

## Influence of the chemical environment on the $\beta$ decay of $^{77}\text{As}$

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The effect of the chemical state on the decay constant  $\lambda$  of the  $\beta$  emitter  $^{77}\text{As}$  has been investigated by means of a differential ionization chamber. The result of the measurement is  $\lambda(\text{metallic } ^{77}\text{As}) - \lambda(\text{Ag}_3^{77}\text{AsO}_4) = (0.93 \pm 0.44) \times 10^{-4} \lambda$ .

[ RADIOACTIVITY  $^{77}\text{As}$ , measured  $T_{1/2}$ , double ionization chamber, chemical effect. ]

The influence of atomic electrons on the nuclear decay modes of electron capture and internal conversion has become the field of fruitful scientific investigations. The goal of these investigations has shifted from finding the chemically induced half-life changes to using them to answer questions in chemical bonding.<sup>1,2</sup> Since Alder *et al.*<sup>3</sup> have estimated that the influence of the chemical environment on the half-life of  $\beta^-$  emitters through changes in the screening potential is a few parts in  $10^4$  only a few measurements have been published.<sup>2</sup> In a study of the  $\beta^-$  decay of  $^{131}\text{I}$  in different chemical forms no effect could be reported within the error of the experiment of  $1.5 \times 10^{-4}$ .<sup>4</sup> A better sensitivity could be achieved in an experiment in which the half-life change of  $^{198}\text{Au}$  in the chemical forms Au metal and  $\text{Au}_2\text{O}_3$  has been studied with the result  $\Delta\lambda/\lambda = (1.0 \pm 0.3) \times 10^{-4}$ .<sup>5</sup>

In the present work the influence of the chemical environment on the decay constant of the  $\beta^-$  emitter  $^{77}\text{As}$  ( $T_{1/2} = 38.8$  h;  $E_\beta = 0.694$  MeV) was studied.  $^{77}\text{As}$  was chosen because its relatively low charge number and  $\beta^-$ -end-point energy indicate a  $\Delta\lambda/\lambda$  in the order of  $1 \times 10^{-4}$  using the calculations of Alder *et al.*<sup>3</sup> Stable compounds in which As is in different oxydation states can easily be prepared and the half-life of 38.8 h is in a range which is very suitable for measuring decay rate variations. Furthermore, the  $^{77}\text{As}$  activity can be produced very easily in a nuclear reactor.

The  $^{77}\text{As}$  activity was obtained as decay product of  $^{77}\text{Ge}^{m,s}$  ( $T_{1/2} = 54$  s and 11.3 h) which itself was produced by irradiating natural Ge of high purity with thermal neutrons in the Munich research reactor. The irradiated Ge was dissolved in the presence of As carrier in conc. HF and 36%  $\text{H}_2\text{O}_2$ .  $\text{As}_2\text{S}_3$  was precipitated from the diluted solution and again dissolved in conc.  $\text{H}_2\text{SO}_4$ . After addition of Ge carrier to the diluted solution Ge was precipitated with tannin and centrifuged out. Again Ge carrier was added and, in the presence of HF,  $\text{As}_2\text{S}_3$  was precipitated which again was dissolved in conc.  $\text{H}_2\text{SO}_4$ . Ge carrier was added and As metal was precipitated by adding sodium hypophosphite to the diluted solution.

Metallic As and  $\text{Ag}_3\text{AsO}_4$  were selected as the chemical compounds in which As is in different valence states (0 and +5) and which are stable against physical and chemical changes.  $\text{Ag}_3\text{AsO}_4$  was prepared from the metallic As by an oxydative dissolution in conc.  $\text{HNO}_3$  and precipitation of  $\text{Ag}_3\text{AsO}_4$  from the diluted solution with  $\text{AgNO}_3$ .

The presence of radioactive contaminants in the metallic As was carefully controlled by using a Ge(Li)  $\gamma$  spectrometer. No contaminant was found to be more than  $10^{-5}$  of the initial  $^{77}\text{As}$  activity which is negligible for the present measurement.

Both compounds were x-ray analyzed. The diffraction pattern confirmed that the As metal was amorphous. The  $\text{Ag}_3\text{AsO}_4$  showed a cubic structure with a lattice constant of  $a = 6.13$  Å.

The radioactive compounds in the form of a thin precipitate were coated and immobilized on a filter paper ( $\phi = 50$  mm) with a solution of an adhesive in acetone. The sources were glued into Al source holders and covered with a  $2$   $\mu\text{m}$  thick Macrofol foil. These cover foils were rendered conductive by coating them with a  $0.045$   $\mu\text{m}$  thick gold layer. They were fixed on the source holder with a conducting adhesive. The samples of each pair of sources were prepared to have equal activities within 1%. For this purpose small 0.5 mm thick Al disks of different but well defined diameters (4–12 mm) were glued with a conducting adhesive on the cover foil of the stronger of the two sources.

The small difference in  $\lambda$  occurring between the two sources of  $^{77}\text{As}$  in different chemical states were measured by the differential ionization chamber method. In this method two radioactive sources are simultaneously measured under as nearly identical conditions as possible and only the difference current produced by the two sources is measured as a function of time for roughly five half-lives.

Since details of the chamber construction and the whole performance of the system were previously reported<sup>6</sup> only the principle of the measurement is given here. Figure 1 shows a schematic diagram of the differential ionization chamber. It consists of two

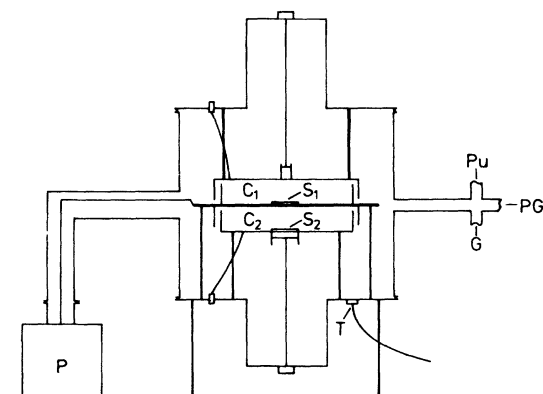


FIG. 1. Schematic diagram of the differential ionization chamber.  $C_1, C_2$ : two identical chambers,  $S_1, S_2$ : sources,  $P$ : preamplifier of vibrating reed electrometer,  $PG$ : pressure gauge,  $Pu$ : pump,  $G$ : gas cylinder,  $T$ : temperature-resistance bulb.

essentially identical parallel-plate ionization chambers in which the two sources are mounted. The electronic circuitry consisted of a high voltage supply, a vibrating reed electrometer, a digital voltmeter and a printer, and timer. The difference ionization current and chamber temperature and pressure were continuously recorded. A mechanical positioning adjustment made it possible to equalize the single ionization currents  $I_1(0)$  and  $I_2(0)$  in the two chambers that a balancing of  $[I_1(0) - I_2(0)]/I_1(0) = 10^{-5}$  could be achieved at the beginning of the measurement. The difference current was measured with the vibrating reed electrometer by means of the rate-of-charge method.

The difference ionization current at time  $t$  is given as

$$\Delta I(t) = e^{-\lambda t} \{ [I_1(0) - I_2(0)] + I_2(0) \Delta \lambda t + R e^{-\lambda t} \} \quad (1)$$

taking into consideration a small recombination term with the parameter  $R$ . The value of  $\Delta \lambda$  is obtained by a least-square analysis of the measured values of  $\Delta I(t)$  with the above equation. The recombination parameter  $R$  is also obtained by the fitting procedure.

The overall performance of the apparatus was checked by using pairs of sources of identical chemical composition. The weighted mean of six single measurements using two sources of  $^{77}\text{As}$  metal and two sources of  $\text{Ag}_3^{77}\text{AsO}_4$ , respectively, is " $\Delta \lambda/\lambda$ " =  $(0.04 \pm 0.33) \times 10^{-4}$ . This value shows that the measuring apparatus is sufficiently stable. A complete description of the source preparation, of the experimental apparatus and measurement and of the evaluation of the experimental data can be found in Ref. 7.

In Fig. 2 a typical run is shown. The difference ionization current multiplied by  $\exp(\lambda t)$  is plotted versus time  $t$ . The solid line represents the least-

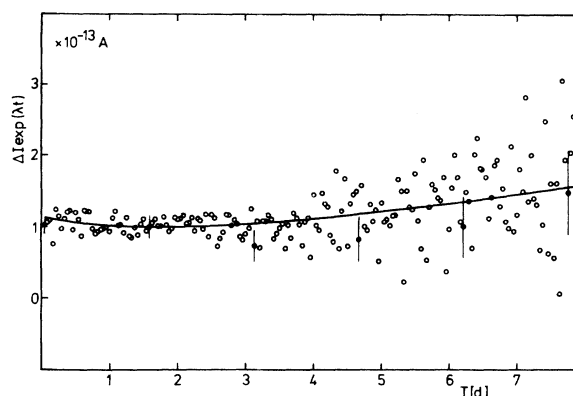


FIG. 2. Difference current vs time for a source pair As metal/ $\text{Ag}_3\text{AsO}_4$ . The solid line represents the least-squares solution of the data. Some data are given with their standard deviation.

squares solution of the data. From five values of  $\Delta \lambda/\lambda$  thus measured, we obtained the result as a weighted mean

$$\begin{aligned} & [\lambda(\text{metallic } ^{77}\text{As}) - \lambda(\text{Ag}_3^{77}\text{AsO}_4)]/\lambda \\ & = (0.93 \pm 0.44) \times 10^{-4} \end{aligned}$$

In the quoted standard deviation of  $0.44 \times 10^{-4}$  are involved the standard deviations calculated from the weighted least-squares analysis of the five single measurements of  $\Delta \lambda/\lambda$  taking into account the stability of the whole measuring system for each corresponding run. The size of the error is mainly caused by the new preparation of the source pairs for each single measurement of  $\Delta \lambda/\lambda$ . Thus a considerable error is introduced by irreproducible, small changes of the mechanical stability of the sources during the single measurements. A  $\chi^2$  test was applied to the data of the single measurements which showed that the data were normally distributed. A detailed error analysis is given in Ref. 7.

The result shows that  $^{77}\text{As}$  nuclei in the amorphous metal decay faster than in  $\text{Ag}_3\text{AsO}_4$  in which the As atoms have the oxydation state +5. An exact theoretical calculation of  $\Delta \lambda/\lambda$  for the presented experiment is difficult. In the calculation of Alder *et al.*<sup>3</sup> the difference between the screened electrostatic potential and the pure Coulomb potential at the nucleus has to be known. This difference is called screening potential  $V^S$ . The total screening potential is the sum of two potentials: the ion potential  $V^S(\text{ion})$  and the lattice potential  $V^S(\text{latt})$  from the surrounding ions. The difference  $V^S(\text{As metal}) - V^S(\text{Ag}_3\text{AsO}_4) = \Delta V^S$  is proportional to  $\Delta \lambda$ .

The fractional change in the  $\beta^-$ -decay constant as a function of  $\beta^-$ -end-point energy and charge number of the nucleus produced by a screening potential

change  $\Delta V^S = 27.21$  eV can be taken from Ref. 3. By means of Hartree-Fock-Slater calculations<sup>8</sup> we have calculated the change of the screening potential which is caused by a modification of the atomic electrons. Due to the electron configurations of the two ionization states 0 and +5 of a free As atom the screening potential changes by 70.7 eV. The As-O bond, however, is not purely ionic. The partial ionic character of the As-O bond was estimated to be 43% using the electronegativities of As and O.<sup>9</sup> Thus the change of the screening potential caused by the transformation of a free As atom into an As-O bond of 43% ionic character in which the As atom is in the formal oxidation state +5 can be estimated to be 30.4 eV corresponding to a  $\Delta\lambda$  of

$$[\lambda(\text{As}^0) - \lambda(\text{As}^{+5} - \text{O})] / \lambda = -0.92 \times 10^{-4}$$

The direction of this theoretically estimated change of

$\lambda$  does not, however, agree with the experimental value. It is obvious from the above rough evaluation that the measured change in the decay rate cannot be explained on the basis only of the removal of five electrons from a free As atom. The influence of the lattice potential has to be considered too. Unfortunately, an exact value of the lattice potential for the complicatedly built molecule of  $\text{Ag}_3\text{AsO}_4$  cannot be derived either by the method of Madelung or from thermodynamic data. For a qualitative interpretation one can state that the increase of the screening potential in  $\text{Ag}_3\text{AsO}_4$  as compared to the one in metallic As must be due to a change of the lattice potential in the order of 60 eV.

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