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Influence of the Chemical State on the Lifetime of a Nuclear Isomer, Tc^{99m}†

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Since a nuclear isomeric transition may take place by emission of either a gamma-ray or an internal conversion electron, the total rate of decay may be expected to vary with any change in electronic environment, such as a difference in chemical state. Differences in the decay constant of the isomer Tc^{99m} (6 hours) in different states of chemical combination were measured by the double ionization chamber balance method. λ for this isomer is determined mainly by the internal conversion probability of a 2-kev transition which is followed promptly by a conveniently measurable 140-kev gamma-ray. Two compounds in the +7 valence state were compared: $\lambda(KTcO_4)-\lambda(Tc_2S_7)=27.0\pm1.0\times10^{-4}\lambda(Tc_2S_7)$. λ for the metal electroplated on nickel and reduced in H_2 at 1000°C for 1 hour $-\lambda(Tc_2S_7)=3.1\pm1.2\times10^{-4}\lambda(Tc_2S_7)$. Errors are standard deviations. There is evidence for diffusion of the Tc into the nickel base and an accompanying decrease in λ(Tc) of $\sim$2 parts in 10^4 compared to pure crystalline metal. λ of the metal was measured directly as 0.1148 ± 0.0005 hr^{-1}, corresponding to a half-life of 6.04 ± 0.03 hours (limit of error). The methods used for internally checking the data and the operation of the apparatus are illustrated, and the statistics of the measurements are discussed.

I. INTRODUCTION

THIS paper presents detailed results demonstrating that the lifetime of a radioactive isomer is influenced by its state of chemical combination.[1]

Experiments to produce and detect alterations in the rate of transformation of radioactive substances were made over a period of thirty years beginning immediately after the discovery of radioactivity. In these early experiments no influence on the characteristic transformation constants could be detected resulting from changes in temperature, pressure, concentration, age, magnetic field, electron bombardment, chemical state, or environment.[2]

More recently Segrè[3] and Daudel[4] suggested that in the case of a substance which transforms by orbital electron capture the period might be altered in different chemical compounds of the substance. Be^7 was selected for study. Leininger, Segrè, and Wiegand[5] found a lower transformation rate for BeF_2 than for BeO. An earlier comparison[6] indicated that BeO decayed more slowly than Be. When BeF_2 was compared with Be metal in an independent experiment by Bouchez, Daudel, Daudel, Muxart, and Rogozinski,[7] a large effect was found,[8] *viz.*, $-\Delta\lambda/\lambda=-[\lambda(BeF_2)-\lambda(Be)]/\lambda(Be)=1$ percent.

Daudel[4] suggested also that the mean life of isomers, whose transformation rates depend in part on internal conversion, might be altered by chemical means. Goldhaber[9] independently suggested the same possibility and emphasized the necessity for using a low energy transition to examine this effect. Tc^{99m} appeared well suited for investigation, since its 2-kev isomeric transition is the lowest energy transition known at present.

Changes in the decay constant of an isomer might be expected to occur if the chemical state of combination can affect the availability of electrons entering into the conversion process. When the transitions from a nuclear isomeric state occur both by internal conversion and by gamma-ray emission, the observed decay constant $\lambda=\lambda_\gamma(1+\alpha)$. Here λ_γ is characteristic of the gamma-ray process alone, and the conversion coefficient α equals the ratio of the number of electrons to the number of gamma-rays emitted per second.

Tc^{99m} (6 hours) is an isomer with a highly converted 2-kev isomeric transition followed prompty by a 140-kev partially converted gamma-ray[10] which can be conveniently measured. The 2-kev transition essentially determines the six-hour half-life. Only 1.4 percent of the level population goes by a crossover transition to the ground state. The daughter product is long-lived Tc^{99}, which provides an effectively inert carrier material when obtained in quantity as a fission product.[11]

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* On leave from Harvard University, Cambridge, Massachusetts.

[1] Bainbridge, Goldhaber, and Wilson, Phys. Rev. **84**, 1260 (1951).

[2] S. Meyer and E. Schweidler, *Radioaktivität* (B. G. Teubner, Berlin, 1927), second edition, pp. 38–41.

[3] E. Segrè, Phys. Rev. **71**, 274 (1947).

[4] R. Daudel, Rev. sci. **85**, 162 (1947); Bouchez, Daudel, Daudel, and Muxart, J. phys. et radium **8**, 336 (1947).

[5] Leininger, Segrè, and Wiegand, Phys. Rev. **81**, 280 (1951); **76**, 897 (1949).

[6] E. Segrè and C. Wiegand, Phys. Rev. **81**, 284 (1951); **75**, 39 (1949).

[7] Bouchez, Daudel, Daudel, Muxart, and Rogozinski, J. phys. et radium **10**, 201 (1949).

[8] This measurement has recently been repeated by Kraushaar, Wilson, and Bainbridge, who find ∼0.07 percent, a value which supports the results of Segrè *et al.* (references 5 and 6).

[9] M. Goldhaber (unpublished lectures).

[10] Medicus, Maeder, and Schneider, Helv. Phys. Acta **22**, 603 (1949); Mihelich, Goldhaber, and Wilson, Phys. Rev. **82**, 972 (1951).

[11] No other long-lived isotope produced by fission is present to as much as 3 percent. Inghram, Hess, and Hayden, Phys. Rev. **72**, 1269 (1947).

II. METHOD OF MEASUREMENT

A. The Differential Method

Rutherford[12] first introduced in 1911 the differential method, which is well suited for the accurate determination of a small difference $\Delta\lambda$ in the decay constants of two sources. $\Delta\lambda$ is determined from the variation with time of the differential current obtained when the intensities of the sources 1 and 2 are compared in two essentially identical ionization chambers A and B connected to collect ions of opposite sign.

The sensitivities of the chambers are defined as S_A and S_B, with a mean sensitivity $\bar{S}=(S_A+S_B)/2\equiv 1$, so that the intensities of the sources at $t=0$ are $\bar{S}I_1$ and $\bar{S}I_2$ divisions of 10^{-14} ampere on the recorder. The difference currents are

$$i_{12}=S_AI_1e^{-\lambda t}-S_BI_2e^{-\lambda t}e^{-\Delta\lambda t}, \qquad (1)$$

and

$$i_{21}=S_AI_2e^{-\lambda t}e^{-\Delta\lambda t}-S_BI_1e^{-\lambda t} \qquad (2)$$

when the sources are interchanged. (The disintegration constant λ is associated with source 1 and $\lambda+\Delta\lambda$ with source 2.)

The average value of the difference currents at time t is

$$\Delta i=(i_{12}-i_{21})/2=\bar{S}(I_1-I_2)e^{-\lambda t}+\bar{S}I_2e^{-\lambda t}\Delta\lambda t. \quad (3)$$

The difference in the chamber sensitivities is obtained from

$$\Delta i_e=(i_{12}+i_{21})/2=(S_A-S_B)(I_1+I_2)e^{-\lambda t}/2 \\ -(S_A-S_B)I_2e^{-\lambda t}\Delta\lambda t/2. \quad (4)$$

In individual experiments on technetium the sensitivities of the chambers S_A and S_B differed over a range of 0 to 10 parts in 10 000 for the chambers used.[13]

B. Calculation of $\Delta\lambda/\lambda$

Since Δi as given in Eq. (3) is not convenient for analysis, it is multiplied by $e^{\lambda t}$ following the practice of Segrè and Wiegand. The resulting equation in t (neglecting the adjustment for chamber sensitivities), $e^{\lambda t}\Delta i=I_1-I_2+I_2\Delta\lambda t$, can be fitted by a least squares analysis to the linear form $y=a+bx$. Here $y=e^{\lambda t}\Delta i$, $x=t$, $a=I_1-I_2=i_0$, the initial difference in intensity of the two sources, and $b=I_2\Delta\lambda$, where I_2 will henceforth be called I_0, the initial current of the source with decay constant $\lambda+\Delta\lambda$. The calculations for a and b and their standard deviations σ_a and σ_b were made by a procedure outlined by Birge.[14]

The standard deviation[15] of the difference current i is proportional to $(2N_0)^{\frac{1}{2}}$, where N_0 is the mean number of ionization events occurring from a single source during the duration D of a single determination of i. Hence, the deviation of $\Delta i=(i_{12}-i_{21})/2$ varies as $N_0^{\frac{1}{2}}$ and that of y_k, i.e., σ_k, is proportional to $(N_0e^{\lambda t})^{\frac{1}{2}}$. The data were weighted with $p_k=c/\sigma_k^2=ce^{-\lambda t_k}$ where $c^{\frac{1}{2}}$ is the standard deviation of y for $x=0$ (making $p_0=1$). The experimental data support the assumption implicit above that the main contribution to the final error in the determination of $\Delta\lambda/\lambda$ is the statistical fluctuation in the number of separate ionization events which have occurred during an observation.

With the quantities I_0, λ, and b, one can now calculate the desired result,

$$\Delta\lambda/\lambda=b/I_0\lambda. \qquad (5)$$

If y is measured for two values of x only, $x=0$ and $x=\omega$, the resulting error in b,

$$\sigma_b=c^{\frac{1}{2}}(e^{\omega\lambda}+1)^{\frac{1}{2}}/\omega, \qquad (6)$$

has a minimum when $(\omega\lambda-2)=2e^{-\omega\lambda}$, i.e., for $\omega=2.22/\lambda$. However, considerably more than two readings were desirable in the actual experiments. If y is measured at equidistant points $x=0$, τ, 2τ, $\cdots n\tau$, where the mean life $\tau=1/\lambda$, the coefficient κ, defined by $\sigma_b=\kappa c^{\frac{1}{2}}/\tau$, decreases with increasing n as shown by the open circles in Fig. 1, whereas κ for only two measurements at $x=0$ and $x=\omega$ is shown in the solid curve. In some experimental runs on Tc^{99m} it was possible to go through all the permutations of the sources in less than the interval τ; in others involving four or more sources more time was required.

In an actual experiment the duration D of a single measurement is $i\cong 1000$ seconds$\cong 0.05T_{\frac{1}{2}}$. This corresponds to a measurement of approximately 4×10^8 ionization events from a single source of strength $I=10^4$ divisions ($\sim 100\mu$C Ra equivalent) so that $c^{\frac{1}{2}}$ is equal

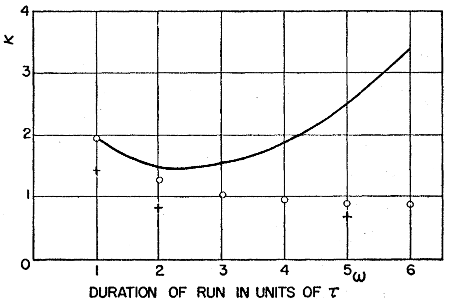

FIG. 1. The coefficient κ occurring in the expression for the standard deviation in b, $\sigma_b=\kappa c^{\frac{1}{2}}/\tau$. The quantity $c^{\frac{1}{2}}$ is the standard deviation of the measurement at $x=0$. The solid curve represents the case where measurements are taken only at $x=0$ and $x=\omega$. The small circles represent the cases where the measurement is made at all integral multiples of τ up to ω. The crosses represent the three cases of eleven equally spaced measurements terminating, respectively, at τ, 2τ, and 5τ.

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[12] E. Rutherford, Wien. Ber. **120**, 303 (1911).

[13] S_{A1} for source 1 in chamber A may differ from S_{A2} for source 2 in chamber A, and strictly

$$e^{\lambda t}\Delta i=(S_{A1}+S_{B1})I_1/2-(S_{A2}+S_{B2})I_2/2+(S_{A2}+S_{B2})I_2\Delta\lambda t/2.$$

No error is introduced into the final result for $\Delta\lambda$ by utilizing the simplified representation. $I_1(S_{A1}+S_{B1})/2-I_2(S_{A2}+S_{B2})/2$ is measured at $t=0$, and $I_1(S_{A1}+S_{B1})/2$ is measured independently so that $I_2(S_{A2}+S_{B2})/2$, required for the determination of $\Delta\lambda$, is known.

[14] R. T. Birge, Phys. Rev. **40**, 225, 226 (1932). $c^{\frac{1}{2}}$ as used here is 1/0.6745 times $c^{\frac{1}{2}}$ in Birge's notation, since standard deviations, σ, rather than probable errors, are being evaluated.

[15] E. V. Schweidler, First International Congress of Radiology and Ionization (Liège, 1905).

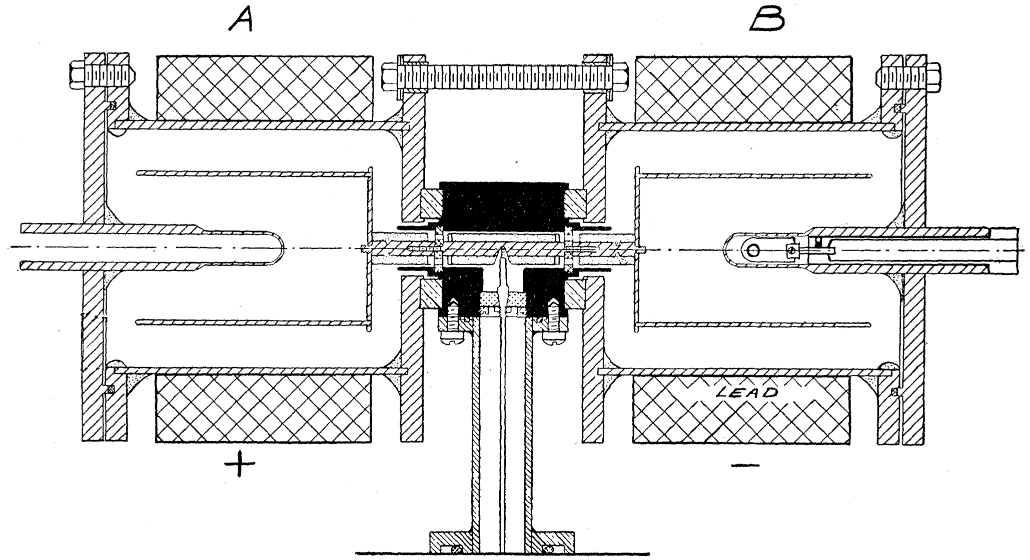

FIG. 2. Welded steel ionization chambers which were tested at 800 and operated at 200 pounds per square inch. chambers are insulated from each other at the central section by cloth Textolite disks bearing against the central grounded section, and at the outside of Textolite washers under the bolt heads. A precision pressure gauge is connected to chamber B. Gas leakage is less than 2 percent per year. The chambers are lagged by 3.5 cm. of cotton to minimize the effect of room temperature changes. Lead sheets in the central region between A and B chambers are not shown.

to ±0.5 divisions. The finite duration of the measurements of i_{12} and i_{21}, and the exponential decay of the sources during that time, does not introduce any error in the final result if t_{12} and t_{21}, respectively, are taken as the midpoints of the periods D_{12} and D_{21} during which the measurements are made. Then the measurements are referred to a common time, $t=\frac{1}{2}(t_{12}+t_{21})$, where

$$y(t)=e^{\lambda t}\Delta i=\tfrac{1}{2}(i_{12}e^{\lambda(t-t_{12})}-i_{21}e^{\lambda(t_{21}-t)}).$$

III. CHAMBER DESIGN

The construction of the welded steel ionization chambers is shown in Fig. 2. The assembly was tested at 800 pounds per square inch. The design was based on an equal probability that, at 2000 pounds per square inch, the cylinders would blow out, or the ends would come off, or the re-entrant source thimbles would collapse. Seven pieces of steel, all but the two cylinders and two thimbles, leaked badly at first. The leaks were corrected by welding at all internal joints, as shown in Fig. 2, and remaking the central grounded assembly (shown in solid black). The latter still leaked and finally had to be impregnated with solder on all external surfaces which do not face the collecting electrode cylindrical support bar. Not shown in Fig. 2 are four one-half inch lead plates on the top and sides, and two at the bottom of the central grounded assembly to aid in shielding each chamber from a source in the opposite chamber. The central rod between chambers had lead cast around it within brass cylinders and end plates which present clean surfaces to the gas filled region. Most of the solid angle from one source which would illuminate the opposite chamber is blocked out by the steel electrode shown in solid black. The radiation which leaks through from one source to the opposite chamber is entirely negligible for Tc^{99m} and Be^7.

The ionization chambers were filled with aged (Rn free) commercial 99.8 percent pure argon to 13.6 atmospheres for the work reported here. At this pressure a satisfactory ion collecting voltage on each chamber was 480 volts for source strengths up to 15 000 divisions or 1.5×10^{-10} ampere. Departure from saturation was evident for sources six times stronger.

The inside surfaces of the cylindrical sections of the re-entrant source holder thimbles were reamed out 1.2×10^{-3} cm greater than the outside diameter of the source holders. The sources could be replaced to better than 10^{-3} cm in position axially and scratch marks were lined up to maintain the same angular position.

The chambers, originally for use with radium and Be^7, were constructed to position the sources in the re-entrant thimbles so that the ionization produced would have a maximum at one position and the effects of small displacements would be negligible. A maximum is attainable for radium and disk shaped Be^7 sources. Unfortunately, it has not been possible to obtain a maximum with simple source holders in the case of Tc^{99m} which emits softer radiations. However, when the salts are properly immobilized in wax and care is taken to return them to the same position, no difficulties are experienced.

IV. IONIZATION CURRENT MEASUREMENTS

Figure 3 illustrates the basic current measuring circuit, which includes certain features that contribute to the accuracy and reliability of the final results.

All measurements are referred to a standard cell which by means of the potentiometer serves to measure the ion currents essentially independently of the gain of the vibrating reed electrometer amplifier, to calibrate the resistors used to measure the individual source intensities I, and to monitor the ion collecting potentials.

The potential assumed by the ion current collecting electrode is constant to within one or two millivolts as complete degenerative feedback is utilized and the open circuit gain of the amplifier is about 1000.

The ion currents are measured by a null method, so that even if the vibrating reed electrometer wanders away from best performance the results are not affected. Null measurements are achieved by using the output of the potentiometer to buck out all but a very small fraction of the IR drop in the case of a measurement of the intensity of one source alone. Then the source decays until the pen crosses the zero line and goes some distance beyond, as illustrated in the top trace on the record in Fig. 3. The full sensitivity of the recorder can be utilized, as the zero has been displaced by the bucking potential 15 to 150 recorder roll widths away (to the right in the case illustrated). The best line drawn through the record gives a mean value which decreases the effects of fluctuations by effectively increasing the time of the measurement. The intercept of the mean trace line with the recorder at zero gives the time at which the voltage iR was equal to the applied bucking potential from the potentiometer. The recorder roll is synchronously driven and is started with reference to the time signals from WWV. Long period excursions of ±20 seconds from true synchronism do occur in the power line but produce a negligible error in the results for λ and $\Delta\lambda/\lambda$.

The small difference currents, varying from $I_0/300$ to $I_0/100\,000$, are measured accurately by determining the rate of potential increase across the 10^{-9} farad condenser. In the usual procedure the potential across the condenser is estimated from the chart record about 600 seconds after the start of the measurement. A bucking potential of twice that reading is inserted from the potentiometer and the condenser continues to charge up until the pen crosses the zero line of the recorder. Then the potential is read from the potentiometer, and the time is obtained from the chart. Again the recorder is used as a null indicator. Two records of this type are illustrated in Fig. 3.

The 10^{-9} farad condenser used for the small current measurements is a well made commercial transmitting condenser in which fused quartz has been substituted for ceramic insulation. The entire condenser is in an evacuated box with a moisture absorber.

The method of calibrating the resistors is illustrated on the left of Fig. 3.[16] High megohm resistors may have a voltage coefficient of resistance capable of introducing errors when the resistor is used in the direct measurement of λ and I_0. The resistors were checked occasionally at various known relative current values by means of the small current generator shown. A fifteen turn, 0.1 percent linear, helical potentiometer is driven by a 1 rps synchronous motor to provide a constant dV/dt source. The potential applied across the helical potentiometer is measured against the standard cell. Induced currents for calibration purposes, varying from $\sim 2\times 10^{-14}$ to 2×10^{-10} ampere, are obtained through the quartz insulated $\sim 25\times 10^{-12}$ farad condenser.

The calibration of a resistance relative to the 10^{-9} farad condenser is made most easily by measuring the same small ionization current, preferably one of less than 8×10^{-12} ampere. Generally, the sources under study were used separately to provide the comparison current when they had decayed to 8×10^{-12} ampere intensity. C and R can be accurately compared by this method down to current values of 15×10^{-14} ampere. In addition a small ionization current produced by a radium source of approximately 5μC strength was used.

This weak radium source and another $\sim$160 times stronger were used to give an over-all simultaneous check of the gas density, resistances, electrometer, and recorder and showed very stable response of the whole balanced ionization chamber and recorder unit over a period of six months, the limits in the variations in the ionization current being ±0.8 percent from the mean value.

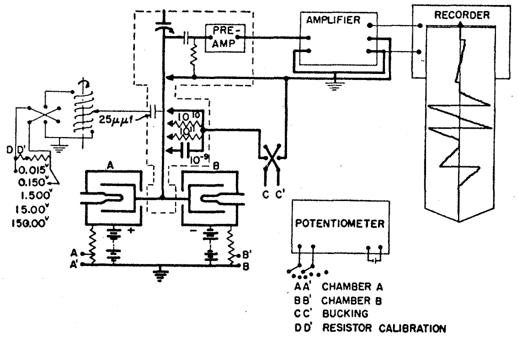

FIG. 3. Schematic of the ionization current measuring system. The currents are measured by means of a vibrating reed electrometer which is used here as a null detector. The potential of the ion collecting system is bucked out by a potential fed from the potentiometer. The potentiometer also serves to monitor the chamber voltages and to calibrate the 10^{10} and 10^{11} ohm resistances.

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[16] The particular system used here was developed by G. C. Ford and K. T. Bainbridge and is described in more detail by G. C. Ford, thesis (1950), Department of Physics, Harvard University. See also A. Wikstrom, Rev. Sci. Instr. 4, 612 (1933), and a reference by Rutherford to Townsend's equivalent device in *Radioactive Substances and their Radiations* (Cambridge University Press, Cambridge, 1913), p. 103.

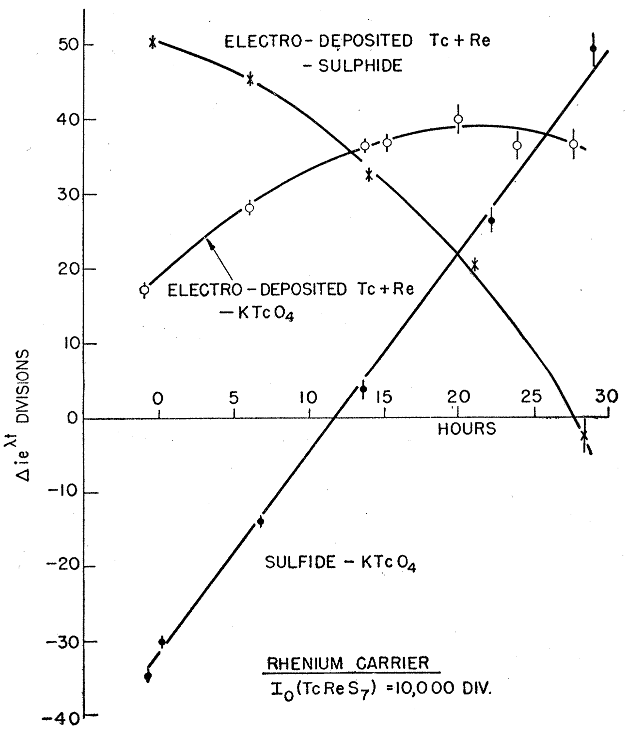

FIG. 4. The source of electrolytically deposited Tc^{99m} and rhenium carrier was not properly immobilized in its source holder in this run. λ for the electrodeposited material behaves as if it were increasing with time. The effect is mainly if not entirely mechanical in origin and was successfully eliminated in all succeeding experiments.

V. PREPARATION OF SOURCES

The Tc^{99m} sources are prepared from the Mo^{99} parent by the methods developed by Perrier and Segrè[17] and by Motta, Larsen, and Boyd[18] and Boyd *et al.*[19]

Mo^{99} obtained by neutron bombardment of Mo metal, with its daughter product Tc^{99m}, is dissolved in a mixture of perchloric and phosphoric acid. The perchloric acid is a strong oxidizing agent and phosphoric acid forms a phosphomolybdate complex, tending to hold the Mo in solution. Mo metal is readily soluble in these acids. The voltatile Tc_2O_7 is carried over by a stream of air bubbling through the solution and also by fumes of the perchloric acid. The TcO_4^- is extremely soluble and the distillate may be collected in water or in dilute H_2SO_4. The Tc^{99} activity begins to distill over at ~120°C and is complete at 200°C. The water fraction, coming over below 120°C and containing no activity, is discarded—thus keeping the active volume to a minimum. The active distillate is then returned to a clean still and inactive Mo added as holdback carrier. The water fraction is again discarded and the distillate collected between 120–200°C. Long-lived Tc^{99}, $\sim 25\mu g$ per source, is added to the distillate as NH_4TcO_4.

Metal

10^{-3} mole of ammonium fluoride is added to an aliquot of the distillate and the solution brought to a *p*H of 5.5. The Tc is electroplated on a polished copper-coated nickel cathode using a platinum stirrer as the anode. The *p*H is quite critical and must be maintained throughout the electrolysis. The reduction at the cathode is complete in ~2 hours at 3–4 volts. The cathode is then reduced in H_2 at 1000°C for 1 hour, transferred to a vacuum vessel and coated with evaporated aluminum.

Sulfide

A fraction of the TcO_4^- distillate is made 5 molar with H_2SO_4. Long-lived Tc carrier is added and the sulfide precipitated by bubbling hydrogen sulfide through the solution at 90°C. The sulfide is digested at this temperature for 1–2 hours, thus coagulating the precipitate and making it easier to centrifuge. The sulfide Tc_2S_7 is washed several times with hot water and then taken to dryness, mounted on its holder, and coated with paraffin.

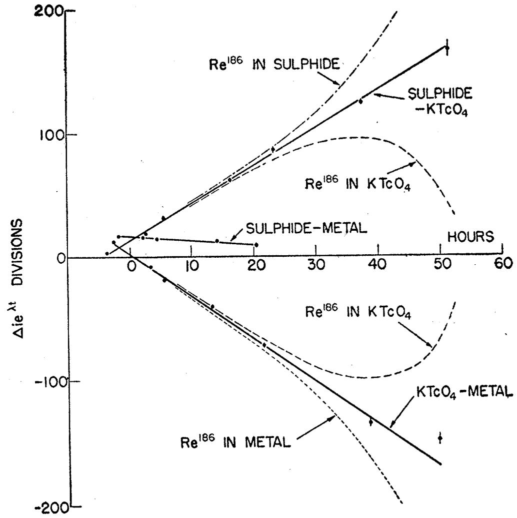

FIG. 5. Effect of hypothetical contaminant Re^{186}. The solid lines are the least squares solutions of the data for the comparisons of the Tc metal, electrodeposited; Tc_2S_7, and the dry salt $KTcO_4$. The ordinates are in units of 10^{-14} ampere = 1 division. The intensity at $t=0$ of the electrodeposited Tc = 10 000 divisions. The long-dashed lines illustrate how the records would appear if Re^{186} had been present in the $KTcO_4$ only, to an intensity of $I_0(KTcO_4)/20\,000$ at $t=0$. The short-dashed line shows the effect of the same amount of contaminant if it had been present in the metal source only, and similarly the dot-dash line applies to the contaminant concentrated in the Tc_2S_7 source.

The duration of the run, $\sim 9T_{\frac{1}{2}}$, contributes little to the accuracy in the determination of $\Delta\lambda/\lambda$ beyond $4T_{\frac{1}{2}}$ or $5T_{\frac{1}{2}}$, but is helpful in furnishing an independent check on the absence of appreciable amounts of contaminants.

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[17] C. Perrier and E. Segrè, J. Chem. Phys. 5, 712 (1937); 7, 155 (1939).

[18] Motta, Larsen, and Boyd, quoted by A. C. Wahl and N. A, Bonner, *Radioactivity Applied to Chemistry* (John Wiley and Sons. Inc., New York, 1951).

[19] Boyd, Cobble, Nelson, and Smith, J. Am. Chem. Soc. 74, 556, 1852 (1952). See also *The Nuclear Chemistry of the New Element Technetium*, G. E. Boyd, Record of Chemical Progress, pp. 67–78 (1951).

Pertechnetate

During the distillation some perchloric acid distills over and when the TcO_4^- solution is neutralized a large bulk of ammonium or potassium perchlorate appears along with the pertechnetate. For this reason the Tc^{99} is first precipitated as the sulfide and then after being washed is dissolved in dilute potassium hydroxide and hydrogen peroxide. The potassium pertechnetate thus formed is very soluble and only appears when taken to dryness. The $KTcO_4$ is thoroughly dried, mounted on its holder and coated with paraffin.

VI. SOURCE CONTAMINANTS

A. Direct Measurement

The purity of the sources of Figs. 4–6 was checked with a NaI scintillation spectrometer. The gamma-ray spectra obtained allowed the identification of contaminants, and in some cases their intensity and period of half-life could be measured also by standard counting procedures. The sources were examined after the Tc^{99m} had decayed to 10^{-7} or less of its initial gamma-ray intensity.

The spectrometer showed that the sulfide and $KTcO_4$ sources of Fig. 4 had equal small amounts of Mo^{99} impurity while the electrodeposited source was uncontaminated.

An entirely negligible trace of Mo^{99} was present in the electrodeposited Tc source of Fig. 5 and the other two sources were uncontaminated.

A radioactive contaminant was found in the sources of Fig. 6 present to the entirely negligible amount of $\sim 5\times 10^{-7}$ of the initial activity of the sources. The contaminant was identified as Re^{186}, as its half-life was found to be ~90 hours, and the radiations observed corresponded to the most prominent gamma-ray and characteristic K radiation emitted by Re^{186}. Mo^{99} which might be transferred in the distillation of Tc^{99m} heptoxide was not found to an appreciable amount. Figure 7 shows spectrometer records of Mo^{99}, of the contaminants identified as Re^{186} from two old sources, and of Re^{186}. The intensities of the contaminants found experimentally in the sources for the different runs illustrated in Figs. 5 and 6 were too small to affect the value of $\Delta\lambda/\lambda$ even if all of the contaminant had been concentrated in one of the sources under comparison. No spectrometer analysis was made of the sources of Fig. 8 but some 14 other sources of reduced Tc prepared in the same way showed only negligible amounts of $Re^{186} \leqslant I_0 \times 3\times 10^{-6}$ in intensity.

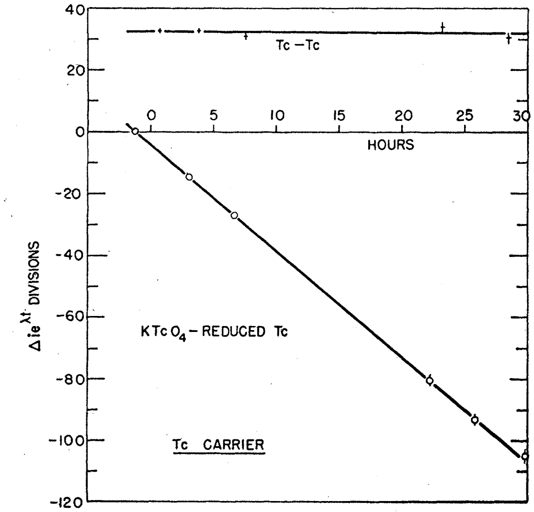

FIG. 6. The dry salt $KTcO_4$ compared with technetium reduced in hydrogen. Two identical metal sources were compared as a test of the over-all operation of the apparatus, which was satisfactory as indicated by the ~zero slope.

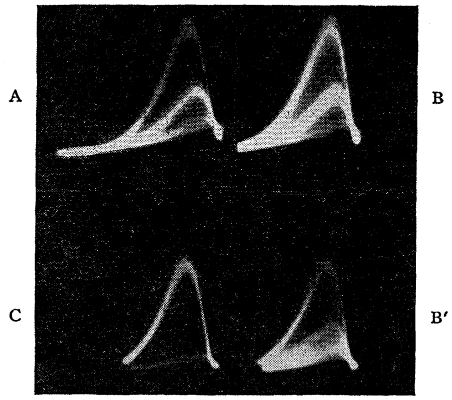

FIG. 7. B and B′ on the right are NaI scintillation spectrometer records of contaminants in old sources in which the Tc^{99m} has decayed to a negligible amount. The spectra are identified with radiations from Re^{186}, A, and not Mo^{99}, C. The period of the contaminant, ~90 hours, corresponds to that of Re^{186}.

Actually the method of preparation of the individual sources adopted from the beginning of the research would act to distribute any Re or Tc activities equally among the sources. Rhenium, the main contaminant found after Mo^{99} had been eliminated, is a chemical homolog of technetium and has a better chance than any other element of accompanying the technetium quantitatively throughout the chemical manipulations in the preparation of the individual sources.

The long-lived Tc^{99} carrier was added to the distillate from which the Tc^{99m} sources were prepared, and then the final sources were matched so that they differed by no more than $I_0/300$. Generally, a better match was obtained. In this way any chemically homologous or isotopic contaminant which could contribute j_0 to the ionization intensity of a single source was reduced to less than $j_0/300$ in the determination of Δi when the sources are interchanged.

The wall of the thimbles, 0.6 g/cm², is sufficient to stop the 0.3 Mev β-rays from Tc^{99} carrier. In a separate determination of its intensity the bremsstrahlung radiation, together with all other radiations from 25μg of Tc^{99}, was less than 0.1 division.

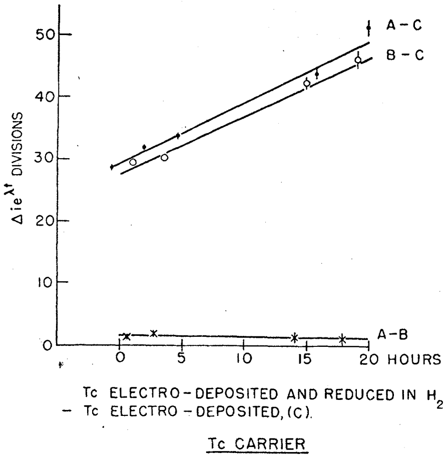

FIG. 8. Three Tc sources are compared, two having been reduced in H_2 at 1000°C for 1 hour and the third used directly. The electrodeposited technetium in this case was not entirely metal and may have contained compounds of shorter $T_{\frac{1}{2}}$ value. Electrodeposited unreduced technetium is not always satisfactory as a reference substance.

Two methods of checking the over-all performance of the apparatus are illustrated. The two reduced sources A and B were compared, as was done in the run of Fig. 6, and the fact that essentially zero slope was recorded indicated satisfactory operation. Also, as in the runs of Figs. 4 and 5, all combinations of the sources were measured and the difference in the ordinates of the plots, (A–C)−(B–C) equals (A–B) over the duration of the experiment and within the range of the errors.

B. Indirect Detection of Contaminants

The existence of a long-lived contaminant in one source alone, present even to an amount as small as $I_0/20\,000$, will produce a marked curvature in the plot of $y=\Delta ie^{\lambda t}$ *vs* t if the measurements are extended through 5 or 6 mean lives. Thus, another check on the possible existence of unbalanced amounts of contaminants in the sources can be obtained by extending the measurements beyond 3 or 4τ. This was tried in the present series of experiments as shown in Fig. 5. If one source alone had an initial strength of contaminant $=I_0/20\,000$ of long life, y at ∼43 hours, or 5τ, would have an additional − and +75 divisions, and the points at $\sim 6\tau$, − and +200 divisions. The corresponding values would be 54 and 136 divisions at 5τ and 6τ, respectively, if 92.8-hour Re^{186} had been present. The departures from linearity which could be caused by errors in the value of λ, or by mechanical or chemical changes in the sources had been eliminated.

VII. DETERMINATION OF λ

The transition constant of the hydrogen reduced metal was measured directly when $\lambda=t^{-1}\log(I_0/I_t)$, yielding the results in Table I. The final result is $\lambda=0.1148\ \text{hr}^{-1}$ with a limit of error of $\pm 0.0005\ \text{hr}^{-1}$. $T_{\frac{1}{2}}$ is 6.04±0.3 hr. Earlier values are 6.6±0.4 hr,[20] 5.98±0.01 hr,[21] and 5.9 hr.[22]

VIII. EXPERIMENTAL RESULTS

The principal result obtained is a demonstration of the influence of different states of chemical combination on the decay of an isomer. A difference in λ was obtained for two compounds of Tc in the +7 state,

$$\lambda(\text{KTcO}_4)-\lambda(\text{Tc}_2\text{S}_7)=27\pm 1\times 10^{-4}\lambda(\text{Tc}_2\text{S}_7).$$

The first series of measurements was made with rhenium as a carrier. Figure 4 is included to illustrate one of the difficulties experienced in this one of four earlier runs. The curvature of the upper two lines in the graph is attributed to gross motion of the electrodeposited source in its holder. An intensity of $I_0/2500$ of Mo^{99} impurity in equal amounts in the sulfide and KTcO_4 sources, but not in the metal source, could approximately account for the observed effects. This possibility was definitely ruled out by the normal results of concurrent determinations of λ for the sulfide source measured over five intervals in the range from ∼12 000 to 79.3 divisions. The departure from a straight line does not correspond either with the calculated effect of an incorrect value of λ, or with the result to be expected from the presence of a short or long period contaminant in the electrodeposited source alone. No such difficulties were encountered in five succeeding runs in which greater care and improved techniques were used in preparing and securing the sources, and in which Tc^{99} was used as a carrier in place of rhenium.

Figure 5 gives a comparison of electrodeposited Tc with the sulfide Tc_2S_7 and the dry salt of potassium pertechnetate, KTcO_4. In this case, the electrodeposited technetium was metallic and not adulterated with appreciable amounts of lower oxides.

The standard deviations in the points on all figures are plotted on the basis that

$$\sigma_y + 0.5(I_0/10D)^{\frac{1}{2}}e^{\lambda t/2}\ \text{divisions.} \tag{7}$$

TABLE I. λ-values for metallic Tc^{99m} measured in two runs with different arrangements of the source and blank source holder. The chambers were connected differentially to minimize the background current. Two different 10^{10} ohm resistors, R_1 and R_2, and the "ideal" quartz insulated condenser were used to measure the currents. The two runs were separated by 18 days.

Run	Chamber *A*	Chamber *B*	Method	Current range 10^{-14} amp	λ hr^{-1}
1	···	source 1	R_1	12 600 to 175.0	0.1147
	···	source 1	R_2	2100 to 202.0	0.1150
	···	source 1	CdV/dt	604 to 7.67	0.1145
2	source 2	···	R_1	15 400 to 110.0	0.1147_5
	source 2	···	R_2	1730 to 106.0	0.1147
	source 2	···	CdV/dt	607 to 17.82	0.1146
	···	source 2	R_1	15 550 to 130.0	0.1148_5
	···	source 2	R_2	1608 to 125.0	0.1153
	···	source 2	CdV/dt	554 to 16.22	0.1150_5
			Average		0.1148
			Limit of error		0.0005

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TABLE II. Summary of data.

Ref. No.	Fig.	Comparison	Carrier	No. of input points	Least squares value of $y=a+bx$						
					$a\pm\sigma_a$*		$b\pm\sigma_b$*		σ_i†	σ_e	σ_e/σ_i
1	4	‡$TcReS_7-KTcO_4$	Re	5	−31.93	0.73	2.700	0.065	0.96	1.04	1.08
2	5	$Tc_2S_7-KTcO_4$	Tc	7	13.165	0.48	3.025	0.063	0.47	0.77	1.64
3	5	Tc_2S_7-Tc	Tc	5	16.031	0.39_6	−0.327	0.049	0.61	0.56	0.92
4	5	$KTcO_4-Tc$	Tc	7	2.134	1.13	−3.466	0.13	0.53	1.69	3.18
5	6	Tc−Tc	Tc	5	32.22	0.53	-0.024_6	0.074	0.50	0.70	1.40
6	6	$KTcO_4-Tc$	Tc	6	−4.20	0.34_5	−3.446	0.042	0.47	0.32	0.68
7	8	Tc−Tc	Tc	4	1.59_4	0.39	−0.011	0.06	0.48	0.40	0.833
8	8	Tc−Tc (electro)	Tc	5	29.47	0.49	1.000	0.078	0.47	0.70	1.49
9	8	Tc−Tc (electro)	Tc	4	27.71	0.81	0.955	0.113	0.50	0.89	1.78
10	none	$Tc_2S_7-KTcO_4$	Tc	6	−5.69	0.47	3.137	0.064	0.50	0.74	1.48

* σ_a and σ_b were calculated from the larger of the two values σ_i and σ_e.
† 38 000 ev per ionization event.
‡ When rhenium is used as a carrier the composition of the sulfide is uncertain, as in a typical source there are only 10^{12} Tc atoms distributed among 3×10^{17} Re atoms.

The standard deviation $c^{\frac{1}{2}}$ of a point of unit weight at $t=0$ is 0.5 divisions for a measurement of duration $D=1000$ seconds with an initial intensity $I_0=10\,000$ divisions $=10^{-10}$ ampere.

Figure 6 gives a comparison between λ for $KTcO_4$ and for the electrodeposited metal reduced in hydrogen. A useful internal check on the behavior of the apparatus is illustrated by the graph of the comparison of two sources of technetium, only one of which was measured against the $KTcO_4$ source (dry salt). There should be zero slope in the comparison of identical sources if everything is working properly, if $\lambda=0.1148$ is correct, and if contaminants are balanced or absent, subject to the errors imposed statistically. In Fig. 6 there is essentially zero slope in the comparison of two technetium sources, starting at an initial difference current $(I_{10}-I_{20})S=i_0=32.4$ divisions, corresponding to an unbalance i_0/I_0 of one part in 308.

In Fig. 8 the initial unbalance of two similar technetium sources has a quite different value of only one part in 6000 to 8000 of I_0. Again the slope is of the magnitude of the slope error, as it should have been if the entire experiment was going satisfactorily.

The other two lines represent a comparison of the individual Tc (metal) sources prepared by reduction in hydrogen at 1000°C with the untreated third of the original electrodeposited source.

In this case the electrodeposited source must have contained a fraction of Tc compounds with λ-values greater than λ(Tc metal) to give

$$\Delta\lambda=8.6\pm0.6\times10^{-4}\lambda(\text{metal}).$$

The results of the experiments illustrated in Figs. 4, 5, 6, and 8 are given in Table II, together with those of a later run and the statistical analysis of the data. σ_i is the standard deviation of a point of unit weight based on the figure 38 000 ev as the mean statistical value for the energy dissipated per ionization event. The chambers were filled with argon which requires 25.4 ev per ion pair created. The value of σ_i differs for different runs with the varying duration D of individual measurements of i. Also, while all runs have been reduced to $I_0=10\,000$, the intensity at the time of the first measurement varied from 15 000 to 9300 divisions.

σ_e is the standard deviation based on external consistency of a point of unit weight, and is equal to $[\Sigma pv^2/(n-2)]^{\frac{1}{2}}$ calculated from the residuals v between the n experimental points and the least squares solution for $y=a+bx=\Delta ie^{\lambda t}=a+bt$.

The ratio σ_e/σ_i has a different significance here than is customary. Usually the difference $(\sigma_e/\sigma_i)-1$ may be compared with a mathematical estimate of the expected probable error, $0.48/(n-2)^{\frac{1}{2}}$, to give an idea of the reliability of the results and to indicate the presence of unsuspected errors.[14] In these experiments σ_i for a point of unit weight and σ for every succeeding measurement of $e^{\lambda t}\Delta i$ in a run has been based on an estimate of the statistical average energy lost per ionization event. An increase of σ_i (unit weight) by 20 percent, corresponding to an increase from 38 000 ev to 55 000 ev per ionization event,[23] leads to values of σ_e/σ_i in reasonable agreement with the statistical expectation except for entry 4 in Table II. Accordingly, if 55 kev is taken as the ionization loss, there remains little evidence of systematic errors in this experiment. The change in σ_i has no influence on σ_e as the relative weights of all of the input data are independent of the value chosen for σ_i (unit weight) and therefore the same least squares solution must be obtained for $y=a+bx$.

Table III lists representative sources of error, and their magnitude, which enter into the determination of Δλ/λ. The statistical error (the origin of which is in the finite number of ionization events observed) supplied 75 to 87 percent of the final error in the measurement of Δλ/λ.

The selection of an easily reproducible reference sub-

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[23] The maximum loss is 49.5 kev and the average loss is ~25 kev for 140-kev gamma-rays in the Compton scattering process. In addition there are contributions to the ionization from the photoelectric absorption in the argon and in the iron walls, and the absorption by both processes of the iron and lead fluorescent x-radiation.

TABLE III. Representative sources of error, and their magnitudes, in the determination of $\Delta\lambda/\lambda = b/I_0\lambda$.

Source of error	Magnitude of error	Standard deviation in $\Delta\lambda/\lambda$, parts in 10 000. Based on duration of run $=4\tau$
1. Statistical. Basis of 1000 sec = duration of an individual measurement	$c^{\frac{1}{2}}/I_0 \cong 1/20\,000$	$\cong 0.5$
2. Uncertainty in λ, limit of error	$\delta(\lambda)/\lambda = 1/200$	$<0.005a + 0.003 I_0 \Delta\lambda/\lambda$
3. Calibration of C relative to R	<1 percent	$<0.01 I_0 \Delta\lambda/\lambda$
4. Unbalanced contaminant, assumed all in one source	$<I_0/300\,000$	<0.12
5. Departure from ideally complete saturation of ionization currents	$-\delta S/\bar{S} \leqslant 1/200$ from $t=0$ to $t= \leqslant 4\tau$	$<0.005 I_0 \Delta\lambda/\lambda$. Opposite in sign to entry 2 when I_0 and λ were determined in the same experiment
6. Error in time measurements	$\cong \pm 50$ sec in 8 hours	Negligible
7. Leak-through of radiation into opposite chamber	$\ll 1$ percent	Negligible
8. Cosmic-ray background and wall contamination effects	0.01 division in measuring i	Negligible

stance for these measurements has been difficult. $KTcO_4$ has the advantage that rhenium can be used as a carrier without altering the composition of the Tc-containing compound. The main disadvantage of $KTcO_4$ lies in the hygroscopic nature of the salt. It will go into solution and migrate if there is any imperfection in the paraffin coating.

Tc_2S_7, which is another possibility, has been reported to include some Tc associated with free sulfur.[24] As the transition rates of Tc and Tc_2S_7 differ by only 3 parts in 10 000, however, it is unlikely that even amounts of Tc up to 10 percent can produce changes outside of the standard deviations of the measurements. Both Tc_2S_7 and metallic technetium suffer from the disadvantage that technetium must be used as a carrier to avoid structural effects on the magnitude of λ, as the lattice conditions play a dominant part in the variations produced in λ.[25]

After the first series of experiments had been completed, Cyril S. Smith pointed out in discussion that the reduction of Tc on nickel at 1000°C in hydrogen might lead to appreciable interdiffusion of the metals. Since the decay rate of Tc associated with nickel could differ from that of Tc in its own crystal lattice, a new series of experiments was undertaken to check the idea of diffusion, and some additional exploratory studies were made.

Tc metal sources, made under different conditions, were compared with Tc metal produced as described in Sec. V, hereafter designated Tc_V. In some cases $KTcO_4$ and Tc_2S_7 were used as reference sources. The results may be summarized as follows: the largest value of λ for the metal $[\Delta\lambda/\lambda = \{\lambda - \lambda(Tc_V)\}/\lambda(Tc_V) = 2.4 \pm 1 \times 10^{-4}]$ was obtained when $KTcO_4$ and Tc_2S_7 were reduced on platinum for one hour at 1000°C; a source consisting of technetium plated on nickel, reduced in hydrogen for two hours at 1000°C, had a lower λ-value than $\lambda(Tc_V)$ $(\Delta\lambda/\lambda = -2.4 \pm 0.7 \times 10^{-4})$; the combined results indicated an effect of diffusion yielding a lower value of λ than for essentially undiffused technetium. As a further test Tc^{99m} *without carrier* was plated on nickel and heated to 1000°C in hydrogen for one hour. Two sources of this type yielded a λ-value less than $\lambda(Tc_V)$, $\Delta\lambda/\lambda = -3 \pm 1 \times 10^{-4}$. It is suggested as a qualitative explanation that the technetium had either diffused into the nickel or had failed to associate into Tc crystals.

In another experiment, bulk Tc_2S_7, which included $150\mu g$ of carrier, was heaped up to permit only minimal contact with a platinum boat and was reduced in hydrogen at 1000°C for one hour. λ for this technetium was less than λ for unreduced Tc_2S_7, i.e.,

$$\Delta\lambda/\lambda = \{\lambda - \lambda(Tc_2S_7)\}/\lambda(Tc_2S_7) = -9.7 \pm 0.6 \times 10^{-4}.$$

This material provided the longest-lived Tc^{99m} which we have been able to produce. The technetium in this case is considered as partly amorphous, approximating the condition of free Tc atoms. As some of this material may have been in crystalline form, it is probable that λ for amorphous Tc^{99m} is even less compared to Tc_2S_7.

The final results from all of the pertinent data except entry 10 in Table II showed that the disintegration constant λ is greater for the dry salt $KTcO_4$ than for the reduced metal (1 hour at 1000°C) by the factor 1.00300 ± 0.00003 and $\lambda(Tc_2S_7)$ is 1.00031 ± 0.00004 times greater than λ for the reduced metal. In our first report on this work the above errors were increased approximately 3 times to 10^{-4} and 1.2×10^{-4}, respectively in accordance with our estimate of possible variations in the reproducibility of the sources when dealing with microgram amounts of technetium. The reproducibility of $KTcO_4$ and Tc_2S_7 sources has been satisfactory. The metal too is reproducible when the detailed preparation described in Sec. V is followed. However, the experimental demonstration of diffusion effects on λ for the metal argues against the continued use of the metal as a standard. Accordingly, our final results, including entry 10, Table II, are $\lambda(KTcO_4) - \lambda(Tc_2S_7) = 27.0 \pm 1.0 \times 10^{-4} \lambda(Tc_2S_7)$, and $\lambda(Tc_V) - \lambda(Tc_2S_7) = 3.1 \pm 1.2 \times 10^{-4} \lambda(Tc_2S_7)$. The range of variations of λ for the metal produced by different reduction treatments has already been discussed.

That the λ-values for both compounds were greater than λ for the pure metal has been explained on physical grounds by the introductory theory developed by Slater.[25] In this report Slater shows that only the elec-

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tron density within ~0.2A of the nucleus contributes to the transition probability for internal conversion. The greater part of the effect is attributed to the $4p$ electrons, which account for possibly one-tenth of the total transition probability. In $KTcO_4$ an increase of 3 percent in the $4p$ electron density in the critical region, compared to the density in Tc metal, could produce an effect of the magnitude and direction observed.

The greater $4p$ electron density of Tc^{99m} in $KTcO_4$ compared to that in Tc metal is attributed to the fact that the Tc atom is constrained to a smaller volume in $KTcO_4$. The Tc$-$O separation in the TcO_4 tetrahedral ion[26] is ~1.75A compared to ~2.73A for the separation of the nearest neighbors in the metal.[27]

The observed effects demonstrate that γ-ray emission and internal conversion take place competitively rather successively, in agreement with the accepted theory of internal conversion. The determination of the changes in the decay constant of isomers in different chemical combinations may help in understanding the electronic structure of these compounds.

An attempt is being made to attain increased accuracy with improved equipment and stronger sources so that the work need not be confined solely to very low energy isomeric transitions.

We are indebted to Mr. M. McKeown for checking the sources with a NaI scintillation spectrometer, to Dr. G. Friedlander for advice on some chemical aspects of this work, to Miss Jean Snover for much valuable help, particularly in the computations, and Dr. V. W. Cohen and Dr. Raymond Davis for their hospitality in providing air-conditioned space for setting up the equipment in their laboratories.

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Inelastic Nuclear Scattering of Photons by Rh^{103}†

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A lower limit to the inelastic nuclear photon scattering cross section of Rh^{103} was determined as function of energy. Rhodium foils were exposed to a bremsstrahlung beam and the yield of Rh$^{103}(\gamma,\gamma')$Rh^{103m} was measured as a function of the upper limit of the spectrum. Activities were counted with a windowless 4π proportional counter and Ta$^{181}(\gamma,n)$Ta^{180} was used as a monitor above 8 Mev, adopting the improved results of the Sasketchewan group. It was ascertained that the fast neutron contamination of the beam contributed but a small fraction of Rh^{103m} activity. The cross section, obtained from the yield curve by customary methods, is found to go through a peak of the order of 10 mb at about 13 Mev and to be appreciable below the Rh$^{103}(\gamma,n)$Rh^{102} threshold (9.35 Mev). The observed location of the peak is considerably lower than would be expected for Rh$^{103}(\gamma,n)$ from the empirical A-dependence of (γ,n) cross sections, and is also at variance with the observations of Katz and Cameron on Au$^{197}(\gamma,\gamma')$Au^{197}, but appears plausible on theoretical grounds as does the magnitude of the cross section.

I. INTRODUCTION

THE importance of nuclear photon scattering, both elastic and inelastic, has long been emphasized in connection with the mechanism[1–3] of electromagnetic absorption in nuclei. Various experiments designed to detect the scattered photons directly have been reported. They differed mainly in the detectors used [cloud chamber,[4] activation of Pr^{141} by (γ,n) reaction,[5] NaI(Tl) crystal with pulse-height selection[6]] and suffered from the common shortcoming of low counting rates and no or insufficient ability to discriminate between elastic and inelastic scattering. Another method, first used at low energies, by the Notre Dame group,[7,8] consists in irradiating a stable isotope possessing an isomeric state with photons and determining the isomeric activity which is induced in a fraction of the inelastic scattering processes. This fraction being unknown experimentally, and but unreliably predictable theoretically, only lower limits to cross sections can be obtained in this way. Furthermore, in the "resonance" region, i.e., at energies above the threshold for neutron emission, this method is unfortunately confined to those isotopes whose isomeric states cannot

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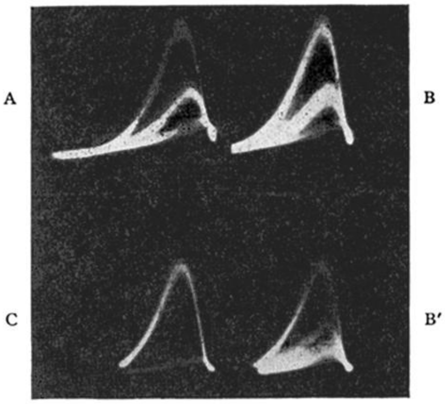

FIG. 7. B and B′ on the right are NaI scintillation spectrometer records of contaminants in old sources in which the Tc^{99m} has decayed to a negligible amount. The spectra are identified with radiations from Re^{186}, A, and not Mo^{99}, C. The period of the contaminant, ∼90 hours, corresponds to that of Re^{186}.