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The Physics and Chemistry of the Reactions of Positrons and Positronium in Polymers

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The problems of the annihilation of positrons in polymers are discussed and the reactions of positrons and positronium, the effect of external electric and magnetic fields, and the influence of various kinds of radiation, temperature, pressure, phase transitions, etc. are examined. The practical value of the positron method for the investigation of polymers is demonstrated.
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I. INTRODUCTION

During the last 10–15 years, there has been an appreciable growth of interest in the study of the reactions of positrons and positronium. The improvement of the experimental technique and methods and the increase of the resolving power of the apparatus, which have become possible as a result of advances in electronics, permitted fairly detailed observations of the reactions of positrons and positronium in matter. At the same time the observed high sensitivity of the characteristics of the electron–positron annihilation to the electronic structure, composition, and defects in the crystal structure of matter, temperature, pressure, phase transitions irradiation, and the effects of external electric and magnetic fields gave rise to the question of a new and in many instances unique method in the physics and chemistry of matter—the positron method.

The aim of the review is to give a systematic account and analyse the experimental and theoretical data, to discuss the main trends in research on the possibilities of the positron method in the physics and chemistry of polymers, and also to attract the attention of specialists in polymer science to the positron method. Without dwelling on the characteristics of the annihilation of positrons in various substances and on the description of the experimental technique and methods (see the relevant reviews, monographs, and corrections[1-15]), we shall proceed to the analysis of the reactions of positrons and positronium in polymers.

II. THE ANNIHILATION OF QUASI-FREE POSITRONS IN POLYMERS

1. The Characteristics of the Electron–Positron Annihilation

It has come to be believed that, as a result of various kinds of energy losses, the fast positrons which arise in the β^+-decomposition of the nuclei of radiative isotopes (^{22}Na, ^{64}Cu, and others) and pass into matter and are slowed down to thermal velocities (thermalisation) long before annihilation. During the retardation process, a proportion of the positrons form positronium. The fraction of positrons annihilated "in flight" is insignificant[2]. The average depth of penetration of positrons (^{64}Cu) is 370.4 ± 20.6 μm in polyethylene (PE) and 156.2 ± 6.1 μm in Teflon (PTFE)†.[15] If the spins of the particles are antiparallel (the singlet state of the e^+e^- pair), the 2γ-annihilation is most probable. On the other hand, for the parallel orientation of the spins of the particles (the triplet state of the e^+e^- pair), the minimum number of annihilation γ-quanta is three (3γ-annihilation). In the 2γ-annihilation the angle of dispersion of γ-quanta differs from π by an amount θ if the e^+e^- pair possesses momentum; the movement of the pair also leads to a Doppler shift ΔE_γ of the energy of the γ-quanta. The probability of the 2γ-annihilation of free particles per unit time in the non-relativistic approximation is, according to Dirac[17], $\lambda = \tau^{-1} = \pi r_0^2 cn$, where $r_0 = 2.818 \times 10^{-15}$ m is the classical radius of the electron, c the velocity of light, and n the number of electrons per unit volume.

The characteristics of the electron–positron annihilation (θ, $\Delta E\gamma$, and τ) correspond to the existing experimental methods based on the following measurements: (a) the angular distribution of γ-quanta in 2γ-annihilation (AD); (b) the distribution of γ-quanta in 2γ-annihilation in terms of the Doppler shift; (c) the time distribution of the annihilation radiation (TD); (d) TD corresponding to different angles θ (combined AD–TD method).

In the general case the TD spectrum consists of several components:

$$p(t) = \sum_i I_i \lambda_i e^{-\lambda_i t}, \quad (1)$$

where λ_i are decomposition constants ($\tau_i = \lambda_i^{-1}$ are the experimental average lifetimes of the positrons) and I_i are the

† Here and henceforth the following notation has been adopted: PE = polyethylene, PTFE = Teflon; PS = polystyrene; PVC = poly(vinyl chloride).

intensities of the components. The probability of the annihilation of the positron in a state i in a many-electron system per unit time with emission of two γ-quanta with an overall momentum p is given by the following expression in the one-particle approximation[18]: $\gamma_i(\mathbf{p}) = \pi r_0^2 c \rho_i(\mathbf{p})$, where

$$\rho_i(\mathbf{p}) = \sum_j \left| \left(\frac{1}{2\pi\hbar}\right)^{3/2} \int \psi_i^+(\mathbf{r}) \psi_j \exp\left(-\frac{i}{\hbar}\mathbf{pr}\right) d\mathbf{r} \right|^2 \quad (2)$$

is the function of the distribution density of the e^+e^- pairs being annihilated in terms of momenta, $\psi_i^+(\mathbf{r})$ is the wave function of the positron, and $\psi_j(\mathbf{r})$ are the one-electron wave functions of the atom (ion, molecule). The summation in Eqn.(2) is carried out over all the electrons in the system. The decomposition rate constant $\gamma_i = \sum_{\mathbf{p}} \gamma_i(\mathbf{p})$ is given by

$$\gamma_i = \pi r_0^2 c n_i^*; \; n_i^* = \sum_j \int |\psi_i^+ \psi_j|^2 d\mathbf{r}, \quad (3)$$

where n_i^* has the significance of the effective number of electrons for annihilation per unit volume of the substance. In the general case $\gamma_i \neq \lambda_i$.

The theoretical AD curves in the case of the isotropic distribution of the e^+e^- pairs in terms of momenta in the Steward approximation[19] can be calculated from the formula

$$I_i(\theta) = 2\pi \int_{p_z}^{\infty} \gamma_i(p)\, p\, dp; \; \theta = p_z/m_0 c,$$

where m_0 is the mass of the electron. The overall distribution is $I(\theta) = \sum_i I_i(\theta)$. The function of the distribution density of the pairs in terms of the momenta $\rho(p)$ and the momentum distribution of the pairs# $N(p)$ can be reproduced from the results of the measurement of the AD:

$$\rho(p) \propto -\theta^{-1} dI/d\theta, \quad N(p) = 4\pi p^2 \rho(p) \propto -\theta\, dI/d\theta.$$

We may also note that the decomposition constant γ_i is equal to the area under the theoretical $I_i(\theta)$ curve:

$$\gamma_i = m_0 c \int_{-\infty}^{+\infty} I_i(\theta)\, d\theta.$$

2. The Annihilation of Quasi-Free Positrons in Polymers

According to Gol'danskii[2], in the general case one can imagine three fundamental mechanisms of the annihilation of positrons in matter: (a) the annihilation of positrons in quasi-free collisions with the electrons of the surrounding medium; (b) the annihilation of positrons in different bound states of the non-positronium type arising on capture of thermalised positrons by ions, atoms, molecules, atom-molecule complexes, and defects; (c) the annihilation of positrons bound in positronium atoms.

In the annihilation of positrons in quasi-free collisions with (valence) electrons, one can infer the distribution densities of the valence electrons in space and with respect to momenta from the results of measurements of their TD and AD parameters. The rate of annihilation of slow quasi-free positrons in a molecular substance can be formulated as follows according to Eqn.(3):

$$\gamma_f = \frac{1}{\tau_f} = \pi r_0^2 c \frac{\rho}{M} N_A \sum_k \nu_k n_k^*, \quad (4)$$

More precisely the distribution of the pairs with respect to momenta, but in the physics of slow positrons the term "momentum distribution of pairs" is used more often.

where ρ is the density, M the molecular weight, N_A the Avogrado number, ν_k the number of atoms (ions) of the kth kind in the molecule, and n_k^* the number of electrons in an atom (ion) of the kth kind which is effective for annihilation. For liquids and solids, $\gamma_f \approx 10^9\ s^{-1}$ according to Eqn.(4) and is proportional to the density of the substance. As an example, Table 1 presents the results of measurements[20,21] of the TD parameters (τ_i and I_i) for certain polymers.

Table 1. The average lifetimes of positrons (and the intensities of the TD components) relative to annihilation in certain polymers[20].

Substance	$10^{10}\tau_0$, s	$10^{10}\tau_1$, s	$10^{10}\tau_2$, s	I_0, %	I_1, %	I_2, %
Polystyrene	4.10±0.20	12.2±0.6	21.0±0.6	49±3	4.3±0.5	29.0±1.5
Polyethylene	3.20±0.12	7.7±0.3	27.4±0.8	61±4	15±1	22.8±1.2
Polyvinyltoluene	3.58±0.13	10.5±0.6	21.0±0.6	50±3	6.9±0.6	31.8±1.6
Polypropylene	3.46±0.10	9.9±0.5	23.5±0.7	74±4	7.5±0.7	14.6±0.8
Cellulose acetate	3.71±0.11	9.5±0.5	22.0±0.7	67±4	6.1±0.6	16.3±0.9
Lucite	3.20±0.10	8.2±0.4	19.6±0.6	63±4	11±1	22.0±1.1
Teflon (Ref.21)	3.3±0.1	9.7±0.5	40.9±0.3	64±4	15.0±1.9	21.0±0.4

Remarks: For polystyrene, polyvinyltoluene, and cellulose acetate, there is a component with $\tau_0' = 1.2 \times 10^{-10}$ and intensities of 18 ± 3, 14 ± 2, and 5.5 ± 0.7% respectively. In order to unify the notation, τ_0, τ_1, τ_2, and τ_3 have been replaced by τ_0', τ_0, τ_1, and τ_2 respectively.

Table 2. The number of electrons n_k^* effective for the annihilation of quasi-free positrons and the number of electrons z in the outer shell of the atom[20].

Atom	n_k^*	z	Atom	n_k^*	z
H	2.36±0.15	1	Si	11.2±0.3	4
B	4.5±0.2	3	S	11.7±0.4	6
C	5.08±0.22	4	Cl	11.4±0.3	7
N	6.6±1.4	5	Br	14.4±0.3	7
O	5.21±0.30	6	I	17.8±0.4	7

Cova and Zappa[20] suggested that $\tau_f = \tau_0 = 1/\lambda_0$ (or $\gamma_f = \gamma_0$) (we replaced the symbol τ_1 used by the above workers[20] for a short lifetime by τ_0). To test this hypothesis, we determined the number n_k^* for H, C, and O atoms from Eqn.(4) putting in the latter $\tau_f = \tau_0$ and substituting the experimental values of τ_0 for molecular liquids[22]. The values of n_k^* were then substituted in Eqn.(4) and the lifetimes τ_f in the polymers were calculated (these are listed in Table 1). It was found that $\tau_f = \tau_0$ to within 5%. The numbers of annihilation electrons calculated[20,22] from the lifetimes of positrons τ_0 in various substances are presented for a series of atoms in Table 2. Theoretically γ_f can be calculated in principle from Eqn.(3).

In the free positron approximation, we have

$$\psi^+(\mathbf{r}) = V^{-1/2} \exp(i\,\mathbf{kr}),$$

where V is the normalised volume and $\mathbf{k}$ the wave vector of the positron. For thermalised positrons, $\mathbf{k} \approx 0$ and the momentum distribution of the e^+e^- pairs

$$N(p) = \int_0^{2\pi} d\varphi \int_0^{\pi} \rho(p)\, p^2 \sin\vartheta\, d\vartheta$$

represents the momentum distribution of the electrons (in practice only valence electrons, in view of the inaccessibility of the inner regions of atoms to positrons).

The function $N(p)$ was calculated (by the method of Coulson and Duncanson[23-26]) by various workers[15,27-34] for low-molecular-weight substances (methane, benzene, hexane, etc.) in accordance with the scheme

$$N(p) = \sum_k \alpha_k N_k(p),$$

where α_k is the relative number of bonds of the kth type in the molecule, $N_k(p)$ is the momentum distribution of electrons in a bond of the kth type. The use of the Hartree–Fock wave functions for the 2s and 2p atomic orbitals of carbon instead of the Slater orbitals leads under these conditions to a much better agreement with experiment[28]. There is a discrepancy only in the region of momenta $p \cong (9-10) \times 10^{-3} m_0 c$. If account is taken of the distortion of the planar wave by the field generated by the atoms, in particular by the nuclei, it is possible to obtain a satisfactory agreement with experiment also in the region of large momenta[30-35]. [Fig.1; the appearance of a low-momentum component in $N(p)$ for liquid methane is associated with formation of positronium; see below]. The momentum distribution of the electrons of covalent bonds is insensitive to the fusion of the substance, as was to be expected (Fig.1).

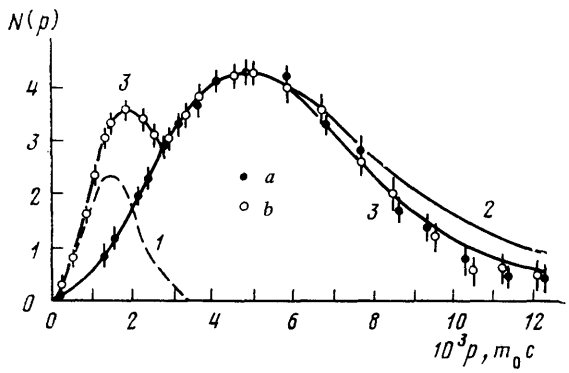


Figure 1. The momentum distribution $N(p)$ for e^+e^- pairs in methane according to AD measurements[30]: *a*) and *b*) experimental points for solid and liquid methane respectively; *1*) momentum distribution of parapositronium atoms; *2*) and *3*) $N(p)$ curves calculated in terms of the approximations of free positrons (curve *2*) and positrons interacting with atoms (curve *3*).

An analogous method can be applied in principle to the calculation of $N(p)$ and hence of the AD curve for high-molecular-weight substances. $N(p)$ for PE can be calculated comparatively simply if the bonds are assumed to be tetrahedral and the ratio of the number of electrons in the C–H and C–C bonds of the $[CH_2]_n$ molecule is assumed to be two in constructing the hybrid orbitals of the carbon atom. The results of the calculation of $N(p)$ and $I(\theta)$ for PE (with Hartree–Fock wave functions) are illustrated in Fig.2.

III. POSITRONIUM IN POLYMERS

1. The formation of Positronium

The properties of the positronium (Ps), i.e. a bound system consisting of an electron and a positron, *in vacuo* are well known (see sub-section 2). The Ps atom is a hydrogen-like atom with a reduced mass equal to $m_0/2$; its ionisation potential is $E_{Ps} \cong 6.77$ eV and its Bohr radius is $a_{Ps} = 2a_0 \cong 0.106$ nm (a_0 is the Bohr radius in the ground state of hydrogen). Parapositronium (*p*-Ps) undergoes spontaneous 2γ-annihilation at a rate $\lambda_s^0 = 8 \times 10^9$ s^{-1} (lifetime $\tau_s^0 = 1/\lambda_s^0 = 1.25 \times 10^{-10}$ s). Orthopositronium (*o*-Ps) is annihilated with emission of three γ-quanta at a rate $\lambda_t^0 = 7.14 \times 10^6$ s^{-1} (lifetime $\tau_t^0 = 1/\lambda_t^0 = 1.4 \times 10^{-7}$ s). As a consequence of the mixing of the substates $^1S_0$ and $^3S_1$ ($m = 0$), in a magnetic field the lifetime of orthopositronium is shortened (magnetic quenching of positronium). The "hydrogen-like" nature, the short lifetime, magnetic quenching, and the possibility of detecting even only one Ps atom [the real density of Ps atoms in matter in the course of the experiment is approximately 10^6 m^{-3} (!)] on the basis of the annihilation γ-quanta make positronium one of the unique research instruments in the physics and chemistry of matter.

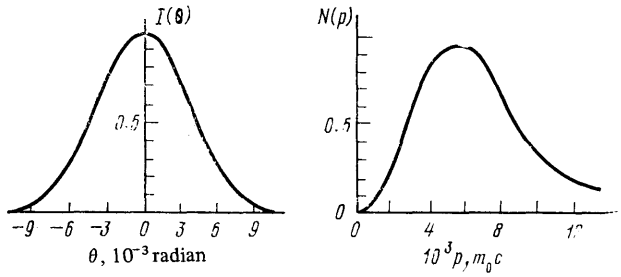


Figure 2. Theoretical AD curves $I(\theta)$ and the momentum distribution curves $N(p)$ for e^+e^- pairs in polyethylene.

The probability of the formation of positronium by retarded positrons in matter is "regulated" by energetic conditions. For a condensed phase, the so-called Ore gap or energy gap, within the limits of which the formation of positronium is most probable, is determined by the following inequality according to Ferrell[2,12,15]: $\mathcal{I} - E_{Ps} - Q_{Ps} < E_+ < E^* - Q_*$, i.e. the energetic condition for the formation and dynamic stability of positronium is represented by the inequality

$$Q_- + Q_+ < E_{Ps} + Q_{Ps},$$

where $\mathcal{I}$ is the ionisation potential and E^* the energy of the electronic excitation of the substance, E_+ the kinetic energy of the positron, and Q_-, Q_+, and Q_{Ps} are the affinities of the substance for the electron, the positron, and the Ps atom.

Even if there is no energetic prohibition of the formation of positronium, not all the positrons form positronium. Some of the positrons are annihilated within the limits of the Ore gap, are captured in non-positronium states ("adhere" to molecules, fall into traps, etc.), are retarded

to an energy $<E_+$ by non-elastic interactions, with individual molecules, etc. All these processes, which have been combined under the name of positronium inhibition processes, depend on the chemical composition, the intermolecular interaction, the structural defects, and other factors.

The so-called spur model of the formation of positronium, proposed[35] to account for the formation of positronium in liquids, has been widely discussed in recent years. It is assumed in this model that positronium is formed when a positron is bound to one of the electrons arising in the trace (spur) of the retarded positron as a result of the ionisation of molecules and accompanying ("escorting") the positron. For liquids (and solutions), it is possible to set up a quantitative theory of the reactions of positrons and positronium taking into account their interaction with the species in the trace of the positron (with electrons, ions, and radicals) and the surrounding medium (see, for example, Refs.15 and 35–41). Attempts have been made to apply the spur model to molecular crystals[36,42], but the problem of its applicability to molecular crystals and polymers has not been finally resolved[36].

2. The Quenching of Positronium

The interaction of positronium with the surrounding medium in matter leads to a significant alteration of its properties compared with a vacuum. Processes such as (a) pick-off annihilation, i.e. annihilation of the positron in the Ps atom by a "foreign" electron, (b) the ortho-para conversion ($^3S_1 \; ^1S_0$) in the interaction of Ps atoms with paramagnetic species M as a consequence (in the simplest case) of the direct spin exchange

$$M(\downarrow) + {}^3S_1(\uparrow\downarrow) \rightleftarrows M(\uparrow) + {}^1S_0(\uparrow\downarrow),$$

and (c) different kinds of chemical reactions of positronium with the molecules of the given substance (addition, substitution, and oxidation) alter the lifetime of positronium compared with τ_S^0 and τ_t^0. For orthopositronium, all the above processes, which open the channel to 2γ-annihilation, shorten the lifetime (compared with τ_t^0) and are therefore combined under the term "quenching" of positronium[2]. If we introduce the quenching rate constant λ_q, then usually $\lambda_t^0 \ll \lambda_q \ll \lambda_S^0$. Parapositronium is therefore relatively insensitive to the above processes. In the general case pick-off annihilation, which shortens the lifetimes of orthopositronium to $\lesssim 10^{-9}$ s, is most significant for polymers.

We shall consider the kinetics of the pick-off annihilation process. Suppose that the probability of the formation of positronium is P. Then at the initial instant $t = 0$ the probability of detecting the positron in a quasi-free state is $P_f(0) = 1-P$ and the probabilities of detecting positronium are $P_S(0) = \frac{1}{4}P$ in the singlet state and $P_t(0) = \frac{3}{4}P$ in the triplet state. The populations of the above states vary with time in accordance with the law

$$P_f(t) = (1-P)\,e^{-\lambda_f t}, \quad P_s(t) = \frac{1}{4}P\,e^{-\lambda_S t},$$
$$P_t(t) = \frac{3}{4}P\,e^{-\lambda_t t},$$

where $\lambda_S = \lambda_S^0 + \lambda_p$, $\lambda_t = \lambda_t^0 + \lambda_p$, λ_f is the rate of annihilation of quasi-free positrons, and λ_p is the rate of pick-off annihilation. The TD spectrum consists of three components with the average durations $\tau_0 = \lambda_S^{-1}$, $\tau_1 = \lambda_f^{-1}$, and $\tau_2 = \lambda_t^{-1}$ and with the intensities $I_0 = \frac{1}{4}P$, $I_1 = 1-P$, and $I_2 = \frac{3}{4}P$. If the TD components with the decomposition constants λ_S and λ_f cannot be resolved, the experimental (average) short lifetime is

$$\tau_1 = \frac{1}{I_1}\left(\frac{I_f}{\lambda_f} + \frac{I_s}{\lambda_s}\right),$$

and $I_1 = I_f + I_S$.

Since the momentum of the p-Ps atom retarded to thermal velocity is comparatively small, the self-annihilation of parapositronium contributes to the AD curve in the region of small angles, while a comparatively narrow peak appears on the AD curve—a narrow $N(\theta)$ component and a low-momentum component on the $N(p)$ curve (see Figs.3 and 4 and also Fig.1). The intensity $I_N = \lambda_S^0 \int_0^\infty P_S(t)dt$ of the narrow AD component is

$$I_N = \frac{1}{4}P\,\frac{\lambda_s^0}{\lambda_s^0 + \lambda_p} \approx \frac{1}{3}I_2, \qquad (5)$$

since usually $\lambda_p \ll \lambda_S^0$. The annihilation of free positrons and the pick-off annihilation of positronium give rise to the broad AD component.

The relative probabilities of the 3γ-annihilation of quasi-free positrons and orthopositronium are $P_{3\gamma}^0 = 1/372$ (Gol'danskii[2]) and $P_{3\gamma}^t = \lambda_t^0 \int_0^\infty P_t(t)dt$ respectively and the overall probability of 3γ-annihilation is therefore

$$P_{3\gamma} = I_2\frac{\tau_2}{\tau_t^0} + \frac{1}{372}\left(1 - \frac{4}{3}I_2\right).$$

The inequality $P_{3\gamma} > P_{3\gamma}^0$ is an "indicator" of the formation of positronium in matter. In polymers $P_{3\gamma} > P_{3\gamma}^0$ (see, for example, Refs.7 and 45–47). Thus we have $P_{3\gamma}/P_{3\gamma}^0 \cong 2.60$ for PTFE and $P_{3\gamma}/P_{3\gamma}^0 = 3-4$ for rubbers[7].

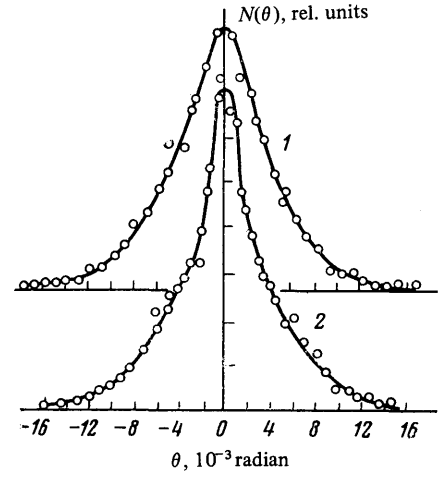


Figure 3. AD curves for Teflon recorded at 77 K (curve *1*) and 525 K (curve *2*).[43]

The positronium formed in the given substance is thus manifested experimentally by the appearance of a long-lived component in the TD and a narrow component in the AD and also by the higher probability of 3γ-annihilation $P_{3\gamma}$ compared with $P_{3\gamma}^0 \cong 0.27\%$. At the same time the relevant measurements make it possible to follow the reactions

of positronium in the substance and its properties on the basis of the TD and AD parameters and $P_{3\gamma}$.

If parapositronium is thermalised and exists in a free state, then its momentum distribution is Maxwellian:

$$N(p) \sim p^2 \exp(-p^2/4m_0k_0T),$$

while the narrow component of AD has a Gaussian form:

$$N(\theta) \sim \exp(-m_0c^2\theta^2/4k_0T).$$

The width of the $N(\theta)$ distribution profile at half its height at the maximum (the half-width of the narrow component) is $\Gamma_N \cong 4.33 \times 10^{-2} T^{1/2}$ mrad. At 295 K we have $\Gamma_N \cong 0.74$ mrad, so that the distribution $N(\theta)$ should be indeed manifested in the given instance by a very narrow peak in the AD. However, in polymers such a narrow distribution is usually not observed.

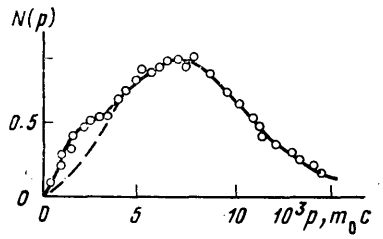


Figure 4. The momentum distribution of e^+e^- pairs in Teflon at room temperature[44] [dashed curve—theoretical calculation of the $N(p)$ function in the region of low values of p].

3. The States of Positronium in Molecular Substances. The "Positronium Capture Model"

There is reason to believe[10,48-51] that positronium can exist in a condensed phase in two states: the quasi-free or delocalised state and the localised state. The localised state arises in the "capture" of a Ps atom by a trap, whose role may be assumed by a macrocavity, a region of reduced density, etc. Bearing in mind that $\lambda_t^0 \ll \lambda_s^0$ and assuming that $\lambda_f \cong \lambda_p$, $\lambda_{pv} \ll \lambda_s^0$, $\lambda_t^0 \ll \lambda_{pv}$, and $\lambda_t^0 \ll \lambda_p + k$, where λ_p and λ_{pv} are respectively the rates of the pick-off annihilation of the quasi-free and localised positronium and k is the rate constant for the capture of positronium by traps, Bartenev and coworkers[49,50] interpreted the observed TD components (when the spectrum was resolved, as usual, into three components) as follows. The long-lived component τ_2 corresponds to the annihilation of o-Ps atoms in a trap, the intermediate component τ_1 corresponds to the annihilation of free positrons, and the short-lived component τ_0 corresponds to the annihilation of o-Ps atoms in a free state and of the p-Ps atoms in free and localised states. The parameters of the experimental TD spectrum are related to the parameters of the model as follows[49,50]:

$$\tau_0 = \frac{1}{4 - 3k/\Lambda_p}\left[\frac{k}{\Lambda_p}\left(\frac{1}{\lambda_{sv}} - \frac{1}{\lambda_s} - \frac{3}{\lambda_t}\right) + \frac{1}{\lambda_s} + \frac{3}{\lambda_t}\right],$$

$$\tau_1 = 1/\lambda_f, \quad \tau_2 = 1/(\lambda_t^0 + \lambda_{pv}) \approx 1/\lambda_{pv},$$

$$I_0 = 1 - I_1 - I_2, \quad I_1 = 1 - P, \quad I_2 = 3/4Pk/\Lambda_p,$$

where $\Lambda_p = \lambda_p + k - \lambda_{pv}$, $\lambda_{sv} = \lambda_s^0 + \lambda_{pv} \cong \lambda_s^0$, $\lambda_s = \lambda_s^0 + \lambda_p + k$, and $\lambda_t = \lambda_t^0 + \lambda_p + k \cong \lambda_p + k$. The form of the narrow AD component is defined by the expression

$$N(\theta) = (\lambda_{sv}/\lambda_s) N_f(\theta) + (k/\lambda_s) N_v(\theta),$$

where the $N_f(\theta)$ and $N_v(\theta)$ components are due to the self-annihilation of the quasi-free and localised parapositronium. The intensity of the narrow component is $I_N \cong \frac{1}{4}P[1-(k/\lambda_s^0)]$.

If the τ_1 component is attributed to the annihilation of free positrons, as suggested by Bartenev and coworkers[49,50], then it is difficult to explain the reason for the long lifetime (for example 1.22 ns in PS; see Table 1) of this fraction of positrons. Furthermore, it follows from the calculations of Cova and Zappa[20] (see above) that $\lambda_f^{-1} \cong \tau_0$. Judging from the value of τ_1, the τ_1 component can be due to the faster, than in the case of the τ_2 component, pick-off annihilation of orthopositronium. There is then a possibility of several versions. For example, traps in the crystalline and amorphous regions of the polymer have different constants λ_{pv} and k (we shall denote them respectively by λ'_{pv}, k, and λ_{pv}, k) and $\lambda_{pv} < \lambda'_{pv}$. Positronium is formed and annihilated, remaining in its own region—crystalline or amorphous. Then $\tau_1 \cong (\lambda'_{pv})^{-1}$, $\tau_2 \cong \lambda_p^{-1}$, $I_1 = 3\chi Pk'/4\Lambda'_p$, and $I_2 = 3(1-\chi) \cdot Pk/4\Lambda_p$, where $\Lambda'_p = \lambda'_p + k' - \lambda'_{pv}$ and $\Lambda_p = \lambda_p + k - \lambda_{pv}$, while χ is the degree of crystallinity of the polymer. In the more general case account may be taken of the "escape" of the Ps atoms from the traps and their diffusion from one region of the polymer to another[52-56]. We shall return to the problem of the nature of the τ_1 component in discussing experimental data.

IV. THE INFLUENCE OF TEMPERATURE, PHASE TRANSITIONS, AND PRESSURE ON THE PROPERTIES OF POSITRONIUM IN POLYMERS. THE "FREE VOLUME" MODEL

1. The Effect of Density in the Quenching of Positronium in Polymers. The "Free Volume" Model

The shortening of the lifetime of the long-lived component (τ_2) of TD with decrease of temperature[57] (for example, $\tau_2 = 3.5$, 2.5, and 1.6 ns for PTFE at 20°, −78°, and −196 °C), the enhancement of the narrow AD component on heating polymers[43,58] (see, for example, Fig. 3), and finally a decrease of the intensity of the narrow component (for PTFE[58]) and at the same time of τ_2(lucite, PTFE, and PE at pressures up to 1.01 GPa)[59] were originally observed in earlier investigations. The decrease of τ_2 both with decrease of temperature and following the compression of the test substance is interpreted as a density effect, i.e. as a consequence of the increase of the density and hence of the decrease of the "free volume" (i.e. of the interstitial volume, the volume of microcavities, the volume of regions with a reduced density, etc.) in which the Ps atom is "located".

The dependence of τ_2 on the "free volume" can be accounted for on the basis of a simple model of the interaction of a Ps atom in a trap with the surrounding medium—as a species with a mass $2m_0$ in the potential well[58,60]. The probability $\mathscr{P}$ of the Ps atom being outside the well, i.e. in the given substance, is determined by the shape, size, and depth of the well. The overlap of the wave function $\psi(\mathbf{R})$, describing the movement of the centre of inertia of the Ps atom, with the wave functions of the surrounding molecules, and therefore the rate of pick-off annihilation of positronium increase with decrease of the size of the well, i.e. of the "free volume", and τ_2 correspondingly decreases. The rate of pick-off annihilation in the "free volume" model can be

formulated thus:

$$\gamma_p = \mathcal{P}\gamma_0;\ \mathcal{P} = 1 - \int_{v_f} |\psi(\mathbf{R})|^2 d\mathbf{R}, \qquad (7)$$

where $\gamma_0 = \pi r^2 c n^*$, v_f is the "free volume" (the volume of the trap), and n^* is the electron density in the given substance effective for the pick-off annihilation of positronium. $n^* = 3.8 \times 10^{29}$ m^{-3}, which corresponds to the electron density in the region where the positron is present in the $P\bar{s}$ ion ($\tau^0 = \gamma_0^{-1} = 0.35$ ns), is frequently chosen for estimates. Calculations of $\mathcal{P}$ have been carried out[61-71] for various geometries of the free volume: spherical (Figs.5*a* and 5*b*), cylindrical (Figs.5c), and planar (Fig.5d).

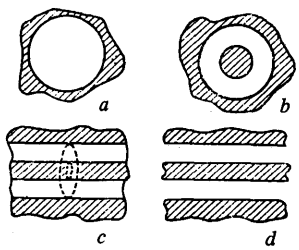


Figure 5. Different geometries of the free volume: *a*) and *b*) spherical geometry; *c*) cylindrical geometry; *d*) planar geometry.

2. Brandt's Free Volume Model

According to Brandt et al.[61,63,64],

$$\mathcal{P} = \frac{1 + G\{\exp[2\xi^2(S, v^*)\langle u^2(T)\rangle/R_0^2] - 1\}}{1 + F(S, v^*)}, \qquad (8)$$

where $S = (4m_0/\hbar^2)U_0R_0^2$ is a dimensionless parameter proportional to the height of a rectangular potential U_0 and the square of the radius R_0 of the core of the cell (i.e. the "excluded" volume v_0) and $v^* = v_1/v_0$ is the reduced "free volume", while v is the volume of the entire cell with a radius R_1 (in the range $R_0 \leq R \leq R_1$ we have $U_0 = 0$ and $n^* = 0$ and the cell constitutes the intrinsic "free volume" $v_f = v_1 - v_0$); the factor G varies from 1/2 to 1 and is approximately given by

$$G \simeq 1 - \frac{1}{2}\, th \frac{\mu - 1}{\xi(S, v^*)},$$

where u = 1, 2, or 3 for the planar, cylindrical (chain), and spherical geometries of the cell respectively. The temperature variation of the reduced mean-square amplitude $\langle\mu^2\rangle/R_0^2$ of the vibrations of the core in the region $\Theta_D \leq T \leq T_m$ is given by the expression

$$\langle u^2\rangle/R_0^2 = v^{*2/\mu}\gamma_m T/T_m,$$

where γ_m is the critical value of $\langle u^2\rangle/R_0^2 v^{*2/\mu}$ attainable on fusion and Θ_D and T_m are respectively the Debye temperature and the melting point. For a melt (T/T_m),

$$\langle u^2\rangle/R_0^2 \simeq v^{*2/\mu}\gamma_m.$$

If $T < \Theta_D$, then $\langle u^2\rangle \cong$ const. and $\mathcal{P}$ depends only on the model parameters S and v^*: $\mathcal{P}[1 + F(S, v^*)]^{-1}$.[71] The functions $\xi(S, v^*)$ and $F(S, v^*)$ have been expressed[64] in analytical and graphical forms. Interpolation formulae for ξ and F are[64]

$$\xi^2(S, v^*) = S[1 - (1+F)^{-2/3}],$$

$$F(S, v^*) = \frac{4}{\pi^3}\{[1 + S^{1/2}(v^{*1/\mu} - 1)]^3 - 1\}.$$

The half-width of the narrow AD component in the free volume model can differ appreciably (is greater) from Γ_N for free thermalised positronium. (The experimentally observed broadening of the narrow component relative to Γ_N for thermalised positronium has served as a basis for the authors' hypothesis[58] concerning the possible localisation of Ps atoms). In Brandt's "free volume" model the half-width of the component (in mrad) is[71]

$$\Gamma_N \simeq 0{,}25 g_\mu^{1/3} \frac{S^{1/2}}{R_0}\left(\frac{\gamma_p}{\gamma_0}\right)^{1/3}, \qquad (9)$$

where $g_\mu = \frac{1}{2}\mu$ for $\mu = 1$ and 2 and $g_\mu = 1/\mu$ for $\mu = 3$; R_0 is measured in nanometers. Thus a relation has been established between Γ_N and γ_p.

3. The "Empty Free Volume" Model (The "Trap" Model).

In the region where the Ps atom is localised is regarded as spherical without a "core" (Fig.5*a*) and the interaction of the Ps atom with the surrounding medium is modelled by a rectangular spherically symmetrical potential well with a radius a and a depth U_0, then $\mathcal{P} = k^2/\alpha(\alpha + aP_0 + k^2/\alpha)$, where $k = (2/\hbar)(m_0E)^{1/2}$, $\alpha = (2/\hbar)[m_0(U_0 - E)]^{1/2}$, $P_0 = (4/\hbar)m_0U_0$, and E is the energy of the Ps atom in the well[65]. Bearing in mind that $\mathcal{P} = \gamma_p/\gamma_0$ and assuming that $E \cong \frac{1}{16}m_0c^2\Gamma_N$, in this model the parameters of the well (or the trap of the Ps atom if the terminology of the "positronium capture" model is used) can be estimated from the experimental values of γ_p and Γ_N as $a \cong 0.77\chi/\Gamma_N$ nm and $U_0 \cong 3.2 \times 10^{-2}(\Gamma_N/y)^2$ eV, where Γ_N is expressed in milliradians and x and y constitute the solution of the equations

$$y = \sin x, \quad \gamma_p/\gamma_0 = y^3/[y + x(1 - y^2)^{1/2}]$$

for cot $x < 0$. In a more rigorous solution of the problem, one calculates in the first place the narrow AD component and then its half-width is determined. For an infinitely deep spherically symmetrical rectangular potential well, the wave function of the Ps atom is

$$\psi(\mathbf{R}) \sim \sin kR/R,$$

and the angular distribution of the annihilation γ-quanta assumes the form

$$N(\theta) \sim \int_\beta^\infty \left(\frac{\sin z}{\pi^2 - z^2}\right)^2 \frac{dz}{z};\ \beta = \frac{m_0 ca}{\hbar}\theta.$$

Numerical calculation of the width of the $N(\theta)$ distribution profile at the level of half its height at the maximum yields[72] $\Gamma_N \cong 1.660\, a^{-1}$ mrad, where a is expressed in nanometers. The $N(\theta)$ distribution for a spherical well with a finite depth[72] and also for a rectangular potential box[73] has also been discussed. The parameters of the well can be determined also from the form of the $N(p)$ momentum distribution[15,67].

4. Dependence of the "Positronium Parameters" of AD and TD on Temperature and Pressure in Polymers and the "Free Volume" Model

Studies on the temperature and pressure dependence of the AD and TD parameters, associated with the reactions of positronium, in various polymers have on the whole confirmed

the conclusions derived from the "free volume" model[1,2,57-63,66,74-87].

In a study[62] of the dependence of the parameters τ_2 and I_2 of the long-lived TD component (the TD component decomposed into two components) on temperature (up to 200 °C) and pressure (up to 6.06 GPa), a relation of the following type was established for a number of substances:

$$\tau_2 \simeq \tau_2^0(T)\,(1-\eta\Delta V/V_0).$$

Here $\Delta V = V_0 - V$ is the volume change under the influence of pressure. The values of τ_2^0 (30 °C) and η, determined from the experimental data, are as follows:

Polymer	Lucite	PTFE	PS
τ_2^0 (30° C), ns	1.7 ± 0.2	3.2 ± 0.2	2.2 ± 0.2
η	4.3 ± 0.9	5.0 ± 0.8	4.3 ± 0.7

Having formulated $\tau_2^{-1} \cong \mathcal{P}\gamma_0$ [see Eqn.(7)] and having defined as the probability that the Ps atom is located outside the limits of a three-dimensional rectangular potential well with a volume v ($\mathcal{P} \propto v^{-0.87}$), so that $\tau_2 \propto v^{0.87}$, the authors[62] based their treatment in essence to the "empty free volume" model. Hence, if one assumes on the basis of compressibility data for polymers that the fraction of vacancies in non-compressed polymers is 20%, it follows that[62]

$$\tau_2 = \tau_2^0(1-5\Delta V/V_0)^{0.87},$$

which corresponds to $\eta = 4.35$ in the empirical $\tau_2(V)$ relation. The calculated and experimental values of η agree within the limits of the error of the measurements.

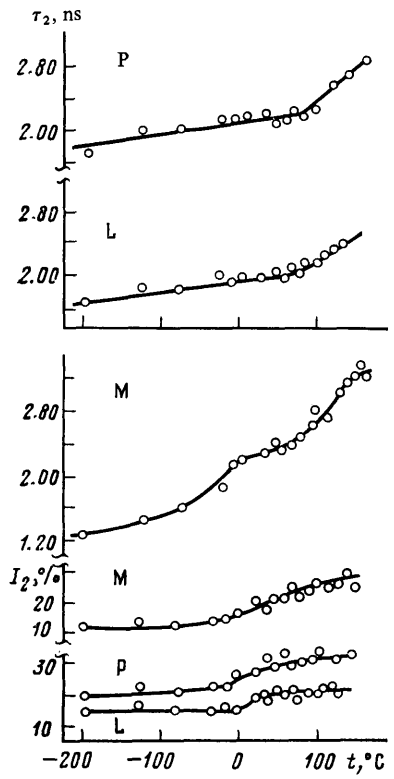


Figure 6. Dependence of the parameters of the long-lived TD component (the lifetime τ_2 and the intensity I_2) in polystyrene (P), lucite (L), and Marlex-50 polyethylene (M).[76]

The ratio I_2/I_2^0 for polymers decreases as the substance is compressed, which, however, is not obligatorily related to the decrease of the probability of the formation of positronium and may be caused, according to the "positronium capture model" [see Eqn.(6)] by the corresponding change in the parameters k, λ_p, and λ_{pv} ($k \propto n$, where n is the number of traps per unit volume of the polymer and λ_p and λ_{pv} are determined respectively by the density of the polymer and the volume of the traps). The decrease of τ_2 in polymers with decrease of temperature and the breaks in the $\tau_2(T)$, $I_N(T)$, and I_2 curves in the region of phase and relaxation transitions[1,2,15,66,76,79,82-86] (Figs. 6 and 7) are also qualitatively consistent with the "free volume" model. The glass points determined from the positronium data are somewhat lower than those found by other methods, which indicates a higher sensitivity of the positronium method to changes in the structure of the polymer[84,86]. In the region of vitrification I_2 is almost independent of temperature[1,75,84,86], i.e. the increase of the size of the microcavities is not accompanied by an appreciable change in their number.

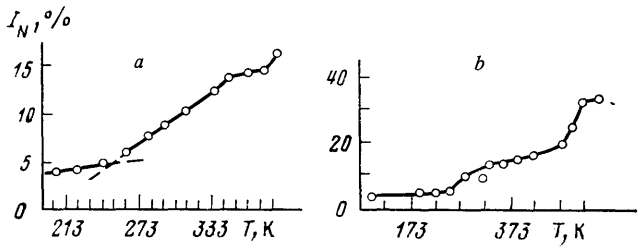


Figure 7. Temperature dependence of the intensity of the narrow AD component in high-pressure polyethylene (*a*) and in Teflon with a degree of crystallinity of 64% (*b*).

One of the causes of the appearance of breaks in the $\tau_2(T)$ curves is "vibrational" movement of atoms (and molecules) and the fluctuations in the density of the substance caused thereby, which lead to the "smearing" of the electron density and hence to an increase of the rate of pick-off annihilation of orthopositronium in contrast to the "free volume" effect, due in this instance to thermal expansion. These effects have been analysed quantitatively[63,70] (they are "inherent" in Brandt's "free volume" model—see above). In polymers the smearing of electron density and hence the associated acceleration of the pick-off annihilation of positronium can arise when the mobilities of particular kinetic units are "switched on" in the temperature range of the relaxation transitions on heating the polymer[51,85].

The TD spectra in polymers contain up to three (or even up to four) components[24,63,87-89] (Table 1). Having measured the temperature dependence of the TD parameters in PE and PTFE (and also in glycerol), Brandt and Spirn[63] concluded that the component τ_2 is due to the pick-off annihilation of the *o*-Ps atoms in the disordered regions of the polymer, while the component τ_1 is due to the annihilation of free positrons; the *p*-Ps atoms located in the disordered regions and the *o*-Ps and *p*-Ps atoms in the ordered regions contribute to the component τ_0. We may note that an analogous interpretation of the TD spectrum has been adopted by the authors of the "positronium capture" model (see Section III).

Fig. 8 presents the experimental values of τ_2 for PE and PTFE and the calculated $\tau_2(\nu^*) = 1/\gamma_p(\nu^*)$ curves based on Eqns. (7) and (8) for $\mu = 2$, $S = 25$, and $\gamma_m = 1/16$ and 1/12 respectively. Extrapolation of the data in Fig. 8 to close packing conditions yields values of τ_2 close to τ_0, which, as it were, confirms the validity of the hypothesis concerning the relation between τ_0 and the pick-off annihilation of positronium in the ordered domains of the polymer. In a subsequent study[71] dealing with the TD spectrum in paraffins, including PE, the above interpretation was wholly retained. At the same time it is assumed that the component τ_1 of TD involves the contribution of the positrons located in the disordered domains in the form of A_+ centres[90] (see also Refs. 6, 9, 10, and 12); on the other hand, the annihilation of free positrons contributes to the component τ_0. According to Brandt[71], the half-width of the narrow AD component in paraffins [see Eqn. (9)] is $\Gamma_N \approx 3.5$ mrad. Measurement of Γ_N for PE yields the same value[82].

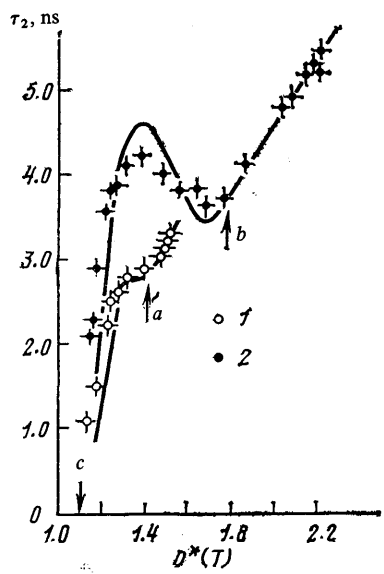


Figure 8. Dependence of the lifetime of positronium τ_2 on the reduced free volume $\nu^*(T)$ in polyethylene (*1*) and Teflon (*2*);[63] symbols—experimental data; curves—calculation; *a*) and *b*) $\nu^*(T_m)$, where T_m = melting point; *c*) close packing.

Thus the dependence of the TD (and also AD) parameters on the reduced "free volume" in molecular substances, including polymers, has been given the same treatment in studies by Brandt and coworkers[63,71]. Nevertheless one must bear in mind that there are discrepancies in the experimental data of different workers (cf. for example, the data in Refs. 63 and 75, on the one hand, and Ref. 77 on the other). The definition of τ_0 as the average lifetime of free positrons or positrons bound in A_+ centres, adopted by Brandt and coworkers[63,71] (see above), is also open to objection. Whereas according to Brandt and coworkers[63,71] the value of τ_0 in PE and PTFE is independent of temperature and that in PE is independent of the degree of crystallinity (Table 3), according to, for example, the data of other workers for PTFE [89] and PE [1,15,91] this is not the case.

Finally, one must bear in mind the approximate nature of the "free volume" model itself, associated with the choice of the form of the potential of the interaction of the Ps atom with the surrounding medium, with the uncertainty of the electron density n^* effective for pick-off annihilation [see Eqn. (7)], with neglect of the details of the formation and reactions of positronium preceding its localisation (such as the probability of the formation of positronium in the crystalline and amorphous region of the polymer, the nature of the population of the "free volumes" by Ps atoms—gas-kinetic or diffusional, etc.), and other factors.

Table 3. Dependence of the TD parameters for polyethylene on the degree of crystallinity χ of the specimens[71] (ρ = density; ν^* = reduced "free volume").

χ, %	$10^{-3}\rho$, kg m^{-3}	ν^*	τ_0, ns	I_0, %	τ_1, ns	I_1, %	τ_2, ns	I_2, %
46	0.917	1.298	0.31	63	0.65	10	2.61	27
51	0.925	1.290	0.33	67	0.81	9	2.67	24
53	0.930	1.280	0.31	69	0.87	9	2.54	22
69	0.948	1.255	0.32	72	0.80	10	2.53	18
80	0.967	1.231	0.34	73	0.75	9	2.54	18

V. DEPENDENCE OF THE PROPERTIES OF POSITRONIUM ON THE STRUCTURE AND DEGREE OF CRYSTALLINITY OF POLYMERS

In the "free volume" model it is in essence assumed that the overall probability of the formation of positronium in molecular substances is independent of temperature, state, and structure. However, numerous experiments (see, for example, Refs. 2, 6, 8, 42, and 92–96), involving observation of the formation of positronium in molecular substances (and in ionic compounds) indicate the opposite behaviour in crystal–liquid and crystal–glass transitions when the conditions and nature of the preliminary treatment are altered. The same applies also to polymers[1,2,15,77,78,80,82–84,91,97–101].

In PTFE with a lower degree of crystallinity (~44%) and density (2.14×10^3 kg m^{-3}), obtained by the rapid cooling of specimens heated to 350 °C, the intensity of the long-lived component $I_2 \approx 23.8\%$ and the sum $I_1 + I_2 \approx 33.1\%$ proved to be appreciably higher than in PTFE with a higher degree of crystallinity (~76%) and density (2.26×10^3 kg m^{-3}), obtained by slow cooling: $I_2 \approx 6.9\%$ and $I_1 + I_2 \approx 21.9\%$.[89] The conversion of PTFE into an amorphous form entails an increase by 6.3% of the fraction of the narrow component in AD.[97]

Later measurements of TD and AD in polymers (PE, PTFE, PS, nylon, and lucite) confirmed the sensitivity of the TD and AD components, bound to positronium, to the degree of crystallinity (Table 3) and to the configuration and conformation of the molecular chains of polymers[1]. In particular, it has been observed[100] that, on passing to a PE "single crystal", the narrow component in AD virtually disappears. Studies on polymeric systems based on epoxy-resins[15,84,86] demonstrated a high sensitivity of the TD parameters to the microstructure of the free volume. According to Grinev et al.[84], the positron method is at present apparently most promising for the study of the microstructure of the free volume of polymers.

In order to elucidate the nature of the long-lived components in molecular substances, attempts have been made[102–105] to employ the combined AD–TD method. Thus McGervey and

Valters[105], who studied PTFE by this method, concluded that the component τ_1 is due to the annihilation of free positrons (the hypothesis of Brandt and Spirn[63]) or the positrons linked to the PTFE molecules. According to Kerr's measurements[44], $I_N \cong I_2/3$ for PTFE and PE. Hence the author concludes [see Eqn.(5)] that only the τ_2 component of TD is due to orthopositronium. On the other hand, other investigators[89,97,99] attribute the component τ_2 to the pick-off annihilation of the *o*-Ps atoms in the amorphous regions and τ_1 to the pick-off annihilation in the crystalline domains of the polymer, i.e. they believe that the ratio $I_1/(I_1+I_2)$ can serve as a measure of the crystallinity of the polymer. The same view is maintained by other investigators[15,86,91]. However, one cannot rule out the possibility that both views on the nature of τ_1 are to some extent valid if it is assumed that a positron–many-electron system, capable of being positronium-like to some extent, can be formed in the polymer. In the simplest case such a system can consist of a positron–exciton complex (see also Section III, sub-section 1).

Chandra and coworkers[106–109] drew attention to a correlation between I_2 and τ_2: a lower intensity corresponds to a longer lifetime and the points on the $I_2-\tau_2$ diagram are arranged in groups, one of which corresponds to liquids, another to polymers, and a third to crystals (Fig.9). According to the "free volume" and "positronium capture" models, the above correlation is due to the fact that γ_p (and hence also τ_2) are determined by the elementary free volume v_f and $I_2 \propto V_f/v_f$, where V_f is the overall free volume. As a result, it is possible to obtain a relation of the type[107,108]

$$I_2 = a'(1+\ln(\tau_2/\tau_c))/[b+\ln(\tau_2/\tau_c)],$$

where a', b, and τ_c are the parameters of the model and $a' \propto v_f$. The theoretical curves in Fig.9 were calculated for $\tau_c = 0.7$ ns, $b = 0.01$, and $a' = 3.375$ (crystals), 12 (polymers), 17 (liquids), and 25 (amorphous bodies).

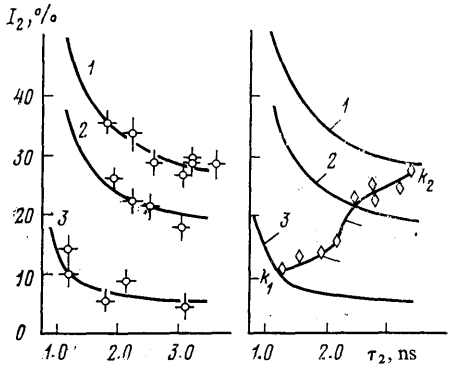


Figure 9. $I_2-\tau_2$ diagrams for simple unassociated liquids and amorphous substances including polystyrene and fused quartz (*1*), partially crystalline substances—poly(vinyl chloride), polyethylene, lucite, and Teflon (*2*), and molecular crystals (*3*); circles—experimental data; lines–calculated data; (*4*) the values of I_2 and τ_2 for Marlex-50 in the range from −196 °C (point k_1) to 142 °C (point k_2).

We shall now quote certain results obtained[49,50] with the aid of the "positronium capture" model. The solution of Eqn.(6) with experimental TD parameters for PTFE with different degrees of crystallinity χ [89] yields $k_1 = (0,32 \pm 0.05) \times 10^9$ s^{-1} and $\lambda_{p1} = (2.5 \pm 0.4) \times 10^9$ s^{-1} for $\chi_1 = 76\%$ and $k_2 = (0.67 \pm 0.10) \times 10^9$ s^{-1} and $\lambda_{p2} = (1.7 \pm 0.3) \times 10^9$ s^{-1} for $\chi_2 = 44\%$. The expected difference $\Delta I_N = I_N(\chi_2) - I_N(\chi_1) = 6 \pm 1\%$ between the intensities of the narrow components, calculated using these constants, agrees with the measured value[97]: $\Delta I_N = 6.3 \pm 0.4\%$. If we put $k = \sigma\bar{v}n$, where σ is the capture cross-section and $\bar{v}$ the average velocity of the thermal movement of the Ps atoms, then, under conditions such that $n \cong (1-\chi)n_a$, where n_a is the bulk density of traps in the amorphous region of the polymer, we have (provided that n_a is independent of χ) $k_1/k_2 = (1-\chi_1)/(1-\chi_2)$, which is confirmed by the above data: $k_1/k_2 \cong 0.48$ and $(1-\chi_1)/(1-\chi_2) \cong 0.43$. If the equilibrium concentration of traps n in the polymer obeys the Arrhenius law, i.e. $n \propto \exp(-E_a/k_0T)$, where E_a is the activation energy for the formation of traps, then the temperature variation of the rate of capture is largely determined by the factor n (Fig.10). The change in the slopes of the $\ln k - 1/T$ linear plots in phase transitions is apparently associated with the change in the activation energy E_a.

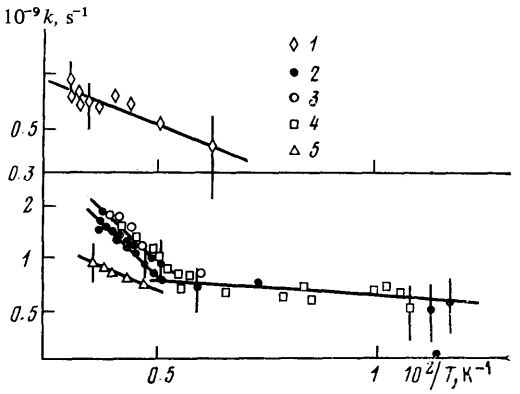


Figure 10. Dependence of the rate constant k for the capture of positronium on the reciprocal of temperature (on the semilogarithmic scale) in Teflon (*1*), polyethylene (*2–4*), and glycerol (*5*) plotted[49] on the basis of data from a series of investigations[49,63,76].

Using the results of TD and AD measurements and the "empty free volume" model (see Section IV, subsection 3) and the "positronium capture model" (see Section IV, subsection 4), Bartenev et al.[50] estimated the radius of the traps, the capture rate constant k, and the bulk density of traps n in high-pressure PE of two types—PEA (autoclave reactor) and PET (tubular reactor). The relation $\sigma = \pi a^2$ was used to estimate n from the measured values of k: $a = 0.45 \pm 0.05$ nm, $k = 1 \times 10^9$ s^{-1} (±30%), and $n = 0.15 \times 10^{22}$ m^{-3} for PEA, and $a = 0.34 \pm 0.05$ nm, $k = 4 \times 10^9$ s^{-1} (±30%), and $n = 1.1 \times 10^{22}$ m^{-3} for PET.

The temperature effects of the annihilation of positrons in polymers do not reduce solely to those discussed above. The TD (I_2 and τ_2)[1,84,110,111] and AD (I_N) [51] parameters are influenced significantly by the thermal degradation of the polymer, since the free radicals arising in this process cause additional quenching of orthopositronium (see below). In the solution

of the problems considered here (and in the previous Section), general approaches have so far been outlined; there is still a need for much tedious theoretical and experimental work in order to achieve an unambiguous quantitative utilisation of the results of measurements of TD and AD parameters in the physics and chemistry of polymers. The results of studies of the reactions of positronium in molecular[42,112-115] and liquid crystals[116-120], haemoglobin[121], aminoacids[122], optical isomers[122,123], etc. may prove to be not without interest from this point of view. In molecular crystals the reactions of positronium are influenced significantly by phase transitions, structural defects, impurities, and the form of the free volume. In liquid crystals the TD parameters (I_2 and τ_2) undergo considerable sudden changes at the phase transition points, and in the isotropic liquid → liquid crystal phase → crystal transitions τ_2 increases abruptly for liquid crystals with negative dielectric anisotropy ($\varepsilon_a < 0$) and conversely decreases for liquid crystals with $\varepsilon_a > 0$. In aminoacids a difference has been observed between the values of I_2 and τ_2 for D- and L- isomers, the sign of the differences ΔI_2 and $\Delta\tau_2$ being positive for some aminoacids and negative for others.

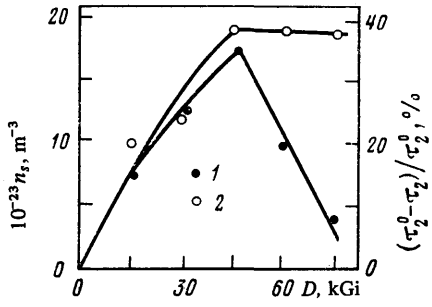


Figure 11. The relative decrease of τ_2 (*1*) and the change in the concentration of free radicals (*2*) in Teflon with increase of the dose of irradiation with ^{60}Co γ-rays (for the non-irradiated specimen, $\tau_2^0 = 3.5 \pm 0.2$ ns).[124]

VI. THE FATE OF POSITRONIUM IN IRRADIATED POLYMERS

1. Teflon

The lifetime of orthopositronium τ_2 in PTFE irradiated with ^{60}Co γ-rays is not determined[124] unambiguously by the concentration of free radicals n_s (Fig.11). The rupture of the C–F and C–C bonds leads to the formation, together with free radicals, of vacancies at the sites of fluorine atoms or in the slit arising in the main polymer chain as a consequence of some compression of its two sections after the dissociation of the C–C bond[124]. The positronium located in these vacancies (type A) can be rapidly "quenched" by the neighbouring unpaired electron (lifetime $\tau_2' < \tau_2^0$). Saturation with respect to the yield of radicals is due to their recombination, but the slits at the sites of dissociation of the C–C bonds are retained under these conditions. Such slits again serve as the locations (type B) of Ps atoms, but here positronium is annihilated after a time $\tau_2'' \cong \tau_2^0$. The authors[124] expressed the observed lifetime of orthopositronium by the formula

$$\frac{1}{\tau_2} = \frac{N_0 + N_B}{N_0 + N_A + N_B}\frac{1}{\tau_2^0} + \frac{N_A}{N_0 + N_A + N_B}\frac{1}{\tau_2'}, \qquad (10)$$

where N_0 is the number of vacancies in the non-irradiated polymer and N_A and N_B are the numbers of vacancies of types A and B. The quantities N_A and N_B are related to the dose D, the radiation intensity I, and the radiation yield in the formation of radicals q by the expressions[2]

$$N_A = N_S\frac{\exp(2N_S ID) - 1}{\exp(2N_S ID) + 1}, \quad N_B = qD - N_A,$$

where $N_S = qI/k_r$, k_r being the rate constant for the recombination of radicals. The limiting value is $N_A = N_S$. The maximum value of τ_2 is attained when $N_0 + qD = \frac{1}{2}N_S\exp(2N_S ID)$. On the other hand, if $D \to 0$ or $D \to \infty$, then $\tau_2 \to \tau_2^0$, which is observed experimentally. It should be noted that Eqn.(10) is inconsistent with the "positronium capture model". In essence, it is assumed in Eqn.(10) that the *o*-Ps atom can undergo pick-off annihilation with a probability $1/\tau_2^0$ and quenching by radicals with a probability $1/\tau_2'$.

When the TD spectrum was resolved into three components, and not two as in the study of Chandra et al.[124], Green and Tao[125] observed a decrease of the "longest time" τ_2 and an increase of the ratio $I_1/(I_1 + I_2)$ with increase of the γ-irradiation dose in PTFE. Green and Tao[125] explained the decrease of τ_2, like Chandra et al.[124], by the quenching of positronium by radicals and the increase of the ratio $I_1(I_1 + I_2)$ by the increase of the degree of crystallinity of PTFE (in conformity with the hypothesis of the same workers[89], mentioned above). Later measurements[21,126-128] confirmed on the whole the results of the above studies[124,125] and at the same time revealed the influence of air on the dependence of τ_2 and I_2 on the irradiation dose, but the results were contradictory (cf. for example, the data of Hsu and Hadly[21] and Khan et al.[126]). Furthermore, according to the measurements of Hsu and Hadley[21], the intensity I_1 of the intermediate component is independent of the irradiation dose (in contrast to the data of Green and Tao[125]). If this is so, it would follow, according to Hsu and Hadley[21], that the component τ_1 of TD is not related to the pick-off annihilation of orthopositronium and the problem of its nature arises again (see above).

The influence of γ-irradiation on TD in PTFE has been studied[129,130] in the region of small doses (up to 30 kGr). Together with TD spectra, measurements were made of the EPR and NMR spectra, the density, and the dielectric constant. It was shown that the dependence of the degree of conversion of positronium in irradiated PTFE on the irradiation dose is influenced by factors such as the change in free volume, free radicals, and crystallinity.

2. Polyethylene

In contrast to PTFE, when PE is subjected to γ-irradiation[131], radiation-induced cross-linking of the chains takes place and not their degradation at C–C bonds. For rapid cross-linking, an EPR signal is not observed. According to X-ray diffraction data[131], the irradiation of PE leads to a decrease of the number and size of the polymer microcrystals with a corresponding increase of the fraction of amorphous low-density regions. Therefore, from the standpoint of the "free volume" model, one may expect an increase of the lifetime τ_2 on irradiation of PE, which has indeed been observed (see Fig.12). (The TD spectrum was resolved into two components[131]). Data concerning I_2 were not presented[131].

Ito and Tabata[132] measured TD in PE obtained from ethylene at high pressure by radiation polymerisation. The polymer was irradiated with γ-rays and the TD was measured at −78 °C *in vacuo*. As a result, it was possible to "reveal" the influence of free radicals on the quenching of orthopositronium in PE; there is a linear relation between the increase of the rate of annihilation of orthopositronium λ_2 under irradiation and the increase of the spin concentration n_S, namely $\Delta\lambda_2 = \lambda_2 - \lambda_2^0 = k_r n_S$, where $k_r \cong 0.22 \times 10^{-17}$ m^3 spin^{-1} s^{-1}. With the increase of the irradiation dose, τ_2 decreases linearly, while I_2 remains almost unchanged (approximately 30%). The decrease of τ_2 in γ-irradiated PE (at low temperatures) was explained[132] by the "quenching" of orthopositronium as a result of the reaction of *o*-Ps atoms with free radicals R: $Ps + R \rightarrow PsR \rightarrow 2\gamma$. The rate of this reaction is an order of magnitude lower than the rate of reaction of *o*-Ps atoms with acceptors in solutions. Assuming that the mobility of the *o*-Ps atoms is determined by diffusion, Ito and Tabata estimated the diffusion coefficient of *o*-Ps atoms: $D_p = (0.58-1.75) \times 10^{-9}$ m^{-2} s^{-1}. The value of D_p obtained is higher than for the reaction of *o*-Ps atoms with DPPH in solid pyridine at −78 °C but lower than, for example, for the diffusion of *o*-Ps atoms in metal oxides.

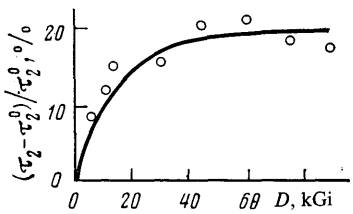


Figure 12. The relative increase of τ_2 in polyethylene with increase of the dose of irradiation by ^{60}Co γ-rays ($\tau_2^0 = 2.0 \pm 0.2$ ns).[131]

3. Polystyrene

Thosar et al.[133] did not observe an influence by γ-radiation (doses up to 250 kGr) on PS—either on τ_2 or on I_2. However, the results of Hsu and Hadley[134] led to the opposite finding. They investigated very dense PS specimens with a low crystallinity, obtained from the monomer by annealing *in vacuo* at 70 °C. The PS specimens were irradiated with ^{137}Cs γ-rays (dose rate 10^3 Gr h^{-1}). The irradiation and the measurement of TD were carried out at room temperature *in vacuo* and in air.

Vacuum irradiation (dose 80 kGr) leads to a decrease of I_2 from approximately 33.8% to approximately 29.3% when TD is measured *in vacuo*; after annealing the irradiated specimens at 70 °C for 24 h and measurement of TD under the same conditions, the previous value of I_2 is found to be restored (approximately 33.5%); on the other hand, measurement in air yields $I_2 \cong 30.4\%$. In air I_2 decreases with increasing irradiation dose from approximately 34.1% to approximately 28.2% for a dose of 150 kGr; τ_2 also diminishes somewhat under these conditions (from 2.33 ± 0.02 to 2.25 ± 0.02 ns). After annealing, the previous value of I_2 is restored, while τ_2 remains unchanged (or decreases slightly: $\tau_2 = 2.23 \pm 0.02$ ns). The changes in I_2 are apparently due to the inhibition of the formation of positronium in γ-irradiated PS by free radicals and also by stable oxygen-containing groups (C=O and OH)—the products of the conversion of free radicals in the presence of atmospheric oxygen[134]. The insensitivity of τ_2 to γ-irradiation is explained by the absence of appreciable changes in the supermolecular structure (i.e. in the "free volume").

Irradiation of PS with neutrons in the thermal column of a nuclear reactor causes a marked decrease of I_2 (by approximately 40% for a dose of approximately 2.4×10^7 kGr), leaving $\tau_2 = 2.2 \pm 0.2$ ns unchanged[133]. Neutron irradiation of PS leads to the breakdown of the benzene rings (according to NMR data) and to the accumulation of free radicals (according to EPR data). Since the formation of positronium in PS is probably associated mainly with benzene rings[133], the breakdown of the latter under neutron irradiation leads to a decrease of I_2. Hence, if Ps atoms are annihilated preferentially in the benzene rings, the quenching influence of the free radicals produced under irradiation outside the benzene rings will be negligible compared with the quenching of the Ps atoms as a consequence of pick-off annihilation by interaction with the electrons of the aromatic rings.

The results of the study of the influence of irradiation on the formation and destruction of positronium in polymers (as in other molecular substances[2] and even in substances such as quartz[10,92]) confirm qualitatively the "free volume" model and the role of order. At the same time it has been observed that in molecular solids (apart from the studies quoted above, see also, for example, Refs. 1, 15, 110, 111, and 135–139), the quenching of positronium by free radicals can play a significant role together with pick-off annihilation. The same conclusion follows also from the analysis of the measurements of the TD and AD parameters in polymers subjected to thermal degradation, which was already mentioned above. One should note that an estimate[111] of the rate of quenching of positronium by radicals in PVC yielded a value greater by 3–4 orders of magnitude than that observed in PE (see above): $\bar{k}_r \cong 8.4 \times 10^{-12}$ kg spin^{-1} s^{-1}. Free radicals (as well as their reaction products) can apparently function not only as quenching agents but also as inhibitors of the formation of positronium.

4. The Quenching of Positronium by Radicals

The mechanisms of the quenching of positronium by free radicals (or stable groups—the products of the reactions of radicals) can be various: *ortho–para* conversion, addition and oxidation reactions, etc. Analysis of the kinetics of the reactions of positronium taking into account the above quenching mechanisms shows that the increase of the rate of quenching of orthopositronium is

$$\Delta\lambda_2 = \lambda_2 - \lambda_2^0 = k = k_r n_s, \qquad (11)$$

where $\lambda_2^0 = \lambda_t^0 + \lambda_p$ and k is the rate constant of *ortho–para* conversion, the addition reaction, the oxidation reaction, etc. In the case of *ortho–para* conversion Eqn. (11) is valid provided that $k \ll \lambda_S^0$ and $\lambda_p \ll \lambda_S^0$. In terms of the approximation indicated, *ortho–para* conversion leaves unaltered the intensity of the long-lived TD component ($I_2 \cong \frac{3}{4}P$) and intensifies the narrow AD component:

$$I_N \simeq \frac{1}{4} P \left(1 + \frac{3k}{\lambda_2^0 + k}\right).$$

As already mentioned, in γ-irradiated PE the intensity I_2 remains almost unchanged as λ_2 increases [in conformity with Eqn. (11)] in the course of the accumulation of free radicals[132].

The addition reaction $Ps + R \rightarrow PsR$ weakens both the long-lived TD component, i.e.

$$I_2 = \frac{3}{4}P\left(1 - \frac{k}{\lambda_p + k + \lambda_{pr}}\right),$$

where λ_{pr} is the rate of pick-off annihilation in the PsR system, and the narrow TD component:

$$I_N \simeq \frac{1}{4}P\left(1 - \frac{k}{\lambda_s^0}\right) \text{ (for } \lambda_p, \lambda_{pr}, k \ll \lambda_s^0).$$

One cannot rule out the possibility that the simultaneous decrease of τ_2 and I_2 (in terms of our notation!) on γ-irradiation of PS is due to the addition reaction[134].

In the oxidation reaction $Ps + R \rightarrow Re^- + e^+$ the I_2 and I_N components are also simultaneously weakened [for example, $I_N \cong \frac{1}{4}P(1-\frac{\lambda_p + k}{\lambda_s^0})$], but, in contrast to the addition reaction, other TD parameters behave differently.

Each version of the quenching of positronium by radicals thus has its specific distinctive features, which make it possible to identify them from experimental data. Other mechanisms of the quenching of positronium by radicals examined above behave analogously. It is easy to see also the possible ways of devising general models taking into account the "free volume" and "positronium capture" models. In order to construct general models taking into account the possibility of the limitation of the rates of reaction by the rate of diffusion of Ps atoms and radicals (as well as traps), one can use the formal treatment developed by Brandt, Seeger, and coworkers[52-56].

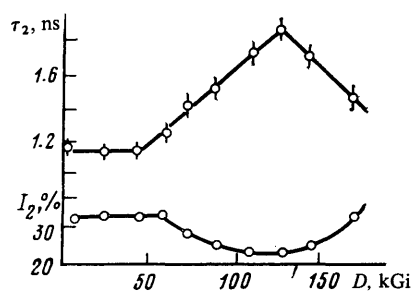


Figure 13. Dependence of τ_2 and I_2 on the irradiation dose for the crystalline monomer *N*-vinylcarbazole (rate of irradiation 7.2×10^{-2} Gi h^{-1}).[136]

VII. THE EFFECTS OF THE MOLECULAR WEIGHT AND COMPOSITION

1. The Effects of the Molecular Weight

In the radical polymerisation of *N*-vinylcarbazole ($C_{15}H_{14}N$), a crystalline monomer, the TD parameters (τ_2 and I_2) associated with orthopositronium depend in a complex manner on the degree of polymerisation[136] (Fig.13). The maximum in τ_2 corresponds to the polymerisation saturation point; further irradiation leads to the accumulation of positronium quenching radicals, which is the reason, according to the authors[136], for the decrease of τ_2 in the region of doses ≥130 kGr. Analogous studies were carried out also for other monomers[1,140-143], but their results showed that the parameters of the TD spectrum are sensitive to the degree of polymerisation and are correlated with EPR data.

Khan[111] studied in detail the influence of temperature on τ_2 (and also on I_2) in PVC, which differs from the polymers studied in most of the investigations quoted above by being thermally unstable. Measurements were made of the long lifetime τ_2, of the intensity of the EPR signal (concentration of free radicals), and of the decrease of the molecular weight as a function of the time t during which specimens of pure and plasticised PVC with different initial molecular weights were heated at a constant temperature (at 150 °C and also, for comparison, at 170 °C). Findings such as the exponential decrease of τ_2 with increase of the duration of heat treatment (the ratio $\tau_2/\tau_2^0 \cong 0.2$ for $t = 7$ days) together with the exponential increase of the concentration of free radicals and decrease of the molecular weight, and the dependence of the rates of the above changes on the molecular weight, temperature, etc. show that the quenching of positronium is due to the free radicals arising in the thermal degradation of PVC.

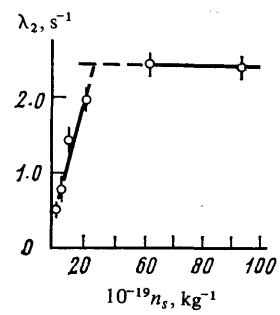


Figure 14. Dependence of $\lambda_2 = \tau_2^{-1}$ on the concentration of free radicals n_S produced by thermal degradation at 150 °C in pure poly(vinyl chloride) powder with $M = 200000$.[111]

Khan believes that positronium is more likely to be quenched by the capture of Ps atoms by free radicals (addition) or the capture of the unpaired electron of the free radical by a Ps atom with formation of the Ps^- ion (formally this mechanism can be regarded as an addition reaction—Section VI) and not via the *ortho–para* conversion mechanism. Evidence in support of the formation of the ion comes from the finding that τ_2 in PVC reaches a minimum value (0.37 ± 0.05 ns) at a spin concentration $n_S \cong 25 \times 10^{19}$ spins kg^{-1} and remains unchanged as n_S increases further (Fig.14). The minimum value of τ_2 is almost equal to the lifetime of the ion Ps in relation to annihilation (0.35 ns).

The dependence of the lifetime of positrons on the average molecular weight M_w has been observed directly[144,145] for polypropylene. The following approximate relation holds for the TD components:

$$\tau_i = \tau_i^0 - \delta_i \bar{M}_w,$$

where τ_i^0 and δi are constants. For polypropylene, $\tau_0(ns) = 0.30 - 0.080 \times 10^{-6}\,\bar{M}w$ and $\tau_2(ns) = 0.48 \times 10^{-6}\,Mw$. Chuang and

Tao[145] attempted to justify this relation in terms of the "free volume" model.

2. Elastomers

Interesting results have been obtained[7,146-148] from measurements of the parameters τ_2, I_2 and $P_{3\gamma}$, characterising the probability of the formation and quenching of positronium in elastomers. On passing from raw rubber to isoprene and then to cured rubber (3% of sulphur), a decrease is observed in $P_{3\gamma}$ (the ratio $P_{3\gamma}/P^0_{3\gamma} = 3.8$, 2.08, and 2.2 respectively) and I_2 (50, 13, and 26% respectively), while $\tau_2 \cong 2.2$ ns remains almost unchanged. On passing to ebonite (32% of sulphur) and to sulphur, τ_2 falls to approximately 0.5–0.6 ns. A more detailed study of the AD and TD parameters (I_N, I_2, and τ_2) for raw rubber and its vulcanised forms with different sulphur contents (up to 10%) and corresponding to different vulcanisation times confirmed the decrease of I_2 [under these conditions, $\Delta I_2 \cong 3\Delta I_N$; see Eqn.(5)] with increase of the sulphur content, I_2 being proportional to the degree of unsaturation. With increase of the vulcanisation time, ΔI_2 increases in parallel with the increase of the relative amount of bound sulphur.

A correlation between the network density and the change in I_2 (at $t = 40$ min, I_2 diminishes by a factor of approximately 2) has been observed[15,84] for sulphur-vulcanised ternary ethylene–propene rubber with increase of the vulcanisation time.

The observed decrease of I_2 from 28% for raw rubber to 8% for raw rubber +10% S, to which corresponds a weakening of the narrow component in AD ($\Delta I_2 \cong 3\Delta I_N$) with a virtually unchanged τ_2 has been attributed[146] to the inhibition of the formation of positronium with decrease of the degree of unsaturation, i.e. of the fraction of double bonds in the rubber (it varies from 95 to 74% respectively). On the other hand, the relation $\Delta I_2 \cong 3\Delta I_N$ indicates the absence of chemical interactions between the Ps atoms and the surrounding molecules and groups and of *ortho–para* conversion (see Section VI, subsection 4). It is suggested that positronium is formed in raw rubber at the sites of double bonds as a result of the capture of π-electrons by positrons. The formation of positronium is apparently inhibited as a result of the annihilation of the volumes in which it can be formed and exist (by analogy with the influence of the neutron irradiation of PS on I_2—see above). The inhibiting effect of the non-static (microheterogeneous) distribution of vulcanisation cross-links on the formation of positronium in raw rubber relative to the static (homogeneous) distribution has been observed[148].

Having applied the "positronium capture" model (see Section III, subsection 3), Arifov et al.[148] estimated from TD parameters the probability P of the formation of positronium and the rate constant k for its capture by traps in elastomers based on the butadiene–styrene rubber: $P \cong 0.6$–0.7 and $k \cong (0.6\text{–}0.7) \times 10^9$ s^{-1}. The extent of the region (trap) in which the Ps atom is localised in the rubber amounts to approximately 0.86 nm, which corresponds to the distance between the groups of neighbouring chains[51,146].

3. Mixtures

Studies have been made[1] on mechanical mixtures of PVC and PE homopolymers and graphite–polyethylene and graphite–4-vinylpyridine copolymers. In the case of macromixtures (grain size more than 10 nm) the annihilation characteristics of the mixture constitute a linear superposition of the annihilation characteristics of the initial polymers; in micromixtures there is no such superposition. It is assumed that in macromixtures positronium is localised in the component where it was formed, while in micromixtures, it is able to diffuse into the other mixture component. The influence of the micromixture on the reactions of positrons and positronium in filled polymers (PE + Al_2O_3 + perlite, polybutadiene + carbon black, etc.) has been investigated[15,86,91,149]. In the case of filled PE it proved possible to elucidate[15,91] the cause of the strengthening of the material (maximum degree of crystallinity) for a specific content of the filler (35%) and also the role of pressure and temperature in the treatment of the material.

Here we shall also point to studies[150-152] in which measurements were made of TD (and AD) in mixed organic crystals and to an investigation[81] in which it was noted that, according to the TD measurements, the vitrification of dry nylon occurs at 50 °C, while in the presence of 0.5% of water it takes place at 30 °C, which indicates yet again a fairly considerable sensitivity of the positron method. There is no theory of the formation and reactions of the positrons and positronium in polymers of complex composition, in elastomers, and in mixtures and compositions.

VIII. THE INFLUENCE OF THE ELECTRIC AND MAGNETIC FIELDS ON THE REACTIONS OF POSITRONS AND POSITRONIUM IN POLYMERS

1. The Effects of the Electric Field

The formation of positronium in matter in the presence of an electric field has been studied theoretically[71,153-155]. On the one hand, the field displaces positrons outside the limits of the Ore gap (see Section III), which leads to a decrease of the probability of the formation of positronium, and, on the other hand, the heating of "slow positrons" increases the yield of positronium. The relative contributions of the two processes are determined by the ratios of the cross-sections for the positronium processes, the loss of energy by positrons, and the annihilation of positrons. In weak fields the first of the above effects of the electric field may predominate the inhibition of the formation of positronium may therefore be observed (see also the considerations put forward by Mogensen[156]). The effect involving the "heating" of positrons by the field, i.e. the increase of the yield of positronium, predominates in strong fields. Experiments with gases on the whole confirmed this picture[2,154,155].

On passing to polymers, we note in the first place that in polymers the probability of the formation of positronium as well as the rate of its quenching depend appreciably on the dipole moment of the molecules: I_2, τ_2, and $P_{3\gamma}$ decrease with increase of the molecular dipole moment of the polymer (see, for example, Refs.7, 89, and 157). For example, the above quantities have the following values for PE and PVC with almost identical valence-electron densities and ionisation potentials but markedly different molecular dipole moments (0 for PE and 6.7×10^{-3} C m for PVC):[7] $P_{3\gamma} = (2.14 \pm 0.3) P^0_{3\gamma}$, $I_2 = 22 \pm 2\%$, and $\tau_2 = 2.1 \pm 0.2$ ns for PE; $P_{3\gamma} = (1.23 \pm 0.15) P^0_{3\gamma}$, $I_2 = 13 \pm 2\%$, and $\tau_2 = 1.23 \pm 0.1$ ns for PVC.

Thus in polymers and, incidentally, in liquids[2] the probability of the formation of positronium diminishes with enhancement of the polarity, i.e. with increase of the molecular dipole moment, while the rate of pick-off annihilation actually increases. The effect of polarity is shown clearly on passing from raw rubbers (non-polar compounds) to isoprene (in which the C–CH_3 bond leads to a dipole moment

of 1.7×10^{-30} C m), cured rubber, and ebonite (32% of sulphur) (polar dielectrics)[7] and from butadiene–styrene rubber with a static (homogeneous) distribution of vulcanisation cross-links to a rubber with a non-statistical (heterogeneous) distribution of such links[140].

The electric field of the dipoles can apparently influence not only the probability of the formation of positronium but also the spatial distribution of positrons and positronium in matter, directing them (positrons and Ps atoms) to specific atomic groups (into the region of enhanced electron density), so that their annihilation is accelerated. Furthermore, the rate of self-annihilation and the half-width of the momentum distribution of Ps atoms can change significantly in the electric field of the dipoles[158].

Static fields up to $E = 12$ MV m^{-1} decrease significantly the lifetime of the long-lived component in PTFE and PE: $\tau_2 = \tau_2^0(1-\alpha E)$, where $\alpha = (9.3\pm1.3)\times10^{-3}$ m MV^{-1}, while in polar polymers (lucite, nylon, and PVC) this type of influence of the field has not been observed[74]. The absence of an effect by the electric field on τ_2 in polar polymers is apparently associated with the fact that in the vicinity of the electric dipoles generated by them the field greatly exceeds the external field.

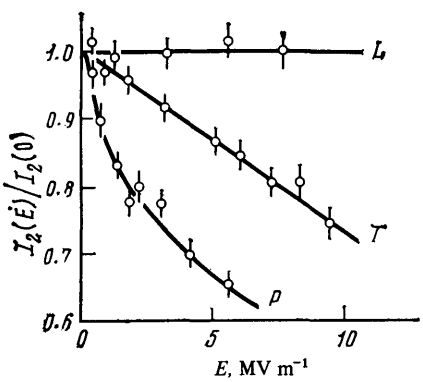


Figure 15. The influence of the electric field on the intensity of the long-lived TD component (τ_2) in lucite (L), Teflon (T), and polyethylene (P).[159]

In typically non-polar polymers like PS and PTFE the probability of the formation of positronium greatly diminishes with increase of the electric field (by 33 and 13% respectively for $E = 5$ MV m^{-1}). On the other hand, in polar polymers (lucite, nylon, and PVC) the electric field does not affect the probability of the formation of positronium (Fig.15)[159] (this may be due to the cause indicated above in the discussion of τ_2). Analogous conclusions were also reached on the basis of the analysis of the results of measurement of $P_{3\gamma}$ in polymers with application of a static electric field: $P_{3\gamma}(E) = P_{3\gamma}(0)(1-\beta E)$ for non-polar polymers, where $\beta \approx 0.80$ m MV^{-1} for PS and $\beta \approx 0.022$ m MV^{-1} for PTFE.[7] The influence of the electric field for PTFE and PE has also been investigated in other studies[71,160-166]. We may note that the results quoted by Patterson and Stewart[160] conflict with the previous ones: no effect of the field (on AD) is not observed up to 11 MV m^{-1}. The absence of a field effect in polar polymers has been confirmed[71].

Bertolaccini et al.[164] (see also Refs.162 and 163) observed a time effect in the influence of the electric field on the probability of the formation of positronium in PE. Immediately after the application of the field, $P(E)$ decreases sharply relative to $P(0)$ and then, when some time has elapsed, the ratio $P(E)/P(0)$ begins to increase and reaches a plateau (Fig.16). On the other hand, in the initial instant the probability of the formation of positronium in PE decreases with increasing field, in conformity with the results of previous measurements. When the field has been switched off, the ratio $P(E)/P(0)$ does not immediately reach unity (Fig.17). It has been suggested[164] that the time dependence of the probability of the formation of positronium in PE, observed when the field is applied and removed, is a consequence of the relaxation of the effective electric field $E(t)$, which in fact acts upon the PS atom in the given substance. The data in Figs.16 and 17 agree with the $E(t)$ relation of the type $E(t) = E(\infty) + [E(0)-E(\infty)]\exp(-t/\tau)$. Thus a whole series of effects of the electric field have been observed in polymers: the effect of the polarity of the polymers, the quenching and inhibition of the formation of positronium, and relaxation effects in the inhibition of the formation of positronium by the electric field.

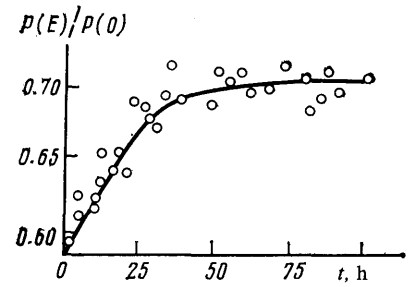


Figure 16. Dependence of the probability of the formation of positronium in polyethylene on the time elapsed from the instant of the application of the electric field $E = 10$ MV m^{-1}.[164]

2. Magnetic Quenching of Positronium in Polymers

The magnetic field (B) is one of the most reliable indicators for the determination of the amount of positronium formed in a given substance. The observed quenching of positronium by the magnetic field constitutes an additional source of information about the properties of positronium in the given substance and hence about the properties of the substance itself.

In the simplest case where the interaction of positronium with the surrounding medium reduces to pick-off annihilation (see Section III), the factors characterising the changes in $P_{3\gamma}$, I_N, and I_2 in a magnetic field as a consequence of the magnetic quenching of positronium are given by the following expressions (see, for example, Refs.2, 12, 33,47, and 167–170) in terms of the approximation $y^2 \ll 1$ {$y = [(1+x_2)^{1/2}-1]/x$, where $x = 4\mu_B B/\Delta E$, μ_B = Bohr magneton, and ΔE is the amount by which the energy of the triplet substate of the Ps atoms exceeds the energy of the singlet substate; *in vacuo* $\Delta E = 8.4\times10^{-4}$ eV}, which is valid for

$\lambda_p \ll \lambda_s^0$ and fields up to $B = 2$ Tl:

$$w_{s\gamma} = P_{s\gamma}(B)/P_{s\gamma}(0) = 2/3 + 1/3(1-Q)^{-1}, \quad (12)$$

$$\varepsilon(B) = [I_N(B) - I_N(0)]/I_N(0) = Q/(1+Q), \quad (13)$$

$$R(B) = \left[\int_{\tau_2}^{\infty} p(t)\,dt\right]_B \Big/ \left[\int_{\tau_2}^{\infty} p(t)\,dt\right]_0 = \frac{1}{3}(2 + e^{-Q}), \quad (14)$$

where $Q = y^2\tau_2/\tau_s^0$ is the parameter of the magnetic quenching of positronium. In still weaker fields, where $x^2 \ll 1$ ($x = 0.275$ V if B is expressed in Tl), one can put $Q \cong 0.151\,B^2\tau_2$ (B expressed in Tl and τ_2 expressed in ns).

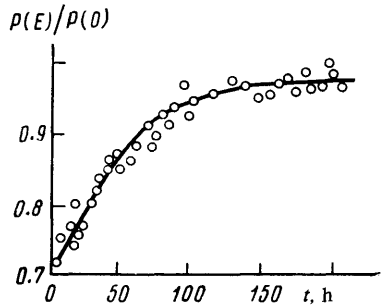


Figure 17. The relaxation of the formation of positronium in polyethylene after switching on the electric field $E = 10$ MV m^{-1}.[164]

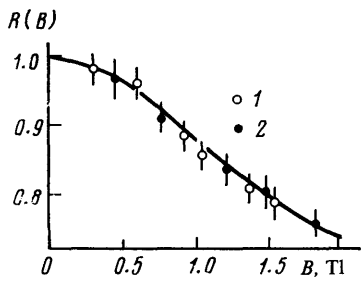


Figure 18. Suppression of the long-lived TD component by the magnetic field in Teflon (*1*) and lucite (*2*); circles—experimental data; lines—calculated data[167].

The nature of the influence of the magnetic field on the experimental characteristics of the annihilation of positronium in matter can be seen directly from Eqns.(12)–(14): in the presence of a magnetic field the probability of 3γ-annihilation [Eqn.(12)] diminishes, the narrow AD component intensifies [Eqn.(13)], and the long-lived component τ_2 of the TD spectrum is suppressed [Eqn.(14)]. The results of the observation of the magnetic quenching of positronium in polymers[2,33,47,167,169,171–177] confirmed the theoretical conclusions (Fig.18). The magnetic quenching of positronium has been investigated[178] within the framework of the "positronium capture" model.

Having analysed the results of the measurements of the factor $R(B)$ in PTFE, PE, PS, PVC, and nylon, Bertolaccini et al.[177] concluded that the Ps atom is "deformed" in polymers (as in ionic crystals[12]). The deformation of the Ps atom in matter can be characterised by the relation $\alpha_m = |\psi(0)|_m^2/|\psi(0)|_0^2$, where $|\psi(0)|_m^2$ and $|\psi(0)|_0^2$ is the electron density at the "zero" point in the Ps atom in matter and *in vacuo*. In polymers $\alpha_m \leq 1$ (Table 4), i.e. the Ps atom exhibits a tendency to "swell"[177]. Within the framework of the phenomenological model of the interaction of positronium with the surrounding medium, proposed by Urbanovich[179], the energy of the interaction of the atom with the molecules surrounding it in a given substance can be estimated, provided that the parameter α_m is known: $U(\text{eV}) = -13.6(1-\alpha_m^{1/3})^2$. As was to be expected, in polar polymers (PVC and nylon) the interaction of the Ps atom with molecules is stronger than in non-polar polymers (Table 4).

Table 4. The "deformation" parameters (α_m) and the energies U of the interaction of the Ps atom with the surrounding medium in polymers.

Substance	α_m (Ref.162)	$-U$, eV
Teflon	1.00±0.09	0
Polyethylene	0.71±0.04	0.16
Polystyrene	0.80±0.06	0.07
Poly(vinyl chloride)	0.060±0.08	0.35
Nylon	0.56±0.4	0.44

The influence of the magnetic field on the intermediate TD component τ_1 in different polymers is manifested unequally[177]: in PTFE no effect of the field is observed, in PE, PS, and nylon the effect is very weak, and in PVC the magnetic quenching of the component τ_1 is clearly observed. It can therefore be suggested (see Section V) that the component τ_1 is due to the positron state which is to some extent positronium-like. One should note that there are still comparatively few data concerning the influence of fields on the AD and TD parameters and $P_{3\gamma}$ and the available data are frequently fragmentary. Such data are necessary to refine our ideas concerning the mechanisms of the reactions of positrons and positronium in polymers and, as already mentioned, to convert "qualitative" information, provided by the method indicated, into quantitative information.

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Fairly extensive experimental data have now accumulated on the properties of positrons and positronium in polymers and we are able to account for the results of the measurements at least qualitatively if not quantitatively. The available data make it possible to claim confidently that positrons effectively "sense" polymers and therefore the positron method can indeed become a valuable supplement to the already existing methods in the physics and chemistry of polymers. Naturally much is still obscure and even contradictory in both experimental results and in their interpretation. There are virtually no data obtained simultaneously by all methods for the observation of the annihilation of positrons (AD, TD, AD-TD, $P_{3\gamma}$, etc.) in the same specimens with

a well known history. There is no rigorous quantitative theory of many of the observed phenomena. Nevertheless studies are being performed along a widening front, the number of investigators is increasing, the experimental technique and methods are being improved, and theoretical studies are being prosecuted; it may be hoped that the positron method will permit the solution of many problems in the physics and chemistry of polymers and other substances[180].

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