs, 500 K, p_{H_2} = 300 mbar (P = relative population).

For Na + H_2, the contribution of the "chemical" mechanism of the quenching of an electonically excited atom (via the formation of the hydride NaH) is not more than 0.5%. For the Mg(^{1,3}P), Ca(^{3}P), Sr(^{3}P), and Zn(^{1,3}P) atoms with energies in the range 2–5 eV, the chemical mechanisms involving the formation of the hydrides MH predominate, the reactions occurring via the insertion of the atom in the molecule in the C_{2v} configuration and with rotational excitation of the hydride MH (for example, the states with $J \geq 30$ are populated in MgH).

The second chemical mechanism is dissociative:

$$Hg(^3P_1) + H_2 \rightarrow Hg(^1S_0) + H + H\,.$$

The energy transfer (the $E-E$ process) makes an important contribution to the quenching, for example:

$$Hg(^3P_1) + Tl(^2P_{1/2}) \rightarrow Hg(^1S_0) + Tl(^2S_{1/2})$$

or

$$Hg(^3P_1) + C_2H_4 \rightarrow Hg(^1S_0) + C_2H_4(^3\Pi_1)$$

with transfer of angular momentum. The $E-E$ processes are important for the pumping of lasers. For example, the functioning of the oxygen–iodine laser is based on the reactions

$$I_2(^1\Sigma_g^+) + O_2(^1\Delta_g,\ v \geqslant 3) \rightarrow 2I(^2P_{3/2}) + O_2(^3\Sigma_g^-)\,,$$
$$I(^2P_{3/2}) + O_2(^1\Delta_g) \rightarrow I(^2P_{1/2}) + O_2(^3\Sigma_g^-)\,,$$
$$I(^2P_{1/2}) \rightarrow I(^2P_{3/2}) + h\nu\,.$$

The conditions for energy resonance are critical for the transfer of the E-energy.

Rydberg atoms (see Section II) are attractive because the conditions for the resonance of small quanta of the E-energy with the V- and R-energies of the molecules are fulfilled in their collisions with molecules and the laws governing the $E-E$ and $E-R$ processes are conveniently investigated in relation to these atoms.

A Rydberg atom can be approximated by a model in which the Rydberg (excited) electron is so remote from the ionic residue of the atom that it can be regarded as a virtually free particle and the collision of the atom with the molecular target can be treated as the interaction of three particles—the Rydberg electron, the ionic residue, and the target particle. It can be accompanied either by the direct $E-V$ or $E-R$ transfer or by the reverse $T-E, V-E$, or $R-E$ transfer, which increases the quantum number n of the Rydberg atom up to its ionisation threshold. The laser-induced fluorescence and selective-field ionisation methods have been developed for the investigation of these processes.

The interaction of the Xe(27f) atom, in which n = 27 for the f electron, with HF proceeds in accordance with the scheme:

$$Xe(27f) + HF(J) \rightarrow Xe(n,\ l) + HF(J-1)$$

i.e. the HF molecule loses a rotational quantum and the Rydberg atom is excited to the states with n = 40 and 41 and different values of l and $|m_l|$. This excitation is very selective: the Xe(n, l) states with n = 39 or 42 are absent, since the energy deficiency for them is approximately 5 cm^{-1}, while for n = 40 and 41 it is much less: ~1.2 and ~2.1 cm^{-1}.

The interaction of the Xe(27f) atom, in which n = 27 for the f electron, takes place for $J \leq 3$. For $J \geq 4$, i.e. for a larger store of the R-energy, the atom ionises:

$$Xe(27f) + HF(J) \rightarrow Xe^+ + HF(J-1) + e\,.$$

However, Xe(23f) behaves in a completely different way:

$$Xe(23f) + HF(J=0) \rightarrow Xe(21,\ l) + HF(J=1)\,.$$

Unlike the previous instance, here the electronic energy is transferred to the rotational levels of the target and the Rydberg atom undergoes partial deactivation with decrease of n. In this case the deficiency of energy resonance amounts to ~1.5 cm^{-1} and this process does not take place with the Xe(26f) and Xe(27f) atoms; although their energies are greater than that of Xe(23f), the resonance deficiency of ~2.6 cm^{-1} completely suppresses this process.

Together with the $E-R$ processes, virtually isoenergetic processes involving no change in n and J also take place, for example:

$$Xe(27f) + HF(J) \rightarrow Xe(27,\ l) + HF(J)$$

in which the change in the orbital electronic momentum is compensated by the change in the translational energy.

The $E-V$ transfer is a still more markedly resonance process. Thus the Na(ns) Rydberg atom induces a rigorously resonance-type vibrational excitation of CH_4 and CD_4: the transition $5s \rightarrow 4p$ (energy 2930 cm^{-1}) excites only the ν_3 vibration in CH_4 (2940 cm^{-1}), the $6s \rightarrow 4p$ transition (1331 cm^{-1}) induces the ν_4 vibration in CH_4 (1340 cm^{-1}), and the $7s \rightarrow 5d$ transition (975 cm^{-1}) excites the ν_4 vibration (965 cm^{-1}) in CD_4. The orbital angular momentum then changes

by $\Delta l = 1$ or 2; processes with $\Delta l = 0$ do not occur. Thus the energy of the transition $8s \rightarrow 7s$ coincides with that associated with the frequency ν_4 in CD_4, but this energy resonance is insufficient to effect the $E-V$ process.

These examples contain a small proportion of what is now known about the atomic-molecular energy dynamics and demonstrates merely the multiplicity of factors involved in this problem, the level of its solution, and the pathways leading to it. The same situation exists also in the energy dynamics of molecules: the examples quoted below give merely an idea about the current state of the problem and about the ways in which it is solved and the aims which have inspired the search for such solutions.

The relaxation of small molecules at low vibrational levels has been thoroughly investigated and has been incorporated in textbooks and monographs. Further progress in this field is being directed to complex molecules and high energies: the characteristic features of relaxation, the mechanisms, and the dynamics are being established. For example, Fig.4 shows how the vibrational energy of acetylene "descends" down the levels and is converted into kinetic energy: there is initially a rapid redistribution among the initial vibrational states (less than 15 collisions are necessary to achieve this), after which follows the slow relaxation of the symmetrical ν_2 stretching vibration (~650 collisions are required) to the ν_4 and ν_5 deformation vibrations, which slowly discard the V-energy into the R- and T-forms. A remarkable feature of this approximate picture is the "bottleneck" effect in the ν_2 vibrations, which can store energy for a long time.

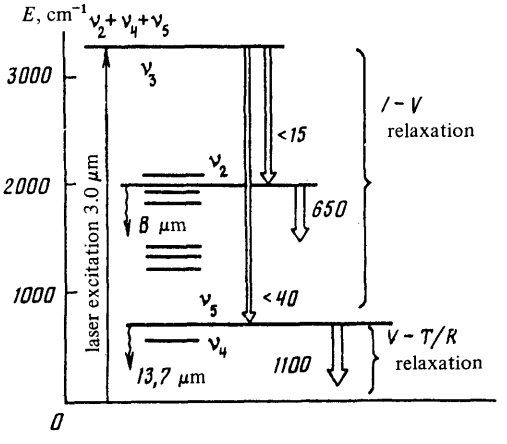


Figure 4. Pathways leading to the relaxation of the vibrational energy in the acetylene molecule among vibrational levels; the numerals against the arrows indicate the number of collisions of the excited molecule required for relaxation from the given level.

Molecules capable of retaining energy are needed for gas lasers and especially for lasers with solar pumping. Natural laser effects are known in the atmospheres of certain planets and the creation of solar lasers constitutes an attractive prospect. The principal requirements which must be met by gases to be used as media in solar lasers are as follows: wide and as far as possible continuous absorption bands to ensure effective pumping; the presence of metastable states and the occurrence of relaxation processes ensuring an inverted population; stability (or capacity for regeneration) of the chemical composition of the laser medium.

In order to find systems capable of transforming solar energy and storing it at excited levels with an adequate density, exceeding the generation threshold, it is essential to know not only the physicochemical structure of the molecules (see Section II), but also their energy dynamics—the lifetimes of the excited states, the mechanisms and cross-sections of the physical and chemical relaxation, and the ways of transforming energy. Examples of solar lasers based on Br_2, I_2, Na_2, Cs_2, IBr, etc. already exist, but their characteristics are far from perfect.

Rotational energy is known to be discarded rapidly, giving T-energy even in collisions with inert gas atoms, since the distances between the rotational levels are small compared with kT. However, for molecules with a small moment of inertia or with a large store of rotational energy (large J), the distances between the rotational levels are comparable to or exceed kT. Under these conditions, the molecule rotates so rapidly that its potential appears to be isotropic to the approaching atom. On the basis of this principle, the atom exhibits a weak perturbation and is ineffective in the $R-T$ relaxation. Because of this factor, the highly excited states of hydrogen halides survive many collisions and lasers based on rotational transitions have been devised using them.

Frequently such molecules with an inverse population of the R levels are formed in photochemical pumping. Thus the photolysis of BrCN at 193 nm yields CN with low E- and V-energies but with a large store of the R-energy (up to 1400 cm^{-1}); the states with J from 30 to 86 are populated under these conditions and the yield of molecules at the maximum of the distribution with respect to J ($J_{max} \cong 60$) is ~4%. These states are metastable (their relaxation by Kr, Ar, N_2, CO, and Xe is relatively inefficient) and are suitable for lasers.

For the majority of polyatomic molecules, the key problem is the intramolecular distribution of energy with respect to the vibrational reservoir. The intramolecular vibrational relaxation (IVR) is a collision-free process resulting from the intramolecular interaction of oscillators—vibrations of different types and having different frequencies. IVR determines the processes leading to the decomposition of molecules and ions on excitation by electron impact or photoexcitation, in chemical activation, and on multiphonon excitation; IVR influences strongly the vibrational and electronic-vibrational fluorescence spectra, chemiluminescence spectra, and the spectroscopy of laser systems.

Excellent methods (picosecond and femtosecond laser spectroscopy) for the generation of coherently pure vibrationally excited states in both electronic ground and electronically excited states have been developed.

A remarkable feature of IVR is the retention of coherence on redistribution and migration of energy among levels, which is manifested by quantum beats, observed on the kinetic luminescence decay curves. The frequencies of the quantum beats are related to the number of levels involved in the energy exchange and the coefficients of the basic vibrational wave functions, from which the overall vibrational wave function of the molecule is made up, can be found from the phase shifts and the amplitude of the modulation of the beats. Furthermore, the Hamiltonian matrix describing the interaction between the oscillators can be found, in principle, on the basis of these beat frequencies and coefficients.

For example, in the anthracene molecule for low vibrational energies (up to 1200 cm^{-1}) there is almost no energy redistribution, the quantum beats are missing, and the vibrational

states generated by the laser excitation relax monoexponentially with $\tau \cong 20$ ns. When the vibrational energy store is 1380–1520 cm^{-1}, strong quantum beats appear with a frequency of ~5 GHz, indicating energy migration in which several levels with migration times of several hundreds of picoseconds are involved. For larger energies, rapid monoexponential loss of the coherence of the initial vibrational states takes place owing to the rapid migration of energy with $\tau \cong 20$ ps.

The redistribution of the V-energy is extremely selective: by no means all the vibrational states participate in the energy exchange. Thus, for a V-energy of 1380 cm^{-1}, only three vibrations interact strongly and participate in the energy exchange, while the density of the vibrational levels corresponding to this energy is ~25 per cm^{-1}, which is characteristic also of other energies in the vibrational reservoir. The number of levels participating in the exchange is much smaller than the density of the vibrational states. Such selectivity of the exchange is associated with the fact that the vibrational states are coupled via the anharmonicity of the vibrations and the latter can obey definite symmetry conditions. Thus, for anthracene (D_{2h} symmetry), this implies that the given vibrational state is coupled by anharmonicity to only $^1/_8$ of the total number of vibrational states.

The population of the rotational levels of the given vibrational state accelerates the vibrational migration and the IVR but does not alter the overall features—the coherence and quantum beats are retained. In principle, one may select on this basis the interaction responsible for the IVR—the anharmonicity of the Coriolis forces. Clearly, if the latter make the main contribution to the energy migration, then the beat frequencies must depend greatly on the rotational temperature and conversely, the absence of such dependence may imply a leading contribution by the anharmonicity.

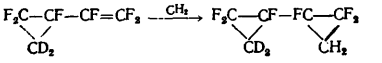
The establishment of the IVR laws is one of the current growing points in energy dynamics. This problem has a direct bearing on the molecular mechanics of vibrations, namely on the question of the relation between coherence and chaos in the vibrational motion of molecules with different stores of vibrational energy. It adjoins the problem of the ergodic nature of molecular systems, which arises in the classical mechanics of Hamiltonian systems of coupled anharmonic oscillators. The famous KAM (Kolmogorv, Arnold, Moser) theorem demonstrates that, for small perturbations (and small energies), the classical movement of anharmonic oscillators is quasi-periodic and regular, whilst for high energies it becomes chaotic. Thus, for the Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda x (y^2 + kx^2),$$

the trajectories (x, y) corresponding to small energies are periodic (Fig. 5*b*), while for high energies they become chaotic (Fig. 5*a*); here x and y are the coordinates, p_x and p_y the moments, and ω_x and ω_y the frequencies.

The relative contributions of order and chaos in IVR depend on the store of the vibrational energy, on the anharmonicity constants of the oscillators and their coupling, and on the density of the vibrational levels. The questions how IVR arises—coherently or chaotically—and at what rate are of fundamental importance for chemical dynamics. Both the pathways leading to the dissociative decomposition of the molecule and the energy pumping of the fragments depend on whether the IVR occurs before the decomposition or whether the decomposition overtakes IVR. In the former case the reaction is described by the statistical theory, while in the latter the reaction takes place "non-statistically", selectively.

As a rule IVR predominates in the competition between IVR and the dissociative decomposition. Thus, in the selective laser excitation of CH_2FCH_2Br, the yield of HBr and HF on decomposition of this molecule corresponds to a statistical distribution of the vibrational energy. In the selective pumping of the fifth overtone of the vibrations of the OH group in the $(CH_3)_3COOH$ molecule, the preferential breakdown of the O–O bond takes place; the energy transfer to this bond occurs over a period of ~2 ps, i.e. before the reaction via the O–H bond. In chemical activation via the exothermic addition of the carbene, i.e.



the vibrational energy, localised initially in the right-hand three-membered ring, is found in the left-hand ring after ~1 ps and the reactions of this molecule occur after IVR.

The number of examples of the non-statistical decomposition or vibrationally excited molecules is much smaller, but they open up pathways to photoselective chemistry, to the laser surgery of molecules, and to "non-statistical" chemistry. Naturally, there exist only limited possibilities for controlling the rate of IVR, but even the knowledge of the

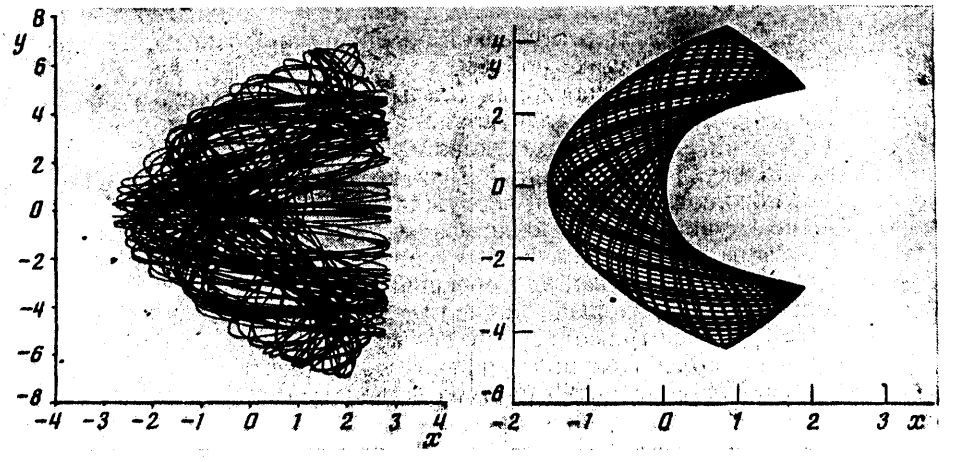


Figure 5. The chaotic (*a*) and quasi-periodic (*b*) trajectories $y(t)$ and $x(t)$ of the Hamiltonian H; $\omega_x = 2\omega_y$.

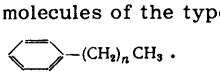
characteristic features of IVR is sufficient to be able to predict which molecules and in which processes are suitable for photoselective chemistry. The identification of the possibilities and principles of the molecular energy organisation of photoselective chemistry is one of the intriguing problems of chemical physics.

The advances in laser spectrocsopy have led to the possibility of investigating the vibrational relaxation of electronically excited states. The method of the ultrasonic expanding flow, in which the flux of molecules with rotational and vibrational temperatures close to the absolute zero is excited by the laser to specific vibrational levels of the electronically excited state and the fluorescence arising from these levels and its decay as a function of time are then detected, has been developed most thoroughly.

The width of the vibronic fluorescence bands increases sharply with increase in the store of the vibrational energy, starting from a certain threshold. This is evidence for a rapid intramolecular vibrational distribution—a rapid escape of vibrational energy from the populated level to a multiplicity of others as a consequence of the anharmonicity of the vibrations and Fermi resonance. When the number of coincident levels (and Fermi resonances) is small, coherent excitation results in the appearance of vibrational quantum beats corresponding to the oscillation of energy between the levels which modulates the decrease of the fluorescence intensity. Incidentally, such beats are also observed in intermolecular energy transfer. Thus, on excitation of HCl in argon, at an overall pressure of 3 bar and an HCl partial pressure of 29 mbar, the $H^{35}Cl$ vibration is pumped at 2963.3 cm^{-1}. Owing to the coherent energy transfer between $H^{35}Cl$ and $H^{37}Cl$ during the time decay of the signal of the trial pulse probing the population of the excited vibrational states, a periodicity (quantum beats) is observed with a period of 15 ps, which corresponds exactly to the difference between the vibration frequencies of the isotopic forms of HCl, amounting to 2.22 cm^{-1}. Under these conditions, the phase coherence is retained much longer, about 50 ps.

If the density of the Fermi resonances is large, there is a pronounced superposition of beats with a large set of frequencies and this situation is referred to as "Fermi bleeding" in IVR. Thus in naphthalene in the S_1 state in the presence of an excess vibrational energy E_V = 3068 cm^{-1}, the density of the vibrational levels is about 1600 per cm^{-1}, the distance between the levels involved in the "Fermi bleeding" is about 0.06 cm^{-1}, and the characteristic IVR time is 10–100 ps. In fluorobenzene the energy threshold of the intense IVR is much lower and begins at a density of levels amounting to 40 per cm^{-1}. In this case the Coriolis interaction, involving the rotational levels in IVR, which increases the density of the levels by the factor $2J$ (for rotational quantum number J), makes a significant contribution.

The role of the density of levels in IVR is illustrated by the popular example of molecules of the type



On excitation of the symmetrical vibration at 993 cm^{-1} of the electronically excited benzene ring, the time taken for the store of the V-energy to leak from the ring to the "tail" of the molecule depends on the density of the vibrational states of the "tail", i.e. on the value of n. Thus, for $n = 1$, this time is long, about 900 ns, whereas for $n \geq 4$, it is reduced to 2–10 ps.

The electronic relaxation of even polyatomic molecules is a much slower process and it is investigated by laser spectroscopic methods with the same high level of "quantification" as the structure of the excited states (see Section II). Thus in benzophenone the electronic energy is lost from the S_1 state (the S_1–S_0 transition) over a period of 50 ps, the transition from the T state to the S_0 state via thermal excitation to S_1 (slow fluorescence) takes place in 1 μs, and the spin-prohibited direct T–S_0 relaxation requires a time of ~1 ms. The rate of relaxation of the E-energy then depends on the store of the vibrational energy in a complex manner. For example, in 9-cyanoanthracene in the presence of an excess of E_V up to 800 cm^{-1}, the quantum yield of the luminescence from S_1 and the luminescence time τ depend little on E_V: $\tau \cong 26$ to 28 ns. When $E_V \cong 1200$–1750 cm^{-1}, both the quantum yield and τ decrease sharply with increase of E_V and, when $E_V \cong 2000$–2500 cm^{-1}, the quantum yield diminishes to 0.1 and τ to 4 ns.

The energy dynamics of the molecules in the gas phase is a multifactorial, multiparameter problem in which none of the factors is of secondary importance: the type of molecules (diatomic, or polyatomic, linear or non-linear), the type of process (intramolecular or intermolecular), the type of energy (E-, V-, R-, or T-reservoir), and the sequence of the energy migration and escape processes (within one reservoir or between reservoirs), the mutual influence of the reservoirs, the anisotropy of the potential of the molecules and the processes ensuring its modulation, the limitations and prohibitions based on the angular momentum, the symmetry and deficiency of the energy, and the rate of movement of the partner species in the region of the overlap of their potentials. The theoretical solution of the problem requires the knowledge of the potential energy surfaces of the ground and excited states and calculations on the dynamics of the motion of the molecular system along the surface—both these problems refer to chemical dynamics (see Section V).

Analogous problems arise in the energy dynamics of the molecules on the surface—namely the problems of the rules governing the transfer of the vibrational, rotational, and electronic energy on impact of the excited molecule against the surface, of which phonons participate in the energy exchange processes (the collective lattice phonon or the localised high-frequency vibrations of the surface atoms), of the ways in which these processes depend on the velocities and masses of the molecules and on the potentials of the molecule and the target, and of the role played by the "roughness" of the surface on the atomic scale.

The greatest experimental progress has been achieved in this instance by the employment of the method of molecular beams, where a monochromatic stream of atoms or molecules in specified quantum states is directed onto the surface and the velocity and angular distribution of the reflected or desorbed species as well as their new distribution among quantum states are then determined. These studies have now assumed a large scale and they are aimed at the fundamental problems of heterogeneous catalysis, the chemistry and physics of surfaces, plasma chemistry, as well as the branches of thermophysics engaged in the questions of the thermal protection of space devices.

2. Migration of Energy in Clusters

The acquisition, storage, and utilisation of energy by molecular systems of finite dimensions (van der Waals molecules, clusters) have become the subject of vigorous investigations quite recently; the interest in this problem is associated with the fact that in such systems the energy spectrum can vary continuously as the dimensions are altered and this leads to the possibility of creating bridges between the energy dynamics of isolated species and the energy dynamics of species in large assemblies (liquids and solids).

The pumping of energy into clusters is achieved by electron impact, by electron capture, or by the laser excitation of one of the species in the cluster. For example, in the van der Waals complex I_2.He, the iodine molecule is promoted by the laser to an electronically excited state with an excess of vibrational energy and probe pulses then detect the fate of the energy and the dynamics of its migration. The principal migration pathway is the transition to the low-frequency vibration of the complex and dissociation, for example:

$$I_2 \cdot He\,(v=7) \rightarrow I_2\,(v=6) + He\,.$$

i.e. one vibrational quantum is sufficient for dissociation. The time taken for energy transfer from the high-frequency to the low-frequency vibration is fairly long but it decreases sharply with increase of the energy store. Thus, for I_2.He with $\nu = 12$, 18, 23, and 25, the time taken for the escape of a vibrational quantum varies in the sequence 200, 100, 50, and 40 ps. Hence it follows that the anharmonicity of the vibrations, which is greater for larger amounts of vibrational energy, is responsible for the energy transfer.

However, this is not the only factor controlling the energy dynamics of clusters. The size of the vibrational quantum, the symmetry and structure of the cluster, the resonance deficiency, and the density of the vibrational states are also important. For example, the time of the vibrational relaxation to dissociative levels is ~100 ps in the I_2.He cluster and ~100 ns in the H_2Ar cluster, i.e. is greater by three orders of magnitude; this is caused by the weaker interaction of the two types of vibrations in H_2.Ar compared with I_2.He. For the same reason, the rate of dissociation in the $(HF)_n$ (n = 2 - 6) clusters (the rate at which HF is split off) in the presence of the enormous excess of vibrational energy of 3000 cm^{-1} amounts to only 10^6–10^7 s^{-1}. In the cluster of pentacene with Ar an energy of 300 cm^{-1} in the aromatic ring is converted slowly (over a period of 10–30 ns depending on the number of Ar atoms in the cluster) into the low-frequency vibration modes of the Ar atoms.

The intermolecular energy transfer and relaxation in gases are frequently preceded by the formation of van der Waals molecules or clusters whereupon new and unexpected features appear. Thus, in order to discard an energy quantum of the HCO deformation vibration, not less than 1500 collisions with the N_2 molecule are necessary but only 10 collisions with NO are sufficient. One might suspect that in the latter case a chemical reaction serves as a powerful relaxation channel, but this is not the case, since the reaction is slow and, furthermore, it is retarded on deformation-vibrational excitation of HCO. It is most likely that relaxation takes place in the complex HCO.NO in which the deformation vibration frequencies of HCO and the low-frequency vibrations of the complex itself do not differ greatly and the energy rapidly slows down to the dissociative levels of the complex.

The relaxation of the energy in clusters has begun to be investigated also by the theoretical methods of molecular dynamics. As an illustration of this approach, we shall consider the Ar_{13} clusters in which the electronic energy is "injected" into one of the central atoms. It organises a localised state—the Ar_2^* excimer, where one of the atoms is of the Rydberg type. The dissociation energy of the excimer, the equilibrium state, and the parameters of the Morse potential are known; next, its interatomic interaction with other atoms of the cluster is "switched on" and the molecular and energy evolutions of the cluster are analysed.

The redistribution of the vibrational energy in the cluster is hindered by two factors: (1) the marked difference between the vibrational frequencies of the excimer and the atoms in the cluster; (2) the local expansion of the cluster around the excimer, occurring when the intermolecular potential is switched on, because the repulsive branch of the excimer–argon atom potential is much steeper than the repulsive potential between the argon atoms. As a result of this, the first stage of the energy relaxation is the "explosion" of the cluster—its rapid expansion (over a period of ~200 fs) around the excimer. The second stage is the slow migration of energy to the vibrational mode of the cluster with its localisation at the predissociation levels of the surface atoms; as a result, the atoms "evaporate" from the cluster and the vibration energy is converted into the kinetic energy of the leaving atoms. This process takes place over a period of 10–100 ns.

The characteristic features of the relaxation of the highly excited (Rydberg) atoms in the lattice, the main one being the local "explosion" of the lattice, can be seen from this example; this is important for the problem of the interaction of strong radiations (laser, electronic, and X-ray) with solids (explosive evaporation, surface erosion, etc.).

The energy dynamics of the clusters aroused increasing interest and has been stimulated by the well-founded hope that the fundamental problems of energy relaxation in liquids and solids can be solved on the basis of the cluster energetics.

3. Energy Dynamics in Liquids

The fluxes of vibrational energy in a liquid are controlled by more complex laws than in a gas or a solid. In gases the vibrational pumping and relaxation are regulated by binary collisions—elastic (when the vibrational states of the partner species are not altered and there is only a shift of the phase of the vibrations) or inelastic (where both the vibrational states and phases change). The first process corresponds to phase relaxation, i.e. to the loss of phase coherence (characteristic time T_2); the second process involves energy relaxation—the removal of the energy to the lattice (characteristic time T_1). The T_1 process determines the escape of energy from the vibrational reservoir to the lattice, while the T_2 process constitutes the migration of energy within the vibrational reservoir without its loss to the lattice.

In a solid, both the phase and the energy relaxation can be interpreted as the interaction of a local vibration (or a vibrational exciton) with the phonon spectrum of the lattice (of a crystal or glass), whereupon the approximation of harmonic phonons is frequently satisfactory.

A liquid is too dense for the treatment to be restricted to the approximation of binary collisions but it is not sufficiently ideal to allow the phonon model to be employed. Furthermore, in a liquid there are low-frequency degrees of freedom (of rotation and of oscillation of the centre of gravity) for which $\hbar\omega \leq kT$ and which can be treated in classical terms as well as high-frequency degrees of freedom ($\hbar\omega \gg kT$), which must be treated only in quantum terms.

The phase coherence of the excited states assumes special importance for the energy dynamics in a liquid, where the density of oscillators is high. The rapid loss of phase coherence implies the rapid migration of the energy in the reservoir, whence $T_2 \ll T_1$. The ratio of T_1 to T_2 is important also for another reason—the energy can be extracted in the form of laser emission only under the conditions of high coherence. If the phase relaxation is limited by the escape of energy to the lattice, then $T_1 = T_2$; in this case, each step involving the removal of a quantum to the lattice also implies the loss of coherence.

For a set (packet) of oscillators of one kind (with one frequency and one phase), the absorption or emission line corresponding to the given vibrational transition is homogeneous

(or homogeneously broadened) with a width T_2^{-1}. For a set of packets, the line constitutes a superposition of the lines of the individual packets; this is an inhomogeneous (or inhomogeneously broadened) line. The causes of the loss of phase coherence are various. Firstly, there is the microstructural inhomogeneity of the liquid when the oscillators in different local environments and the phases fall out of step at different rates under different conditions. This is especially significant for rapid phase relaxation, where molecular dynamics is incapable of averaging out the microstructural inhomogeneity during a period shorter than T_2. Secondly, there is the resonant transfer of vibrational quanta between oscillators; each step involving the migration of a quantum is accompanied by a loss of phase coherence. Thirdly, the intramolecular interaction of oscillators with anharmonic coupling between them can also become a cause of the system going out of phase: the excitation and relaxation of one oscillator modulate the frequency and phase of another oscillator. Other causes are the vibrational-rotational interaction, Fermi resonance, and the formation of clusters.

In the energy dynamics in a liquid, one can trace the same trend as in clusters: the greater the frequency isolation of the oscillator, the longer the period during which it retains the energy. A striking example is provided by the N_2 molecule in liquid nitrogen for which T_1 at 77 K has the record value of 45–60 s, while $T_2 \cong 150$ ps, i.e. $T_1/T_2 \gg 1$. In the presence of admixtures (CO, CO_2, CH_4, O_2), the relaxation of N_2 is directed to impurities and from them to the lattice. For SO_2 in liquid SO_2, we have $T_1 \cong 45$ ns and it is independent of temperature, while for HCl ($v = 1$), $T_1 \cong 1-2$ ns in liquefied HCl and decreases with increase of temperature. The HCl ($v = 1$) relaxation cross-section in liquid xenon is 3×10^{-8} and is almost the same as in a gas for collisions with argon atoms. In CH_3F, the ν_3 vibration has a relaxation time of 375 ns in liquid O_2 and 1300 ns in liquid argon.

In polyatomic and "low-frequency" molecules, the relaxation times are shorter by several orders of magnitude and lie in the picosecond range. Thus the CH stretching vibrations in CH_2Cl_2 and CH_3COCH_3 lose energy over periods of 50 and 65 ps and these are nevertheless long times, because the deformation vibrations are of the low-frequency type and the Fermi resonance is suppressed. In CH_3OH, the second overtone of the CH_3 deformation vibration has virtually the same frequency as the stretching vibration and the Fermi resonance shortens the relaxation time of the stretching vibration to 1.5 ps. In ethanol, the Fermi resonance is slightly weakened and T_1 increases to approximately 20 ps. In $CHCl_3$, $T_1 \cong 115-140$ ps and depends on temperature; for SF_6, $T_1 = 27$ ps in liquid oxygen and 160 ps in liquid argon.

The vibrational relaxation of polyatomic molecules as a rule takes place in two stages: (1) rapid redistribution of energy among the vibrational modes (or their combinations) within the molecule over a period of 1–2 ps and (2) slow escape of energy from the vibrational reservoir to the lattice over a period of tens or even several tens of picoseconds. For example, in anthracene and azulene, the intramolecular migration of energy via vibrations takes place over a period of 1–2 ps and the removal of energy to solvent molecules takes 20–40 ps.

Rapid intramolecular energy fluxes are associated with a high density of the vibrational states and a strong interaction (via anharmonicity and Fermi resonance). Thus, for molecules containing ~30 atoms, the density of the vibrational levels is $\sim 10^6$ per cm^{-1}. The slow relaxation is associated with the transfer of the V-energy to the librational and translational degrees of freedom of the solvent molecules and this reservoir is "disconnected" from the vibrational reservoir as regards frequencies.

The study of the energy relaxation in large molecules in both ground and excited states has steadily advanced to the femtosecond region; the aim of such advance is to find new possibilities for laser-coherent effects and for selective "non-statistical" chemistry.

The theory of vibrational relaxation in a liquid has developed predominantly in two directions. The first originated from the gas model of binary collisions into which "collective" elements are introduced—correlations of pairs, triplets, etc. The second direction employs the model of collective movements and the rate of relaxation is determined in terms of the Fourier components of the correlation functions of the non-diagonal matrix elements of the perturbing Hamiltonian. A purely hydrodynamic theory based on model representation of a species "trembling" in a viscoelastic medium has also been developing; the theory reproduces collectively the effects of viscosity and density, but it is too simplified to reproduce all the characteristic features of the relaxation. An approach based on the generalised Langevin equation (see Section III) has also been developed. In all cases the theory is based on intermolecular interactions and the relaxation is a result of a complex interplay of attractive and repulsive forces; the prediction of the result of this interplay and the determination of its rules and characteristics is a complex and serious combined problem in molecular and energy dynamics.

4. Energy Relaxation in Solids

The relaxation and transfer of electronic energy in solids (especially in crystals) is a thoroughly developed field of physics and chemical physics with long traditions. The principal laws governing the transfer and quenching of energy and the mechanisms of its degradation have been formulated, the dependences of the transfer cross-sections on the oscillator strengths, on the distances between the donor and the acceptor, and on the orientation of the dipole moments of the optical transitions of the donor and acceptor are being refined, and the characteristic features of the electronic relaxation in excimers and exciplexes are being investigated. The aspects of this problem associated with photosynthesis, phosphors, and solid lasers are developing particularly vigorously.

In vibrational relaxation, the main problem is the dynamics of phonon excitations and the relaxation of the vibrationally excited impurity centres as reflected in the phonon spectrum. The lifetimes of the optical phonons in crystals are measured by coherent laser spectroscopic methods; thus in diamond their lifetimes T_1 are 2.9 and 3.4 ps at 295 and 77 K respectively and the A_{1g} vibration of the CO_3^{2-} anion in $CaCO_3$ relaxes over a period of ~3 ps.

The relaxation of impurity centres is of interest for the same reasons that the centres themselves are of interest (see Section II). The "burning of holes" in an inhomogeneously broadened spectrum (optical or vibrational), i.e. the saturation of optical or vibrational transitions for the given packet of centres of molecules, is used for their investigation. Conclusions about the rates and mechanisms of relaxation and about the contributions of the T_1 and T_2 processes to the relaxation are reached on the basis of the elemination of the "hole".

Direct results can be obtained from the spectroscopy of impurity centres in single crystals. For example, the width of the lines in the vibrational spectrum of SiF_6 in a xenon single crystal at 14 K is 0.028 cm^{-1}; it is homogeneously broadened, i.e. all the SiF_6 molecules in the xenon crystal are identical and constitute a single vibrational packet. The

line width is determined by T_2, i.e. by the loss of phase coherence as a result of the phase falling out of step in the elastic scattering of the lattice phonons by the vibrations of the impurity centres (SiF_6 molecules).

Furthermore, it is possible to discover which phonos are responsible for the phase relaxation. At low temperatures (14–50 K), the temperature dependence of the line width (T_2^{-1}) is described satisfactorily on the assumption that the local phonons with the following parameters are responsible for the phase coherence: frequency 4 cm^{-1}, lifetime 8 ps, constant for the coupling of the SiF_6 vibrations to local phonons 0.08. At high temperatures (>50 K), the bulk-phase (Debye) phonons of the crystal play the main role with a coupling constant of 0.05 and a frequency maximum of 42 cm^{-1} (this corresponds to a Debye temperature of 62 K). For ReO_4^- in ionic crystals of alkalis, the line width is also determined by T_2^{-1} and the phase coherence is lost to Debye phonons.

One of the new aspects of the energy dynamics in solids is the relaxation of charge carriers and excitons in semiconductors. For example, the pulse excitation of carriers (duration of pulse 50 fs) in the GaAs superlattice (65 periods in GaAs having a thickness of 96 Å with barrier layers of $Al_{0.3}.Ga_{0.7}As$ having a thickness of 98 Å) generates a packet of excited carriers, whose relaxation takes place over a period shorter than 100 fs. The average energy of the carrier then remains unaltered, i.e. only energy exchange between the packet of excited carriers and the remaining carriers in the conductivity band takes place during 100 fs. The elimination of energy and the descent of the carriers to the bottom of the conductivity band take place over a period of the order of picoseconds (over a period of ~5 ps in GaAs) and the relaxation to the valence band requires ~7 ps.

The examples presented here are few in number but they demonstrate the high technical level of the experiments and the high time and frequency resolution. Little has been done as yet in energy dynamics in solids, but progress in this field is constantly accelerating.

V. REACTION DYNAMICS

This is the science of the development of chemical processes in time, which constitutes the central component of chemical physics. It answers or attempts to answer fundamentally important questions such as which reactions can occur and which are prohibited, in what ways and by what means is it possible to remove the prohibition, how chemical reactions can be controlled, and how the rate and direction of the reaction can be influenced. Chemical dynamics is the fundamental basis for the creation of new and the improvement of existing technologies. A second important aspect of chemical dynamics is analysis of the ways of transforming energy in elementary reactions in order to search for high quality chemical laser systems.

1. Potential Energy Surfaces and Theories of Reaction Dynamics

The task of the theory is the development of methods for the calculation of rate constant or cross-sections for specified quantum states of the reacting species; potential energy surfaces (PES), i.e. the dependence of the total energy of the reacting atomic-molecular system on the coordinates of the atoms, are needed for this purpose. The PES is the "conductor" of the chemical reaction, controlling the trajectories of the transitions from reactants to products and determining the reaction channels, the reaction cross-sections, and the distribution of energy in the product.

The calculation of PES is the first problem of chemical dynamics. Non-empirical (*ab initio*) computational methods are being developed; they are laborious, since they require the calculation of a large number points on the surface, but the main difficulties are associated with the correct allowance for the electronic correlation energy. Furthermore, subsequent employment of this PES in the calculation of trajectories requires an analytical, functional representation of the entire PES (which is virtually impossible) or of its section in the vicinity of the trajectory to be calculated. Semiempirical quantum-chemical methods are also being developed (for example, the method of diatomic complexes in the molecule—DCM), but the most popular are the even simpler methods based on the familiar London equation for the energy of a triatomic system. Among them, the LEPS (London–Eyring–Polanyi–Sato) PES is widely used. Semiempirical methods for the calculation of the one-dimensional profile of the reaction path from the reactants valley to the products valley are also known (for example, the "bond energy–bond order" method); it is useful in approximate calculations where only the rate constants are of interest and the entire PES need not be known.

Examples of PES for the $O + H_2$ reactions are presented in Fig. 6. For linear $O(^3P) + H_2$ collisions, the forms of the PES obtained by the *ab initio* and DCM methods differ. The crossing point in the former is displaced towards the valley of the initial reactants and in the latter towards the valley of the products. This difference is of fundamental importance for the possibility of activating this reaction and the fate of the energy. It is seen from Fig. 6*c* and 6*d* that the PES for the reaction $O(^1D) + H_2 \rightarrow OH + H$ with a linear configuration of the atoms and for the insertion reaction $O(^1D) + H_2 \rightarrow H_2O$ differ sharply from the PES for the $O(^3P) + H_2$ reactions.

The accuracy of the PES is a painfully acute problem in chemical dynamics: any errors in the calculation and distortions in the PES entail marked deformations of the trajectories. The reaction trajectories and cross-sections are so sensitive to the details of the PES that one frequently resorts to the solution of the converse problem: the trajectories and cross-sections are assumed on the basis of a calculated PES and then the results of the calculations are compared with reliable experimental data and the PES is "corrected" until "satisfactory" trajectories reproducing the experimental data are obtained.

The construction of the PES is the first part of chemical dynamics; the second part involves the calculation of the trajectories in the movement of the reaction system on the surface. If the calculation is based on the equations of classical mechanics, then the procedure is called the method of classical trajectories; if the quantum states of the internal degrees of freedom (rotations and vibrations) are taken into account in the equations, then the trajectories obtained are assumed to be quasi-classical in the sense that their initial conditions take into account the quantum character of the rotations and vibrations, but they do not represent rigorous solutions of the quantum equations of motion.

Examples of quasi-classical trajectories for the reactions $C(^1D) + HI \rightarrow CH + I$ and $C(^1D) + HI \rightarrow CI + H$ are presented in Figs. 7*a* and 7*b*. Both trajectories describe the mutual approach of three atoms (the C atoms move along the normal to the centre of the H–I bond) with formation of a complex having a lifetime of ~0.8 ps along the first trajectory and ~0.4 ps along the second. The periodic changes in interatomic distances, i.e. bond vibrations (between 0.5 and 1.3 ps) are very marked in the complex; the highest frequency is that of the C–H vibration and the lowest frequency is that of

the C–I vibration. The lifetime of the complex is comparable to the time required for the intramolecular migration of the vibrational energy (see Section IV) and its statistical distribution therefore holds in the reaction products.

The trajectories of the same reactions occurring in a linear collision do not reveal the existence of a complex. They have the form typical for the generalised reactions A + BC → AB + C (Fig.7c). The absence of a long-lived bound state in such reactions is the cause of the non-statistical distribution of energy in the products.

The method of quasi-classical trajectories does not take into account the quantum effects of the motion and of the tunnelling under the barrier. Such problems do not arise in quantum calculations, being exotic rather than usual. The experience gained in the calculations has demonstrated that the introduction of quantum corrections to the quasi-classical trajectories with a one-dimensional potential barrier is insufficient and that it is necessary to solve the problem with a multidimensional barrier and that a method capable of describing the classical movement of the reactants along the PES over long distances and tunnelling over short distances is needed.

Definite advances have been made on these lines: a method of complex trajectories has been developed, within the framework of which it is possible to combine the mutually exclusive concepts of tunnel and classical trajectories. A complex trajectory becomes real when the real time is replaced by the imaginary time ($t \to it$) and the PES is replaced by the inverted PES ($U = -U$). In this method there are difficulties associated with the choice of the boundaries and contour of the trajectories, but overall it is an effective procedure whereby one can obtain "quantum" results from quasi-classical equations of motion.

Calculation of the trajectories on a single PES is frequently insufficient, since there are several PES in very close proximity in individual regions or even quasi-intersecting. The unusual problem of allowing for the non-adiabatic nature of the process, i.e. for the "jump" of the reaction system

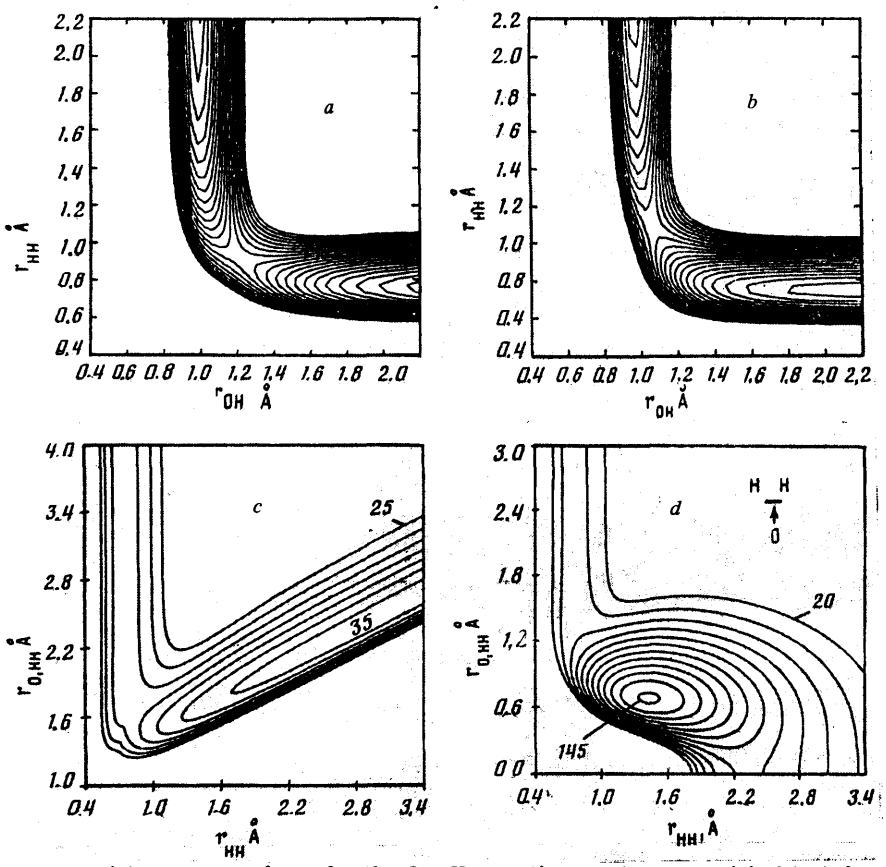
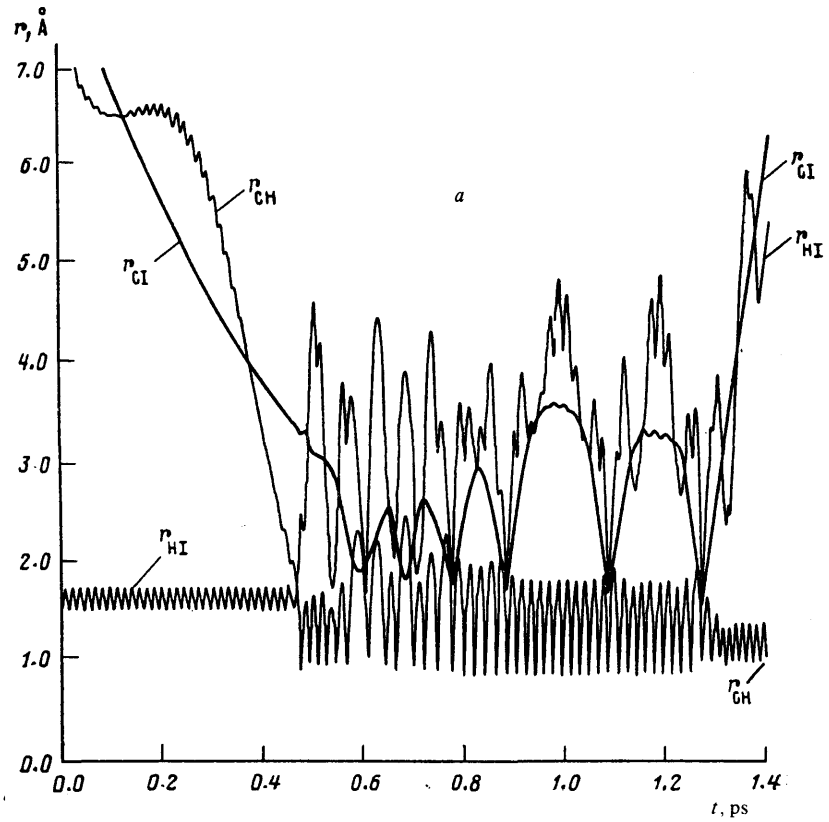
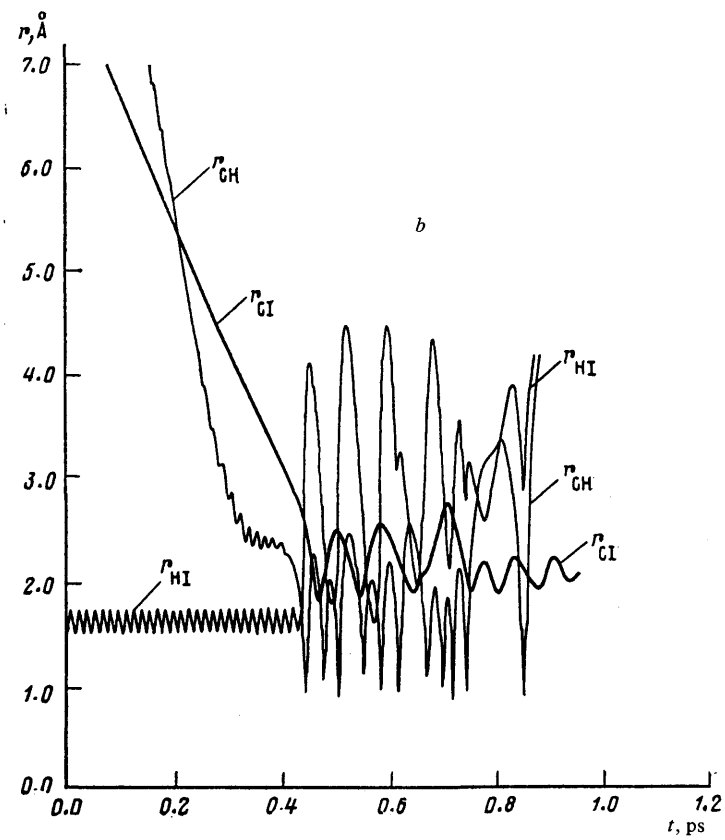


Figure 6. The potential energy surfaces for the O + H_2 reactions: *a*) non-empirical PES for $O(^3P)$ + $H_2 \to OH + H$ (linear complex, $r^*_{OH} = 1.216$ Å, $r^*_{H_2} = 0.920$ Å, 12.58 kcal mol^{-1} barrier); *b*) PES obtained by the DCM method for $O(^3P) + H_2 \to OH + H$ (linear complex, $r^*_{OH} = 1.061$ Å, $r^*_{H_2} = 1.103$ Å, 13.35 kcal mol^{-1} barrier); *c*) PES obtained by the DCM method for $O(^1D) + H_2 \to OH + H$ (linear complex, $r_{O,HH}$ = distance from O to the centre of the H–H bond, $r^*_{O,HH} = 1.66$ Å, $r^*_{HH} = 0.78$ Å, 0.80 kcal mol^{-1} barrier); *d*) PES obtained by the DCM method for $O(^1D) + H_2 \to H_2O$ (complex with C_{2v} symmetry, reaction involving the insertion of O in the centre of the H–H bond, no barrier). Constant energy lines have been drawn from 1 to 20 kcal mol^{-1} at 1 kcal mol^{-1} intervals (for *a* and *b*), from 35 to 25 kcal mol^{-1} at 10 kcal mol^{-1} intervals (for *c*), and from −145 to 20 kcal mol^{-1} at 15 kcal mol^{-1} intervals (for *d*); r^* = coordinates of the apex of the barrier.





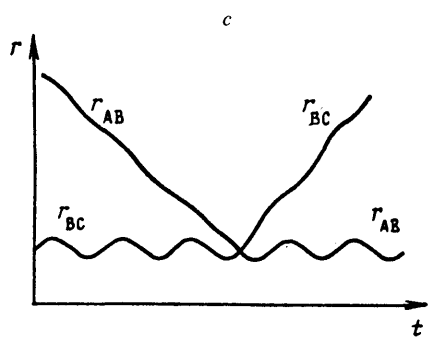


Figure 7. Examples of reaction trajectories: *a*) for $C(^1D) + HI \rightarrow CH + I$; *b*) for $C(^1D) + HI \rightarrow CI + H$; *c*) generalised trajectory for the forward reaction $A + BC \rightarrow AB + C$.

between different PES in regions where they approach one another or quasi-intersect, then arises. Such jumps distort the reaction trajectories and allowance for them constitutes a serious problem in chemical dynamics.

In trajectory dynamics, account is taken of many trajectories for a given reaction (by no means all cross the bridge between the reactants valley and the products valley), and then the overall reaction cross-section in the specified states of the reactants is obtained by averaging the results with respect to the initial (starting) conditions governing the trajectories; one of the popular methods of selecting the initial conditions (but not the only one) is the Monte Carlo method.

Dynamic trajectory calculations yield the most complete information about the chemical reaction and provide answers to the following questions: what reaction channels exist, what are their probabilities, how is the energy of the reactants utilised in the reaction, how is it redistributed in the products, and at which modes of the motion is it localised. However, they are laborious and are by no means always fully realisable, being used predominantly for the simplest reactions. Simpler versions of the theory are therefore being developed, among which the method of the reaction pathway Hamiltonian merits special attention.

In this version of the theory, the classical Hamiltonian of the molecular reaction system is constructed and the reaction pathway as well as orthogonal oscillations (deviations from the reaction pathway in the closest regions of the PES along the pathway) are found. In principle, this approach makes it possible to carry out calculations for polyatomic systems and has definite practical advantages: the entire PES is not needed, only a small proportion of the latter being required (the region corresponding to the valley on the reaction pathway), but these advantages entail the sacrifice of the physical rigour and completeness of the calculation.

Together with dynamic trajectory theories, statistical theories are also being developed in chemical dynamics. They are suitable for reactions proceeding via a long-lived intermediate complex (resembling those which can be seen on the trajectories in Figs. 7*a* and 7*b*). The formation of the complex and its decomposition are then independent events. If during the lifetime of the complex τ_c, a statistical distribution of the energy takes place (subject to the conservation of the energy and the momentum), then the reaction complex can be treated as a statistical system and its behaviour can be described in terms of statistical laws.

The criterion which determines whether the reaction can be described by the statistical theory is not always definite; it is frequently assumed to be represented by the condition $\tau_c \gg \tau_{rot}, \tau_{vib}$, i.e. the lifetime of the complex is longer than the rotational and vibrational relaxation times. However, this condition is not unambiguous and statistical theories are frequently applicable even if this condition is not fulfilled and, conversely, they are not applicable when it is fulfilled. In order to predict the properties of the reaction complex, it is important to know the behaviour of van der Waals molecules (Section II), while information derivable from energy dynamics is important for the prediction of its "statistical nature" (Section IV).

The transition state theory is frequently included among statistical theories; strictly speaking, this is not correct, because the configuration of the atoms at the top of the crossing ridge (it is referred to as the transition state or the activated complex) decomposes only via the direct channel and is not a statistical system. This is associated with the fact that one degree of freedom, corresponding to the reaction coordinate, has been differentiated in the method itself (in its physical aspect) and, by definition, it is isolated from the other degrees of freedom of the reaction system. On the other hand, in the transition state theory an equilibrium distribution is adopted, but it is a consequence of the equilibrium nature of the initial reactants. In other words, it leads to the activated complex together with the reactants but is not created in it and in this sense the claim that the transition state theory belongs to the class of statistical theories can be regarded as correct.

In the transition state theory, there is no dynamics of motion along the PES, only the knowledge of the energy spectrum of the reaction system moving along the PES being required. During its long history, the theory has received new formulations and justifications and many versions of this theory have been created: the canonic theory [calculation of the rate constants $k(T)$], the microcanonic theory [calculation of the cross-sections $\sigma(E)$], the variational theory (ensuring allowance for only the one-way reaction trajectories), the adiabatic transition state theory (it takes into account the quantum-mechanical partition functions and tunnel corrections), and, finally, the variational quantum-mechanical (or generalised) theory.

At the present time the transition state theories are the most productive, although they are more in the nature of recipes and not all their approximations are reliable. It has been demonstrated for a large number of collinear reactions over a wide temperature range that the rate constants usually agree with the quantum-mechanical calculations and with experiment to within an error not greater than 30%, although there are instances where the discrepancies in the constants amount to a factor of several tens and hundreds and it is not possible to estimate *a priori* this artibrary aspect.

The question when does the description of the reaction require dynamic trajectory calculations and when are statistical theories sufficient is a problem in statistical and non-statistical, selective chemistry. It is important especially in the chemistry of highly excited states; the emphasis laid on this problem is a tribute to technical progress. Hence follows the sharp increase of interest in ergodic systems. Chemical dynamics is beginning to adopt on a wide scale the approaches based on the ideas of the ergodic hypothesis, theories of order and chaos in chemical reaction systems are being developed, and problems of the chemical dynamics of periodic, oscillating reactions are being discussed. The endeavour to move outside the framework of adiabatic models and to develop effective methods whereby non-adiabatic conditions can be taken into account is associated with these factors.

The chemical dynamics of reactions in the condensed phase adds a new problem to all the difficulties and problems of gas-phase dynamics—that of allowing for the influence of the medium whose molecules act on the atomic-molecular reaction systems and are, strictly speaking, participants in the reaction and the question to what number of participants can the treatment be restricted has no definite answer. The first attempt to solve this problem arose in the familiar Kramers theory based on the solution of the equation of diffusional motion along the reaction coordinate. This theory introduced the concept of friction along the reaction pathway and was later developed in different versions—on the basis of the Fokker–Planck equation in terms of various approximations (Kramers himself obtained his initial equation in terms of the Stokes–Smoluchowski approximation—see Section III) and then on the basis of the Langevin equations. It was shown that the Kramers theory can also be obtained from the simple Langevin equation, i.e. subject to the condition that the random force acting from the direction of the molecules of the medium on the reaction system moving along the reaction coordinate is described by a Markov process. The generalised Kramers theory can be obtained from the generalised

Langevin equation and is equivalent to the problem of the attainment of the apex of a one-dimensional potential barrier by a Brownian particle when the random force is described by a non-Markov stationary Gaussian process. The generalised Kramers theory is then equivalent to the generalised transition state theory. The physical significance of the analogies is clear—the molecules of the medium (thermostat) act as a perturbing trajectory of the motion of the reaction medium along the reaction coordinate. The prospects for the development of a theory based on the quantum-mechanical version of the generalised Langevin equation have also been considered, but this is a difficult problem requiring the knowledge of the nature of the thermostat and of the details of the interaction of the reaction system with the thermostat at the quantum-mechanical level.

There have been definite advances in the development of theories of charge transfer reactions; they are based on the idea of the reorganisation of the medium as a result of fluctuations in dielectric polarisation. Such reorganisation produces potential wells and barriers, i.e. produces a potential surface, and this process is described by the classical theory, while movement along the reaction coordinate can be described within the framework of any dynamic theory (in particular, a purely tunnel version can be considered for electron transfer). A generalised quantum-mechanical-clasical theory, in which the classical treatment of the movement of nuclei is combined with the quantum-mechanical description of the movement of electrons is also being developed.

The state of the theory of chemical reactions in the condensed phase is such that the theory and experiment are developing almost independently; the theory predicts merely general qualitative features but is incapable of making quantitative predictions. The difficulties are associated with the fact that many important details of the physics of the reactions are obscure—it is not clear what is the main factor which needs to be taken into account and what is of secondary importance and negligible in the theory.

2. Energetics in Reaction Dynamics

This problem has two aspects. The first involves the question of how the reacting molecules utilise the energy supplied to them, what energy is most effective and for what reactions, and under what conditions do the molecules employ their energy with the maximum benefit for the reaction. These questions have a direct bearing on the selective pumping of the energy to the degrees of freedom responsible for movement along the reaction coordinate—the control and stimulation of selected reactions. The second aspect involves the questions how energy is liberated in the chemical reaction, where it proceeds, where and in what forms it is localised, and how can it be concentrated and utilised. These questions have a bearing on the creation of laser media and effective pumping procedures in chemical lasers.

In principle, the answers to the majority of these questions are provided by trajectory calculations, but the laborious nature of the calculations and the limited accessibility of the PES has stimulated an alternative, experimental procedure, involving the use of modern laser spectroscopy, which makes it possible to produce and detect molecules in any quantum-mechanical states.

We shall deal first with the first set of questions—the ways of controlling reactions by pumping energy to the reacting species. These questions have no general answer; it depends on the type and topology of the PES, on the type of reaction, on the value of the energy, and on the type of the energy reservoir—E, V, R, or T.

When the electron reservoir is pumped up, electronically excited states are created, but even they exhibit a selectivity in reactions: each type of reaction is stimulated only by an electronic excitation of a definite type. The pumping of energy into the electron shell by no means stimulate every reaction despite the enormous amount of energy stored. One of the problems is to discover the nature of the selectivity, to learn how to predict it, and to employ it economically in the photostimulation, radiation-stimulation, and plasma-stimulation of processes.

The question of the relative contributions of the kinetic and vibrational energies to the activation of reactions is important. Thus, for reactions with a large barrier, there exists a kinetic energy threshold above which the reaction cross-section increases to a maximum and then diminishes. For endothermic reactions, the vibrational energy is much more effective than the kinetic energy, while for exothermic reactions the opposite situation obtains. The vibrational pumping of molecules is of special interest for two reasons: the vibrational energy relaxes with difficulty (at any rate much less easily than the kinetic and rotational energies) and should therefore be retained for a long time in the vibrational modes; the availability of powerful lasers operating in the vibrational-frequency range makes the question of practical significance.

The efficiency of vibrational energy in reactions depends on the heat of reaction, on the topology of the PES, on the height of the barrier, on the size of the vibrational quantum, on the adiabatic conditions, on the type of reactions (transfer of an atom, metathesis), on the complexity of the molecules, on the density of the vibrational states, on whether the reaction is of the direct, single-step type, or whether it proceeds via an intermediate statistical complex. Only one important feature has been reliably established and justified theoretically: the vibrational excitation is effective in overcoming the endothermic component of the potential barrier and hardly influences the overcoming of the barrier in thermally neutral and exothermic reactions. Its origin is inherent in the topology of the PES: for endothermic reactions, the barrier is encountered at an "early" stage, being displaced towards the initial reactants valley, while for exothermic reactions the barrier occurs at a "late" stage, being displaced towards the products valley.

For example, the reactions Ca(Sr) + HF → CaF(SrF) + H are accelerated by a factor of 10^4 already by the first vibrational quantum absorbed by HF, while the reaction F + HCl → HF + Cl with vibrationally excited HCl ($v = 1$) is accelerated only by a factor of 4. The reaction $CH_3 + H_2 \rightarrow CH_4 + H$ with participation of $H_2(v)$ is accelerated, while the excitation of CH_3 can accelerate, suppress, or altogether fail to influence the reaction, depending on the type of vibration excited. In the reaction K + HCl → KCl + H, HCl ($v = 1$) molecules react 100 times faster than HCl($v = 0$) and only 10 times faster if the same amount of energy is "thrown" into the kinetic degrees of freedom. In the reaction $OH + H_2 \rightarrow H_2O + H$, the $H_2(v = 1)$ molecules react 150 times faster than $H_2(v = 0)$, but the acceleration in the pumping of OH to the $v = 1$ state is only by a factor of 1.3. Neither the pumping of OH nor the pumping of CO alters significantly the rate of the reaction $OH + CO \rightarrow CO_2 + H$, while the reaction $O_2 + CN \rightarrow CO_2 + N$ is actually retarded by the pumping. The excitation of the HCO vibrations inhibits the HCO + NO reaction and this is evidence that it proceeds via a statistical complex.

An enormous number of such facts and observations exist for gas-phase reactions and by no means all have been explained satisfactorily. In the condensed phase the problem in activation is complicated by the rapid vibrational relaxation (see Section IV). There are very few data for

reactions on solid surfaces (for example, it is known that the reaction $N_2O + Cu \rightarrow CuO + N_2$ is accelerated by a factor of 10^3–10^4 when vibrationally excited N_2O molecules participate in it), but this field will develop vigorously.

The influence of rotational pumping on reactions has been investigated mainly by the method involving the selection of rotational states in quadrupolar fields and by laser methods. The rate constants $k(J)$ for the reactions $Na + HF \rightarrow NaF + H$ and $Na + HCl \rightarrow NaCl + H$ decrease with increase in the rotational quantum number J to $J_{min} = 11$ (for the first reaction) and 7 (for the second), and then increase with increase in $J > J_{min}$. The reaction $K + RbF \rightarrow KF + Rb$ is exothermic, $k(J)$ falling with increased J; the reaction $H + OH \rightarrow H_2 + O(^1D)$ is also exothermic, but $k(J)$ increases with increased J. The rotation of OH accelerates the reaction $NO + OH \rightarrow NO_2 + H$, while the rotation of NO accelerates the reaction $NO + O_3 \rightarrow NO_2 + O_2$. In the reaction $H + HBr \rightarrow HBr + H$ with $v = 0$, J does not influence the reaction, but, when $v = 2$, the constant $k(J)$ increases with increasing J, i.e. the effect of the rotational R-energy depends on the vibrational state. The reaction $Br + HBr \rightarrow HBr + Br$ with HBr ($v = 0$) is insensitive to J up to $J \leq 10$, but is accelerated sharply for $J > 10$.

The influence of the R-energy depends on the kinetic energy: for a high kinetic energy (above the threshold), the influence of the R-energy is insignificant, which is understandable: for high rates, the time of contact between the species is much shorter than the period of the rotation and the rotational state of the reactant becomes insignificant for the reaction. The inhibition of the reaction by rotation, i.e. the decrease of $k(J)$ with increase of J, is also understandable to a first approximation: the reaction requires a definite orientation of the reactants, an appropriate orientation throughout the contact time, while rotation disrupts this arrangement. This is the effect involving the gyroscopic stabilisation of molecules: a rapidly rotating molecule averages out the perturbing potential of the incoming partner and this "saves it" from reaction.

However, these are only the few features which are understandable; much remains obscure and difficult to predict. The principal factor is apparently the ratio of the angular velocity of the rotating molecule to the relative velocity of the movement of the partners—it determines the efficiency of the R-energy in the reaction and so far there is no general solution to this problem.

An attractive problem involves the search for non-traditional and sometimes non-evident methods of controlling reactions using energetically weak influences. This is possible in systems with degenerate states, which, however, differ in reactivity. Then even weak influences induce almost isoenergetic transitions from one less reactive state to another, more reactive state. This is in fact the principle of magnetic influences on chemical reactions (see Section VI); this is also possible in laser chemistry, where the direction of the reaction can be altered by weak coherent radiation.

The idea can be illustrated by an example: suppose that the molecule decomposes into different products for a certain energy, which means that it possesses a series of degenerate continuous states, each of which is correlated with a definite composition of the products. The key question is how to intensify the selectivity of the molecules in relation to these states—how to achieve their selective population. This requires the control of the composition by a coherent linear superposition of these degenerate states. It can be achieved if the initial molecule is prepared by coherent irradiation with superposition of bound states and is then dissociated in a specified state. This idea has been realised experimentally in the photolysis of CH_3I via two channels:

$$CH_3I \rightarrow CH_3 + I(^2P_{1/2})$$
$$CH_3I \rightarrow CH_3 + I(^2P_{3/2}).$$

Using two-frequency laser irradiation (one frequency for the superposition of the coherently bound states and the other for photodissociation via one or other channel), it is possible to increase by a factor of two the quantum yield of the decomposition for an unchanged energy expenditure and to alter the competition between the channels. This is in essence the first example where energetic coherence has been manifested in chemical reactions.

We shall now turn to the second range of questions, concerning the fate of the heat of reaction. A most attractive procedure is to convert the heat (when it is sufficient) into an "intensive" form of energy—electronic energy. The efficiency of the electronic pumping into the reaction product depends on many factors—the magnitude of the heat of reaction, the orbital and spin prohibitions, the quasi-intersections of the PES, and the non-adiabatic nature of the trajectories on the PES. For these reasons, the quantum yield of the electronic pumping in different reactions (usually determined from the chemiluminescence yield) varies by many orders of magnitude—from 10^{-11} to ~1. It is important to establish the characteristics of the electronic pumping for the prediction of laser effects. They are widely investigated in the flames of metal vapours in CO, N_2O, O_2, O_3, etc. atmospheres, in the reactions of alkali metal atoms with halogen molecules, in the recombination of the N, O, etc. atoms on surfaces, etc. The search for chemical laser systems is one of the most vigorously developing fields of chemical physics.

The vibrational pumping of products is determined also by the topology of the PES: if there is an attractive potential between the reactants and the ridge separating the valleys occurs at an "early" stage, i.e. is displaced towards the reactants valley, the kinetic energy of the reactants is converted preferentially into the vibrational energy (V-energy) of the products; for a repulsive potential and a "late" ridge, the energy liberated remains in the kinetic form. Adiabatic conditions with respect to both ΔV and ΔR are frequently retained, i.e. the vibrational and rotational energies of the initial reactants are fully retained in the products. General characteristics have been scarcely established in this field hitherto, the adiabatic (or non-adiabatic) conditions, depending on the energy stored, the topology of the PES, and the vibrational-rotational coupling. For example, in the reaction $Cl + HD \rightarrow HCl + D$, the rotational energy is retained, while in the similar reaction $Cl + HD \rightarrow DCl + H$, the rotational energy of the initial molecule is converted almost fully into the kinetic energy of the products.

The energy pumping of the product frequently serves as the criterion of the reaction mechanism. Thus the reaction $Cs(7P_{1/2, 3/2}) + H_2 \rightarrow CsH + H$ proceeds via the harpoon mechanism: the optical electron of the excited Cs atom is thrown like a harpoon from Cs to H_2 over long distances and the $Cs^+ + H_2^-$ ion pair is maintained as a result of the Coulombic potential and decomposes slowly into CsH and H. This mechanism agrees with the dynamic trajectory analysis of the PES on which the ionic and covalent energy levels "intersect". An important consequence of this mechanism is the strong rotational excitation of CsH: J_{max} reaches 17 and the maximum pumping has been achieved for $J = 10$–12.

The photolysis of H_2S in the gas phase at 193 nm leads to the formation of an H atom with an HS radical in the $^2\Pi_{3/2}$ or $^2\Pi_{1/2}$ states, their ratio being 3.75, which corresponds to an electronic temperature of 410 K. Vibrational excitation is almost completely absent and the rotational temperatures of

the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ states are 375 and 220 K, i.e. the electronic and rotational temperatures are close to the temperature of the photolysis, which means that the energy of the photolysing quantum is converted into the kinetic energy and the decomposition takes place non-statistically. The opposite case is represented by the decomposition reaction $CF_3NO \rightarrow CF_3 + NO$. The distribution of CF_3 and NO with respect to v is nearly statistical and the rotational temperature of NO ($^2\Pi_{1/2}$) is 900 K and is very close to the statistical limit of 1025 K; the V- and R-energies of CF_3 and NO are close to this limit. The times corresponding to the appearance of CF_3 and NO at 670, 640, and 500 nm are 18.5, 8.8, and 4.3 ns and agree with the lifetimes of the "energised" CF_3NO molecules measured independently. Clearly, CF_3NO decomposes via a long-lived statistical complex.

The present experimental level of research into pathways leading to energy pumping is demonstrated by the analysis of the energy states of the products in the following reactions:

$$H+O_2 \rightarrow OH+O; \quad \Delta H = 16.6 \text{ kcal mol}^{-1};$$
$$H+CO_2 \rightarrow OH+CO; \quad \Delta H = 25.4 \text{ kcal mol}^{-1};$$
$$H+H_2O \rightarrow OH+H_2; \quad \Delta H = 14.8 \text{ kcal mol}^{-1}.$$

All these reactions are endothermic, but the H atoms generated by the photolysis of HI are hot and the energy of the collision of H with its reaction partners (O_2, CO_2, H_2O) is 60 kcal mol^{-1}, which greatly exceeds the endothermicity. Despite the high collision energy in the $H + CO_2$ and $H + H_2O$ reactions, there is no vibrational excitation of OH (there are none in states with $v = 1$), but in the $H + O_2$ reaction there is significant vibrational pumping: the population of OH ($v = 1$) is only a factor of 2 smaller than the population of OH ($v = 0$).

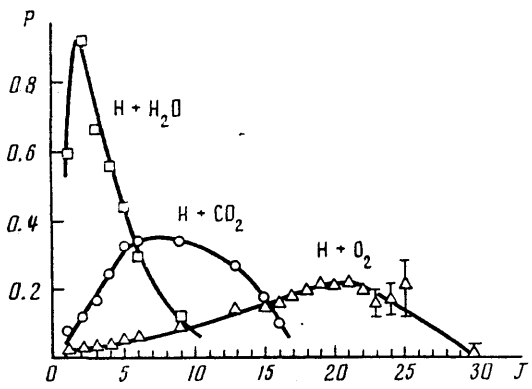


Figure 8. The populations P (in relative units) of the rotational states of OH ($v = 0$) in the reactions of a hydrogen atom with H_2O CO_2, and O_2 (pressure 0.2 mmHg, probing pulse delay time 100 ns).

The rotational excitation of OH in the $H + O_2$ reaction is very hot (J is large—Fig.8), while in the $H + H_2O$ reaction it is virtually absent, although the energetics are the same. In the $H + H_2O$ reaction the rotational distribution does not correspond to the statistical distribution, while in the $H + O_2$ reaction the statistical distribution obtains but this does not mean that the reaction can be treated statistically. This agreement is fotuitous: trajectory calculations have shown that the transition complex HO_2 on the non-empirical PES in the vicinity of the ridge has a lifetime of ~0.1 ps and the distribution of the rotational energy agrees with the experimental distribution in the absence of statistical equilibrium.

The spin-orbit doublets $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ are populated statistically, but the population of the Π^+ component of the Λ doublet takes place preferentially in all three reactions by a factor of 3–6. This means that an angular momentum is generated in all the reactions in the plane containing the bond undergoing dissociation, i.e. that the output channel in these reactions lies in a single plane. Otherwise, an angular momentum would have been created in the reaction around the bond being dissociated and this would have entailed the preferential population of the Π-component of the Λ doublet.

These features of the dynamics and energetics of all three reactions presented are associated with the characteristics of their PES and indicate how effectively the PES "conducts" both the chemical and energy dynamics.

3. Chemical Kinetics and Reaction Mechanisms

Chemical kinetics as the science of process rates and mechanisms is part of reaction dynamics; it has long outgrown their traditional framework and has reached a new level. Formal kinetics has been converted into a routine technique, the new level of modern kinetics being determined by the wide-scale application of a wide variety of physical methods permitting the reliable identification of the majority of intermediate species with a high time resolution (down to tens of femtoseconds). Reliable methods, characteristics, and criteria have been developed, whereby it is possible to achieve a sufficiently full determination of any mechanism.

The knowledge of the mechanism is not the ultimate aim; it is necessary to determine the rate-limiting stage, to establish the main and secondary pathways, and to select the method of controlling the process in order to increase its productivity and selectivity. The knowledge of the mechanism is the most important element on the way to creating intensive highly selective and energy saving chemical technologies.

A considerable proportion of chemical physics is devoted to kinetic studies and chemical mechanisms. It is concerned with the mechanisms of the reactions in molecular beams, ion-molecule reactions, the reactions of excited species, oxidation-reduction reactions, metal complex, acid–base, heterogeneous, micellar, and enzyme catalysis, and electrochemical reactions. Priority has been given to catalytic processes, plasma chemistry, combustion processes, reactions in solids, and processes associated with chemical energetics (new current sources, chemical methods for the accumulation and transformation of energy, etc.). Among them, we may mention the creation of new combustion regimes—the solid-phase oxygen-free combustion (self-propagating high-temperature synthesis), the creation of a "superadiabatic" regime with extremely high effeciencies approaching 100%, and combustion coupled with energy consuming processes. In the chemical physics of solid-phase reactions, valuable low-temperature chemical "explosions", induced by the mechanical stresses in strongly cooled glasses, and the quantum-mechanical limits of the rates of low-temperature reactions have been discovered and new types of mechanochemical processes, induced by shear deformation at high pressures and by shock waves, have been observed. There has been a sharp growth of interest in the problem of the macroscopic storage of mechanical energy and the utilisation of this store for the activation of chemical processes is a tentative basis of promising technologies.

A remarkable property of chemical reactions in solids has been established—even in the kinetic regime the reactions are controlled by the molecular dynamics of the solid so that the molecular organisation of the transition state and not the chemical step proper becomes the rate-limiting stage. This alters, in principle, the concept of the reactivity of species in a solid and leads to new ways of controlling reactions via the physics and mechanics of the solid.

VI. SPIN DYNAMICS

Spin dynamics includes the dynamics of the populations of the spin states of atomic-molecular species and matter, the dynamics and mechanisms of the pumping and relaxation of spin states, and the dynamics of the change of the angular momentum. It can be subdivided into two components—spin dynamics in systems without a chemical reaction and spin dynamics in reactive systems.

The first component is the traditional field adjoining magnetic resonances and magnetic resonance spectroscopy as a method in chemical physics. It includes an enormous number of problems—magnetic relaxation of electrons and nuclei, the dynamics of spin systems in UHF and microwave frequency fields, the exchange of magnetic energy between the Zeeman and magnetic-dipolar reservoirs, joint electronic-nuclear relaxation and the orientation of nuclei (dynamic nuclear polarisation), electron–electron relaxation and electron–electron double resonance, spin–orbit coupling and its contribution to the spin dynamics, and the spin relaxation and transition between the spin states of triplet moelcules, ions, carbenes, metal complexes, clusters, etc. A special branch of spin dynamics is associated with the optical orientation of electrons and nuclei: these phenomena are known in gases, in plasma, in molecular crystals, in impurity centres of a solid, and recently also in liquids.

Spin dynamics is controlled by magnetic perturbations and their time variation, being determined by the amplitude of the perturbation and the duration of its action and it therefore carries simultaneously information both about the structure and about the dynamics of the perturbations (molecular or chemical information). This is important for magnetic microwave spectroscopy as a physical method for structural analysis and for the identification of chemical species and substances and also for magnetometry (including quantum-mechanical magnetometry).

However, spin dynamics can be sensitive also to non-magnetic, purely electrostatic interactions. For example, the rate of singlet–triplet conversion in the carbene Ph_2C depends on the polarity of the solvent. This is possible owing to the Coulombic polarisation of the electron shell (on complex formation, solvation, etc.); this effect can alter the contribution of the spin–orbit coupling to the spin relaxation and can alter the spin dynamics. Another example: the electron-spin relaxation of the Na, K, Rb, and Cs atoms in the inversely populated state $^2S_{1/2}$ depends greatly on the nature of the "buffer" gas (He, Ne, H_2, CH_4, NH_3, C_6H_6, etc.). The cause of the effect is as follows: in the impact of an atom against the buffer molecule, Coulombic forces induce an orbital moment, while the spin–orbital coupling induces in its trun spin relaxation. Here not only the rate of relaxation but also the extent of the hyperfine magnetic interaction of the electron with its nucleus in the metal atom depends on the nature of the buffer gas. Thus highly polar molecules diminish the hyperfine interaction constant, because, in strong collisions between an atom and such molecules, the electron shell of the atom is polarised and a *p* orbital with a zero-point hyperfine interaction becomes mixed with the spherically symmetrical *s* orbital.

The dynamics of the exchange of the angular momenta (orbital and spin) between the molecules play a significant role in many processes, including the functioning of lasers. For example, in the iodine laser with emission based on the transition $I(5^2P_{1/2}) \rightarrow I(5^2P_{3/2}) + h\nu$, the inverse population is restored in the process $I(5^2P_{3/2}) + O_2(^1\Delta g) \rightarrow I(5^2P_{1/2}) + O_2(^3\Sigma\bar{g})$, i.e. the electron-spin momentum is transferred from oxygen to the angular momentum of the iodine atom.

The spin dynamics in chemically reacting systems ensures an even greater richness of phenomena. In chemical reactions prohibitions based on the angular momentum (both orbital and, especially, spin momentum) are very strong, i.e. reactions requiring a change in the angular momentum are strictly prohibited; only reactions which are not accompanied by a change in momentum are allowed. The evidence for this postulate is numerous and reliable. Thus molecular, ion-molecule, and even radical substitution and addition reactions in solutions are not accompanied by the polarisation of the nuclear spins, which is a feature of the change in the electron spin. Even in reactions with participation of atoms with strong spin–orbit coupling, the spin is retained:

$$F(^2P_{1/2}) + Br_2 \rightarrow FBr + Br(^2P_{1/2})$$
$$F(^2P_{3/2}) + Br_2 \rightarrow FBr + Br(^2P_{3/2})$$
$$Br(^2P_{3/2}) + IBr \rightarrow Br_2 + I(^2P_{3/2})$$

(these reactions are significant in gas lasers based on halogen atoms).

The rigour with which the spin is retained and the rigour of the spin prohibitions of chemical reactions are evident from simple physical considerations alone. The intrinsic time of the elementary reaction is a fraction of a picosecond and magnetic or spin–orbit perturbations exerting an enormous force are necessary to alter the spin during this period. As a rule, such high-energy perturbations do not occur in the transition states of reactions. For this reason, spin is conserved in the vast majority of chemical reactions. Exceptions may be expected only in rare cases [for example, in reactions with a long-lived statistical complex (see Section V)]. The spin prohibitions in chemical reactions are stronger than the energy prohibitions: the latter are statistical in character (an energy fluctuation sufficient to overcome the barrier can always occur), while the former are absolute.

The existence of spin prohibitions has long been suspected, but their importance and scale have been estimated only recently and their consequences observed—magnetic effects in chemical reactions: the influence of weak magnetic fields on photophysical and photochemical processes in molecular solids, the influence of magnetic fields on chemical reactions, the dependence of the reaction rates on the magnetic moments of the nuclei of the reactants (the magnetic isotope effect), chemically induced dynamic nuclear polarisation, the microwave frequency maser-chemical effect, chemically induced magnetic electron polarisation, and the influence of high-frequency electromagnetic fields on chemical reactions. The discovery of these effects is a striking illustration of the definition of creativity as a way of converting the unpredictable into the inevitable. Fairly soon after their discovery, these effects passed from the class of intriguing incomprehensible phenomena to the class of self-evident phenomena with a simple and clear physics.

In order to remove the spin prohibition, i.e. in order to alter the spin, long-acting magnetic perturbations are needed. An example of long-lived states with magnetic interactions is provided by a pair of two radicals in which two unpaired electrons can exist in two spin states—singlet or triplet. The generation of molecules from the singlet pair is spin-allowed, while the generation from the triplet pair is

prohibited. The reaction in the triplet pair stops and "waits" until magnetic interactions (Zeeman, hyperfine, or dipolar) alter the spin pairing and cause its transition from the triplet to the singlet states. In this spin-prepared pair prohibition of the reaction has been removed and reaction restarts. Thus the source of magnetic effects is the spin selectivity of chemical reactions.

Long-lived states with magnetic interactions are realised in pairs with participation of radicals, triplet molecules, electrons, paramagnetic holes, ions, and solitons—all are species with unpaired electrons. Magnetic interactions induce in these pairs transitions between various spin states and remove the prohibition of spin-selective chemical reactions in such pairs. Magnetic effects are therefore observed in varied processes—photoconductivity and photoluminescence, dark conductivity of organic semiconductors, the annihilation of broken bonds in mechanically deformed inorganic semiconductors, photosynthesis, changes in the rates of chemical reactions and product yields, etc.

Magnetic perturbations in pairs, which removes the spin prohibition, depend on the external magnetic field and are a source of magnetic field effects. They also depend on the magnetic electronic-nuclear interaction, on the magnetic moment of the nuclei, and on the magnetic spin and its projection—a dependence which leads to the magnetic isotope effect and to chemically induced nuclear polarisation. When the polarisation of the nuclei is high (and it can reach record values in the range 10^4–10^6 which are unobtainable in physics) and exceeds the generation threshold, the movement of the nuclear spins becomes coherent and a new property of chemical reactions is observed—the ability to generate a microwave frequency field, i.e. the chemical reaction becomes a kind of molecular quantum generator with chemical pumping—a chemical maser.

The spin state of the pairs and hence their reactivity can also be altered by the action of high-frequency fields. This leads to new possibilities for controlling chemical reactions and for developing new magnetic resonance methods; appreciable advances have already been made on these lines.

Quantum beats have been observed in the triplet–singlet conversion in the pairs and hence in the reactivity of these pairs and in the yields of the chemical products of their reactions. Ways of controlling the coherence of the spin dynamics of pairs with the aid of high-frequency fields have been found; this is the second example where coherence "operates" in chemistry (for the first, see Section V).

We may note a difference between the spin and magnetic effects. Spin effects, i.e. spin prohibitions, exist in all the states of matter—gases, liquids, solids, and plasma. However, in gases and plasma the duration of contact between the species is 10^{-13}–10^{-14} s and is too short for the occurrence of the magnetically induced spin conversion of the pairs. Only in liquids and solids are the spin effects accompanied by magnetic effects, since only under these conditions is the lifetime of the pairs of reacting species comparable to the spin evolution time and magnetic forces act for a sufficiently long time to alter the spin.

The spin evolution of pairs is induced via two channels. The "useful" channel includes evolution as a result of the Zeeman and hyperfine interactions and leads to all the magnetic effects enumerated above. The second channel includes the spin evolution induced by the dipolar interaction of the electrons and the spin–orbit coupling. It depends little on the magnetic field and involves the nuclear-spin system to only a slight extent and for this reason it makes possible the "leakage" of the spin states, lowers the scale of the magnetic effects and in this sense it is "harmful" and difficult to control.

Control of spin dynamics is one of the important problems of chemical physics: the scale of the magnetic effects depends on it. Thus the magnetic isotope effect and the efficiency of the separation of magnetic and non-magnetic isotopes in chemical reactions are determined by the spin, molecular, and chemical dynamics. In other words, they depend on the spin evolution and the competing processes involving the dissociation of pairs into isolated species (molecular dynamics) and the chemical reaction of the pairs, which restrict the spin evolution time. However, the problem is not only that of creating favourable "physical" conditions for spin evolution (adequate magnetic interactions, optimum lifetimes of the pairs, favourable molecular dynamics, minimum "leakage" via the harmful channel) but it is also necessary to "organise" chemistry and chemical reactions with respect to the specified physics (to create the required pairs with an intense Zeeman or hyperfine interaction, to specify a favourable starting spin state of the pairs, and to drive the reactions via the specified pathway). Clearly the problems of controlling spin dynamics are the problems of controlling the physics and chemistry of reactions.

Spin dynamics has two remarkable advantages: the first is that it reliably controls chemical reactions in the pairs and in its turn is itself controlled by weak magnetic interactions with negligibly small energies. This factor leads to non-traditional ways of controlling many physicochemical processes with the aid of weak magnetic and electromagnetic influences.

Pairs of spin-containing species, in which long-acting magnetic perturbations operate, altering the spin state of such pairs, are not the only type of magnetosensitive systems. Another type comprises electronically excited molecules or ions in which there is a set of energy states with different spin multiplicities. During the lifetime of these excited molecules, magnetically induced conversion takes place between these energy states, including conversion to predissociation levels at which the molecules decompose. This leads to a dependence of the luminescence and the decomposition of the molecules on the magnetic field. Effects of this type have been observed in the gas phase (where the lifetime of the excited molecules are sufficiently long) and they constitute one of the new fields in the chemical physics of gas-phase reactions.

VII. CONCLUSION

A reader with a rigorous viewpoint will say that the limits of chemical physics outlined in this article have been enormously extended, and he is right: in by no means all the fields and problems mentioned here has a leading position been attributed to chemical physics. Many of them are being worked out and solved in related chemical sciences—physical and quantum chemistry, the chemistry of high energies, electrochemistry, photochemistry and radiation chemistry, biochemistry, the chemistry of high-molecular-weight compounds, etc. Chemical physics overlaps (and this is natural) with solid state physics, molecular physics, biophysics and, to an especially great extent, physical and quantum chemistry. However, when one is dealing with the physics of chemical processes, the physics in chemistry, then one is concerned with chemical physics—it is its characteristic feature and reliable criterion.

There is an interesting feature in the development of chemistry. The traditional chemical and chemical engineering fields, which constitute the basis of chemical industry (petrochemistry, the manufacture of fertilisers, fundamental organic synthesis, etc.) have been established and have

developed almost independently of chemical physics. However, new fields (microelectronics, laser and plasma chemical technologies, modern catalysis, chemical lasers, modern chemical materials science, modern analysis and diagnostics, etc.) are firmly based on chemical physics and the development of future or predicted fields (such as molecular electtronics, the new generation of superconducting materials, chemical bionics, organic ferromagnetics, etc.) is altogether unthinkable without chemical physics.

The current emphasis, priorities, and growing points in chemical physics have been noted in various sections of the present article; they can be generalised and grouped around the following principal fields:

Physical principles governing the creation of new materials with new or extreme properties;

control of chemical processes and the development of chemical and physical principles of the control of reactivity and chemical dynamics—the "tuning" of reacting species to a specified reaction and a specified rate;

energy dynamics, the creation of new chemolasers and methods for the transformation and accumulation of chemical energy;

the principles of molecular organisation, chemical dynamics, and the functioning of molecularly organised systems as a basis of a new generation technology.

---o0o---

The article represents a generalisation and a combination with the author's views and ideas of a large number of results, facts, ideas, and postulates described in numerous articles, communications, reviews, and books. The idea of this article arose in 1984 in connection with work on the analysis of the problems of modern chemistry (see V.A.Legasov and A.L.Buchachenko, Uspekhi Khimii, 1986, 55, 1949 Russ. Chem.Rev., 1986(12)), V.I.Gol'danskii, V.A.Legasov, and V.A.Benderskii for many useful, interesting, and inspiring discussions.

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow