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The Chemistry of New Atoms†

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The physicochemical interaction of hydrogen-like positronium and muonium atomic systems, in which the proton is replaced by a positron or a μ^+-meson, and mesonic atoms containing a μ^-- or a π^--meson instead of an electron have been examined. The nuclear-physical methods for the investigation of processes involving the new atoms have yielded information which significantly supplements that available from the usual research techniques.
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I. INTRODUCTION

The last two decades have been distinguished by the appearance and development of a new research field intermediate between the physics of elementary particles and chemistry. It concerns the chemistry of "new atoms" in which either an electron or a proton is replaced by another negatively or positively charged elementary particle.

Atoms in which there is a negative meson instead of one of the electrons are called mesonic atoms. On forming a chemical bond with other "ordinary" atoms, mesonic atoms can form also the so called mesonic molecules.

The most thoroughly investigated examples of new atoms of this type are the μ- and π-mesonic atoms. They will be the only ones considered in the appropriate sections of the present review.

However, in principle, there is also a possibility of the existence of K-mesonic atoms and new atoms in which instead of an electron there is a negative hyperon, an antiproton, or an antihyperon.

The radius of the nth Bohr orbital is $a_n = \hbar^2 n^2/\mu Z e^2$, in which $\mu = Am_e m_N/(m + Am_N)$ is the reduced mass, m the mass of the particle in the orbital, m_N the mass of the nucleon, A the mass number of the nucleus, and Z its charge.

Therefore the radii of the first Bohr orbitals of the hydrogen-like μ- and π-mesonic atoms are respectively about $2.5 \times 10^{-11}/Z$ cm and $1.9 \times 10^{-11}/Z$ cm, which are closer to nuclear rather than atomic dimensions. This is

† In the compilation of this review data known to the authors by 1st March 1970 were employed.

even more true of the K-meson, antiproton, and hyperon atoms (for example $a_1 \simeq 5 \times 10^{-13}$ cm for K-mesonic sodium and $a_1 \simeq 2.7 \times 10^{-13}$ cm for antiproton-sodium). As a result, the effective charge of the nucleus of the mesonic atom or an even heavier new atom of this type is z only for large values of n, of the order of $n \simeq \sqrt{m/m_0}$ (m_0 is the mass of the electron), and decreases by unity when the particle replacing the electron passes to the first orbitals.

Atoms in which the proton is replaced by another positive particle are named after the particle with the ending "onium". The penetration of any positive particle into the nucleus is hindered by electrostatic repulsion which can be counteracted only by attraction due to nuclear forces. Therefore, for the lightest positive particles (leptons), i.e. the positron and μ^+-meson, which do not enter into nuclear interactions, atoms of the "onium" type are possible only without a nucleonic nucleus, the positive leptons replacing the sole nucleon (the proton). An atom comprising a positron and an electron is called positronium (Ps) and an atom comprising a μ^+-meson and an electron is called muonium (Mu). Both positronium and muonium may be regarded as light hydrogen isotopes, positronium being the lightest of all the new atoms—it is at the same time the only atom altogether without a nucleus. Indeed, since both constituent particles of positronium have equal masses, the centre of gravity about which they both rotate does not approach either of them (such a particle would have played the role of a nucleus) but is located exactly in the centre.

A nuclear proton can be replaced also by a positively charged hyperon just as a neutron can be replaced by neutral hyperon. This gives rise to the so called hypernuclei and the corresponding hyperatoms. However, the structure of the electron shells of hyperatoms and their chemical properties hardly differ from those of the atoms with the same nuclear charge and therefore hyperatoms are not usually included among the "new atoms".

All the new atoms are unstable. The upper limits to the lifetimes of atoms with charged μ- or π-mesons are the intrinsic lifetimes of these particles in a vacuum ($\tau_\mu \simeq 2.2 \times 10^{-6}$ s, $\tau_\pi \simeq 2.5 \times 10^{-8}$ s) in relation to the decomposition processes $\mu^\pm \rightarrow e^\pm + \nu(\tilde{\nu}) + \tilde{\nu}_\mu/(\nu_\mu)$ and $\pi^\pm \rightarrow \mu^\pm + \nu_\mu(\tilde{\nu}_\mu)$ (ν is a neutrino and $\tilde{\nu}$ an antineutrino).

Each of the constituent particles of positronium is itself stable but, being a particle and an antiparticle, the electron and positron annihilate one another with emission of gamma-quanta, which is the reason for the instability of positronium and its very short lifetime (10^{-7}–10^{-10} s in a vacuum).

From the chemist's point of view, the main interest of the study of new atoms consists in the fact that chemical and crystalline environments influence their lifetimes and various characteristics of their destruction.

The first stage of studies in the chemistry of new atoms is the elucidation of the laws governing such influence and the verification of how specified changes in the chemical or crystal structure of the substance or the changes established in independent experiments influence the fate of new atoms.

The second stage of such investigations of the greatest importance to chemistry, in which chemistry assumes the role of a "consumer", is the determination of new structural-chemical data on the kinetics and mechanism of chemical processes based on the observation of particular characteristics in the formation, transformation, and destruction of new atoms.

At present, the mesochemical studies on μ- and π-mesonic atoms and muonium are still in the first stage, while the work on the physical chemistry of the positron and positronium have already passed to the second stage and has begun to yield new information of general importance to chemistry.

II. POSITRONIUM

1. General Characteristics of the Annihilation of Positrons and the Physical Properties of Positronium

The annihilation of positrons and the formation and destruction of positronium have been described in monographs[1,2], reports at the 1965 Conference in Detroit (USA),[3] compilation tables[4], many reviews[5–18] and articles containing an extensive bibliography (see, for example, Refs. 19 and 20), and about 400 original papers. The aim of the present review is not to give any sort of complete list of literature on this problem and we shall confine ourselves to the description of the general information of the greatest significance to chemists, concentrating attention on the latest work.

The positron, predicted theoretically by Dirac and discovered in 1932 by Anderson, is the antiparticle of the electron having the same mass ($m_0c^2 = 0.511$ Mev) and the opposite positive electrical charge ($e = 4.8 \times 10^{-10}$ CGSE). The hitherto unknown mutual annihilation process was first observed for the positron (e^+) and the electron (e^-); the process is characteristic of the interaction of particles and antiparticles in general and in the present case is accompanied by the emission of γ-quanta. The annihilation on collision between an electron and a positron can involve the emission of either two or in rare cases (probability 1/373) of three γ-quanta. One-quantum or quantumless annihilation require the participation of a third body and their probabilities are altogether low.

In laboratory experiments positrons are obtained from radioactive isotopes, for example sodium-22 or copper-64, which emit positrons with a maximum energy of several hundred keV. The positrons emitted by the sources initially behave like electrons—they are retarded expending their energy on the ionisation and excitation of the surrounding molecules. Up to energies of several tens of electron-volts, the role of annihilation is negligibly small and almost all the positrons "survive" until the attainment of the above low energies and are only then annihilated. By virtue of the possibility of recording the annihilation quanta, the positron is, as it were, a labelled electron the fate of which, from its appearance in the substance until its destruction by annihilation, can be followed. According to Dirac, the 2γ-annihilation cross-section for the positron and electron moving relative to one another at a velocity $v \ll c$ ($c = 3 \times 10^{10}$ cm s^{-1}) is

$$\sigma_D = \pi r_0^2 \frac{c}{v} = \pi \left(\frac{e^2}{m_0c^2}\right)^2 \cdot \frac{c}{v} \simeq 7.4 \cdot 10^{-15} \cdot \frac{1}{v} \text{ cm}^2 . \qquad (1)$$

There exist three principal variants of the annihilation, each of which can be isolated experimentally and each provides certain specific information about the properties of the medium in which the annihilation takes place.

The first pathway involves the annihilation in free or quasi-free (i.e. without the involvement of the ionic framework) collisions of positrons with electrons. If the two particles were at rest at the instant of mutual annihilation, then the two annihilation quanta would have absolutely identical energies (equal to m_0c_2) and the angle of their divergence would be exactly 180°. The experimentally

observed negligible deviations of the energies (by several electron-volts) and angles (by several milliradians) from the above values permit a direct recording of the count distribution of the conductivity and valence electrons which annihilate the positrons (their penetration to the region of the inner atomic orbitals is prevented by the Coulombic repulsion by the nucleus) and the observation of the anisotropy of such distribution relative to particular specified directions in crystals and molecules and the changes in it during phase transitions.

Another annihilation pathway is via the formation of combined states of the positron with neutral molecules (e^+M) or with anions (e^+A^-). From a theoretical standpoint, the structure and analysis of the wave functions of molecules of the type e^+H^- or, what amounts to the same thing, positronium hydride PsH, are of interest[20]. One cannot rule out the possibility of the formation of a completely new type of chemical bond of the kind He$-e^+-$He. The formation of a virtual or combined level of the e^+M system (as a result of the polarisation by the positron of the electron cloud of the atom or molecule) leads to a characteristic "resonance annihilation" phenomenon the cross-section of which is sometimes tens and hundreds of times greater than the Dirac σ_D. There is also a possibility of the formation of collective (polaron) states of the positron or bonds between the positron and lattice defects in ionic crystals. Of the problems which are not considered in a monograph by one of the present authors[1], we shall mention here only the model of the optical positron[21] and new experimental methods, based on it, for the determination of a parameter of great importance for structural chemistry—the effective charges of the anions (atoms of Group VII and VI elements) from data for the angular correlation between the annihilation quanta[22] and the lifetimes of positrons[23] in ionic media.

We shall also mention recent interesting observations[24] which established a very marked influence of even low concentrations of F-centres in KCl (approximately 3×10^{-4} of the number of regular Cl^- sites) on the type of angular correlation of the annihilation γ-quanta and thereby again demonstrating the high sensitivity of positron methods to any kind of breakdown in the regularity of crystal lattice structures.

The third pathway for the annihilation of positrons—via the formation of positronium atoms—is of greatest interest for a wide range of problems in modern physical chemistry and is in fact considered below.

The possibility of the existence of combined states of the electron–positron system was postulated in 1934,[25] the name "positronium" was proposed for the electron–positron atom in 1945,[26] and the chemical symbol Ps was put forward in 1959.[27] The existence of positronium was demonstrated experimentally by Deutsch in 1951.[28] The mass of positronium is 920 times smaller than the mass of the hydrogen atom but its reduced mass $\mu_{Ps} = m_0/2$ is only twice as small as the reduced mass of the hydrogen atom $\mu_H \simeq m_{i0}$. Accordingly the ionisation potential of positronium in the ground ($1s$) state $V = e^4\mu z^2/2\hbar^2n^2$ ($\mu = m_{i0}/2$, $z = 1$, and $n = 1$) is twice as small as the value for hydrogen and amounts to $V_{Ps} \simeq 6.77$ eV. The distance between the positive and negative charges, which in the case of hydrogen is defined as the radius of the first Bohr orbital, is twice as large in positronium and is close to 1.06 Å (when $n = 1$). In the present case this distance is, however, not the radius but the diameter of the atom.

There exist two ground states ($1S$; $n = 1$) of positronium—the triplet state $^TPs(^3S_1)$ or orthopositronium o-Ps with parallel spins of e^- and e^+ and the singlet state $^SPs(^1S_0)$ or parapositronium p-Ps with antiparallel spins of e^- and e^+. The total moment of o-Ps is $J_T = 1$ and in this case three substates are possible, differing in the magnetic quantum numbers: $m = +1$, 0, or -1. For p-Ps, $J_S = 0$ and $m = 0$. Correspondingly, the statistical weight $2J_T + 1$ of o-Ps is three times larger than for p-Ps and in the formation of positronium o-Ps arises in 75% of cases and p-Ps in only 25% of cases.

In accordance with various selection rules, p-Ps is annihilated with the emission of two γ-quanta and o-Ps with the emission of three γ-quanta. As a result, the intrinsic lifetime of singlet positronium is much shorter than that of triplet positronium. The lifetime of p-Ps in a vacuum is

$$\tau_S^0 = 2\frac{\hbar^2}{m_0e^2} \cdot \frac{1}{cr_0^2} = 1.25 \cdot 10^{-10}\text{s}. \qquad (2)$$

while that of o-Ps is higher by a factor $9\pi/4(\pi^2 - 9)(\hbar c/e^2) = 1115$ and amounts to $\tau_T^0 = 1.4 \times 10^{-7}$ s.

As a result of the hyperfine splitting of the $1S$ state of positronium, the energy of o-Ps exceeds that of p-Ps by an amount

$$\Delta W = {}^TW - {}^SW = \frac{7}{12}\left(\frac{e^2}{\hbar c}\right)^4 m_0c^2 = 8.4 \cdot 10^{-4}\text{ eV} \qquad (3)$$

(to within the so called radiation corrections).

In fairly strong external magnetic fields, a "good" quantum number is no longer the total moment of positronium J but m, the states with $m = 0$ and $J = 1$ and with $m = 0$ and $J = 0$ are mixed, and the contribution by the 2γ-annihilation of positronium increases (in a vacuum) from 25 to 50%. External fields alter the energies of the sublevels with $m = 0$, increasing the energy for the state with $m = 0$ and $J = 1$ and correspondingly decreasing it for the state with $m = 0$ and $J = 0$ by $\Delta W(1 + x^2)^{1/2}/2$, where $x = (2e\hbar/m_0c)(H/\Delta W) = 2.75 \times 10^{-2} H$ (kilogauss), but do not affect the energies of the $m = \pm 1$ states. An additional decrease of the probability of the 3γ-annihilation of triplet positronium can arise due to the magnetic dipole transitions ($m = \pm 1$) $\rightarrow$ ($m = 0$) in a high-frequency electromagnetic field at the resonance frequency

$$\nu = \frac{\Delta W}{2\hbar}[\sqrt{1 + x^2} - 1].$$

For fields of about 10 kG, the frequency $\nu \simeq 3000$ MHz, so that the experiments on the quenching of the 3γ-annihilation of positronium by a high frequency field, which were carried out for the first time by Deutsch[29] and made it possible to determine with high accuracy ΔW, were the first experiments on the microwave spectroscopy of positronium.

2. General Chemical Properties of Positronium. The Quenching of Positronium. Principal Differences between Positronium and Hydrogen

Positronium, which is the lightest hydrogen-like atom and constitutes a model free radical, is also a kind of labelled atom, the properties, the lifetime, and the mechanism of the destruction of which greatly depend on the properties of the surrounding medium. The short intrinsic lifetime of orthopositronium makes it possible to use this time as a convenient standard in the investigation of rapid reactions involving atoms of the hydrogen type and to observe and study the role of diffusion and quantum (tunnel effect) factors in the kinetics of such reactions.

As a rule the duration of chemical reactions in which positronium is involved lies within the limits between the characteristic lifetimes of the long-lived form (orthopositronium, 10^{-9} s in the condensed phase, 10^{-7}–10^{-8} s in gases, $\tau_T^0 = 1.4 \times 10^{-7}$ s in a vacuum) and of the short-lived form (parapositronium, $\tau_S^0 = 1.25 \times 10^{-10}$ s). Therefore a decrease of the lifetime (the quenching of positronium) constitutes in the first place the quenching of orthopositronium, the replacement of the annihilation of the positron in the ^{T}Ps state by other types of annihilation.

The processes involving positronium which lead to the quenching of ^{T}Ps include the following: (1) annihilation by "foreign" electrons at the instant of collision between Ps and other atoms or molecules—the so called "pick-off" annihilation; (2) ortho-para conversion in the interaction with paramagnetic species, for example $^T\mathrm{Ps}(\uparrow\downarrow) + \dot{\mathrm{N}}\mathrm{O}(\downarrow) \rightarrow {}^S\mathrm{Ps}(\uparrow\downarrow) + \dot{\mathrm{N}}\mathrm{O}(\uparrow)$; (3) substitution reactions, for example, $\mathrm{Ps} + \mathrm{Cl}_2 \rightarrow \mathrm{PsCl} + \mathrm{Cl}$; (4) addition reactions, for example, $\mathrm{Ps} + (\mathrm{CF}_3)_2\dot{\mathrm{N}}\mathrm{O} \rightarrow (\mathrm{CF}_3)_2\mathrm{NOPs}$, as a result of which the positron is brought into the field of many electrons, as in pick-off annihilation; (5) oxidation reactions, for example, $^T\mathrm{Ps} + \mathrm{Fe}^{3+} \rightarrow e^+ + \mathrm{Fe}^{2+}$, which lead to the formation of a rapidly destroyed free positron.

In substitution, addition, and oxidation reactions, positronium behaves as a chemical analogue of hydrogen. However, because of the very great difference between the masses of hydrogen and positronium, there are many differences in the structure of their compounds, the energies of their formation, and the kinetics of their chemical reactions.

While an HA molecule (A is any atom) should be regarded as a two-centre molecule, its analogue PsA = e^+A^- is better characterised as a one-centre molecule, namely as an A atom with mixed electron and positron clouds. This is markedly reflected in the bond energy—for example, while the A_2 bond energy is close to 4.5 eV, the energy for HPs is estimated as 0.657 eV [20] and for Ps_2 as 0.11 eV.[30] The stability of any PsA molecule must be lower than that of HA if only because, with increase of the reduced mass μ of the molecule, the energy of the zero-point vibrations, from which the dissociation energy is reckoned, must increase. In principle $\hbar\omega_0 \propto 1/\sqrt{\mu}$, but in fact that ratio $(\hbar\omega_0)_{PsA}/(\hbar\omega_0)_{HA}$ probably never reaches the value

$$\sqrt{\frac{\mu_{PsA}}{\mu_{HA}}} \simeq \sqrt{\frac{m_H}{m_{Ps}}} \simeq 30 .$$

Nevertheless any reaction involving the substitution of H by Ps, HA + Ps → PsA + H, is probably endothermic.

As stated above, the ionisation potential of the H atom is twice as high as for Ps. Therefore in the gas phase the oxidation of positronium by hydrogen is a highly exothermic process: $H^+ + Ps \rightarrow H + e^+ + 6.8$ eV. Since however the heat of hydration (and in general the heat of solvation) of the proton, which is close to 11 eV, is much higher than for the positron (one can assume arbitrarily that this heat is 1.5–2 eV, as for the electron), the oxidation of positronium by hydrogen in aqueous solution is endothermic and hardly occurs to an appreciable extent: $H^+_{aq} + Ps_{aq} \rightarrow H_{aq} + e^+_{aq}$ (~ 2.5 eV). The electron affinity of the hydrogen atom (0.75 eV) also exceeds the analogous quantity for positronium (estimated [31,32] as ~ 0.20 eV).

In comparing the rates of reaction of hydrogen and positronium, one should bear in mind not only the difference between the heats (the heat of an endothermic reaction is equal to its minimum possible activation energy), the pre-exponential factors (the thermal velocity of Ps atoms is about 30 times higher than that of H), and the diffusion coefficients, which reach $D \simeq 3 \times 10^{-4}$ cm^2 s^{-1} for Ps in various solvents (Becquerel [1], Chapter VII), but also the possibility of tunnel transitions within a particle as light as positronium under conditions where such transitions are virtually ruled out for H atoms. We obtained in our investigations [33,34] the temperature T_{tun} below which tunnel transitions predominate exponentially over the Arrhenius (over-the-barrier) transitions: $T_{tun} = (\hbar/k\pi d)\sqrt{E/\mu}$, where k is the Boltzmann constant, μ the reduced mass of the tunnelling system, d the width of the potential barrier, and E its height. For free positronium, the temperature T_{tun} is approximately 30 times higher than for H atoms and sometimes amounts to hundreds of degrees. Therefore in gas-phase reactions of positronium, a non-activation tunnel mechanism is extremely likely.

The appearance of a tunnel effect is not the sole expression of the wave properties of positronium associated with its low mass and consequently with its high De Broglie wavelength. For a thermal positronium atom at room temperature, $\lambda\!\!\!^{-} \simeq 9$ Å, so that the cross-sections for processes involving positronium can reach in principle $4\pi\lambda\!\!\!^{-2} \simeq 10^{-13}$ cm^2.

Yet another kinetic difference between the reactions of hydrogen and positronium, due to the unusually low mass of the latter, consists in the fact that the electron transitions between positronium and another atom cannot be regarded as adiabatic, without a change in the distance between the positron and the nucleus of the other atom.

Finally the low mass of positronium leads to an unusual form of the excitation functions for its endothermic substitution reactions (Ps + AB → APs + B), which differ appreciably from those for H atoms, but are close to the excitation functions for dissociative electron capture ($\bar{e}$ + AB → A$\bar{e}$ + B). The cross-sections for the above reactions of Ps and an electron have a sharp maximum directly at the threshold and the maximum cross-section is very sensitive to the threshold energy and provides a method for its determination. When the energy increases above the threshold value by an AB vibration quantum, the substitution cross-section decreases sharply [35].

The above factors make it difficult to transfer directly the results of positron studies to reactions of hydrogen atoms, but they give rise to the possibility of many specific applications of the positron method in chemistry, which will be described below.

3. The Probability of the Formation of Positronium and Its Inhibition Processes

One of the principal characteristics of the annihilation of positrons is the probability P of the formation of positronium. The simplest estimate of this quantity is provided by the so called Ore model [36] illustrated in Fig. 1. Here V denotes the ionisation potential of the molecules of the medium and E the excitation energy for their first electronic level. As long as the kinetic energy of positrons exceeds E and particularly V, the energy expenditure on ionisation and excitation predominates. On the other hand, when the energy of positrons is lower than $V - 6.8$ eV, the formation of positronium is simply

impossible on energy grounds. The range of positron energies between E (upper limit) and $V - 6.8$ eV (lower limit), in which the dominant positron interaction process is the formation of Ps, is called the Ore gap. For a rectangular spectrum of retarded positrons, the Ore model gives $6.8/V > P > [E - (V - 6.8)]/E$, which holds fairly well for simple gaseous systems. For example, for argon $V = 15.8$ eV and $E = 11.6$ eV, whence $0.43 > P > 0.22$, while experiment gives $P = 0.30$.

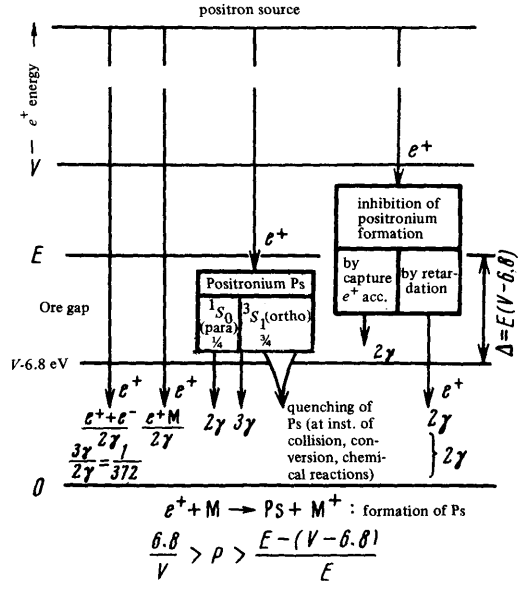


Figure 1. A schematic representation of the processes involving the formation and destruction of positronium, illustrating the Ore model and possible deviations from it.

In the condensed phase predictions based on the Ore model must be appreciably modified if only because account must be taken of the affinity of the medium for electrons, positrons, and positronium atoms. However, even without these complicating factors, the situation may alter (even in gases) in consequence of various inhibition processes, which lower the probability of the formation of positronium (Fig. 1). These are the capture of positrons, competing with the formation of positronium and with the elastic retardation of positrons (resulting in their slow passage through the Ore gap), which altogether removes positrons "from play", and non-elastic retardation of positrons, which rapidly brings them below the Ore split into the region of low energies, where positronium is no longer formed.

Both types of inhibition—by capture (capture inhibitors) and retardation (retardation inhibitors)—may be due to the medium itself in which the annihilation is investigated (auto-inhibition) and to different additives (inhibition by impurities) at varying concentrations.

The foregoing shows that the observation of changes in the probability of the formation of positronium and the study of various processes involving the inhibition of such formation can yield information about the various ways in which positrons are captured (for example, capture from a complex with annihilation: $e^+ + AB \rightarrow ABe^+ \rightarrow 2\gamma$, or capture with dissociation: $e^+ + AB \rightarrow A + Be^+ \rightarrow 2\gamma$), about their non-elastic retardation, and about the excitation of the electronic, vibrational, and rotational levels of the inhibitor molecules. An additional source of information comes from the increase of the probability of the formation of positronium when static external electric fields are applied, because the field accelerating positrons can return to the Ore gap some positrons with an energy less than $V - 6.8$ eV. The combination of such accelerating effects of the field and the loss of positron energy in elastic and non-elastic collisions is comparatively readily susceptible to calculation and can serve as a basis for the estimation of the cross-sections for different types of interaction involving positrons.

Thus different ways become available for obtaining data about the competition between the ionisation of molecules, their electronic excitation, and the capture of electrons by positrons with energies of the order of several electron-volts and about the relative contributions of the cross-sections for the elastic and non-elastic scattering and the capture of positrons.

When applied to the gas phase, the relevant field of study has been called by Massey "positronics" [37] and constitutes a useful addition to gaseous electronics. In the condensed phase positronic research techniques are applicable also under conditions where the corresponding data are altogether lacking even for electrons. In this connection, one of the most interesting problems is, for example, the study of the changes in the nature of the retardation of positrons on passing from a gas to a liquid and further to a solid, as a result of the appearance of collective interactions.

4. Principal Experimental Methods in Positronium Chemistry

According to the foregoing, the main subject of observations in experiments with positronium is two characteristics of the annihilation of positrons: (a) the probability of the formation of positronium, the decrease of which is caused by various inhibition processes, and (b) the rate of destruction of positronium atoms in various interactions with molecules, atoms, radicals, etc. owing to all possible positronium quenching processes.

For laboratory isotope sources of the usual power (up to several hundred millicuries), the steady-state concentrations of positrons or any products of the combination of positrons with electrons, anions, and molecules, do not exceed several units per cm^3. Clearly there can be no question of any classical methods for the observations of chemical reactions involving positronium—it is necessary to employ the experimental techniques of nuclear physics whereby the fate of each individual positronium atom can be followed.

Different arrangements for the measurements are presented in Fig. 2. The top figure shows a triple collision scheme, in which orthopositronium annihilation acts with emission of three γ-quanta incident on $C1$, $C2$, and $C3$ grids, are recorded. A disadvantage of this method consists in the fact that the counting rate $C_{3\gamma}$ of the γ-coincidences is proportional to the product of two variable factors—the probability P of the formation of positronium (the fraction of orthopositronium $I_2 = 3P/4$) and the probability of its spontaneous annihilation (with emission of three γ-quanta), which is $\omega_{3\gamma} = \tau_2/\tau_T^0$, where τ_2 is the

actual lifetime of orthopositronium in the substance, shortened relative to $\tau_T^0 = 1.4 \times 10^{-7}$ s in consequence of various quenching processes. Therefore the decrease of $C_{3\gamma} \propto I_2\tau_2/\tau_T^0$ may be due to both the quenching of positronium (τ_2 decreases) and the inhibition of its formation ($I_2 = 3P/4$ decreases), whereas it is in fact desirable to separate the contributions by these two types of interactions.

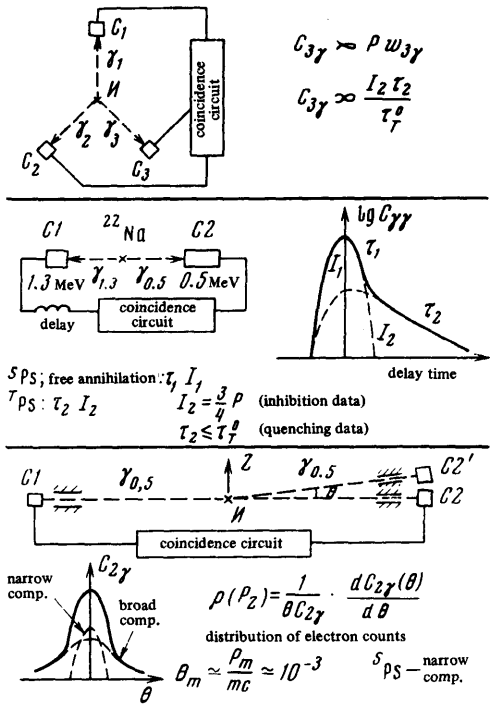


Figure 2. Schematic representation of different procedures for the observation of the fundamental characteristics of the annihilation of positrons. Upper figure—recording of 3γ-coincidences; middle figure—recording of the time spectrum of delayed $\gamma\gamma$-coincidences; lower figure—recording of the angular correlation of the annihilation γ-quanta.

The greatest variety of information is provided by observations of the time spectrum of the annihilation of positrons (the central part of Fig. 2) with the aid of delayed coincidence circuits. The coincidences $C_{\gamma\gamma}$ of the 1.3 MeV nuclear γ-quantum (C1 counter), emitted almost simultaneously with the ejection of a positron from a ^{22}Na nucleus, with the 0.5 MeV γ-quantum (C2 counter) emitted in the 2γ-annihilation of this positron, are recorded. In the simplest case the spectrum consists of two components[38]. The short-lived component with a lifetime τ_1 and a relative intensity I_1 is due to the annihilation of the positron in quasi-free collisions with electrons and in parapositronium and the long-lived component (τ_2, $I_2 = 1 - I_1$) is due to the annihilation of the positrons forming the triplet orthopositronium. The usual order of magnitude of the τ_i in the condensed phase amounts to a fraction of a nanosecond for τ_1 and several nanoseconds for τ_2. In the gas phase τ_2 increases as the pressure is reduced, tending to τ_T^0.

The improvement of the resolving capacity of coincidence circuits made it possible to determine finer details of the time spectra of the annihilation of positrons. Thus four sections of such spectra were observed in the gas phase[39]: an "instantaneous" peak (τ_p) due to the annihilation of parapositronium and the destruction of positrons above the Ore gap, followed by a "shoulder" whose length is inversely proportional to the gas pressure (treated as the lifetime of positrons between emission below the Ore gap and capture), and then sections corresponding to the exponential destruction of positrons with the characteristic annihilation times τ_1 (quasi-free and resonance annihilation) and τ_2 (orthopositronium) (see Fig. 3).

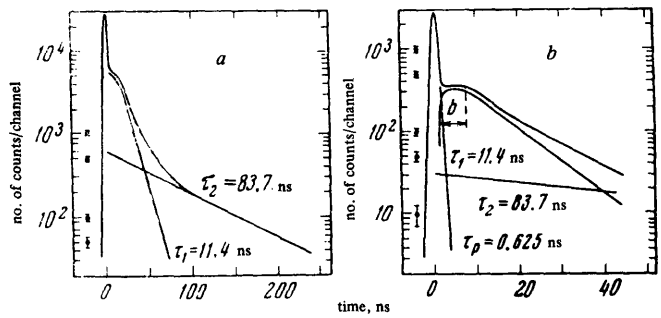


Figure 3. Curves for the distribution of the annihilation of positrons in pure argon with respect to time[39]: *a*) argon pressure 17.2 atm, duration of experiment 1223 min, $\tau_1 = 11.4$ ns, $\tau_2 = 83.7$ ns; b) argon pressure 16.8 atm, duration of experiments 928 min; *b*) width of "shoulder" $\tau_1 = 11.4$ ns, $\tau_2 = 83.7$ ns, $\tau_p = 0.625$ ns—limiting "instantaneous time" accessible to measurement, obtained by the extrapolation of the lifetime of singlet positronium.

For glycerol and many polymers (polyethylene, Teflon, and others) a third component, intermediate between τ_1 and τ_2, was also noted; it is treated here as an effect of annihilation in quasi-free e^+e^- collisions[40].

Finally, in powdered oxides (Al_2O_3, MgO, SiO_2, etc.) the presence of two characteristic long lifetimes—not only τ_2 (several nanoseconds), which is usual for a condensed phase, but also τ_3 (many tens of nanoseconds, up to $\tau_T^0 = 1.4 \times 10^{-7}$ s), caused by the spontaneous annihilation of orthopositronium atoms during their diffusion between the oxide particles, has been established[41-43].

The time method makes it possible to separate clearly the quenching of positronium and the inhibition of its formation. In the simplest case of "pure" inhibition, the intensity of the long-lived component I_2 decreases without further decrease of the slope of its "tail" characterising its lifetime τ_2.

On the other hand, in the case of "pure" quenching, τ_2 falls but I_2 remains unchanged. Two examples taken from Gol'danskii et al.[44], illustrating inhibition and quenching, are presented in Fig. 4, where the distance between two adjacent points in the spectra corresponds to approximately 0.1 ns. Fig. 4*a* illustrates the inhibition of the formation of positronium in benzene by added iodobenzene—probably as a result of positron capture by the iodobenzene—and

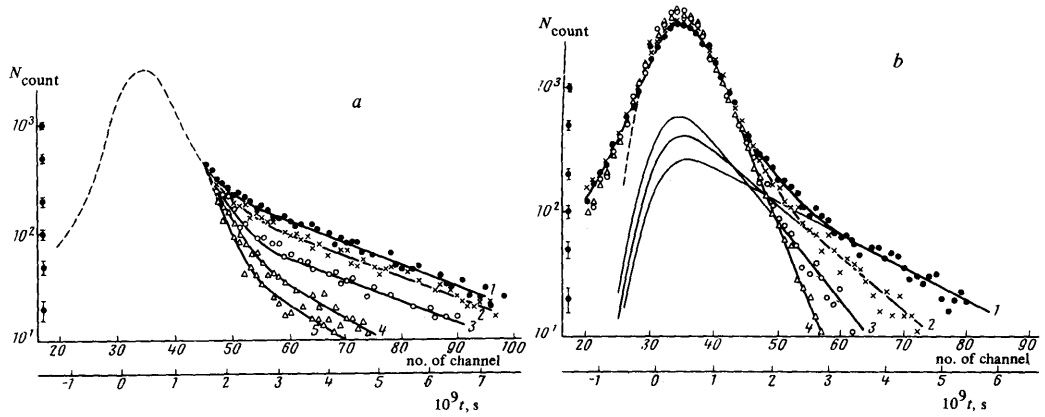


Figure 4. Positron annihilation spectra. *a*: 1) benzene; 2)–4) solutions of iodobenzene in benzene [2) 0.004 M; 3) 0.02 M; 4) 0.34 M]; 5) iodobenzene. *b*: 1) water; 2)–4) aqueous solutions of $K_2Cr_2O_7$ [2) 0.005 M; 3) 0.015 M; 4) 0.025 M]. Power of ^{22}Na source 10 μc.

Fig. 4*b* illustrates the quenching of orthopositronium in aqueous solution by a powerful oxidising agent ($K_2Cr_2O_7$).

The third main experimental method for the investigation of the annihilation of positrons—the observation of correlation curves, i.e. the relations between the counting rate $C_{2\gamma}$ of the coincidence of two 0.5 MeV annihilation γ-quanta and the angle θ, equal to the difference between 180° and the angle between the directions at which the two quanta are emitted—is illustrated schematically in the lower part of Fig. 2. Differentiation ($dC_{2\gamma}/d\theta$) makes it possible to determine the count distribution function for the electrons in the substance. The narrowest component at the angular distribution of the coincidence counting rate $C_{2\gamma}(\theta)$ on the complex correlation curve corresponds to the annihilation of singlet parapositronium. Therefore, by dividing the correlation curves for a series of numerous experiments into narrow and broad components, one can obtain important information, in addition to that from the annihilation time spectra about the chemical reactions of positronium, namely, the contributions by various types of quenching of positronium may be separated. Indeed pick-off annihilation of orthopositronium, as well as the formation of its chemical compounds or oxidation to a positron, correspond to the annihilation of positrons by valence electrons, the kinetic energy of which (T_e) amounts to several electron-volts. Correspondingly, the width of the correlation curves $\Delta\theta \propto \sqrt{T_e/mc^2}$ amounts under these conditions to several milliradians. Nevertheless the ortho-para conversion and subsequent 2γ-annihilation of the slow ^{S}Ps atoms contribute to the correlation curves a central narrow peak near $\theta = 0$, the width of which is about 1 milliradian (the so called narrow component with an intensity I_N). An example of the combination of the time and correlation methods is provided by Fig. 5, where data for aqueous solutions of two manganese salts are presented—the paramagnetic converter $MnSO_4$ and the diamagnetic oxidant $KMnO_4$.[45] The addition of these two salts shortens τ_2, i.e. they behave as quenching agents for positronium. However, the ortho-para converter increases at the same time the intensity of the narrow component of the correlation curve by $\Delta I_N = 15\%$, while the oxidant decreases its intensity by $\Delta I_N = -7\%$, since not only triplet but also singlet positronium is oxidised. The possibility of detecting the oxidation of singlet positronium demonstrates the applicability of positron methods to the observation of reactions occurring over periods as short as 10^{-10} s. A clear confirmation of this possibility is also provided by recent observations of the changes in the intensity of the narrow component ΔI_N for aqueous solution of the $CoCl_2.6H_2O$ converter, the $CuCl_2.2H_2O$ oxidant, and their mixtures[46]. In accordance with the kinetic equations taking into account the oxidation of ^{S}Ps among other processes, the changes in ΔI_N for mixed Co^{2+}–Cu^{2+} solutions are by no means additive relative to the analogous data for Co^{2+} and Cu^{2+} separately (Fig. 6).

The combination of various experimental techniques, supplemented by the variation of a number of parameters (composition, temperature, concentration of additives, and viscosity for liquid systems and composition, temperature, and pressure for gaseous systems) over a wide range makes it possible to verify and analyse in detail different versions of kinetic equations and to determine the kinetic constants for elementary chemical reactions involving positronium.

5. Examples of Information of General Chemical Importance Obtained from Observations on the Annihilation of Positrons

Using various methods described above, the investigators in a number of countries (USSR; USA—Berko, Brandt, Celitans, Lee, McGervey, Tao, and others; Canada—Bell, Hogg, Pohl, and others; France—Paulin and others; India—Thosar and others; Italy—Germagnoli and others; Australia—Green; Norway—Trumpy, etc.) observed fairly numerous examples of all classes of chemical reactions of positronium‡.

Our task is not, however, the description of the chemistry of positronium itself; this new atom is of interest to us as a means of obtaining information of

‡ In the present review we have examined only the reactions of positronium and not the annihilation of slow positrons in general. This is the only reason why we have not mentioned here I. Ya. Dekhtyar, V. L. Fedov, and others (the USSR), de Benedetti, Stewart, Roellig, and others (USA), Massey, Osman, and others (England), Zappa, Colombino, Ferranti, and others (Italy), etc.

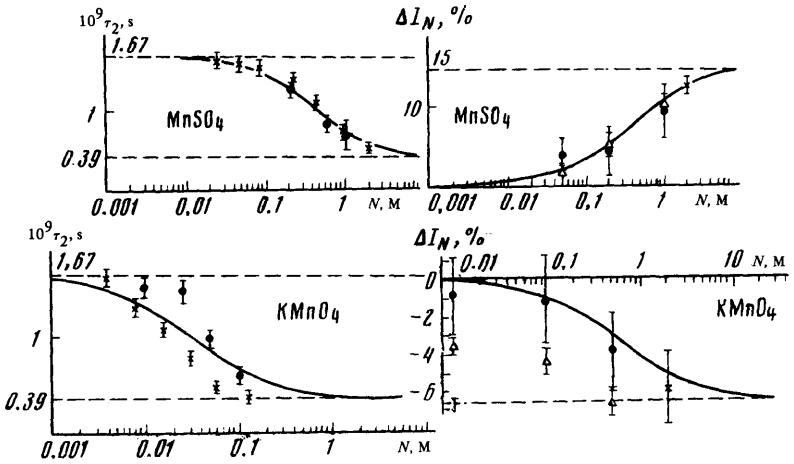


Figure 5. Variation of the lifetime of positrons (τ_2) (on the left) and of the intensity of the narrow component of the correlation curves (ΔI_N) (on the right) in the annihilation of positrons in aqueous solutions of an ortho–para converter ($MnSO_4$; upper figure) and an oxidant ($KMnO_4$; lower figure) as a function of the concentration of additives[1,45]. Power of ^{64}Cu or ^{22}Na source in the experiments on angular correlations—tens of millicuries or several millicuries respectively.

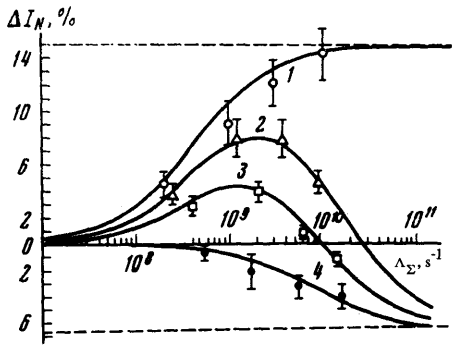


Figure 6. Variation of the intensity of the narrow component of correlation curves in an aqueous solution of converter ($CoCl_2$) and oxidant ($CuCl_2$) salts as a function of the overall rate of conversion and oxidation. Curves *1*–*4* correspond to the contributions by conversion to the overall rates of quenching, which is 100, 80, 50, and 0% respectively, the quenching rate constants being k_{conv} $(2.0 \pm 0.3) \times 10^9$ litre mole^{-1} s^{-1} and $k_{ox} = (5.4 \pm 0.4) \times 10^9$ litre mole^{-1} s^{-1}.

general chemical interest. We shall now consider examples of such information.

In the gas phase the rate of conversion quenching of positronium may serve as a fairly sensitive measure of the concentration of paramagnetic centres—quenching agents. For example, the rate constant for the quenching of positronium by paramagnetic nitric oxide NO, determined by various methods (from annihilation time spectra[28], an increase in the counting rate of the 2γ-coincidences[47], and a decrease in the counting rate of the 3γ-coincidences[48]), amounts to $(1-4) \times 10^{-10}$ cm^3 s^{-1}.

The latest value obtained from observations of the narrowing of the correlation curves is $(2.1 \pm 0.5) \times 10^{-10}$ cm^3 s^{-1}.[49] Adopting this value and assuming that the observation of a change in the counting rate of coincidences by 1% is a real effect, we obtain $n \simeq 10^{13}-10^{14}$ cm^{-3} (at room temperature; with increase of temperature, the sensitivity of the method is unchanged if $\sigma_{conv}v$ = const. and increases when σ_{conv} = const.) as the lower limit of the concentration of the paramagnetic centres recorded in the gas phase by the positron method.

The conversion of positronium includes in all probability the formation of the positronium–converter complex as the first stage. The positronium annihilated in such a complex does not give rise to the narrow component of the correlation curves characteristic of the destruction of free thermalised parapositronium. Therefore the correlation method makes it possible to establish whether the positronium–converter complex became stabilised in new collisions before annihilation or whether the complex decomposed with ortho–para conversion. By varying the concentration of the converter and the overall gas pressure, it is possible to determine on this basis the lifetimes of various positronium complexes; this is important also for other gas-phase reactions. The complexes formed on collision between positronium and NO are very unstable—even at a gas pressure of hundreds of atmospheres they decompose before collision with gas molecules. However, more complicated excited complexes, of the kind of $PsNO_2^*$ or $(CF_3)_2NOPs^*$, which have a larger number of degrees of freedom, have been shown experimentally[50] [for example, by measurement of the correlation curves in argon or oxygen at 30–150 atm with the addition of $5 \times 10^{-4}-0.8$ atm of $(CF_3)_2NO$] to survive for about $(1-2) \times 10^{-12}$ s and to have sufficient time to transfer their excitation energy in new collisions.

We shall now turn to the liquid phase. In the discussion of the mechanism of oxidation–reduction reactions in solutions, the problem of whether an electron is transferred from the reductant to the oxidant by a long-range tunnel transition or via the formation of an intermediate oxidant–reduction complex has been frequently discussed.

In the study of the kinetics of the chemical reduction of anions, Frumkin and coworkers[51] rejected the hypothesis of a long-range tunnel effect. An analogous conclusion was arrived at also on the basis of the comparison of the rate constants for the reactions of hydrogen and positronium atoms with Fe^{2+} and Fe^{3+}, the results of which are presented below (the constants are listed in litre mole^{-1} s^{-1}):

Acceptor	(Ac)	H	Ps	$\frac{k_{Ps}}{k_H}$
$Ac + Fe^{2+}$ →	$[FeAc]^{2+}$	$2 \cdot 10^{7}$ [52]	$2 \cdot 10^{9}$ [54]	100
$Ac + Fe^{3+}$ →	oxidation	$9 \cdot 10^{7}$ [53]	$1.2 \cdot 10^{10}$ [54]	130

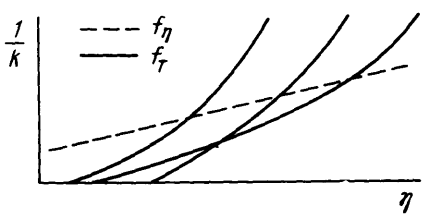
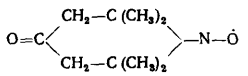


Figure 7. Variation of the reciprocal of the rate constant for the quenching of positronium in the mixed diffusion–kinetic region ($1/k$) with the viscosity of the solution η.[18,55] Dashed straight line—variation of f_η at a constant temperature and a variable solvent composition. Continuous curves—variation of f_T at a constant solvent composition and a variable temperature.

Radiation-chemical studies have shown that the reaction between H and Fe^{2+} proceeds via an intermediate complex, but the mechanism of the reaction between H and Fe^{3+} requires explanation. The fact that the rate of reaction of positronium, which is almost 1000 times lighter, with both Fe^{2+} and Fe^{3+} exceeds to approximately the same extent (by two powers of ten) the rate of reaction of hydrogen suggests that the mechanism of both reactions (with Fe^{2+} and Fe^{3+}) is the same. If a tunnel effect obtained in the second case, there would be no reason to expect such a sharp difference between the rates of the reactions of Ps and H with Fe^{3+}.

Another example of the use of positronium for the investigation of the mechanism of reactions in the liquid phase concerns the development of a method whereby the role of diffusion and kinetic factors can be distinguished[55]. This method, which has been applied to the quenching of positronium, can be readily extended to any other system, which would be of considerable importance to the study of the kinetics of liquid-phase reactions[56].

The method is based on the idea that the viscosity η of a solvent, in which the quenching of positronium by different free radicals [for example, diphenylpicrylhydrazyl (DPPH) $(C_6H_5)_2N-N-C_6H_2(NO_2)_3$ or 2,2,6,6-tetramethyl-4-oxopiperidine 1-oxide



(TMOPO)] takes place, is varied into waves. The viscosity is first increased by altering the composition of the solvent at a constant temperature T_0, for example by adding to water small amounts of glycerol, and then by reducing the temperature ($T < T_0$) for an unchanged composition of the solvent. Under these conditions, the reciprocal of the rate constant for the quenching of positronium ($1/k$) varies as follows:

$$\frac{1}{k} = f_\eta = \frac{\eta}{b}\left(\frac{1}{T_0} + \frac{a'}{\eta\sqrt{T_0}\,P} \cdot e^{E/RT_0}\right)$$

or

$$\frac{1}{k} = f_T = \frac{\eta}{b}\left(\frac{1}{T} + \frac{a}{\eta\sqrt{TP}} e_{E/RT}\right), \qquad (4)$$

where the activation energy E and the solvent parameters b and P are constant and a and a' are very similar. The experiments were carried out in octanol between −12° and 130°C, in ethyl ether between −90° and 25°C, and in cyclohexanol–acetone and water–glycerol mixtures at room temperature. The first type of variation of η is indicated in Fig. 7 by the linear function (dashed straight line) $1/k = f_\eta(\eta)$ while the second type of variation is more pronounced [$1/k = f_T(\eta)$] and is represented by continuous lines. By comparing $f_\eta(\eta)$ and $f_T(\eta)$ and also the slopes of the plots of $\ln k$ and $\ln(1/\eta)$ against $1/T$, it is possible to estimate the activation energy for the quenching of positronium by radicals despite its extemely low value ($E \simeq 1$ kcal mole^{-1}), against the background of the diffusion activation energy $E \simeq 2-6$ kcal mole^{-1}.

To complete the range of examples of the chemical applications of the positronium method in the liquid phase, we shall consider its use in the investigation of the structure of the coordination sphere of the complexes of paramagnetic ions (Co^{2+}) and electron-accepting oxidant ions (Fe^{3+}) in aqueous, alcoholic, and aqueous-alcoholic solutions.

In the first experiments of this kind, the results of which are presented in Fig. 8, the rate of quenching of positronium by the paramagnetic salt $CoCl_2$ (as a result of ortho–para conversion) was compared with the rate of reaction of this salt with TMOPO and DPPH radicals. The quenching was observed from the shortening of τ_2 and the reaction of $CoCl_2$ with the radicals from the broadening of the lines of the radicals in the ESR spectra. The observations were made in propanol, water, and their mixtures of various compositions. A change in solvent composition entails a rearrangement of the structure of the outer coordination sphere of the Co^{2+} complex—the tetrahedral (blue) form $Co(H_2O)_2Cl_2$ characteristics of the alcohol is transformed in water into the octahedral form $[Co(H_2O)_3]\cdot Cl_2$. In this example delocalised unpaired electrons, smeared over the coordination sphere of the complex and concentrated mainly at Cl^- ions in the pure alcohol and at the oxygen atom of the hydroxy-groups in water (the main part of the spin density is of course localised at the Co^{2+} ions themselves, "screened" from positronium by the ligand environment), behave as a quenching agent for positronium (or an agent interacting with radicals). In the mixed solvents the formation of hydrogen bonds between water and the alcohol and also the steric hindrance

due to the propyl radicals in the coordination sphere make the delocalised electron least accessible and retard the reaction of $CoCl_2$ with positronium and other radicals. Fig. 8 shows that under these conditions positronium is in fact the most sensitive detector of changes in the spin density of the delocalised unpaired electron—on passing from propanol and water to their mixtures, the rate of the paramagnetic quenching of positronium falls by a factor of several tens.

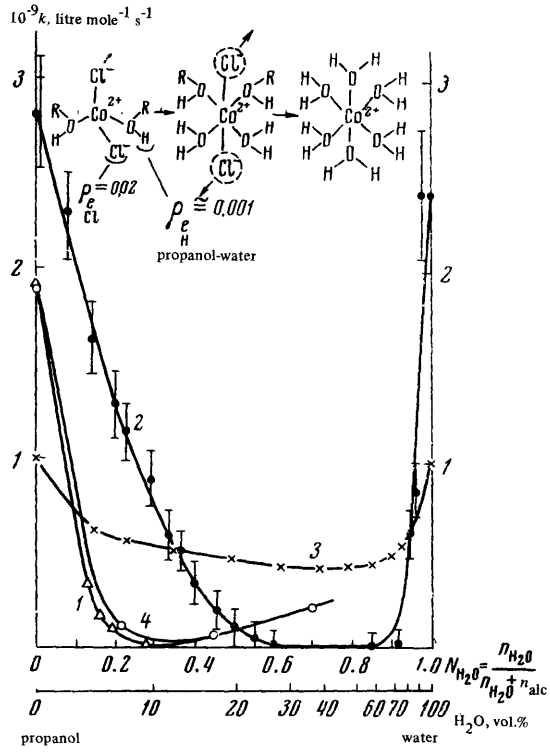


Figure 8. Variation of the rate of reactions of positronium and free DPPH and TMOPO free radicals with the composition of propanol–water mixtures[1,18,57]: 1) concentration of the tetrahedral (blue) form of the complex; sum of concentrations 4.5×10^{-2} M; 2) rate of reaction of Ps with $CoCl_2$ (0.4 M); 3) rate of reaction of TMOPO with $CoCl_2$ (6×10^{-2} M); 4) rate of reaction of DPPH with $CoCl_2$ (4.3×10^{-2} M).

Subsequent experiments on the quenching of positronium by the $FeCl_3$ oxidant in various alcoholic solutions[58] showed that positronium is extremely sensitive also to the delocalisation responsible for the oxidising effect of the Fe^{3+} acceptor orbital.

The observations of a sharp increase in the rate of reaction of positronium with other radicals when solutions are frozen, for example in octanol and benzene[18,59], are very remarkable and hitherto unexplained. For example, the rate of reaction of Ps with TMOPO in frozen octanol at −20°C is higher by a factor of almost 30 than in the liquid at −12°C, i.e. 3 degC above the melting point. These results may indicate both an increase in the rate of diffusion of Ps atoms in the solid phase and the presence of interaction mechanisms specific to the solid state, which operate in the liquid to a much lesser extent and which may play a role not only in the reactions of positronium but in solid-phase reactions in general.

The interpretation of the majority of the data concerning the formation and destruction of positronium in the solid phase is based on the so called "free volume model" examined for the first time by Wallace[60] and developed to the greatest extent by Brandt and coworkers (see, for example, Refs. 61 and 62).

The term "free volume" is applied to all vacancies, defects, and traps and all irregularities in the structure of the crystal lattice where Ps atoms may be located. In the simplest version of the free volume model[60], positronium is distributed in the interstices—a potential well with a periodic inner and exponentially decaying outer wave functions. We have the following quantity normalised to unity:

$$\Psi^2_{outer} = \frac{k^2/\alpha}{\alpha + \frac{2m_0 u}{\hbar^2} a + \frac{k^2}{\alpha}}, \qquad (5)$$

where

$$\alpha = \frac{\sqrt{2m_0(u-E)}}{\hbar}, \; k = \frac{\sqrt{2m_0 E}}{\hbar},$$

u is the depth of the well, a its radius, and E the energy of the level occupied by positronium. With decrease of the radius of the well a, i.e. of the free volume, Ψ^2_{outer} increases, which implies an increase in the overlapping of the wave function of positronium with the electron clouds of the surrounding molecules, an increase in pick-off annihilation, and a decrease of τ^2.

In principle it is clear that the changes in free volume must influence not only the lifetime (τ_2) of the Ps atoms in the traps, but also the very probability of the formation of positronium $P = (4/3)I_2$.

Among the factors which may lead to changes in free volume and hence may influence τ_2 and I_2, one must mention in the first place a change in temperature, the contraction of solids, fusion, and various phase transitions[1,62,63].

Having analysed the data for three groups of substances, namely (a) liquids and amorphous materials, (b) polymers, and (c) crystals, Thosar and coworkers[64], concluded that, within the limits of each group, the increase of τ_2 is accompanied by a decrease of I_2, and they obtained the following semiempirical relation:

$$\frac{4}{3} I_2 = a \cdot \frac{1 + \ln \tau_2/\tau_1}{b + \ln \tau_2/\tau_1}, \qquad (6)$$

where

$$a = K\frac{V_f}{v_0}, \; b = \frac{v_1}{v_0}, \; \tau_2 = \tau_1 \exp\left(\frac{v - v_1}{v_0 - v}\right),$$

V_f is the overall free volume, and K a constant (Fig. 9).

The significance of Eqn. (6) is that the free volume v corresponding to one positronium atom may vary from $v_{min} = v_1$ (here $\tau_2 = \tau_1$) to $v_{max} \to v_0$ (here $\tau_0 \to \infty$) and correspondingly $K = V_f/v$ is in the range $K(v_f/v_0) \leqslant P \leqslant K(V_f/v_1)$. Expressing I_2 as a percentage and τ_2 in nanoseconds, the authors[64] quote the following values of the parameters a and b: $a = 23$ and $b = 0.01$ for liquids, $a = 16$ and $b = 0.01$ for polymers, and $a = 4.5$ and $b = 0.01$ for crystals.

Owing to the different values of the parameter a for the above three groups of substances, the transition from one group to another may involve a change in τ_2 and I_2 in the same direction, for example, in the fusion of naphthalene (the dashed curve N in Fig. 9) or in the crystal–glass transition for Marlex-50 polyethylene (the dot–dash curve M in Fig. 9), where both τ_2 and I_2 increase.

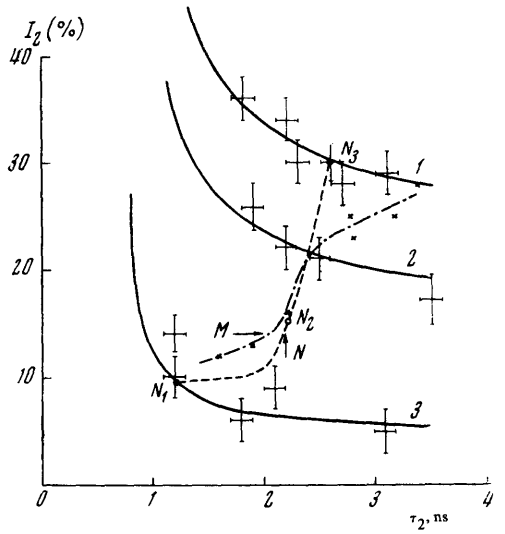


Figure 9. I_2–τ_2 correlation curves for liquid and amorphous materials, polymers, and crystals[64]: 1) liquids and amorphous materials (fused quartz, polystyrene, isopropyl alcohol, liquid naphthalene, benzene, and cyclo-octatetraene); 2) polymers [poly(vinyl chloride), polyethylene, poly(methyl methacrylate), Teflon]; 3) crystals (phenanthrene, naphthalene, stilbene, polyoxymethylene, and Sb_4O_6). N—heating and fusion curve for naphthalene (30 to 80.2°C); M—heating (between −196° and 142°C) and glass-formation curve (−20°C) for crystalline Marlex-50 polyethylene.

The factors which influence the probability of the formation of positronium in solids and its lifetime include also radiation effects and therefore their study must be regarded as one of the promising applications of positron methods.

The after-effects of radiation which may influence the annihilation of positrons are extremely various—they include the appearance of all possible radiation-induced effects (the possibility of the study of which by annihilation methods has been examined[65]), the generation of F-centres to which the annihilation of positrons proved to be extremely sensitive[24], the formation of ions and paramagnetic centres, etc.

The first experiments on the influence of radiation on the characteristics of the annihilation of positrons were performed as early as 1957–1958.[56] Subsequently it was shown that, as a result of the irradiation of solid anthracene with neutrons, positronium begins to form, as in liquid anthracene and in contrast to non-irradiated crystals, both τ_2 and I_2 increasing with radiation dose[67], although τ_2 does not in fact reach the value characteristic of liquid anthracene.

The wide variety of the effects of radiation is shown, for example, by the fact that, following the γ-irradiation of Teflon, the opposite behaviour is observed—τ_2 and I_2 decrease with radiation dose[68,69], which has been attributed to the increase of the degree of crystallinity of Teflon on irradiation and the quenching of positronium by the free radicals formed.

Indeed it has been shown[65] that the variation of τ_2 in the γ-irradiation of Teflon is correlated with the radical concentration determined by ESR. At the same time, according to the data of Indian investigators, the breakdown of the microcrystals and the increase of the proportions of low-density amorphous regions in irradiated polyethylene lead to an increase of τ_2,[70] while the rupture of benzene rings in polystyrene on neutron irradiation leads to a decrease of I_2,[71] since the formation of positronium in compounds of this kind is in fact mainly localised at aromatic rings.

Recently the positron method was applied in Japan (Tabata and coworkers[19,72]) in observations on radiation-induced solid-phase polymerisation of a number of monomers (acrylonitrile, methacrylonitrile, acetaldehyde, N-vinylcarbazole, and dimethyl and diethyl itaconates).

A number of factors influencing the formation and destruction of positronium arise in the course of polymerisation. As the polymeric chain grows, the number of defects and dislocations in the crystalline monomer increases—the systems of monomeric units contract after polymerisation. All these factors are responsible for a general increase in free volume, which alone would lead to an increase of τ_2. At the same time, the presence of terminal active centres (usually paramagnetic) of the growing polymeric chains at the free volume boundaries is responsible for a multiplicity of ways in which positronium can be destroyed and thus shortens its lifetime—together with pick-off annihilation there is the possibility of ortho–para conversion and positronium capture. Ultimately fairly different types of relation between τ_2 and I_2 may arise. With increase of radiation dose D from 5 to 20 Mrad, a correlation similar to that described by Thosar et al.[64] is observed for N-vinylcarbazole—initially τ_2 increases and I_2 falls and then (starting with $D \simeq 13$ Mrad) the opposite variation is observed, τ_2 decreasing and I_2 increasing. On the other hand, in dimethyl itaconate an increase of the degree of polymerisation is accompanied by an appreciable increase of the probability of the formation of positronium (Fig. 10), while τ_2 remains almost constant.

Apart from radiation-induced polymerisation, the positron method has recently been applied for the first time to another kinetic problem in polymer chemistry, namely in the study of the ageing of poly(vinyl chloride) due to thermal oxidation[73]. Prolonged heating of this polymer leads to a sharp reduction of τ_2, while I_2 increases with temperature. In the vicinity of the phase transition of the polymer at 195°C, τ_2 passes through a minimum ($\tau_2^0/\tau_2 \simeq 3$) and I_2 passes through a very sharp maximum ($I_2/I_2^0 \simeq 2$, where τ_2^0 and I_2^0 correspond to room temperature). The decrease of τ_2 was compared with the accumulation of free radicals detected by ESR and with the weight loss by the polymer owing to the elimination of HCl. The clear correlation between the above quantities has been interpreted[73] as confirmation of the mechanism of the quenching of positronium by combination with radicals or double bonds, or by ortho–para conversion, or finally by the interaction of Ps with HCl or HCl_2^-.

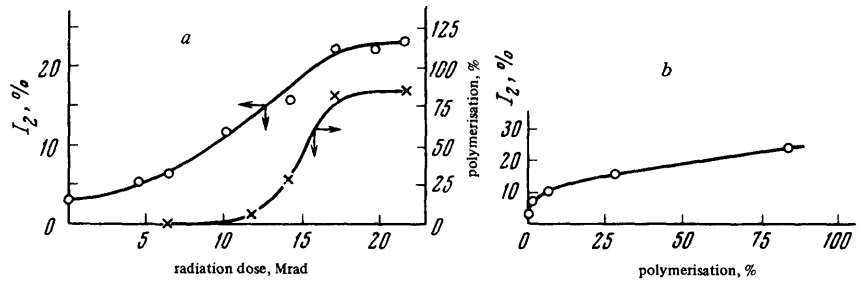


Figure 10. *a*) Variation of I_2 (%) and percentage polymerisation with radiation dose (^{60}Co γ-radiation) in the radiation-induced solid-phase polymerisation of dimethyl itaconate[69]; *b*) variation of I_2 with percentage polymerisation of dimethyl itaconate[69].

Thus the first, not altogether fully defined possibilities of the new chemical applications of positron methods have been outlined, namely in observations on the kinetics of solid-phase reactions accompanied by marked changes in the structure of the solid.

6. Characteristics of the Annihilation of Positrons in Porous Media

In conclusion of the section on positronium, we shall consider the most interesting observations on the characteristics of the annihilation of positrons in highly dispersed media and the wide variety of prospects for the employment of the results of these observations.

As already mentioned, in the study of the positron annihilation spectra in powdered oxides (Al_2O_3, MgO, SiO_2), Paulin and Ambrosino[41] observed two long-lived components—with a lifetime τ_2 of the order of several nanoseconds, characteristic of pick-off annihilation in the solid, and τ_3 of the order of several tens of nanoseconds, up to $\tau_T^0 = 1.4 \times 10^{-7}$ s. With increase of the degree of dispersion of the powders, i.e. with increase of the proportion of free volume $v_f/v = (\rho_0 - \rho)/\rho_0$ (ρ_0 is the density of the monolithic substance and ρ its density), an increase was observed in the intensity of the most long-lived component I_3 owing to the decrease of the contribution by the pick-off component I_2. An example is provided by Table 1.

The τ_3 component arises as follows. The positrons retarded in the porous solid can ultimately form Ps atoms. Part of these atoms undergo pick-off annihilation in the solid itself, while others emerge into the free volume between the particles. The probability of the capture of such atoms on impact against the surface of the particles is very low—they are much more likely to undergo repeated reflection (albedo) being ultimately destroyed in the pore volume (in flight)—either by pick-off annihilation in the pores filled with gas or in consequence of spontaneous annihilation. The relative contributions of these two processes may be assessed from the fact that the value of τ_3, reaching 140 ns in a vacuum, decreases by a factor of 2 when experiments with SiO_2 are performed in air or oxygen at the normal pressure.

Brandt and Paulin[42] calculated from the data of Paulin and Ambrosino[41] the characteristics of the diffusion of Ps atoms in the particles of solid oxides—the diffusion coefficients in the range between $D = (5.8 \pm 1.9) \times 10^{-5}$ (SiO_2) and $D = (1.4 \pm 0.7) \times 10^{-3}$ (MgO) cm^2 s^{-1}, the activation energy for diffusion $E = 700 \pm 370$ cal mole^{-1}, and the overall paths traversed before annihilation $\lambda = \sqrt{2D\tau}$ (46 ± 7 Å in SiO_2 and 270 ± 80 Å in MgO—for orthopositronium). Apart from the powdered oxides enumerated above, Bartenev et al.[43] observed the τ_3 component also in powdered BeO but not in the sintered oxide. Observations on the angular correlation of the annihilation quanta demonstrated the presence of a narrow component in BeO, MgO, SiO_2, and Al_2O_3 powders and its absence in monolithic specimens of these oxides. One cannot rule out the possibility that the results of the above investigations[41-43] explain the high probability of 3γ-annihilations in certain alkali metal halides and particularly in BeO and MgO, discovered and investigated by Italian workers[74,75] (see also Refs. 1 and 63), which for a long time appeared to be a puzzling anomaly. In all probability, these findings are not due to the molecular properties of the materials investigated but to their high degree of dispersion—indeed the entire anomaly in the counting rate of the 3γ-coincidences for MgO disappeared on passing to single crystals[76].

Table 1. Characteristics of the annihilation of positrons in highly dispersed oxide powders.

Substance	Specific surface m^2 g^{-1}	ρ, g cm^{-3}	τ_2, ns	I_2, %	τ_3, ns	I_3, %
SiO_2	50	0.3	1.77±0.2	28±2	140±4	4±0.5
SiO_2	180	0.06	1.89±0.2	10.7±0.8	142±3	11.6±1
SiO_2	300	0.05	2.1±0.2	4.5±1	132±3	12±1
SiO_2	380	0.05	3.4±0.4	4±1	137±3	15±1
Al_2O_3		1	3.6±0.4	2.5±1.5	87±3	15.7±1
MgO		0.35	2.9±0.3	1.8±1.5	126±3	25.6±2

The extension of the range of substances investigated by positron methods in a highly dispersed state constitutes an urgent problem. Possibly the formation of positronium in fine-pored specimens will be detected also in substances where its existence has been hitherto ruled out—for example, metals.

Other consequences of the above studies[41-43] are also of interest—the observations of the reactions of positronium with atoms and molecules adsorbed on surfaces or

filling adsorbent pores and the development of positron methods for the investigation of the physical chemistry of surface phenomena, adsorption, and heterogeneous catalysis are promising.

The probability of the capture of hydrogen atoms (ϵ_H) on impact against various surfaces is known to vary within extremely wide limits—from $\epsilon_H = 10^{-4}-10^{-5}$ for SiO_2 to $\epsilon_H \simeq 1$ for graphite and $ZnO.Cr_2O_3$.[77] Moreover, ϵ_H depends markedly on temperature: $\epsilon_H \propto \exp(-E/RT)$, where $E = 9000-13\,000$ cal mole^{-1}.

There is reason to expect similar relations also for positronium and comparison of data for positronium, with its exceptionally low mass and large de Broglie wavelength, and hydrogen is of particular interest.

The interest becomes even greater in connection with the recent theoretical demonstration by Kagan[78] that a neutron can also give rise to a long-lived bound state in porous substances: the porous medium behaves as a kind of "sponge" which sorbs neutrons into a bound state with a binding energy of the order of 10^{-7} eV and a characteristic lifetime, which reaches tens and hundreds of seconds at the helium temperature.

The annihilation spectra of positrons in silica gel, alumina gel, and aluminosilicate catalyst specimens of moderate porosity, having specific surfaces in the range 130–230 m^2 g^{-1} and an average pore radius of about 40 Å, were recently compared[79] at a number of points on the water desorption isotherm at room temperature. As long as the water vapour pressure p is close to the saturated vapour pressure p_S ($p/p_S \gtrsim 0.3$), the τ_3 component in the time spectra is altogether absent, since the pore volume is entirely filled by liquid water. On the other hand, in the region of low values of p/p_S, corresponding to a more or less depleted monolayer of physically adsorbed water, a correlation was noted between the catalytic activity of the specimens in the dealkylation of cumene (i.e. the strength of the Brönsted acid centres) and the values of τ_3. For catalytically inactive silica gel and alumina gel, the desorption of water with decrease of p/p_S hardly affected τ_3, while for the aluminosilicate catalyst τ_3 decreased appreciably under these conditions, apparently due to the reaction $H^+ + Ps \rightarrow H + e^+$, which is energetically possible only for non-hydrated protons weakly bound to the surface of the pore, i.e. only for strong proton acid centres. The effect of the desorption of water on τ_3 in the region of low values of p/p_S for catalyst specimens containing sodium cations was much weaker and the values of τ_3 themselves were higher. Indeed the reaction $Na^+ + Ps \rightarrow Na + e^+$ is endothermic ($Q = -1.63$ eV) and therefore it could not play an appreciable role. Thus a change in the probability of the capture of positronium ϵ_{Ps} as a function of the state of the surfaces of adsorbents and catalysts was demonstrated[79].

The observation of the annihilation of positrons in porous materials in an atmosphere of different gases is frequently more convenient than experiments with the gases themselves—the volume of the highly dispersed system necessary for the effective retardation of positrons is much smaller than for pure gases and the positronium atoms traversing the labyrinth between the grains of the highly dispersed powders do not leave the field covered by the counters recording the annihilation γ-quanta up to the very instant of annihilation.

These advantages were fully reflected in the work of Chuang and Tao[80], who observed the annihilation of positrons in iodine and carbon tetrachloride adsorbed on silica gel. In our remark in subsection 4 that a decrease of I_2 for a constant value of τ_2 corresponds to "pure" inhibition of the formation of positronium and a decrease of τ_2 for a constant I_2 corresponds to its "pure" quenching, we simplified the situation somewhat.

If fast positronium atoms enter into an endothermic threshold reaction, which is possible only up to their retardation and "thermalisation" and leads to instantaneous annihilation, the annihilation spectrum shows an additional component with a short lifetime virtually indistinguishable from τ_1. The conversion of some of the orthopositronium atoms into this component is detected as a decrease of I_2—in other words the quenching of fast Ps atoms is recorded as apparent inhibition. This type of apparent inhibition, due to the reaction $Ps + Cl_2 \rightarrow PsCl + Cl$, was in fact observed by Tao[81] after the addition of chlorine to argon. The possibility of distinguishing true quenching agents and inhibitors on the basis of their influence on annihilation in the adsorbed state has been demonstrated[80]. The authors[80] believe that the adsorption of the quenching agent on the surface of silica gel alters significantly the potential for the interaction of Ps with the surface or, using the terminology adopted above, by increasing the probability of the capture of positronium ϵ_{Ps} it thereby shortens τ_3. At the same time the adsorption of the quenching agent should lower also the value of I_3, since the presence of the quenching agent on the surface of the adsorbent reduces the probability of the liberation of Ps atoms from the bulk of the silica gel globules into pores. Both these effects, the decrease of τ_3 and I_3 with increasing amount of the adsorbed substance, have been observed for iodine, which is therefore believed[80] to be a true quenching agent for positronium. Different results have been obtained for the "pseudoinhibitor" carbon tetrachloride—over a wide range of its concentrations (up to the saturation of a monolayer on the surface of silica gel), I_3 decreased, while τ_3 remained unchanged. This implies that the presence of carbon tetrachloride on the silica gel surface does not increase ϵ_{Ps}.

The total experimental data obtained by Paulin and Ambrosino[41] and subsequent investigators for the annihilation of positrons in porous media and also the relevant theoretical considerations indicate the possibility of creating effective highly dispersed positronium sources (it must be stressed that these are in fact positronium sources and not simply positron sources), which are particularly promising for the study of chemical reactions in gases over a wide range of temperatures and pressures.

III. MUONIUM

1. The Nuclear-physical Characteristic of the μ^+-Meson and Muonium

Muonium (atomic system consisting of a μ^+-meson as the central nucleus and an electron) is a hydrogen-like atom—a model light analogue of atomic hydrogen. The μ^+-meson (an elementary particle) (mass 206.76 $m_e \simeq \frac{1}{9} m_p$; lifetime with respect to the decomposition into a positron, a neutrino, and an antineutrino 2.2×10^{-6} s; spin 1/2; magnetic moment 8.89 nuclear magnetons) arises in the decomposition of π^+-mesons formed in charged-particle accelerators as a result of nuclear reactions above the meson generation threshold. It is significant that in the decomposition of π^+-mesons in flight the resulting μ^+-mesons are fully polarised longitudinally in consequence of the non-conservation of parity in the $\pi\mu e$ decomposition,

i.e. the spin of the ejected μ^+-meson is oriented in opposition to the direction of its motion. The ejection of the position in the μe decomposition ($\mu^+ \rightarrow e^+ + \nu + \tilde{\nu}$) takes place preferentially in the direction of the spin of the meson and there is a steric asymmetry with the impulse of the positron.

In the theory of the two-component neutrino[82-84], the asymmetry coefficient c, defined as the ratio of the difference between the "forward" and "reverse" decompositions (along and in opposition to the initial direction of the spin of the μ^+-meson) to their sum, averaged over the entire energy spectrum of the decomposition positrons, is 1/3 (polarisation $P = 1$) for fully polarised μ^+-mesons. The change in the polarisation of μ^+-mesons in the medium as a function of the experimental conditions is a characteristic of the interactions with matter.

When the meson is retarded to velocities of the order of that of atomic electrons of the medium, a charge-transfer stage ensues, which is completed by the capture of an electron and the formation of a stable μ^+e^- atomic system, i.e. a muonium atom (ionisation potential 13.539 eV, Bohr radius 0.532 Å, mass $207.76m_e$). Since the initial direction of the spin of the μ^+-meson is arbitrary, the formation of muonium with parallel and antiparallel orientations of the meson and electron spins is equally probable (the $^3S_1$, $m = 1$ triplet state with a population of 1/2 and superposition of the $^1S_0$, $m = 0$ and $^3S_1$, $m = 0$ states with populations of 1/4 in each case). In the first case the spin of the μ^+-meson in the absence of external perturbations retains its initial polarisation in the course of the lifetime of the meson; in the second case there are harmonic oscillations between the (1,0) and (0,0) states, the frequency of which (ω_0) is determined by the hyperfine splitting energy ΔW ($\omega_0 = \Delta W/\hbar = 2.804 \times 10^{10}$ s^{-1}). Thus in a period of the order of about 10^{-10} s the para-state of muonium undergoes irreversible depolarisation and the overall asymmetry coefficient decreases to the level of 1/2 of the initial value. Processes involving the exchange of electrons having opposite spins with the medium (conversion) can lead to further depolarisation of the μ^+-meson down to zero.

We may note that the "thermalisation" time of the μ^+-meson in condensed media and gases at a pressure greater than 50 atm does not exceed $10^{-12}-10^{-13}$ s, which is significantly less than the characteristic depolarisation time ($1/\omega_0$). Consequently depolarisation during the retardation time is insignificant; repeated charge transfers in the inhibition of the meson do not lead to a change of its spin and the probability of the formation of the ortho- or para-state of muonium depends only on the last electron capture step.

In fairly strong longitudinal (in the direction of the spin of the μ^+-meson) external magnetic fields, the interaction of the magnetic moments of the meson and the electron in the muonium atom disappears; both populated states (+1/2, +1/2 and 1/2, −1/2) retain the initial polarisation of the μ^+-meson. A critical condition for which the magnetic energy of muonium in the external magnetic field is equal to the hyperfine splitting energy is that $H_0 = \Delta W/2(\mu_e - \mu_\mu) = 1585$ G. Since ΔW depends on the cube of the distance between the interacting magnetic moments [$\Delta W = f(r^{-3})$], it is clear that H_0 is extremely sensitive to changes in the distribution of electron density in the molecule incorporating muonium. The last factor allows an additional identification of the form in which muonium is present in the medium. In transverse magnetic fields there is a Larmor precession of the spin (or a system of spins) with a frequency determined by the magnetic moment and the spin. Since the magnetic moment in the triplet state of muonium is determined largely by the magnetic moment of the electron and the spin is unity, the precession frequencies of the μ^+-meson and triplet muonium differ by a factor of about 103 and can be readily distinguished experimentally.

A typical apparatus for the measurement of the asymmetry coefficient for the angular distribution of μe-decomposition positrons (Fig. 11*a*) incorporates two telescopes comprising two scintillation counters, each recording the passage of charged particles. The arrest of a μ^+-meson by the target *5* is recorded by the counters *1* and *2* in the absence of coincidences with the counters *2* and *3*, giving rise to a "start" pulse signal. In the decomposition of a μ^+-meson on the target, positrons are recorded by the counters *3* and *4*, giving rise to a "stop" signal in the absence of coincidences with the counters *2* and *3*. The pulses produced according to the $12\overline{23}$ and $34\overline{23}$ scheme control the operation of the time–amplitude converter.

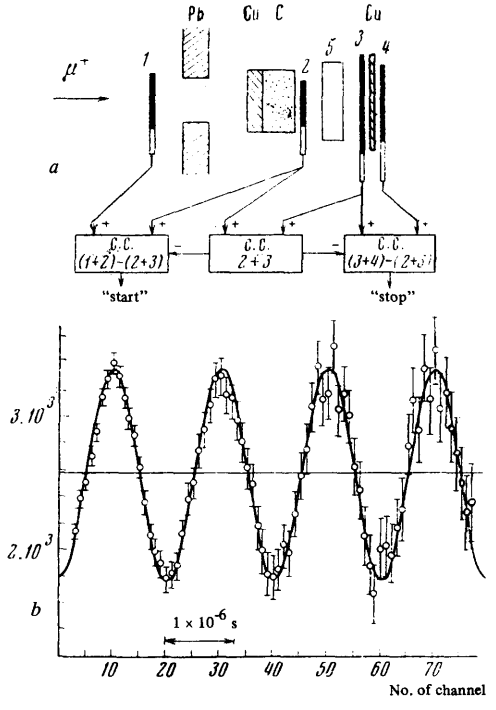


Figure 11. *a*) A typical arrangement of the apparatus for the measurement of the asymmetry coefficient for the angular distribution of μe decomposition positrons [1)–4) scintillation counters; 5) target; C. C.—coincidence circuits]. The magnetic coils are not shown in the Figure. *b*) The precession curve in bromoform. The numbers of readings in the channels are corrected for the background and the exponential decomposition of μ^+-mesons.

The latter transforms the time interval between the pulses into a variable amplitude signal recorded by a multichannel analyser. The use of a transverse magnetic field of the required strength leads to the modulation of the exponential decomposition curve for the Larmor precession of the μ^+-meson or triplet muonium. After the correction of experimental data for the random coincidence background and the decomposition of the μ^+-meson, a

typical precession curve has the form shown in Fig. 11*b* (in this case the magnetic field strength was 50 G and the precession period about 1.5×10^{-6} s).

2. Physicochemical Principles of the Interactions of Muonium

a. Kinetic scheme. Calculation of the rate constants for the chemical reactions of muonium. In the majority of cases the behaviour of muonium (Mu) described is complicated by its involvement as a hydrogen-like atom in chemical reactions with the molecules of the medium, with formation of fairly strong chemical bonds in a manner analogous to the reactions of atomic hydrogen. In view of their wide occurrence, the reactions of atomic hydrogen have been investigated in detail by chemical kinetic methods in the course of several decades (see, for example, the relevant fundamental monographs[85,86]).

The incorporation of muonium in the molecule after chemical reaction alters fundamentally the factors governing its depolarisation in the medium[87,88]. In the reaction with an unsaturated covalent compound (for example, $C_8H_{18} + H \rightarrow H_2 + C_8H_{17}^{\cdot}$; the dot designates the unpaired electron of the radical product), which is typical for atomic hydrogen, the hydrogen atom enters into the composition of a molecule with a closed diamagnetic shell, where the electron spins are compensated in pairs. A similar reaction involving muonium has the same consequences. Thus the magnetic field created by electrons at the point where the μ^+-meson is located in the molecule is zero. Under these conditions, there is no coupling of the magnetic moments of the meson and the electron and depolarisation by the above process does not occur. However, the interaction with the magnetic moments of the adjacent nuclei of the molecule is possible, provided of course that the latter are not even–even. Under real conditions, allowance for the rotational states of molecules, in particular for gases and liquids, leads to a virtually negligible contribution by depolarisation factors to the formation of the diamagnetic electron shell; for solids, this depolarisation mechanism can play an appreciable role only when $r \lesssim 1$ Å.

It is significant that the Larmor precession for muonium incorporated in the molecule occurs at a frequency corresponding to a free μ^+-meson. Indeed the absence of magnetic interactions between the meson and the electrons of the diamagnetic shell of the molecule corresponds to an independent interaction of the magnetic moment of the μ^+-meson with the external field. This factor resolves the apparent contradiction in the earlier experimental studies, where the search for the precession of triplet muonium was unsuccessful, but the precession of the spin of the μ^+-meson was observed[89,90].

Thus the involvement of muonium in the composition of a diamagnetic molecule leads to the "freezing" of the depolarisation processes at a level which depends on the rate of reaction of muonium with the medium. For a fairly short characteristic time of the chemical reaction τ, the para-state of muonium (Mu^S) is involved in the process, which prevents depolarisation when $\tau \ll 1/\omega_0$; then precession at the frequency of the free μ^+-meson (the meson component) has the maximum amplitude. With increase of τ, there is a possibility of partial or complete depolarisation of Mu^S; the probability of the reaction of triplet muonium (Mu^T) and Mu^S which has retained its polarisation corresponds to the observation of the meson precession with an amplitude depending on the value of τ. Finally, for large values of τ (for example, $\tau > \tau_{\mu^+}$), the absence of chemical interactions makes it possible to observe the precession of the frequency of triplet muonium (the muonium component). Consequently, a qualitative treatment yields the relation between the rate of the chemical reaction of muonium and the experimental polarisation at the corresponding (meson or muonium) frequency. We may note that, in the absence of conductivity electrons, the conversion exchange is appreciably suppressed, since it apparently requires an energy expenditure on the scale of the triplet excitation energy of molecules and for covalent compounds the rate of such exchange does not exceed the rate of decomposition of the μ^+-meson.

We shall now formulate the characteristics of the muonium method for the investigation of chemical processes. Firstly, one of the characteristic conditions associated with the specific features of the experimental method is the presence throughout the bulk of the test substance only of single muonium atoms. Thus the reaction kinetics are studied in the initial stage when there are no complications associated with the formation and accumulation of secondary reaction products in the bulk phase. Secondly, the use of nuclear-physical constants as independent time standards permits the determination of the absolute rate constants for a wide range of fast reactions. Thirdly, the observation of the behaviour of the spin and the magnetic moment of the μ^+-meson allows the study of the factors determining the spin interactions during the process or at steady state, which is one of the unique characteristics of the method. Fourthly, the typical independence of the recording method of the external experimental parameters significantly increases the scope of the investigation; in particular, the method becomes universally applicable to various states of aggregation of matter.

From the standpoint of the experimental characteristics associated with the method (the observation of the meson and muonium precession frequencies in an external magnetic field), it is desirable to classify in appropriate groups the products obtained as a result of the reaction. We shall include in the first group molecules which incorporate muonium and have a diamagnetic electron shell; the second group includes reaction products with an unpaired electron (radicals). In the absence of an effect of the magnetic moments of the surrounding nuclei, the products of the first group are observed at the meson frequency. We may note that, in the reaction of muonium with a molecule having different substituents, parallel pathways are possible, but, since the molecular products are indistinguishable in terms of experimental technique (in the concrete example of the interaction of muonium with chloroform, MuH and MuCl are formed, the precession occurring at the meson frequency in both cases), the probability of the formation of the sum of the molecular products is determined. In the formation of radical products incorporating muonium (for example in the reaction involving addition to a multiple bond: $Mu + H_2C = CH_2 \rightarrow H_2MuC-CH_2^{\cdot}$), the interaction of the magnetic moments of the μ^+-meson and the unpaired electron (complicated by the change of the average effective distances and the nature of the delocalisation of the electron in the molecule) persists. In this case there is no precession at the meson frequency, but the "latent" polarisation may be determined either from its restoration in longitudinal magnetic fields in consequence of a change in H_0 or from the competition between various reactions of muonium in

homogeneous mixtures of compounds (the method of competing acceptors).

We shall now consider a kinetic scheme for the reactions of muonium with matter[88,91]. The time interval between the individual steps involving the entry of a μ^+-meson into the space occupied by the test compound is much longer than its lifetime. Consequently the number of mesons in the system is unity (the time interval between the decomposition of a μ^+-meson and the entry of the next particle is insignificant, since no processes occur during this interval) and the statistical conditions for a steady state are fulfilled; the rates of appearance and loss of reaction intermediates are then equal. In the general case it is necessary to take into account the following competing processes: reactions with formations of molecular and radical products, reactions involving conversion spin exchange with the electrons of the molecules of the medium, irreversible depolarisation of Mu^S in consequence of spin flip, and the decomposition of the μ^+-meson. We may note that any chemical reactions of a depolarised muonium atom (Mu^D) naturally yield products with an isotropic angular distribution of decomposition positrons. The interaction of muonium with hydrogen-containing compounds can be formulated schematically as follows:

$$\begin{aligned}
&(1).\ Mu^T\ (Mu^S) + RH \xrightarrow{k_1} MuH + R^{\cdot}\ ,\\
&(2).\ Mu^T\ (Mu^S) + RH \xrightarrow{k_2} RMuH^{\cdot}\ ,\\
&(3).\ Mu^T\ (Mu^S) + RH \xrightarrow{k_3} Mu^S\ (Mu^T) + RH\ , \qquad (1)\\
&(4).\ Mu^S \xrightarrow{k_4} Mu^D\\
&(5).\ Mu^T\ (Mu^S, MuH, RMuH^{\cdot}, Mu^D) \xrightarrow{k_5} e^+ + \nu + \tilde{\nu}\ .
\end{aligned}$$

By fitting the function $\exp(-\lambda t)$ to the average polarisation of Mu^S ($1/\omega_0 t.\sin\omega_0 t$), we find the depolarisation rate constant $k_4 = \frac{2}{\pi}\omega_0$; the decomposition rate constant is $k_5 = 1/\tau_{\mu^+}$.

Using the method of steady states, we obtain expressions relating the rate constants for reactions (1)–(5) to the experimental asymmetry coefficients c_1', c_2', and c_3' determined under various conditions:

$$\frac{2k_5 + 2(k_1+k_2)[RH]}{k_4}\cdot\frac{1}{1+\dfrac{2k_3[RH]}{(k_1+k_2)[RH]+k_5}} = \frac{c_1'}{fc-c_1'}\ , \qquad (2)$$

$$\frac{k_1[RH]}{k_2[RH]+k_5+\dfrac{k_4}{2+\dfrac{k_4}{(k_1+k_2)[RH]+2k_3[RH]+k_5}}} = \frac{c_2'}{fc-c_2'}\ , \qquad (3)$$

$$\frac{k_2[RH]+k_5}{k_1[RH]+\dfrac{k_4}{2+\dfrac{k_4}{(k_1+k_2)[RH]+2k_3[RH]+k_5}}} = \frac{c_3'}{fc-c_3'}\ , \qquad (4)$$

where f is the degree of polarisation of the initial beam of μ^+-mesons, which depends on the kinematic conditions of the formation of the meson beam in accelerators. Formula (2) corresponds to the case where the depolarisation of the μ^+-meson is due solely to reaction (4) and characterises the overall reactivity of the compound via all reaction pathways. Formulae (3) and (4) are applicable to experiments by the precession method in transverse magnetic fields and describe the meson and muonium components respectively. We may note that, for reaction rates comparable to ω_0, the inaccuracy of the approximation employed for the average polarisation of Mu^S limits the applicability of the formulae. In this case it is necessary to take into account the oscillatory nature of the depolarisation of Mu^S when reactions (3) and (5) are neglected owing to their small contributions[92].

The statistical accuracy of the determination of the absolute rate constants for the reactions of muonium depends on the magnitude and accuracy of the determination of the asymmetry (polarisation) coefficients. The current experimental techniques ensure an accuracy in the determination of the reaction rate constants for a pure compound reaching under favourable conditions 10–20%.

Table 2. Rate constants for the reactions of muonium.

Compound	Formula	k_1	k_2
Cyclohexane	C_6H_{12}	$(2.4\pm0.2)\cdot10^9$	—
Methanol	CH_3OH	$(5.6\pm1.1)\cdot10^8$	—
Octane	C_8H_{18}	$(2.9\pm0.4)\cdot10^9$	—
Chloroform	$CHCl_3$	$(4.2\pm1.4)\cdot10^9$	—
Benzene	C_6H_6	$(3.0\pm1.1)\cdot10^8$	$(3.1\pm0.4)\cdot10^9$
Bromoform	$CHBr_3$	$(1.1\pm0.2)\cdot10^{10}$	—
Diphenylpicrylhydrazyl (DPPH)		$(7.6\pm2.2)\cdot10^{10}$	

With a correct choice of the second solution component, the method of competing acceptors makes it possible to obtain the maximum accuracy in all necessary cases; moreover, this method allows the detection, from the results of the measurements of the meson frequency, of radical product formation processes.

b. Experimental data for a number of compounds. We shall examine one specific example[92,93] the determination of the absolute rate constants for the reaction of muonium by the method of competing acceptors. In order to observe the precession in a transverse magnetic field at the meson frequency, measurements were made of the asymmetry coefficients for individual substances (listed in Table 2) and their binary solutions. Some of the data obtained for the variation of the asymmetry coefficient with the concentration of the substance in solution are presented in Fig. 12. We may note that for heterogeneous mixtures, where the competition between parallel reactions is appreciably suppressed, or in the absence of chemical interactions, the dependence of the asymmetry coefficient on the concentration of the mixture components should be linear, while for competing acceptors the form of the analogous relation is determined by the ratio of the overall (via pathways involving the formation of both molecular and radical products) reactivities of the compounds. The curve for $C_6H_6-CHBr_3$ is typical in this sense (Fig. 12*a*).

The form of the curve for the $C_6H_6-CH_3OH$ mixture is important (Fig. 12*b*)—despite the lower asymmetry coefficient at the meson frequency for benzene, the overall consumption of muonium in the interaction with benzene is higher than in the interaction with methanol, which leads to a deviation of the curve relating the asymmetry coefficient to concentrations towards smaller values. This is evidence of the predominance of the "latent" polarisation due to the radical pathway of the reaction of muonium with benzene involving the formation of $C_6H_6Mu^{\cdot}$.

Quantitative calculation for the system as a whole yielded the reaction rate constants (in litre $mole^{-1}$ s^{-1}) listed in Table 2. These data may be used to calculate the

rate constants for the corresponding reactions of atomic hydrogen, provided that the activation energies for the processes are known (see below).

c. Gas-phase reactions of muonium. The study of the reactions of muonium in the gas phase is of considerable interest, since it permits a direct comparison with the gas-phase kinetics involving atomic hydrogen.

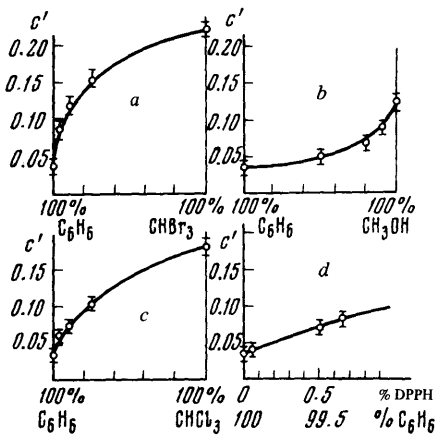


Figure 12. Variation of the asymmetry coefficients at the meson frequency with the concentration of the solution components (in mole %): *a*) $C_6H_6-CHBr_3$; *b*) $C_6H_6-CH_3OH$; *c*) $C_6H_6-CHCl_3$; *a*) C_6H_6–DPPH.

The presence of an inert buffer gas, which is necessary for the retardation of μ^+-mesons, permits the use of low concentrations of the test substance, i.e. a significant reduction of the rate of reaction, and the usual kinetic curves for the decrease in the amount of muonium with time at a given acceptor concentration may be studied. Calculation of the reaction rate constants is in this case trivial—the characteristic time of depolarisation (equivalent to the decrease of the concentration of muonium) is equal to the duration of the chemical reaction and is inversely proportional to the rate of reaction (V) with the acceptor at a concentration [Ac]:

$$\tau = \frac{1}{V} = \frac{1}{k\,[\mathrm{Ac}]} \quad . \qquad (5)$$

The calculations quoted below are based on the experimental data of Hughes and coworkers[94,95]. The inert buffer gas employed was carefully purified argon under a pressure of about 50 atm to which small admixtures of the test compounds (NO, O_2, NO_2, C_2H_4, H_2, N_2, etc.) were added. As an example, Fig. 13 presents the variation of the muonium depolarisation factor with time for various concentrations of ethylene at room temperature. The linear relation between the rate of depolarisation and the concentration of ethylene, which is evident from Fig. 13 (compare curves *1* and *2*), is evidence that the rate-limiting stage of the process is the formation of the radical $C_2H_4Mu^{\cdot}$, in which the depolarisation of the μ^+-meson takes place owing to the exchange interactions of the unpaired electron.

Standard kinetic treatment of the data in Fig. 13 leads to the characteristic times for the decrease of the polarisation of muonium (by a factor e) $\tau = (8.4 \pm 2.2) \times 10^{-6}$ s (curve *1*) and $\tau = (2.7_5 \pm 0.7) \times 10^{-6}$ s (curve *2*). The corresponding reaction rate constants $k = (1.7_5 \pm 0.4_5) \times 10^9$ litre mole^{-1} s^{-1} and $k = (1.4 \pm 0.4) \times 10^9$ litre mole^{-1} s^{-1} agree within the limits of experimental error. By combining the data, we have

$$K(\mathrm{Mu} + C_2H_4) = (1.6 \pm 0.3) \cdot 10^9 \text{ litre mole}^{-1}\,\text{s}^{-1}\,.$$

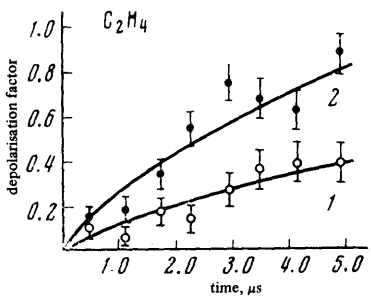


Figure 13. Kinetic curves for the decrease of polarisation (increase of the depolarisation factor) for muonium with time in the reaction with ethylene (according to Mobley et al.[94]): 1) $[C_2H_4] = 4.1 \times 10^{16}$ mol. cm^{-3}; 2) $[C_2H_4] = 15.8 \times 10^{16}$ mol. cm^{-3}.

The calculation for the analogous reaction of atomic hydrogen (according to collision theory, the rate constant ratio is about 3; in view of the low activation energies for the reactions of H and Mu with C_2H_4, it is not necessary to allow for the difference between them) yields the

$$k(\mathrm{H} + C_2H_4) = (5.3 \pm 1.0) \cdot 10^8 \text{ litre mole}^{-1}\,\text{s}^{-1},$$

in satisfactory agreement with the literature data[96,97] for the kinetics of the gas-phase reaction of H with C_2H_4 at 18°C, which gave

$$K(\mathrm{H} + C_2H_4) = (5.1 \div 7.5) \cdot 10^8 \text{ litre mole}^{-1}\,\text{s}^{-1}.$$

Experiments in longitudinal magnetic fields[95] showed that the strength of the critical magnetic field for NO and O_2 is consistent with the value of H_0 for the free muonium atom, confirming thereby the hypothesis of the dominant role of conversion processes in reactions with the given compounds. At the same time the critical field for C_2H_4 is significantly weaker (about 100 G), which is evidence of an increase of the effective distance between the meson and the unpaired electron as a result of the formation of the ethyl radical $C_2H_4Mu^{\cdot}$.

d. Temperature variation of the rates of the reactions of muonium. The activation energy for the process is one of the most important criteria of the reactivity of compounds. Having determined by the method described above the rate constants for the reactions at different temperatures, it is possible to obtain with an adequate statistical accuracy (which depends, in particular, on the width of the temperature range) the principal parameters of the chemical reactions of muonium

(the pre-exponential factor, the steric factor, and the activation energy).

Similar measurements have been made[98] for the substances listed in Table 3. Particular attention has been devoted to the phase transition point. For organic compounds, the continuous variation of the asymmetry coefficient during the change in the state of aggregation permitted the determination of the activation energies for the corresponding reactions of muonium. It is striking that, for the compounds investigated, the activation energies are low and do not exceed 1.5 kcal mole^{-1}. It is probably necessary to take into account the possible decrease of the activation energies for substitution reactions involving atoms with a smaller mass[99].

Table 3. Activation energies for the reactions of muonium.

Compound	Temp. range, °K	E, kcal mole^{-1}
C_6H_{12}	303÷77	1410±50
C_6H_5Br	303÷80	970±80
$CH Br_3$	303÷77	⩾670±50
H_2O (liq.)	363÷273	135±320
H_2O (solid)	273÷77	10±30

The abrupt change of the asymmetry coefficient for the water–ice phase transition (Fig. 14), corresponding to a decrease of the reaction rate constant by two powers of 10, is of interest. The interpretation of this effect must be related to the presence of hydrogen bonds in the crystal structure of ice[100]. When the temperature is reduced during the crystallisation of ice, a closed-coordination system of hydrogen bonds is formed, which gives rise to a sharp decrease of the rate of the process on transition to the crystal structure. In this case the free muonium atom in the ideal ice lattice migrates in the crystal owing to the impossibility of stabilisation by addition to hydrogen bonds. The evident conclusion is that muonium may be identified in ice, which has in fact been demonstrated[101]. The absence (within the limits of experimental error) of an activation barrier in the reaction of muonium with water and ice is also consistent with the specific nature of the process involving addition to the hydrogen bond.

The problem of barrier tunnelling interaction of muonium is of interest. Estimates based on a number of studies[33,34] showed that the temperature limit at which the rates of activation and tunnel processes become comparable may be reached at 30–70°K for muonium (for E = 1000–2000 cal mole^{-1} and an effective half-width of the activation barrier of 2–3 Å). Comparison with the analogous data for positronium, muonium, and atomic hydrogen will probably allow a solution of this theoretically important problem.

3. Reactions of Muonium with Unsaturated Compounds

a. Ratio of the rate constants for the formation of molecular and radical products. The interactions of muonium, like those of atomic hydrogen, with aromatic and other unsaturated compounds can occur, as already stated, by parallel pathways—substitution reactions with the removal of an atom and the formation of a diamagnetic molecule incorporating muonium and addition to a multiple bond with formation of a radical. The effect of the functional groups and substituents in the molecule and the role of factors involving the conjugation of different types of bonds were discovered in the study of the variation of the reaction rate constants associated with a successive logical alteration of molecular structure.

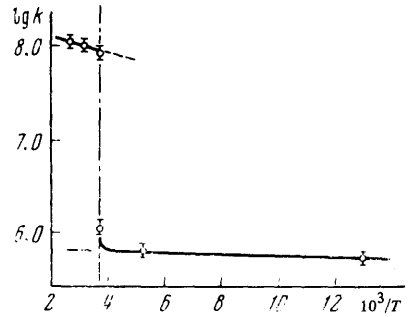


Figure 14. Temperature variation of the rate constant for the reaction of muonium with H_2O; the dot–dash line represents the temperature of the water–ice phase transition.

Table 4. Ratio of the rate constants for the reactions of muonium with methyl-substituted (in the ring) benzene derivatives.

Compound	k_2/k_1	$k_1\times10^{-9}$	$k_2\times10^{-9}$
C_6H_6	10.5±4.2	0.30±0.11	3.1±0.4
$C_6H_5CH_3$	3.3±1.0	0.77±0.20	2.5±0.7
$C_6H_4(CH_3)_2$	2.7±0.8	0.82±0.23	2.5±0.8
$C_6H_3(CH_3)_3$	2.3±0.6	1.03±0.22	2.4±0.7
$C_6H_2(CH_3)_4$	2.2±0.6	1.08±0.24	2.3±0.7
$C_6(CH_3)_6$	0.84±0.26	1.85±0.34	1.5±0.5

We shall examine, for example, the results[92] for two homologous series—for the successive methylation of the benzene ring and for the successive introduction of methyl groups into a side chain. In the first case (Fig. 15*a*) the polarisation increases relatively slightly up to the introduction of four methyl groups [as in durene (tetramethylbenzene)] but there is a subsequent increase of the asymmetry coefficient for hexamethylbenzene associated with the screening of the ring by CH_3 groups. These data indicate that the reaction involving the addition of muonium to the multiple bond predominates even under the conditions of partial screening of the benzene ring. It is significant that the polarisation for hexamethylbenzene is nevertheless appreciably less than for saturated compounds (octane and cyclohexane). One may suppose that this difference is caused by the attack of muonium in the plane of the benzene ring with formation of a π-complex. Quantitative calculation yields the reaction rate constants (litre mole^{-1} s^{-1}) listed in Table 4.

We may note that the overall reaction rate constants hardly change in this series, but there is a redistribution of the reactivity of the molecule with respect to parallel reaction pathways.

The analogous relations for normal (unbranched) alkylbenzenes are of a different type (Fig. 15*b* and Table 5). With increase of the length of the side chain, there is a monotonic increase of the asymmetry coefficient and an equivalent increase of the rate constant for the formation of molecular products. This change corresponds to the absence of a redistribution among parallel reaction pathways. This result is of very general importance, since it indicates the independence of the interactions of muonium with aromatic rings and the side chains when the chain length is sufficiently long (more than two carbon atoms).

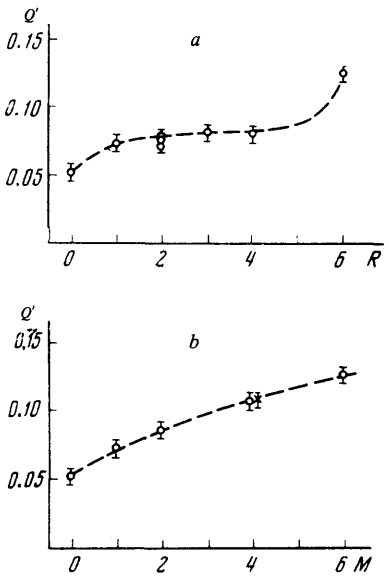


Figure 15. Variation of the asymmetry coefficient with the number of methyl groups R in the benzene ring (*a*) and with the number of carbon atoms (M) in the side chain of n-alkylbenzenes (*b*); X = $C_6H_5CH(C_2H_5)C_3H_7$.

The hypothesis that in many cases the interaction does not take place with the molecule as a whole but with individual fragments is confirmed by the experiment with 3-phenylhexane for which the reaction rate constants agree for the analogous values for n-butylbenzene (Table 5).

Many other results confirming the probable future value of this research technique for the investigation of the relation between the reactivity of the molecule and its chemical structure are quoted in the literature[92,93,102].

b. The restoration of polarisation in longitudinal magnetic fields. The effect of external magnetic fields on the polarisation of the μe decomposition when muonium interacts with unsaturated compounds revealed the presence[103-105] of as a rule two polarisation components. The first component, which is independent of the strength of the transverse magnetic field, is due to a substitution reaction with formation of diamagnetic molecular products containing muonium. The second component depends on the longitudinal magnetic field; however, both the initial (at $H \simeq 0$) polarisation and the critical magnetic field strength are not consistent with the hypothesis of a simple Paschen–Back effect associated with the prevention of depolarisation owing to the uncoupling of the magnetic moments of the μ^+-meson and the electron in a free (isolated) muonium atom.

Table 5. Ratio of the rate constants for the reactions of muonium with alkylbenzenes.

Compound	$(k_1+k_2)\times10^{-9}$	k_2/k_1	$k_1\times10^{-9}$
C_6H_6	3.4±0.3	10.5±4.2	0.30±0.11
$C_6H_5CH_3$	3.3±0.4	3.3±1.0	0.77±0.20
$C_6H_5C_2H_5$	3.6±0.8	2.4±0.8	1.05±0.30
$C_6H_5C_4H_9$	4.3±0.9	1.4±0.3	1.8±0.6
$C_6H_5C_6H_{13}$	5.7±1.0	0.78±0.22	3.2±0.7
$C_6H_5CH(C_2H_5)C_3H_7$	4.3±0.9	1.4±0.3	1.8±0.6

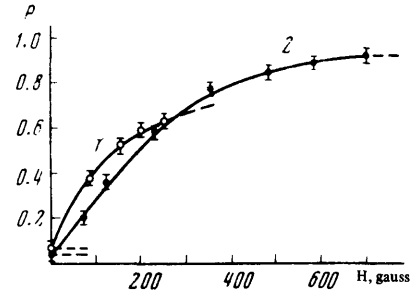


Figure 16. Variation of polarisation with longitudinal magnetic field strength. The lower dashed lines correspond to polarisation in a transverse magnetic field: 1) benzene; 2) naphthalene.

In these cases when a muonium atom adds to a multiple bond forming a radical with an unpaired electron, a complex system of spin interactions of the magnetic moments of the delocalised (in the general case) electron, the μ^+- meson, and the adjacent nuclei (protons) in the molecule is achieved and leads to depolarisation. The latter is removed when the strength of the longitudinal magnetic field corresponds to a change in the average effective distance between the meson and the delocalised electron in the molecule, the limiting asymptotic value of the polarisation corresponding to the overall rate of interaction via the molecular (component independence of the transverse magnetic field strength) and radical reaction pathways.

We shall consider as an example the results obtained[105] for the restoration of polarisation in crystalline benzene (−196°C) and naphthalene (30°C) specimens. The reason for the use of a solid phase is that molecular rotation during the period of observation may lead to an averaging of the interactions of the magnetic moments[87]. If the moment of inertia of the molecule is sufficiently high, the rotation during a period of the order of the lifetime of the μ^+-meson can be of course neglected. Fig. 16 shows that the polarisation is restored along curves with different parameters and there are differences between both the asymptotic limits to which the polarisation tends with increasing field strength and between the critical magnetic field strengths. Using the overall values for the reactivity

of benzene obtained by the method of competing acceptors, we find that at $-196°C$, $P = 0.79 \pm 0.03$, which is in satisfactory agreement with the asymptotic limit (Fig. 16). The estimates based on the difference between the reactivities of benzene and naphthalene in reactions involving addition to a multiple bond[86,106] show that, within the limits of the accuracy of the measurements, the asymptotic polarisation limit for naphthalene should be unity, in agreement with experimental data.

The difference between the critical magnetic field strengths (86 ± 6 G for benzene and 168 ± 11 G for naphthalene) is qualitatively consistent with the hypothesis concerning the effect of quaternary carbon atoms on the distribution of the probability density of the unpaired electron in the $C_{10}H_8Mu^{\cdot}$ radical. Quantitative analysis of the results requires detailed quantum-chemical calculations. Adopting the very rough approximation that the nature of the interaction of the magnetic moments of the μ^+-meson and the electron in the radical is the same as in the muonium atom and depends only on the average effective distance (r_{eff}), we obtain $r_{eff} = 1.40 \pm 0.03$ Å for benzene and $r_{eff} = 1.12 \pm 0.02$ Å for naphthalene. Without carrying out a specific physical interpretation of these values, we shall only point out the high experimental (but not computational) accuracy of the determination of r_{eff}.

4. Other Types of Interaction of Muonium

Like atomic hydrogen, the free muonium atom can also enter into redox reactions with variable-valence ions involving electron transfer (for example, $Mu + Fe^{3+} \rightarrow \mu^+ + Fe^{2+}$). However, these reactions are less specific for muonium, since, firstly, the indeterminacy of the further behaviour of the meson (or of the system in which it is incorporated) remains, secondly, the interaction with a solvent, which is inevitably present, becomes important, and, thirdly, the role of conversion exchange is much more pronounced for paramagnetic species.

Certain experiments on Cu^{2+}, Fe^{2+}, and Fe^{3+} ions[93] showed that the accuracy of the determination of the rate constants for the reactions of muonium in these cases is low and there is only a qualitative correspondence with the analogous reactions of atomic hydrogen investigated in the radiation chemistry of aqueous solutions[107]. The study of redox reactions with ions in solution is most promising for processes involving positronium, since there is for the latter a specific relation between the lifetime and the change in electronic state.

Conversion exchange is most important for compounds with unpaired electrons (NO, O_2, etc.). Despite the high rates of chemical reactions with these compounds, conversion exchange involving them predominates and the cross-sections for the processes are close to the gas-kinetic collision factors[94].

Interesting possibilities arise in the study of diamagnetic molecules incorporating muonium under conditions where there is a relation between the magnetic moments of the μ^+-meson and of an adjacent nucleus. Precession in a magnetic field which is not strong enough to uncouple the magnetic moments of the meson and the nucleus should be determined by the overall magnetic moment and the spin of the system. In particular, as a result of the vector addition of the magnetic moments and the spins of the proton and meson, the precession frequency in the transverse field for certain states of the MuH molecule should be 0.343 and the asymmetry coefficient should be half of the corresponding value for the precession of the μ^+-meson incorporated in the molecule. This constitutes the basis of one of the possible ways of identifying individual products[91] formed in the reactions of muonium with matter.

Among other aspects of the application of the μ^+-meson and muonium, we may mention the study of their interactions with a crystal lattice, which is of interest for the physics of solids and semiconductors. The slow (of the order of several microseconds) depolarisation effect during the time of observation found for a number of substances (B_4C, LiH, etc.[90,108]) is significant in the study of the spin–lattice relaxation of a polarised ion, of crystal structures, and of the role of local magnetic fields. In semiconductors[109,110] the introduction of alloying additives and also a change of temperature revealed a complete spectrum of polarisation changes as a function of the concentration of charge carriers in the specimen. Identification of the precession of triplet muonium in germanium single crystals at 77°K demonstrated[110] a low contribution by the exchange interaction with the electrons of the medium under the given conditions. The role of possible conversion exchange processes involving the lattice anions has been elucidated for the single crystals of a number of alkali metal halides[111,112]. The study of crystal lattice defects demonstrated that the latter are appreciable but do not alter the overall nature of the observed phenomena.

IV. MESONIC ATOMS

A number of very interesting effects are observed in the study of the effect of chemical structure on the atomic capture of μ^-- and π^--mesons in various substances. Negatively charged mesons retarded in a given medium are ultimately captured by atomic orbitals forming mesonic atoms in which they play the role of "heavy electrons". Initially the capture takes place usually in orbitals with high quantum numbers ($n = 10-15$) and then, as a result of a series of cascade transitions with emission of mesonic X-rays, the meson reaches the ground energy state in the inner $K(1s)$ shell of the given atom. As already stated, the radii of a mesonic atom orbital are close to nuclear dimensions and the atom of mesohydrogen, for example, behaves as a single electrically neutral particle. It can approach various nuclei and interact with them without the interference normally caused by the electrostatic repulsion between the nucleus and the proton. In particular mesonic hydrogen can behave as a kind of catalyst of the cold mesonuclear synthesis of helium from hydrogen[113].

In the capture of a μ^--meson, there arises both a characteristic mesonic X-ray emission spectrum and the lifetime of the μ^--meson in the 1s shell changes as a function of the atomic number z of the nucleus. By studying these factors in various compounds, it was possible to establish the probability of the atomic capture of μ^--mesons by individual components.

Theoretical hypotheses concerning the additivity of capture in a multicomponent system give rise to the expression (the Fermi–Teller z law)

$$W_i = \frac{n_i z_i}{\Sigma n_i z_i} \quad ,$$

where W is the probability of the capture of the μ^--meson, n the concentration of the atoms of the ith component, and z the atomic number. Numerous experiments showed that this relation does not constitute the rule but is a rare exception—it holds satisfactorily only for metallic alloys.

A detailed study[114] of the probabilities of the atomic capture of μ^--mesons in a number of oxides ($z = 4-82$) led to the conclusion that the ratio of the capture probabilities per nucleus of the given element $[W(z)]_\mu$ and oxygen $[W(0)]_\mu$ varies periodically. The experimental relation $[W(z)/W(0)]_\mu = f(z)$ is plotted in Fig. 17.

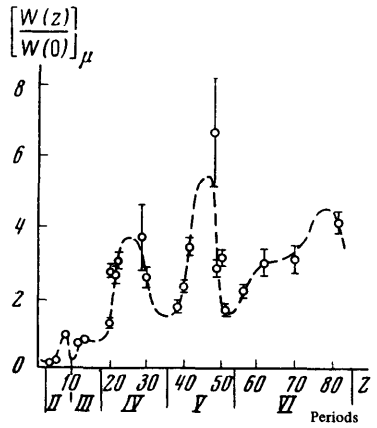


Figure 17. The ratio of the probabilities of the atomic capture of μ^--mesons in oxides. $W(z)$ and $W(0)$—probabilities of meson capture per nucleus z and per oxygen nucleus respectively.

Such periodicity is quite unexpected in terms of the concepts concerning the capture of mesons directly by atomic orbitals. However, it can be satisfactorily explained within the framework of the "model of large mesonic molecules"[115], according to which the mesons are initially captured by generalised mesonic molecular levels, the quantum numbers of which are so large that they correspond to the usual atomic dimensions (about 10^{-8} cm), despite the fact that the linear scale of mesonic atoms is smaller by a factor of 200 compared with the usual atoms. Thus the μ^--meson is located in an asymmetric double potential well (Fig. 18). The probability of the transfer of the meson to lower levels of one or other atom in cascade transitions to the region where the mesonic levels of the two atoms are separated depends on the properties of the electron shells of both. Clearly the periodicity of the structure of the outer shells of one of the atoms while that of the other remains unchanged (in the given case of oxides, this is oxygen) may lead to the appearance of a periodic variation of the probability ratio $[W(z)/W(0)]_\mu$.

The ratios of the probability of the capture of μ^--mesons by atomic orbitals are equivalent to the ratio of the effective atomic dimensions in complicated compounds. Thus there is a possibility of investigating the distribution of electron density in molecules, i.e. of a quantitative experimental determination of the amount of ionic character (covalence) of chemical bonds in polyatomic compounds.

The model of large mesonic molecules has been applied also to relations governing the capture of slow π^--mesons in mixtures and in chemical compounds involving hydrogen. In hydrogen such capture is accompanied by a charge-transfer reaction:

$$\pi^- + p \rightarrow \pi^0 + n$$

(the capture takes place partly according to the mechanism $\pi^- + p \rightarrow \gamma + n$) and the resulting slow π^0-meson decomposes after about 10^{-16} s into two γ-quanta moving apart at an angle of 180°C. In the capture of π^--mesons in complex nuclei, there is no charge transfer or the second process indicated above; in this case the capture of π^--mesons is accompanied by the ejection of numerous nucleons ("star"). Therefore the determination of the yield of π^--mesons, for example, by recording the coincidences due to the 2γ-quanta, constitutes a reliable criterion for the determination of the fraction of π^--mesons captured in complex systems by hydrogen atoms.

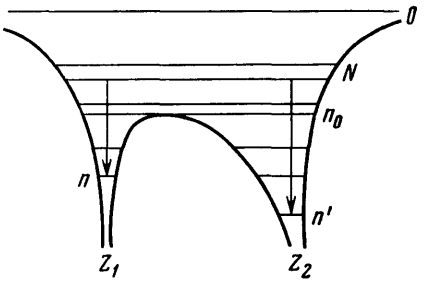


Figure 18. Schematic representation of the meson levels in an asymmetric diatomic molecule z_1z_2. The levels above n_0 are common mesomolecular levels; the mesonic atomic levels z_1 and z_2 are shown below.

It has been shown in a series of studies[116-118] that the ratio of the probabilities of the capture of slow π^--mesons by protons and nuclei with a charge Z differs sharply for simple mixtures and chemical compounds (Z and H). Whereas for $Z_m + (H_2)_n$ mixtures the ratio is $[W(H)/W(Z)]_\pi \simeq 2n/mz$, in binary compounds of analogous composition the ratio is smaller by a factor Z^2. For example in the $N_2 + 2H_2$ gas mixture the probability of the capture of π^--mesons by hydrogen is 30%, while in hydrazine (N_2H_4) the probability is reduced almost to 1/200. The finding that $[W(H)/W(Z)]_\pi$ depends on the nature of the chemical bond is even more interesting. Thus for ethylene (C_2H_4) $[W(H)/W(Z)]_\pi$ is higher than for acetylene (C_2H_2) by a factor of 2.5 and not 2. Thus fine differences between the $H_2C{=}CH{-}H$ and $HC{-}C{\equiv}H$ bonds are shown in the capture of π^--mesons, and are probably reflected in a slightly higher C–H bond energy in acetylene compared with ethylene.

We may note that the method applied provides a sensitive criterion for the determination of the difference between hydrogen involved in exchange interactions (in the molecule) and free hydrogen[119], which is very useful for the elucidation of many problems in structural chemistry, kinetics, and catalysis of chemical reactions. In particular, such problems may include the kinetics and catalysis of reactions of the type $Z + H_2 \rightarrow Z_mH_n$, the nature and kinetics of adsorption, sorption, and chemisorption phenomena, the role of water of crystallisation in compounds, the structure of ice at low temperatures, and the nature of hydrogen bonds.

As an illustration, one may point to the lower probability of the capture of π^--mesons by hydrogen in titanium hydrides[120] compared with the theoretical values, which is

probably due to the characteristics of the hydrogen bond in pseudohydrides. Although the nature of the hydrogen bond with the metal in compounds of this kind has not been finally elucidated, it has been suggested that in pseudohydrides the hydrogen is partly involved in chemical interactions and partly ionised and exists in the form of a proton gas[121]. Since only chemically combined hydrogen is involved in the capture of π^--mesons, it is reasonable to expect a lower probability of their capture in pseudohydrides compared with the usual hydrogen-containing compounds. Thus the result obtained confirms the above hypothesis: it is also possible to estimate the fraction of ionised hydrogen (protons) in pseudohydrides. Experiments on the problem of the spatial and temporal delocalisation (this problem has been considered theoretically by Blyumenfel'd et al.[122]) of π^--mesons among systems comprising several identical ZH groups in symmetrical compounds of the type $R(ZH)_q$,[120] and also on the problems of the determination of the amounts of ionic character of O–H bonds in various oxygen-containing acids, are being carried out. A number of interesting data concerning the intensity ratio of π^--mesonic X-ray emission lines associated with changes in chemical structure have been obtained[123].

At the present time both the development of theoretical concepts and of the techniques of mesochemical experiments are far from complete. Nevertheless, comparison of the experimental probabilities of meson capture with theoretical estimates already yields very interesting data. So far, experiments with μ^-- and π^-- mesonic atoms reduce as a rule to the study of the effect of the known properties of various compounds on the catpure characteristics. The converse problem now arises in nuclear chemistry—the employment of the properties of mesoatomic systems to obtain hitherto unknown characteristics of chemical bonds, i.e. the problem of creating mesochemical research methods.

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The scope of studies with the aid of elementary particles constitutes, as a whole, a novel set of nuclear-physical methods which may prove suitable for the solution of many physicochemical problems. The principal aim of this review was to outline the range of problems where these methods yield information of interest for chemical research. Undoubtedly further expansion of studies in this field will reveal other important aspects of the application of the chemistry of new atoms.

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