

## CONTRIBUTION TO THE THEORY OF THE CHEMICAL REACTIONS OF MUONIUM

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The possibility of classifying the character of the chemical reactions of muonium in media and of experimentally determining the rates of these reactions is considered on the basis of the phenomenological theory of depolarization of the  $\mu^+$  meson in media. Cases are considered when the reactions possess both "ordinary" channels and the so-called hot chemistry channel, and the resultant products can be both diamagnetic and long-lived ( $\tau > 10^{-5}$  sec) radical compounds. An analysis is presented of all the available possibilities, particularly, additional information, which can be obtained by investigating the dependence of the observed polarization on the time, is investigated. Relations are obtained which make it possible to determine experimentally both the reaction rates and the relative importance of the different channels for muonium, as well as other phenomenological parameters of depolarization theory.

1. The possibility of investigating the depolarization of the  $\mu^+$  meson in condensed phases to determine the rates of chemical reactions between the hydrogen like atom muonium and matter was first pointed out by Firsov and Byakov<sup>[1]</sup>. Subsequently<sup>[2,3]</sup>, a number of experimental investigations were performed, in which it was shown that the depolarization of the  $\mu^+$  meson depends essentially on the addition of chemically active impurities to the depolarized medium. The dependence of the degree of depolarization on the chemical activity of the medium becomes obvious if it is recognized that after the muonium enters into the chemical bond, the conditions under which it is situated change radically. The depolarization of the  $\mu^+$  meson either stops completely if it is in a chemical compound with saturated valence bonds, where the magnetic field produced on the  $\mu^+$  meson by all the valence electrons vanishes<sup>[4]</sup>, or else, if the  $\mu^+$  has entered in a compound of the radical type with an unpaired valence electron, the depolarization can occur, but its rate, generally speaking, differs significantly from the depolarization rate of the  $\mu^+$  meson in the chemically free muonium atom ( $\mu^+e^-$ ).

2. Inasmuch as the directly observed quantity is the  $\mu^+$ -meson polarization, it is obvious that to determine the rate of the reaction of the muonium atom in a given substance it is necessary to have an analytic expression relating the polarization  $P$  with the reaction rate, or, which is the same, with the mean lifetime  $\tau$  of the muonium prior to its entry in the chemical reaction, which is inversely proportional to the reaction rate. The concrete character of this dependence is determined primarily by the entire prior history of the life of the  $\mu^+$  in the substance before it enters the reaction, and secondly by the behavior of its polarization after the  $\mu^+$  meson enters into the chemical bond with the molecules of the substance.

3. We consider further the situation in which the  $\mu^+$  meson is decelerated in a diamagnetic substance, capturing an electron during a certain stage of the deceleration, and forming the ( $\mu^+e^-$ ) atom. It is of great importance for what follows that we confine ourselves here to an analysis of the "pure muonium" mechanism of the polarization, i.e., we assume, first,

that there is no charge exchange at all, second that the muonium is in the 1S state and the admixture of excited states is small, third that the reaction occurs either very rapidly, before the depolarization has begun in practice, or slowly enough to permit full thermalization of the muonium atoms. The conditions mentioned above are dictated by the fact that only in the latter case is there available a consistent depolarization theory, as developed in<sup>[4,5]</sup>. Whether these conditions are satisfied in each concrete case is a question that must be answered by experiment. We shall formulate below a number of attributes which make it possible to establish whether the "pure muonium" mechanism is realized in a given substance. A theoretical analysis was performed earlier in<sup>[1]</sup>, but the relations obtained there are generally erroneous<sup>1)</sup>, although at certain values of the parameters characterizing the medium they can lead to results that are close to the correct ones.

4. We begin the analysis with the case when the depolarization of the  $\mu^+$  meson ceases after entering the chemical stage ("radical-less case"). Then the asymptotic value of the polarization, observed when the depolarization process is finished, is determined by the relation (see<sup>[5]</sup>)

$$P = 1 - \frac{\tau^2 \omega_0^2 (1 + 2\nu\tau)}{2[(1 + 2\nu\tau)^2 + \tau^2 \omega_0^2 (1 + \nu\tau + x^2)]} \equiv F(\tau, \nu, \omega_0, x). \quad (1)$$

From this we have immediately

$$\frac{P}{2(1-P)} = \frac{1 + 2\nu\tau}{\tau^2 \omega_0^2} + \frac{1/2 + x^2}{1 + 2\nu\tau}. \quad (2)$$

Here  $\tau$  is the average lifetime of the free muonium;  $1/2\nu$  is the average relaxation time in the medium of the electron spin in the ( $\mu^+e^-$ ) atom;  $\omega_0$  is the characteristic frequency of the hyperfine splitting in the medium;  $x = \omega'(1 + \xi)/\omega_0$ , where  $\omega'$  is the precession frequency of the electron spin in the external magnetic field, and  $\xi = m_\mu/m_e = 1/207$  is the ratio of the magnetic moments of the  $\mu^+$  meson and the electron. We note immediately that the quantities  $\nu$ ,  $\tau$ , and

<sup>1)</sup>The error lies primarily in the fact that the muonium depolarization rate has been invalidly averaged in [1].

$\omega_0$  are phenomenological parameters and are determined by the nature of the substance. Therefore in the given scheme they should be determined experimentally.

We note that if the investigated object is a sufficiently homogeneous mixture of several substances then, generally speaking, neither  $\nu$  nor  $\omega_0$  can be additive quantities in the mixture concentration. However, with respect to  $1/\tau$ , the assumed additivity is perfectly reasonable in the case when a new chemical compound is not produced when the two substances are mixed, and there is no catalytic effect. Thus,

$$1/\tau = c_1/\tau_1 + c_2/\tau_2. \quad (3)$$

Here  $c_1$  and  $c_2$  are the specific concentrations of the mixture components, and  $\tau_1$  and  $\tau_2$  are the times of entry in the chemical reaction for each of the components. The generalization to include multicomponent mixtures is trivial. It is also obvious that formula (3) determines the chemical lifetime also in a homogeneous medium, if the latter has two reaction channels.

5. We now list the variants of the chemical behavior of the muonium, which will be considered in this paper.

1. Muonium reacts chemically with the substance and forms a diamagnetic compound. Further relaxation of the  $\mu^+$ -meson spin can be due then only to its interaction with the field of the paramagnetic impurities (if they are present in the given substance) or to the interaction with the magnetic moments of the lattice nuclei. We assume further that there are no paramagnetic impurities in the substance, and as to relaxation resulting from the interaction with the nuclear spins, the estimates given in<sup>[4]</sup> show that under the most unfavorable circumstances the characteristic depolarization time is of the order of  $10^{-5}$ – $10^{-6}$  sec. We can therefore assume that after the  $\mu^+$  meson becomes bound in the diamagnetic molecule it is no longer polarized in practice.

2. One of the reaction channels for the muonium leads to the formation of a long-life ( $\sim 10^{-6}$ – $10^{-5}$  sec) radical paramagnetic compound. Here, obviously, the depolarization of the  $\mu^+$  mesons contained in a compound of this type continues after the formation of the chemical bond, and, generally speaking, the characteristic times of the total depolarization do not exceed  $10^{-7}$  sec. Therefore, the  $\mu^+$  meson should be completely depolarized during its lifetime. In this case the  $\mu^+$ -meson depolarization, just as in muonium, is due to the interaction with the spin of the unpaired electron and can be described phenomenologically in adequate fashion.

3. There is a channel of a fast chemical reaction which occurs within times on the order of  $10^{-11}$ – $10^{-12}$  sec after the entry of the  $\mu^+$  meson in the substance. We shall henceforth call this the "hot chemistry channel." Reactions of this type may be connected with a great variety of factors (in particular, with the reaction of the  $\mu^+$  meson with active compounds formed in the  $\mu^+$ -meson track). For our purposes the concrete mechanism of the reaction is immaterial, and importance attaches only to the fact that the  $\mu^+$  meson, which reacts within times on the order of  $10^{-12}$ – $10^{-11}$  sec, enters in the chemical compound fully polarized. Obviously, in this case compounds of the radical type

can be formed, a fact that will be accounted for subsequently.

We begin the analysis with the consideration of the first variant. In this case, in longitudinal magnetic fields, we have the relation<sup>[5]</sup>

$$\frac{H_2^2 - H_1^2}{H_3^2 - H_1^2} = \frac{(P_2 - P_1)(1 - P_3)}{(P_3 - P_1)(1 - P_2)}. \quad (4)$$

Here  $H_1$  and  $P_1$  are the values of the magnetic field and the corresponding values of the residual polarization.

As noted in<sup>[5]</sup>, relation (4) signifies that, by determining the residual polarization at two arbitrary values of the external magnetic field, we can predict the values of  $P(H)$  at any field. It is clear therefore that if we confine ourselves to measurements of the asymptotic polarization in longitudinal fields, then we obtain only two independent equations, in place of the three necessary to determine the phenomenological parameters  $\tau$ ,  $\nu$ , and  $\omega_0$ . On the other hand, an experimental verification of formula (4) can serve perhaps as the most distinct criterion of whether a "pure muonium" mechanism of depolarization is effected with subsequent formation of only diamagnetic compounds.

In the case when the radical reaction channel is present, the polarization of the  $\mu^+$  meson in the muonium atoms forming the stable radical drops to zero after a sufficiently long time. We then have for the asymptotic value of the polarization

$$P = \left( \frac{1}{\tau} - \frac{c_{\text{rad}}}{\tau_{\text{rad}}} \right) \int_0^{\infty} P(t) e^{-t/\tau} dt, \quad (5)$$

where  $c_{\text{rad}}$  and  $\tau_{\text{rad}}$  are the specific concentration of the centers, on which radical production is possible, and the lifetime of the muonium relative to the radical channel. Accordingly formula (2) takes the form

$$\frac{P}{2(\alpha - P)} = \frac{1 + 2\nu\tau}{\tau^2\omega_0^2} + \frac{1/2 + x^2}{1 + 2\nu\tau}, \quad (6)$$

where

$$\alpha = 1 - \frac{\tau}{\tau_{\text{rad}}} c_{\text{rad}}. \quad (7)$$

By determining experimentally the polarization at three different values of the field, we can find  $\alpha$  in accordance with the formula

$$\alpha = \left[ \frac{(P_3 - P_1)(H_2^2 - H_1^2)}{(P_2 - P_1)(H_3^2 - H_1^2)} P_2 - P_3 \right] \left[ \frac{(P_3 - P_1)(H_2^2 - H_1^2)}{(P_2 - P_1)(H_3^2 - H_1^2)} - 1 \right]^{-1}. \quad (8)$$

It is obvious that by using measurements made at a fourth value of the field and eliminating  $\alpha$ , we obtain an analog of formula (4)—a four-point relation which makes it possible to establish experimentally whether the situation under consideration is realized in practice. By determining the parameter  $\alpha$  from (8) we thus find the relative reaction rate in the radical channel. When  $\alpha$  is known, then, as before, we are left for the system of phenomenological parameters  $\tau$ ,  $\nu$ , and  $\omega_0$  with two independent equations, and for a complete determination we must again resort to additional information.

6. We consider separately the "hot chemistry" case. Assume, as before, that there are two reaction

channels, diamagnetic and radical. We introduce two parameters  $\beta$  and  $\delta$ , which represent respectively the probabilities of entering in the diamagnetic compounds during the "hot chemistry" stage and in the usual manner. We then have for  $P_\infty$

$$P_\infty = \beta + \delta F(\tau, \nu, \omega_0, x). \quad (9)$$

and in analogy with (2) and (6) we obtain

$$\frac{P - \beta}{2(\beta + \delta - P)} = \frac{1 + 2\nu\tau}{\tau^2 \omega_0^2} + \frac{1/2 + x^2}{1 + 2\nu\tau}, \quad (10)$$

where  $\tau$  as before is determined by formula (3). From this we can readily see that  $\delta + \beta$ , which is the total probability of the reaction in the diamagnetic channel, is determined as before by relation (8). It is therefore obvious that so long as the radical channel is missing, then the three-point relation (4) is satisfied also in the case of the "hot chemistry." Thus, in this case we already lack two equations for the determination of all the experimental parameters.

7. We shall show that by supplementing the data obtained in longitudinal fields by an investigation of the depolarization of the  $\mu^+$  in perpendicular magnetic fields it is possible in principle to determine all the parameters of interest to us, as well as the character of the chemical reactions of muonium. We recall once more that measurements in longitudinal fields are necessary primarily for the clarification of the fact that the depolarization is actually described by the "pure muonium" mechanism. The decisive criterion consists of relations (4) and (8).

The complex polarization in a perpendicular magnetic field is determined by the relation<sup>[5]</sup>

$$P = \left\{ 1 + \frac{i(\omega_0\tau)(A+B)B}{2[AB^2 - (A+B)]} \right\}^{-1},$$

$$A = i\left(\frac{2}{\tau\omega_0} + \frac{4\nu}{\omega_0}\right), \quad B = i\left(\frac{2}{\tau\omega_0} + \frac{4\nu}{\omega_0}\right) - 2x. \quad (11)$$

We recall now the physical meaning of the complex asymptotic polarization. In a perpendicular magnetic field, obviously, precession of the  $\mu^+$ -meson polarization vector will be observed. At the initial instants, the amplitude of the precession sinusoid attenuates (the depolarization process takes place) and after a certain time it reaches a certain asymptotic value<sup>2)</sup>. This value of the amplitude is the modulus of the complex polarization. The complex polarization reflects the fact that in a perpendicular field, during the muonium stage, the polarization vector of the  $\mu^+$  meson not only decreases in magnitude, but also rotates through a certain angle  $\varphi$ . Obviously

$$\operatorname{Re} P = |P| \cos \varphi, \quad \operatorname{Im} P = |P| \sin \varphi. \quad (12)$$

In the simplest case, when there is no radical channel and it is possible to neglect the reaction in the "hot chemistry" stage in perpendicular fields, the analog of relation (2) is of the form

$$\frac{1}{2} \operatorname{Re} q = \frac{1}{2} \operatorname{Re} \left( \frac{P}{1-P} \right) = \frac{\dot{a}}{2\omega_0\tau} \left( 2 - \frac{d^2}{d^2 + x^2} + \frac{2}{d^2 + 4x^2} \right), \quad (13)$$

$$\frac{1}{2} \operatorname{Im} q = \frac{1}{2} \operatorname{Im} \left( \frac{P}{1-P} \right) = \frac{x}{2\omega_0\tau} \left( \frac{d^2}{d^2 + x^2} - \frac{4}{d^2 + 4x^2} \right). \quad (14)$$

Here  $d = 2(1 + 2\nu\tau)/\omega_0\tau$ .

It is easy to see that

$$\operatorname{Re} q = -1 + \frac{1 - \operatorname{Re} P}{(1 - \operatorname{Re} P)^2 + (\operatorname{Im} P)^2},$$

$$\operatorname{Re} P = 1 - \frac{1}{(1 + \operatorname{Re} q) + (\operatorname{Im} q)^2 / (\operatorname{Re} q + 1)},$$

$$\operatorname{Im} q = + \frac{\operatorname{Im} P}{(1 - \operatorname{Re} P)^2 + (\operatorname{Im} P)^2}, \quad \operatorname{Im} P = \frac{\operatorname{Im} q}{(1 + \operatorname{Re} q)^2 + (\operatorname{Im} q)^2} \quad (15)$$

Naturally, the condition  $|\operatorname{Re} P|^2 + |\operatorname{Im} P|^2 \leq 1$  is realized. Generally speaking, all the parameters  $\nu$ ,  $\tau$ ,  $\omega_0$  of interest to us can be determined by measuring the polarization at three different values of the field and using further formula (11) or, what is more convenient practically, formula (13).

We note, however, that this can raise considerable difficulties of experimental nature. A simple analysis of relations (13) and (14) shows that when the ratio  $(1 + 2\nu\tau)/\omega_0\tau$  increases the changes of the polarization as a function of the field turn out to be less and less noticeable. As shown in<sup>[5]</sup>, even when this ratio is comparable in order of magnitude with unity, the polarization changes by 5–10% when the field changes in the interval  $0 < x < 2.5$ . If  $\omega_0$  in the substance is close to the vacuum value, then the value  $x = 2.5$  corresponds to an external field of approximately 4 kG. Since, on the one hand, the use of stronger fields entails definite experimental inconveniences, and, on the other hand, the present experimental accuracy makes it possible to determine the absolute value of the polarization with accuracy 0.05, it may be impossible in a number of cases to determine the parameters of the theory with the aid of measurements of the absolute value of the polarization in perpendicular fields. However, in perpendicular fields there appears an additional possibility connected with the measurement of the polarization phase.

Indeed, it may turn out that in those cases when the absolute magnitude of the polarization is small or depends little on the external field, the phase, obviously, which equals zero in the absence of the field, can assume values up to 20–30°. In this connection, let us analyze the behavior of the phase as a function of the field in the region  $d = 2(1 + 2\nu\tau)/\omega_0\tau \gg 1$ . We confine ourselves to this range for  $d$ , since when  $d < 1$  the necessary information can be obtained by investigating the changes of the absolute value of the polarization. From (12) and (15) we have

$$\operatorname{tg} \varphi = \frac{\operatorname{Im} P}{\operatorname{Re} P} = \left[ \operatorname{Im} q + \frac{\operatorname{Re} q}{\operatorname{Im} q} (1 + \operatorname{Re} q) \right]^{-1}. \quad (16)$$

We then get from (13) and (14)

$$\operatorname{Im} q = \frac{d}{\omega_0\tau} \frac{h}{1 + h^2}, \quad \frac{\operatorname{Re} q}{\operatorname{Im} q} \approx \frac{1}{h} + 2h. \quad (17)$$

Here  $h = x/d$ . Accordingly we get

$$\operatorname{tg} \varphi = \frac{\operatorname{Im} P}{\operatorname{Re} P} \approx \left[ \frac{d}{\omega_0\tau} \left( \frac{1}{h} + 4h \right) + \left( \frac{1}{h} + 2h \right) \right]^{-1}. \quad (18)$$

On the other hand, in our case, the following relation holds with good accuracy:

<sup>2)</sup>Naturally, in constructing the precession sinusoid for the polarization vector, corrections are introduced to allow for the observed damping due to the  $\mu^+$ -meson decay.

$$\operatorname{Re} P \approx \frac{\operatorname{Re} q}{1 + \operatorname{Re} q} \approx \left[ 1 + \frac{\omega_0 \tau (1 + h^2)}{d(1 + 2h^2)} \right]^{-1}. \quad (19)$$

By determining the maximum of  $\tan \varphi$  from  $h$ , we find that the value of  $|P|$ , which approximately equals in our case  $\operatorname{Re} P$ , is smaller than 0.5 in the absence of a field, then the phase should reach 10–20° when  $x \sim d$ . With increasing value of the residual polarization, the maximum phase decreases rapidly.

Inasmuch as the maximum of the phase should be observed at external fields satisfying the condition  $x \gg 1$ , it is obvious that from the experimental point of view it is most convenient to use for the observation of the phase substances in which  $\omega_0$  is appreciably smaller than the vacuum value.

When  $d \sim 1$ , generally speaking, both cases in which the phase is close to zero and situations when it is appreciable can be realized. When  $d \ll 1$ , in principle, the phase can be raised to 90°. However, in this region there is a noticeable dependence of the absolute magnitude of the polarization on the perpendicular field, and consequently the information obtained by measuring the phase is not necessary. Incidentally, it is useful as a control method in determining the parameters of the theory.

8. We now consider, in a perpendicular field, the case when the reaction proceeds in the ‘‘hot chemistry’’ stage and, in addition, there is a radical channel. In this case the analog of (11) is

$$P = \beta + \delta \left\{ 1 + \frac{i\omega_0 \tau (A+B)B}{2[AB^2 - (A+B)]} \right\}. \quad (20)$$

The notation is the same as in (9) and (11). We now have in lieu of (13) and (14)

$$\frac{1}{2} \operatorname{Re} \left( \frac{P - \beta}{\delta + \beta - P} \right) = \frac{d}{2\omega_0 \tau} \left( 2 - \frac{d^2}{d^2 + x^2} + \frac{2}{d^2 + 4x^2} \right), \quad (21)$$

$$\frac{1}{2} \operatorname{Im} \left( \frac{P - \beta}{\delta + \beta - P} \right) = \frac{x}{2\omega_0 \tau} \left( \frac{d^2}{d^2 + x^2} - \frac{4}{d^2 + 4x^2} \right). \quad (22)$$

In principle, by measuring the polarization at different values of the field, it is possible to extract from (21) all the parameters of interest to us. In practice, however, to determine the parameters it is convenient to make use of the results obtained in the investigation of the substance in longitudinal fields, i.e., to carry out the processing in accordance with (10) and (21) simultaneously.

The qualitative analysis presented for the phase in Sec. 7 remains in force in the present case, too.

9. This section is of methodological character. We shall show that experiments in oblique magnetic fields cannot yield any new information on the macroscopic parameters of the substance, if measurements have been made in parallel and perpendicular magnetic fields.

Indeed, in the case when the field  $H$  is directed at an angle to the initial direction of the polarization vector, by choosing one of the coordinate axes along the field, it is easy to find that the system of equations for the components of the density matrix<sup>[4,5]</sup> breaks up into two independent subsystems. One of these subsystems contains only a polarization component in the field direction, and the system of equations itself, naturally, is identical with that considered above for

the case of the longitudinal field of magnitude  $H$ .

The second subsystem is identical with the case of a perpendicular field of magnitude  $H$  and depends only on the polarization component perpendicular to the field. It is therefore obvious that measurements in inclined fields can in principle not yield any additional information compared with the data obtained in longitudinal and perpendicular fields.

In conclusion, let us analyze the variation of the  $\mu^+$ -meson polarization vector in an oblique field. The initial values of the polarization components in the direction of the field and in a direction perpendicular to the field are  $P_0 \cos \theta$  and  $P_0 \sin \theta$ . Accordingly, the modulus of the polarization vector is

$$|P| = [P_{\parallel}^2 \cos^2 \theta + |P_{\perp}|^2 \sin^2 \theta]^{1/2}. \quad (23)$$

In this case the polarization vector will obviously process around the field direction, forming a cone. Inasmuch as the ratio  $|P_{\perp}|/P_{\parallel}$  decreases monotonically with time, tending to a certain asymptotic value, the angle between the polarization vector and the field decreases accordingly.

10. We now consider those additional possibilities for the determination of the phenomenological parameters of the theory, which appear in the case when it is possible to observe the dependence of the polarization on the time.

We start the analysis with the case when muonium is directly observed in the substance. In this situation, the additional information, which can be extracted by studying the time variation of the polarization, is maximal.

Let us consider first the picture which will be observed in a perpendicular field. First, there is a damped sinusoid with the muonium frequency. The doubled value of the amplitude determines the number of free atoms of muonium which are present in the substance at the given instant of time. By extrapolating the amplitude to the zero point, we can determine the relative number of muonium atoms produced in the substance during the thermalization stage. The presently available experimental technique<sup>[6]</sup> makes it possible to start the analysis with times on the order of  $5 \times 10^{-9}$  sec, and therefore the extrapolation is quite reliable.

As shown in<sup>[5]</sup>, the muonium frequency can be observed in small fields ( $x \ll 1$ ) and in the case of slow relaxation of the electron spin  $4\nu/\omega_0 \ll 1$ . If  $x^2 \ll 4\nu/\omega_0$ , the damping of the polarization is determined by the term  $\exp\{-t(1/\tau + \nu)\}$ , and if  $x^2 \gg 4\nu/\omega_0$ , it is determined by the term  $\exp\{-t(1/\tau + 3\nu/2)\}$ . Thus, in principle, by varying the field and accordingly going over from one case to another, we can measure  $\tau$  and  $\nu$ . In practice it is probably more convenient to supplement the study of the time variation of the polarization in perpendicular fields by investigations in longitudinal fields.

As shown by elementary manipulations, the dependence of the polarization on the time in a longitudinal field at  $4\nu/\omega_0 \ll 1$  is given by

$$P(t) = \frac{1 + 2x^2}{2(1 + x^2 + \nu\tau)} + \frac{(1 + 2x^2)\nu\tau}{2(1 + x^2)(1 + x^2 + \nu\tau)} \exp\left\{-t\left(\frac{1}{\tau} + \frac{\nu}{1 + x^2}\right)\right\}. \quad (24)$$

for  $\tau, t \gg [\omega_0^2(1 + x^2)]^{-1/2}$ .

It must be emphasized that whereas the analysis in perpendicular fields pertained to the most general case, formula (24) is valid only in the absence of "hot chemistry" and of a radical channel.

The "hot chemistry" channel is revealed in simple fashion if it is possible to observe in the given substance, besides the muonium frequency, also the precession frequency corresponding to the free  $\mu^+$  meson. The latter obviously describes the  $\mu^+$  mesons captured in the diamagnetic channel during the "hot chemistry" stage.

Since we are considering the "pure muonium" mechanism, we assume that the medium does not contain any free thermalized  $\mu^+$  mesons at all. We note, incidentally, that inasmuch as the free  $\mu^+$  mesons retain their polarization practically completely, such  $\mu^+$  mesons cannot be distinguished in principle from the muonium atoms that react in the "hot chemistry" stage.

The probability of the reaction in the radical channel of "hot chemistry" can be readily determined from the balance condition. Actually, the probability of formation of muonium atoms in the substance is determined by double the value of the muonium amplitude at zero, and the probability of the reaction in the diamagnetic channel of "hot chemistry" is given by  $\mu^+$ -meson amplitude.

11. Let us consider further the time variation in the case of large relaxation rates of the electron spin  $\gamma = 4\nu/\omega_0 \gg 1$ . We shall not analyze the case of medium relaxation rates  $\nu \sim \omega_0$ , since such a relaxation leads to a very rapid vanishing of the time dependence (within times on the order of  $1/\omega_0$ ). The latter circumstance can be readily seen already from the fact that in the case of slow relaxation the damping time is  $\sim 1/\nu$ , and in fast relaxation, as will be shown later,  $\sim \nu/\omega_0^2$ . We note only that if  $\omega_0$  in the substance is much smaller than the vacuum value and, in principle, a possibility appears of observing the time variation in the case of medium relaxation rates of the electron spin, too, then the observed picture will differ appreciably from both limiting cases, since the curve of precession of the polarization in a perpendicular magnetic field will be the superposition of several sinusoids.

We write down first the general relation for the polarization, observed at the instant of time  $t$  in a perpendicular field. As shown in<sup>[5]</sup>, the observed complex polarization is determined by the relation

$$P(t) = e^{i\zeta\omega t} \int_0^t \rho(t') \exp \left\{ - \left( \frac{1}{\tau} + i\zeta\omega' \right) t' \right\} \frac{dt'}{\tau} + \rho(t) e^{-t/\tau}, \quad (25)$$

where  $\rho(t)$  is the polarization of the  $\mu^+$  mesons that are in the muonium stage. In (25) it is assumed that the precession frequency of the chemically bound  $\mu^+$  meson is the same as that of the free  $\mu^+$  meson. Inasmuch as  $\rho(t)$  is given by<sup>[5]</sup>

$$\rho(t) = \sum_{k=1}^4 A_k e^{\lambda_k t}, \quad (26)$$

we get

$$P(t) = e^{i\zeta\omega t} \sum_{k=1}^4 \frac{A_k [\exp\{[\lambda_k - (1/\tau + i\zeta\omega')t] - 1\}]}{\tau[\lambda_k - (1/\tau + i\zeta\omega')]} + \rho(t) e^{-t/\tau} \quad (27)$$

We shall show further that in the case when  $\gamma \gg 1$  we

have  $\rho(t) = e^{\lambda t}$ . Indeed, as shown in<sup>[5]</sup>, the characteristic equation for  $\tilde{\lambda} = 2\lambda/\omega_0$  is

$$\begin{aligned} & \tilde{\lambda}^4 - [2(a+b') - \gamma]\tilde{\lambda}^3 + [4 + (a+b')^2 + 2ab' - \gamma(2b'+a)]\tilde{\lambda}^2 \\ & - [2ab'(a+b') + 4(a+b') - \gamma b'(b'+2a) - 2\gamma]\tilde{\lambda} + (a+b')^2 \\ & + a^2b'^2 - \gamma ab'^2 - \gamma(a+b') = 0, \end{aligned} \quad (28)$$

where

$$a = \frac{2i\zeta x}{1+\zeta} \quad b' = - \left[ \gamma + \frac{2ix}{1+\zeta} \right].$$

Introducing the variable  $\mu = \tilde{\lambda} - a$ , we get

$$\begin{aligned} & \mu^4 - [2b - \gamma]\mu^3 + [4 + b^2 - 2\gamma b]\mu^2 - [4b - \gamma b^2 - 2\gamma]\mu \\ & + b^2 - \gamma b = 0. \end{aligned} \quad (29)$$

Here  $b = -(\gamma + 2ix)$ .

We begin the analysis of (29) with a search for roots satisfying the condition  $|\mu| \ll 1$ , since the time dependence of the polarization can be observed experimentally only when such roots exist. As can be readily seen from (29), there is only one root satisfying the condition  $|\mu| \ll 1$ . It is determined from the equation

$$\gamma b^2 \mu + b^2 - \gamma b = 0. \quad (30)$$

Accordingly

$$\frac{2\lambda_1}{\omega_0} = \left[ \frac{\zeta}{1+\zeta} + \frac{1}{\gamma^2 + 4x^2} \right] 2ix - \frac{1}{\gamma} - \frac{\gamma}{\gamma^2 + 4x^2}. \quad (31)$$

The results (30) and (31) were obtained with relative accuracy  $1/\gamma^2$ . As seen from (30), when  $\gamma \gg 1$  the root actually satisfies the condition  $|\mu| \ll 1$  and therefore our procedure is justified.

Further analysis of (23) shows that the three remaining roots satisfy the condition  $|\mu| \gg 1$ . With this,  $\text{Re } \mu \approx -\gamma$ . We note incidentally that for the analysis it is convenient to rewrite (29) in the form

$$\left( \frac{1}{\mu + \gamma} + \frac{1}{\mu + \gamma - 2ix} \right) \left( \frac{1}{\mu} + \frac{1}{\mu + \gamma - 2ix} \right) = -1. \quad (32)$$

Determining then the coefficients  $A_k$  corresponding to these roots, we can see that they are close to zero, with good accuracy. Accordingly, the coefficient  $A$  for the root  $|\mu| \ll 1$  is equal to unity, with the same accuracy. Thus, when  $\gamma \gg 1$  the polarization takes the form

$$\begin{aligned} P(t) = \exp \{ i\zeta\omega t \} & \left\{ P_\infty + (1 - P_\infty) \exp \left[ \frac{ix\omega_0 t}{\gamma^2 + 4x^2} \right] \right. \\ & \left. \cdot \exp \left[ - \left[ \frac{1}{\tau} + \left( \frac{1}{\gamma} + \frac{\gamma}{\gamma^2 + 4x^2} \right) \frac{\omega_0}{2} \right] t \right] \right\}. \end{aligned} \quad (33)$$

The residual polarization  $P_\infty$  is determined here by formula (11), and in our case is given by

$$P_\infty = - \frac{1}{\tau[\lambda - 1/\tau - 2i\zeta\omega]} = \left\{ 1 - \frac{\tau\omega_0}{2} \left[ \frac{2ix}{\gamma^2 + 4x^2} - \frac{1}{\gamma} - \frac{\gamma}{\gamma^2 + 4x^2} \right] \right\}^{-1}. \quad (34)$$

When  $x \ll \gamma$ , formulas (33) and (34) go over into the relations obtained in<sup>[4,6]</sup>. If there exists a "hot chemistry" channel and there is no radical channel, then relation (33) remains in force, except that the residual polarization  $P_\infty$  should be calculated by means of formula (20). In a longitudinal magnetic field at  $\gamma \gg 1$ , a similar analysis leads to the result

$$P(t) = P_\infty + (1 - P_\infty) \exp \left\{ -t \left[ \frac{1}{\tau} + \frac{\omega_0\gamma}{\gamma^2 + 4x^2} \right] \right\}, \quad (35)$$

where

$$P_{\infty} \approx \beta + \delta \left[ 1 + \frac{\omega_0 \tau}{\gamma(1 + 4x^2/\gamma^2)} \right]^{-1}. \quad (36)$$

Thus, in those cases when a dependence of the time variation of the polarization on the field is observed, we can determine all the theory parameters of interest to us.

12. We note in conclusion that the entire problem of determining the phenomenological parameters is trivial in the case when the value of  $\omega_0$  for hydrogen has been determined in the given substance with the aid of EPR. Then, obviously, to determine  $\nu$  and  $\tau$  it suffices to measure the residual polarization in longitudinal magnetic fields. It can be assumed that the use of muonium as an object simulating atomic hydrogen is quite promising, particularly for the study of the kinetics of fast chemical reactions ( $\tau \sim 10^{-10} - 10^{-11}$  sec) and for "hot chemistry" of hydrogen. Particular interest, in our opinion, attaches to an investigation of reactions with formation of unstable short-lived ( $10^{-6} - 10^{-10}$  sec) radicals. We note, however, that in this case the theory developed earlier should be modified somewhat. This question, as well as the semi-phenomenological theory of "hot chemistry" of muonium, will be considered in our next paper. We indicate only that  $\mu^+$  mesons may turn out to be a very convenient tool for the study of hydrogen reactions on a surface. Indeed, in the case of strongly developed surfaces, their influence on the depolarization process can be readily observed, and thus we obtain a new method of investigating finely dispersed phases. It is known that

problems of this type arise in the most diverse branches of physical chemistry and are of great practical interest.

Finally, it can be noted that a study of processes of depolarization of the  $\mu^+$  meson in electrolytes of different concentrations, particularly in concentrated acids, may possibly explain a number of problems in the chemistry of these systems, such as for example the determination of the concentration of the free ions  $H^+$ .

<sup>1</sup>V. G. Firsov and V. M. Byakov, *Zh. Eksp. Fiz.* **47**, 1074 (1964) [*Soviet Physics JETP* **20**, 719 (1965)].

<sup>2</sup>V. G. Firsov, *ibid.* **48**, 1199 (1965) [**21**, 786 (1965)].

<sup>3</sup>A. I. Babaev, M. Ya. Balats, G. G. Myasishcheva, Yu. V. Obukhov, V. S. Roganov, and V. G. Firsov, ITEF Preprint No. 388, 1965.

<sup>4</sup>V. G. Nosov and I. V. Yakovleva, *Zh. Eksp. Teor. Fiz.* **43**, 1750 (1962) [*Soviet Physics JETP* **16**, 1236 (1963)].

<sup>5</sup>I. G. Ivanter and V. P. Smilga, *ibid.* **54**, 559 (1968) [**27**, 301 (1968)].

<sup>6</sup>I. I. Gurevich, L. A. Makar'ina, E. A. Meleshko, B. A. Nikol'skii, V. S. Roganov, V. I. Selivanov, and B. V. Sokolov, *ibid.* **54**, 432 (1968) [**27**, 235 (1968)].