Applications of Nuclear Methods to Chemical Physics

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Ten years ago the U.S. National Academy of Sciences and the National Research Council jointly published a current review on nuclear chemistry.[1] Its introduction ended with the words: "It is difficult to give a universally acceptable definition of nuclear chemistry. For the purposes of this survey, included as research in nuclear chemistry are: most of the research of nuclear structure, reactions, and radioactive transformations being carried out by persons trained as chemists; research by chemists on atomic and molecular phenomena, insofar as nuclear processes are involved more than incidentally; and research by chemists on geological, astronomical, or other problems, where nuclear processes are intimately involved."

In the present survey preference will be given to such aspects of nuclear chemistry as the interconnection and mutual influence of transformations of atomic nuclei and elementary particles and the properties of their molecular and crystalline environment.[2-5]

Such an approach can be illustrated schematically as in Figure 1, which shows the position of nuclear chemistry in present science and its partial overlap with three other sciences, namely, with nuclear physics, chemical physics, and radiochemistry. The overlap of nuclear chemistry with chemical physics will be the main topic of this Account.

Chemical physics, as defined by one of its founders, Nobel Prize winner Professor Nikolai N. Semenov,[6] is the physics of chemical conversions and of the structure of molecules. It is particularly important for the progress of chemistry that chemical physics has introduced into chemistry a physical approach to chemical methodology, and to some extent, the physical attitude of mind.

The creation of chemical physics was stimulated by the spread of theoretical physics and experimental physical methods. At the early stage of chemical physics, workers in this field largely used the ideas and methods of atomic physics and electronics. Beginning with the middle of our century, chemical physics made use of an increasing number of nuclear phenomena, nuclear instrumentation, nuclear methods, and even ideas taken from nuclear and elementary particle physics.

Nuclear properties are represented in most modern methods of chemical physics, in the studies of the structure of matter and of various chemical conversions, since such methods imply various hyperfine interactions between the nuclei and their electronic environment. However, in writing here about the nuclear applications to chemical physics we restrict ourselves to methods based on transformations of nuclei and elementary particles and imply that such transformations can be affected by the molecular and crystalline environment. They can, therefore, serve as probes, which sense and respond to the properties of the environment and their changes.

Several phenomena of nuclear and elementary particle physics displaying environmental effects, e.g., Mössbauer effect, annihilation of slow positrons, and decay of pions and muons, have been explored by our department (now called the Section of Structure of Matter) at the Institute of Chemical Physics of the Academy of Sciences, U.S.S.R. Some results of these studies are described in the present survey.

Mössbauer Spectroscopy and Some Problems of Chemical Physics

Most attention was given to the field of chemical Mössbauer spectroscopy, which we entered 15 years ago. The problems investigated and the main results have been described in two books[7,8] and in several surveys

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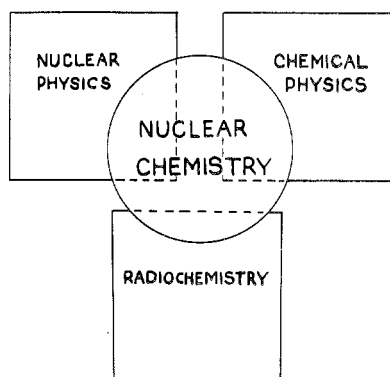
Figure 1. Scheme of arrangement of nuclear chemistry between nuclear physics, chemical physics, and radiochemistry.

presented at various national and international conferences devoted to use of the Mössbauer effect in structural chemistry,[9] in the studies of organometallic compounds,[10] of surface phenomena[11] and heterogeneous catalysis,[12] in study of the physics and chemistry of polymers,[13] and to γ-ray lasers.[14] I will dwell here on only two lines illustrating the fruitfulness of the use of Mössbauer spectroscopy in investigations carried out by chemical physicists.

Electron Delocalization. It should be emphasized that one of the main problems of modern chemical physics is the relation between the structure of molecules and their reactivities. It must be made clear why and how the change of the electronic state—of some atom or some group—can lead to chemical conversion of molecules, or to a conformational transition or to any other kind of motion on a molecular, macromolecular, or cellular level. That is, we must elucidate the causal relation and the ways and mechanisms of transmission and perception of the signal starting this causal relation. Purely structural, static data are insufficient for the solution of these important problems; dynamical information is also needed. Like all other methods using hyperfine interactions, and even to a much larger extent, Mössbauer spectroscopy is highly informative from both a structural and dynamical point of view, and that accounts for its particular value.

It may well be that the most fundamental problem of chemical physics at present, one where the combination of static and dynamic structural information is of particular importance, is the problem of spatial and time-dependent delocalization of electrons in molecules or more complex systems.[15] It is obvious that, if we deal with a system of two potential wells separated by a barrier, then the levels located above this barrier

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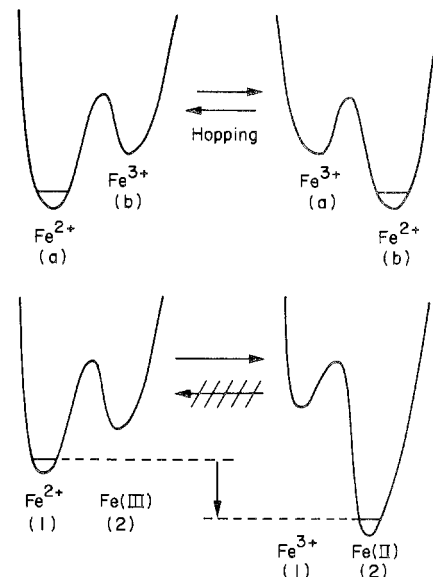
Figure 2. Schemes of the spatial and time-dependent delocalization of electrons in systems possessing two potential wells each. (a) Upper case: two potential wells of left and right systems (if both these wells are without or with an electron) are the same, and therefore the right system is a mirror reflection of the left system. (b) Lower case: left and right potential wells of Fe(III) as well as of Fe(II) are different, e.g., one well corresponds to a high-spin, the other well to a low-spin state of iron. Therefore the right and left systems are completely different and possess different energies.

belong to neither the left nor the right well but describe the whole system. The system is more complicated for subbarrier levels. Let us treat, for example, the simplest case of behavior of some particle, e.g., of an electron in two equal potential wells, when the electron is occupying some of the subbarrier levels. It would seem that in this case we may consider an electron as being either in a left (wave function ψ_l) or in a right (wave function ψ_r) well. However, neither the state with the electron in the left well nor the state with the electron in its right well is in fact the eigenstate of such a system. The eigenstates are the symmetric $\psi_s = (1/2^{1/2})(\psi_l + \psi_r)$ and antisymmetric $\psi_a = (1/2^{1/2})(\psi_l - \psi_r)$ combinations of wave functions ψ_l and ψ_r with their energies differing by $\Delta E_{as} = \hbar/\tau$. The magnitude of the energy splitting is thus related to the characteristic time of delocalization, τ_d, or, in other words, the time of electron oscillation (or hopping) between the left and right wells. Only if this time, τ_d, is long compared to the characteristic time of measurement of the given experimental method (τ_{exp}) can one observe spatially localized states ψ_l and ψ_r, e.g., the left- and right-handed forms of optically active organic compounds.

One should take into account that the appearance of an electron in one of the two potential wells changes the interaction of this particular well with the environment, destroys its identity with another well, and decreases the delocalization probability, in other words, increases the hopping time. For example, if we put an electron into a system where two equal potential wells are represented by two equal high-spin ferric Fe^{3+} ions (ion a and ion b), the wave function ψ_l will now describe the state $Fe_a^{2+} - Fe_b^{3+}$, and the wave function ψ_r the state $Fe_a^{3+} - Fe_b^{2+}$ (Figure 2a). Each of the two (a and b) ions appears to spend half of the time in the high-spin ferrous state, Fe^{2+}, and the other half in the ferric state, Fe^{3+},

Fe^{3+}. The characteristic time of measurement in Mössbauer spectroscopy is the mean lifetime of the excited Mössbauer level: $\tau_{exp} = \tau_M$, which in the ^{57}Fe case is equal to $\tau_M = 1.4 \times 10^{-7}$ s. If the time of the hopping of the electron between two wells is comparable to the lifetime, $\tau_d \gtrsim \tau_M$, two Mössbauer spectra representing both Fe^{2+} and Fe^{3+} will be observed. On the other hand, if the hopping time is much shorter than the Mössbauer transition time, $\tau_d \ll \tau_M$, only one spectrum will be observed. This spectrum will be representative of some intermediate (between Fe^{2+} and Fe^{3+}) valence state. In such a way Mössbauer spectroscopy allows us not only to establish the very fact of spatial delocalization of electrons but also to investigate in a quantitative way the time scale appropriate to the hopping of electrons between various states.

The use of emission Mössbauer spectroscopy opens new possibilities. Suppose that two potential wells, e.g., two ferric ions, differ in their properties even in the absence of an additional electron, e.g., one of them is in a high-spin state and the other in a low-spin state (Figure 2b). In this case the presence of an additional electron in one of these potential wells would be energetically more favored than its presence in the other well and, consequently, only one of two possible states—the lower state—is often represented in ordinary (absorption) Mössbauer spectra.

However, let us assume that at the moment of formation of the excited Mössbauer nuclear level the corresponding atom finds itself in an upper, unstable electronic state of the system and only later is the system transformed into a stable state, with the characteristic time of transformation being close to or longer than the lifetime of the Mössbauer level. In this case it would be possible to detect in the emission Mössbauer spectra the contribution of the initial unstable state of the system. This can be particularly important for short time intervals just after the formation of Mössbauer level. (The case represented in Figure 2b deserves special attention as an example of a very peculiar kinetic problem of the potential barrier between initial and final states, the shape of which depends on the direction of reaction (one shape of barrier for A → B, another shape for the inverse B → A reaction).)

We have tried to use and to study all of the above-mentioned circumstances by combining the simple (absorption) Mössbauer method with the additional possibilities of emission spectroscopy. In such a way we have succeeded in obtaining fairly extensive evidence on electron delocalization. This, it may be emphasized, has been done for inorganic compounds, while earlier studies of this problem of chemical physics, using the ESR method, were devoted, as a rule, to organic compounds.

The results obtained are briefly as follows. The phenomenon of superexchange (indirect) induction of magnetic fields on the nuclei of diamagnetic atoms,[16] found for tin introduced in yttrium–iron ferrites–garnets, is an interesting consequence of the spatial delocalization of electrons. All spectral parameters—the isomer shift (equal to that of SnO_2), the zero quadrupole splitting (showing the identity of all tin bonds), the high value of the recoil-free fraction and its weak temperature dependence—confirm the absence of direct Sn–Fe bonds and the existence of only Sn–O–Fe bonds.

Nevertheless, the six-component Zeeman splitting of the Mössbauer line indicates a quite strong magnetic field at the tin nuclei (ca. 200 kOe at 77 K), which vanishes only at the Curie point, simultaneous with the disappearance of the magnetic splitting of the iron spectral lines. The sign of the field is the same as of the magnetic field at iron in the octahedral sublattice.[17]

Measurements of the conductivity and its temperature dependence have shown that the magnetic effect of the unpaired iron electrons could not pass to tin via the conduction electrons, and thus we deal here with delocalization of iron 3d electrons in an inorganic system with only σ bonds. Such delocalization shows in the polarization exchange interaction of an unpaired iron electron with the inner s electrons of tin.

Another peculiar example of electron delocalization was observed by Makarov et al.[18] for the antimony compounds Cs_2SbCl_6 and $RbSbCl_6 \cdot 2Rb_3SbCl_6$, from the Mössbauer spectra of ^{121}Sb ($\tau_M \sim 3.5 \times 10^{-9}$ s). Two lines, corresponding to trivalent ($SbCl_3^{3-}$) and pentavalent ($SbCl_5^-$) antimony, were observed in the absorption spectra at 80 K. However, at a higher temperature (130 K) there appeared additional complex lines between the isomer shifts associated with Sb(III) and Sb(V), i.e., lines formally corresponding to tetravalent Sb(IV). The fraction of this state in the spectra increased with temperature, while the fractions of Sb(III) and Sb(V) decreased. At 130 K more than 30% of the antimony was found to be in the Sb(IV) region of spectrum. Calorimetric and ESR data showed the absence of phase transitions (at least of first order), and no electrons in conduction bands could be observed in the compounds studied.

The authors came to the conclusion that they were observing the fast hopping of electron pairs: Sb(III) ⇌ Sb(V), with a short characteristic time, $t < \tau_M$ (see also the survey[19]). This research is continuing, with particular attention being paid to the shape of the intermediate antimony line over a broader temperature range.

The last example I am going to use here in illustrating the applications of the Mössbauer effect to the study of electron delocalization seems to be of particular interest. It deals with compounds known to all chemists from early college years—the ferricyanide–ferrocyanide complexes called Prussian blue and Turnbull's blue. Even in the first years of Mössbauer spectroscopy it was shown in many laboratories that, whatever the preparation of these complexes (see Figure 3), only one product was obtained, namely, Prussian blue, with low-spin ferrous (Fe(II)) ions in the sites having carbon atom nearest neighbors, i.e., surrounded by strong-field ligands, and high-spin ferric (Fe^{3+}) ions in sites having nitrogen atom nearest neighbors, i.e., surrounded by weak-field ligands. The impression was that Turnbull's blue does not exist at all and that the electron is

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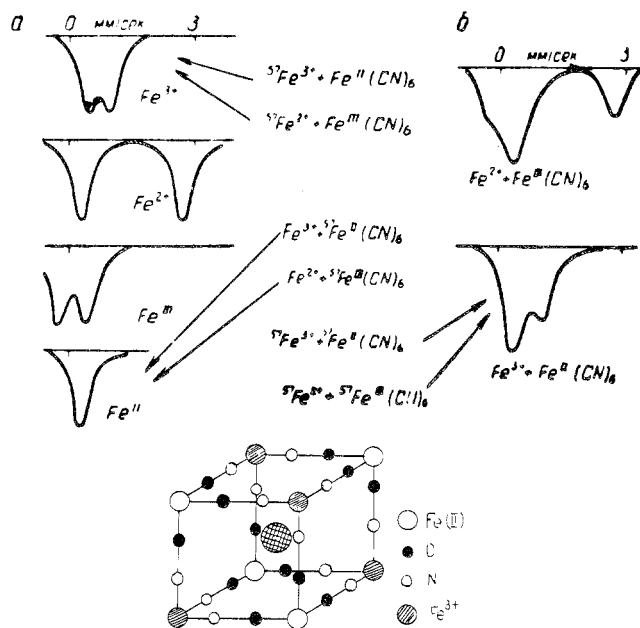
Figure 3. Mössbauer spectra of ferricyanide–ferrocyanide complexes: (a) spectra of high-spin and low-spin ferric and ferrous iron; (b) spectrum of Turnbull's blue (upper) and Prussian blue (lower). Only the spectra shown by arrows are realized in corresponding interactions. The structure of ferricyanide–ferrocyanide complexes is also given.

Figure 4. Emission Mössbauer spectra of cobaltoferricyanides, $^{57}Co^{2+}[Fe^{III}(CN)_6]$, taken with variable delayed coincidence between the 123-keV pre-Mössbauer γ-ray and the 14-keV Mössbauer γ-ray. Upper: integrated over the time of delay ($t = 0-\infty$); lower; with the gate of delay: $t = 0-60$ ns. Narrow Fe^{3+} doublet and broad Fe^{2+} doublet are shown.

localized on the low-spin iron in all ferricyanide–ferrocyanides.

Such a conclusion was particularly convincing for experiments based on the method proposed by us as early as 1965 and called "Mössbauer effect as an analyzer in a tracer method".[20,21] This technique is particularly convenient for the study of structures, of kinetics, and of mechanism of transformations of systems containing Mössbauer atoms in various functional states. In the case of ferricyanide–ferrocyanides, Mössbauer spectra were obtained which showed the presence of four different forms of iron involved in these complexes. The ^{57}Fe label was introduced either into one or into both interacting forms (Figure 3).

Besides confirming the production of Prussian blue, but not Turnbull's blue, in all cases investigated,[22] the method of Mössbauer isotope labels provided evidence that the sequence of formation of soluble and insoluble ferri–ferrocyanides was quite different, sometimes even completely opposite to what was believed before. It also showed that the ionic isotope exchange proceeded via the solution. However, these problems will not be discussed here, and we pass to experiments on emission Mössbauer spectroscopy.

Emission spectra of complexes with labeled cobalticyanide anion ($[^{57}Co^{III}(CN)_6]^{3-}$) and labeled cobaltoferricyanide ($^{57}Co_3[Fe^{III}(CN)_6]_2$) gave important additional information concerning the peculiar intramolecular oxidation–reduction conversion in ferri–ferrocyanides, where low-spin iron acts as oxidizer and the high-spin iron as reductant.[23]

A well-defined doublet assigned to the ferricyanide anion was observed in the emission spectra of cobalticyanides ($M^{n+}[^{57}Co^{III}(CN)_6]^{3-}$) with cations $M^{n+} = Ni^{2+}$, Co^{2+}, Cu^{2+}, Fe^{3+}. In such a way evidence was obtained that K capture in ^{57}Co as such does not change the chemical state of the product (iron) compared to the oxidation state of the initial cobalt. However, the emission spectrum of ferrocobalticyanide (Fe^{2+}-$[^{57}Co^{III}(CN)_6]^{3-}$) was that of a typical ferrocyanide singlet, which means that the electron passed inside the coordination sphere. Similar results were obtained from emission spectra of cobaltoferricyanide ($^{57}Co^{2+}$-$[Fe^{III}(CN)_6]^{3-}$); a typical narrow doublet of high-spin ferric iron was observed.

Combination of emission spectroscopy with delayed γ,γ coincidences of pre-Mössbauer 123-keV and Mössbauer 14-keV γ rays made it possible to introduce the time factor. Detailed observations of emission spectra of cobaltoferricyanide showed a broad doublet corresponding to the Turnbull's blue cation, that is, corresponding to high-spin ferrous iron, Fe^{2+}. The fraction of this state was quite small (ca. 7%) in Mössbauer spectra integrated over all γ,γ coincidences delay times (from 0 to ∞) as shown in Figure 4. However, when γ,γ coincidences were selected by the delay gate from 0 to 60 ns, the Fe^{2+} fraction increased to ca. 30%. In such a way we were able to detect the previously elusive Turnbull's blue and to estimate as 10–20 ns (at 80 K) the duration of intramolecular transfer of the electron converting this compound to Prussian blue.[23] More detailed conclusions concerning the mechanism of electron transfer require further emission spectroscopic measurements at lower temperatures.

A development of the method described above would seem to be very promising for study of electron transport in biological materials, e.g., in organelles such as mitochondria and chloroplasts and in heterogeneous and homogeneous catalytic processes.

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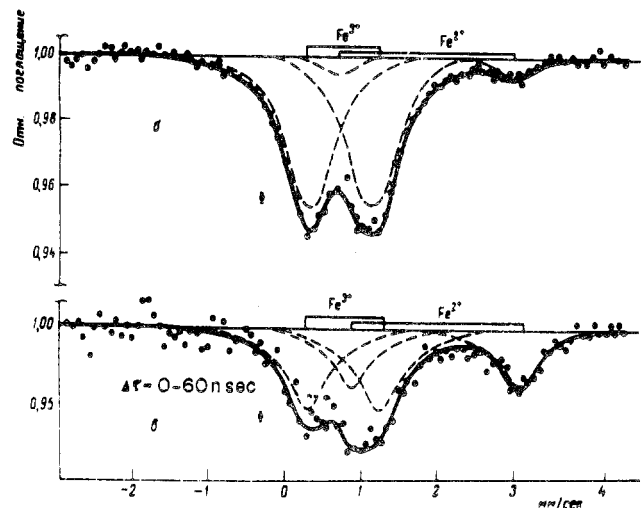(23) V. P. Alekseev, V. I. Goldanskii, V. E. Prussakov, A. V. Nefedjev, and R. A. Stukan, *Sov. Phys. JETP Lett. (Engl. Transl.)*, **16**, 43 (1972).

On γ-Ray Lasers (Gasers). Mössbauer measurements are known to hold a high record in relative precision, fixing changes in γ-ray energies of less than 10^{-15}–10^{-16}, thus exceeding the relative precision of NMR by five or six orders of magnitude. However, the absolute values of Mössbauer transition energies typically amount to several tens of keV, being in such a way almost a trillion times larger than the energies of NMR transitions. The spread of local electric and magnetic fields in crystals, the existence of various defects, dislocations, etc., lead to the appearance of very strong inhomogeneous broadening of spectral lines.[14,24,25] Such broadening is much more important for Mössbauer spectra (because two different nuclei emitter and absorber participate in these transitions) than in NMR spectra where two sublevels of the same nucleus are involved. Therefore, the smallest values of the Mössbauer line width obtained so far are ca. 10^{-10} eV, which is ten million times broader than the narrowest NMR lines (for liquids). This circumstance was decisive in the failure of all earlier attempts to create gasers—attempts that were dropped some 12 years ago. However, fundamentally new ideas of gaser creation were put forward recently in the U.S.S.R.

First, there is the design of gasers based on lines of a relatively large natural width (with lifetimes up to ca. 0.01 s) requiring very intense neutron impulse beams for their pumping. The first estimate of the necessary neutron fluxes[26] gave a value of 10^{19}–10^{20} cm^{-2}. Later, ideas of two-stage pumping and of use of the Borrmann effect indicated the possibility of decreasing these fluxes by two to four orders of magnitude. This variant was developed mainly by Kagan and the author.[14,24,25,27]

Second is the design of gasers based on relatively long-lived radioactive crystals (with lifetimes up to ca. 1000 s), but using new ideas about the suppression of inhomogeneous broadening of Mössbauer lines. This approach was started by Khokhlov,[28] who also showed how to suppress the inhomogeneous broadening due to quadrupole interactions, by combination of Mössbauer and NMR methods. Later on we proposed means for the suppression of another source of broadening, which is most specific for Mössbauer spectroscopy, namely, the distribution of chemical (monopole) shifts. These means are based either on the proportionality between small variations in spin density and total density of the s electrons at the nucleus, as in the case of Fermi contact interaction,[27] or on the motion of γ-emitting atoms in periodic fields.[29] Letokhov has developed an ingenious laser method of separating excited Mössbauer emitters from the same nuclei in the ground state.[30]

Research on creation of gasers seems to be of particular interest for chemical and biochemical physics—in connection, for instance, with the problem of microholography. Even if the gaser as such is unattainable, any success in the narrowing of Mössbauer spectral lines is of high importance for

practically all natural sciences.

Positron Annihilation as a Tool in Chemical Physics

Among the phenomena of elementary particle physics which can be used as a tool of chemical physics is the annihilation of positrons, and we have focused considerable attention on this field. The results of these studies were summarized in a book[31] and in several surveys or invited talks at International Positron Annihilation Conferences.[2-5,32-37] Slow positrons annihilate with electrons via three mechanisms: in quasi-free collisions (free annihilation), by attachment to molecules (e^+M) or to anions (e^+A^-), and by the formation of a bound positron–electron system, the positronium (Ps) atom. This atom was discovered in the United States in 1951 by Martin Deutsch, and is the lightest atom in the universe (919 times lighter than hydrogen), being the only atom without a heavy nucleus. It can exist in two forms in the ground (1s) state: as triplet or orthopositronium ($^3S_1$), with a lifetime of 1.4×10^{-7} s and 3γ annihilation, and as singlet or parapositronium ($^1S_0$), with a lifetime of 1.25×10^{-10} s and 2γ annihilation.

Both the probability of positronium formation and its subsequent fate depend on the properties of the environment. The inhibition (suppression) of Ps formation and its quenching (i.e. acceleration of annihilation of ortho-Ps) belong to the main phenomena studied by the annihilation method—many examples of such processes studied in our laboratory are listed in Table I.

Because of the very short lifetimes of e^+ and Ps in matter, their steady-state concentrations in routine experiments using radioactive sources (^{22}Na, ^{64}Cu) do not exceed several particles per centimeter cubed. Therefore any classical chemical methods for the detection of these species are certainly inapplicable here. But the detection of various types of γγ coincidences opens up the possibility of following the fate of every single positron or Ps atom and of studying the inhibition of positronium formation and its quenching by processes which increase the rate of annihilation of orthopositronium.

By supplementing the time and angular (or energy) characteristics of γγ coincidences with broad variations in external conditions, such as medium composition, admixture concentrations, temperature, pressure, etc., it is possible to obtain comprehensive chemical information about the behavior of positrons and Ps atoms and about the dependence of this behavior on the properties of the environment.

A positron can be treated as a specifically labeled electron, and positronium as the lightest radioactive

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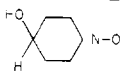
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Table I

Inhibition of Positronium Formation

Inhibition by capture	(a) Annihilation from the bound state: $e^+ + NO_3^- \rightarrow e^+ NO_3^- \rightarrow 2\gamma$;	(liquid)
	(b) With dissociation: $e^+ + R - HaL \rightarrow R + e^+ HaL$ $\underline{\qquad\qquad} \rightarrow 2\gamma$	(liquid)
Inhibition by slowing down	Excitation of vibrational, rotational and electron levels of M: $e^+ + M \rightarrow (e^+)' + M^+$ (acetone in acetic acid)	(liquid)

Positronium Quenching

Pick-off annihilation	$Ps + M \rightarrow e^+ (M^-) \rightarrow 2\gamma$	
	M: N_2, Ar, He (P up to 150 atm)	(gas)
	$CH_3(CH_2)_nX$; X = Br (n = 2, 5, 10, 11, 16); Cl, (n = 2, 3, 5, 13); OH (n = 0, 1, 3, 7, 11); CH_3 (n = 4, 6, 7, 9, 14)	(liquid)
Conversion	$^3Ps + M(\uparrow) \rightleftarrows {}^1Ps + M(\downarrow)$	
	M = NO, O_2 (gas); Co^{2+}, Mn^{2+}, Ni^{2+}, Fe^{2+}	(liquid)
Oxidation	$Ps + Fe^{3+} \rightarrow e^+ + Fe^{2+}$	
Substitution	$Ps + Cl_2 \rightarrow PsCl + Cl$	(gas, liquid)
Addition	$Ps + DPPH \rightarrow (PsDPPH) \rightarrow 2\gamma$	(liquid, solid)
	$Ps + (CF_3)_2NO \rightarrow [Ps(CF_3)_2NO] \rightarrow 2\gamma$	(gas)
Donor-acceptor interaction	$Ps + M(\colon C^+) \underset{t}{\rightleftarrows} (PsM) \rightarrow 2\gamma$	(liquid)

$^3Ps + ac(\uparrow) \rightarrow [Psac(\uparrow)]$ with branches to $^1Ps + ac(\downarrow)$ and 2γ

Conversion-chemical interaction	$ac = NO_2(gas)$:	(liquid)

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isotope of hydrogen, with all the characteristics of its radioactive decay, such as lifetime, number, or energies and angles of emitted γ rays, depending on the properties of the environment. Moreover, the variations of these parameters can be studied in an effort to understand the characteristics of the environment.

As a result of detailed research carried out since 1963 using both time and angular methods (i.e., measuring the lifetime of Ps and the angular correlation of annihilation γ rays) we succeeded in studying extensively the chemistry of extremely short-lived ($\tau \lesssim 10^{-7} - 10^{-9}$ s) radioactive atoms, including the kinetics and mechanism of their chemical interactions. The very short lifetime of Ps is an advantage, rather than an obstacle, in kinetic studies, because it serves as a reference in the determination of rates of ultrafast reactions and of the lifetimes of ultrashort-lived Ps-containing intermediates.

Let me mention briefly several examples of the results which were obtained by the positron method and which seem to be of general interest for chemical physics (or even for chemistry as a whole). To begin, I shall discuss the kinetics and mechanisms of chemical processes.

Our first application was to the determination of the mechanism of oxidation of H atoms by transition-metal ions in solutions. Two possible mechanisms of oxidation–reduction conversions in solutions have been discussed. One of these is assumed to involve electron transfer from reductant to oxidizer via long-range tunneling; the other, the formation of an intermediate complex consisting of the reductant–oxidizer pair. Radiation-chemical data on the reactions of H atoms and our observations of Ps interactions with Fe^{2+} and Fe^{3+} ions in aqueous solutions[38] yielded the values of the corresponding rate constants at room temperature.

It was known from radiation-chemical data that the reaction of H with Fe^{2+} proceeds via an intermediate complex. The mechanism of reaction of H with Fe^{3+} had to be established. It was observed that the ratio of rate constants of Ps and H atoms is practically the same both for Fe^{2+} and Fe^{3+} (ca. two orders of magnitude). This observation suggests the operation of similar mechanisms of reactions with these two ions. If tunneling were responsible for oxidation of H and Ps with Fe^{3+} ions, one would hardly expect the same strong difference between the rates of H and Ps oxidation as for their reactions with Fe^{2+} ions via a mechanism involving complex formation. A conclusion against the tunneling mechanism in such types of interactions was made also by A. N. Frumkin in studying the kinetics of electroreduction of anions.

A further example of the application of positron annihilation studies is to elucidate the distinction between diffusion and kinetic factors for reactions in solutions, even at very low activation energies.[39] This method was tested for positronium quenching by stable free radicals such as diphenylpicrylhydrazyl (DPPH) and 2,2,6,6-tetramethyl-4-oxopiperidine 1-oxide (TMOPO). Experiments were performed in octanol (–12 to +130 °C), in diethyl ether (–90 to +25 °C), in cyclohexanol–acetone, and in glycerol–water mixtures (at room temperature).

The viscosity of the solutions was increased either by variations in the solvent composition (e.g., addition of small quantities of glycerol) at fixed temperature or by cooling of the pure solvent. In the first case the inverse reaction rate constant K^{-1} rises linearly with viscosity η; in the second, the K^{-1} vs. η dependence is stronger than linearity. The activation energy of positronium quenching, E_{Ps}, can be determined from experimental

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(39) V. I. Goldanskii and V. P. Shantarovich, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 809 (1970).
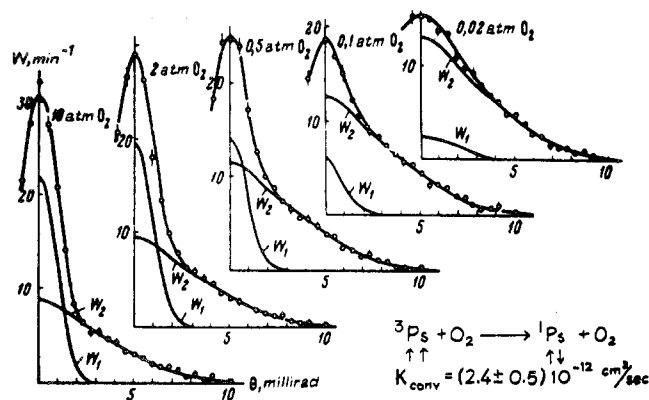
Figure 5. Angular correlation curves of 2γ annihilation in gas mixtures of argon and oxygen (argon pressure is equal to 120 atm).

results even against the background of the much higher diffusion activation energy, E_η ($E_{Ps} \sim 1$ kcal/mol; $E_\eta \sim$ 2–6 kcal/mol).

It is also possible to exploit positron annihilation methods in the study of fast reaction rates and of the lifetimes of short-lived intermediates. In such studies, carried out using angular correlation measurements for gas-phase quenching, positronium acts as a labeled analogue of the hydrogen atom. Small amounts of paramagnetic admixtures to an inert gas lead to a strong narrowing of the correlation curves for annihilation γ rays (Figure 5 shows the effect of addition of oxygen to 120 atm of argon[40]), and such narrowing could be used to obtain the ortho–para conversion rate constant. According to the results obtained in this way for NO, the sensitivity of the positron method in detecting free radicals in gases is ca. 10^{13} cm^{-3}.

Since the collision of Ps with a paramagnetic center yields an excited complex, and annihilation within such a complex does not show the narrow component of angular correlation, a necessary condition for conversion is that the complex decomposes before being stabilized by other collisions. Therefore, the shape of the correlation curves can serve to determine the lifetime of the complex, even if this time is as short as ca. 1% of the para-Ps intrinsic lifetime. Our experiments[41] have given lifetimes of excited complexes PsNO$_2$* and (CF$_3$)$_2$NOPs* as (1–2) $\times$ 10^{-12} s, whereas the lifetime of PsNO* is even shorter; even at several hundred atmospheres it decomposes before the next collision occurs.

Correlation curves similar to those in Figure 5, but changing in an inverse sequence (i.e., from left to right), are observed when increasing amounts of chlorine are added to 120 atm of oxygen.[42] This is due to the substitution reaction: Ps + Cl$_2 \rightarrow$ PsCl + Cl. In such a way one can determine the rate constant also of this type of reaction ($K = 4 \times 10^{-9}$ cm^3/s) and of the competing process of inelastic scattering of positronium atoms. Furthermore, knowing the cross section of substitution reactions and using the method developed in ref 43, it is possible to estimate the reaction

threshold, in other words, the corresponding binding energy for positronium (e.g., $Q_{Ps-Cl} \sim 2.2$ eV).

Passing next to an application of Ps chemistry to the study of structural problems we consider the high-sensitivity detection of carbonium ions in the structures of organic compounds. The data on Ps quenching by diamagnetic organic molecules show that the presence of a low-lying vacant molecular orbital makes these electron acceptors (ac) effective quenchers. The vacant orbital is involved in the formation of a Ps–ac complex, which either decomposes immediately to an ac anion and a free positron (with subsequent fast annihilation of the latter) or provides the 2γ annihilation of the positron within the complex. The carbonium ion (:C$^+$) represents a typical example of a functional group having a low-lying vacant orbital and acting both as electron acceptor and positron quencher.

The data on Ps quenching by large numbers of diamagnetic organic molecules, combined with calculations by the LCAO method, have confirmed that the diamagnetic organic positronium quenchers (which all possess conjugate bonds) actually contain a vacant electron level about 2 eV lower than that of benzene and aniline.

It was found that organic structures with a carbonium ion show particularly large quenching rate constants, between 10^{10} and 3.3×10^{11} L/mol-s, making the positron method an extremely sensitive probe for the presence of such structures.[37]

Finally we may consider the application of Ps techniques to the determination of the resistance of various functional groups in organic molecules to intramolecular redistribution of the electron density. The redistribution of electron density in molecules with conjugated bonds is known to be induced by donor (e.g., NH$_2$) and acceptor (e.g., NO$_2$) substituents. The magnitude of the inductive effect of amino and nitro groups directly bound to the benzene ring is similar, but opposite in sign. As a result, the *p*-amino group cancels the tendency of the *p*-nitro group to form a carbonium ion in the para position, and the positronium quenching rate for *p*-nitroaniline is two orders of magnitude lower than that for nitrobenzene:

$$R_B = \frac{K^P_{C_6H_4NO_2NH_2}}{K^P_{C_6H_5NO_2}} = \frac{10^8}{1.1 \times 10^{10}} \approx 9 \times 10^{-3}$$

One may take this ratio as being characteristic of the benzene ring property reflecting unit resistance of the functional group to intramolecular redistribution of electrons.

It is now possible to introduce groups of atoms into the chain between the NO$_2$ and the NH$_2$ groups. With increasing resistance of these bridges to electron redistribution, the quenching rate will obviously approach that for nitrobenzene. If there are μ bridges and β benzene rings in the chain, and the quenching rate constant equals K_X, then the resistance of each bridge (in R_B units) can be define as:

$$r_X = \frac{1}{\mu}\left(\frac{K_X}{K^P_{NA}} - \beta\right)$$

In the case of 4-nitro-4-aminophenyl phenyl sulfide (NH$_2$C$_6$H$_4$SC$_6$H$_4$NO$_2$) $\beta = 2$, $\mu = 1$, $K_X = 2.8 \times 10^9$ L/mol-s, so that $r_X = 26$. This implies that the –S–

(40) A. D. Mokrushin and V. I. Goldanskii, *Sov. Phys. JETP (Engl. Transl.)*, 26, 344 (1968).

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bridge resistance is 26 times higher than that of the benzene ring.

The results obtained in this way may prove useful in achieving a more complete description of the properties of organic semiconductors containing bridges such as -S-, -O-, -NH-, -CH=CH-, -N=N- between the aromatic rings in the structure.

Since this Account is restricted to applications of nuclear methods in chemical physics I shall not dwell here on radiation solid-state physics and the problems of radiation damage to various materials, and will only mention in passing that the positron method has recently become a very important tool in these fields and promises even more for the future.

Some Other Connections between Nuclear and Chemical Physics

I give now a short exposition of the field called mesochemistry. The main problem in this field is represented at present by muonium atoms, the μ^- and π^- mesic atoms and molecules.

The largest contributions to chemical physics of muonium were made principally by three research groups, those of V. G. Firsov and I. I. Gurevich in the U.S.S.R. and of Vernon Hughes in the U.S.A. (see the surveys, ref 33 and 44).

As to the chemistry of μ^- and π^- mesic atoms, pioneer experimental research was carried out by A. I. Mukhin, Yu. D. Prokoshkin, V. S. Evseev, and their colleagues on the Dubna synchrocyclotron, while a crucial part in interpretation of the results obtained was played by Ponomarev's model of "large mesic molecules".[45]

Only the application of the partial deuteration method to mesochemistry is mentioned here. Recently, this method has made it possible to establish the character of π^- distribution between various hydrogen-containing groups in multifunctional compounds.[46]

The charge-exchange reaction: $\pi^- + p \rightarrow \pi^0 + n$ is known to proceed only in normal hydrogen, but not in deuterium. Therefore, the comparison of charge-exchange probability in compounds such as $Z_mH_nZ'_pD_q$, $Z_mD_nZ'_pH_q$, $Z_mH_nZ'_pH_q$ allows a direct determination of the fractions of π^- mesons captured by hydrogen from Z_mH_n and from Z'_pH_q groups. Additional experiments with μ^- mesons[47] made it possible to observe the initial distribution of π^- mesons between Z and Z' atoms at the stage of mesic capture by atomic orbitals and to find considerable (1.5–8 times) deviations from the Fermi–Teller Z law even at this stage.

The totality of the data obtained to date shows the necessity of further development of modern theoretical ideas and of a general dynamic theory of highly excited states of mesic molecules. Such theories must take into account the formation, deexcitation, and decomposition of such molecules, including possible breaking of Z-(π^- H) bonds during the mesic intraatomic x-ray transitions, repeated formation of free mesohydrogen and its reentering the chemical interactions, the role of Cou-

lomb repulsion between various groups in multicharged positive ions, correlation between mesochemical as well as radiation-chemical processes, as for instance, the reactions between (π^- H) atoms and hot hydrogen atoms.

Among some other promising aspects of nuclear chemistry which deserve special attention, I will mention as an example the problem of the direct measurement of superstrong magnetic fields produced at nuclei for very short times by holes in the K shell.[48] This problem can probably be solved by comparing $\gamma\gamma$ and $e_K\gamma$ angular correlations, when the conversion K electron is detected instead of the first γ ray.

An interesting and specific effect of nuclear transformation in matter can be represented by shock waves expanding cylindrically around the tracks of fission fragments or heavy multicharged ions.[49] The amplitudes of such shock waves around the fission fragment tracks in water would reach 50–60 kbar; in more dense media they would be even larger, proportional to the cube of density (at fixed elemental composition). Shock waves are known to induce various phase transitions in condensed matter, and even chemical conversions, such as prompt polymerization and polycondensation (e.g., transformation of amino acids in polypeptides). Therefore a comprehensive study of shockwave hydrodynamic effects in energy losses of fission fragments and heavy ions in condensed media seems to be a promising area of further study.

Another mechanism of transformation of the kinetic energy of fission fragments can well be of great practical interest, i.e., conversion of kinetic energy to light, particularly to coherent laser light. It might appear that radiation photochemistry will serve as a most rational basis for complex uses of nuclear reactors, for production both of energy and of valuable chemical products.

There certainly also exist many other connections between the laser action on substances and nuclear transformations, including the laser-induced fusion of light nuclei, the possible effect of laser beams in the change of rates of isomeric transitions with internal conversion and of electron capture processes, and the possible pumping of isomeric nuclear level in laser-produced plasma by the mechanism of inverse internal conversion.[50]

Finally, I should note here the extremely tempting problem of interconnection between the nonconservation of parity in weak interactions (taking into account neutral currents) and asymmetry in the bioorganic world. This problem is still obscure and contradictory both in experimental results and in their interpretation, but as such is especially interesting.

In general, new problems in the applications of nuclear methods to chemical physics still arise at a rate much higher than that of the solution of the problems already formulated, and this fact is the best guarantee of a fast development of our field of science in the future and a challenge to nuclear chemists for active creative participation in bringing closer this fascinating future.

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