

K-Electron Ejection in the Beta Decay of S^{35} *

WILLIAM RUBINSON AND J. J. HOWLAND, JR.†

Department of Chemistry, Brookhaven National Laboratory, Upton, New York

(Received September 3, 1954)

By means of proportional-counter pulse-height analysis, it is found that S^{35} sources emit K photons of chlorine with a probability of $2.47(\pm 0.6) \times 10^{-4}$ photon/beta (the indicated error being an extreme), equivalent to a probability for K -hole production of $2.3(\pm 0.7) \times 10^{-3}$ K hole/beta. The theory, which has about the same accuracy as the experiments, predicts 3.0×10^{-3} K hole/beta.

I. INTRODUCTION

IN continuation of experimental studies at this laboratory^{1,2} on the transitions suffered by an extranuclear electron of an atom when the nucleus undergoes radioactive transformation, we have investigated the case of K -electron ejection in the beta decay of S^{35} .

The apparatus and the general procedure for such measurements are described at length in reference 1. By means of a proportional counter and pulse-height analyzer, one makes a pulse-height analysis of the photon spectrum emitted from a source at known geometry and of known radioactive disintegration rate, establishes that the photons under study are characteristic x-radiations of the daughter atom, and makes appropriate corrections on the observed rate of emission of these photons to obtain their total emission rate. This total emission rate is divided by the radioactive disintegration rate of the source to give the "photon yield," i.e., the probability, per decay, of emission of the x photon in question. Then the probability of electron ejection from the shell in question is the photon yield divided by the appropriate fluorescence yield.

In the case of beta emitters, the x-ray peaks are superposed on a relatively intense bremsstrahlung background which varies considerably with energy, so that special consideration must be given to background subtractions.

II. PREPARATION OF THE S^{35} SOURCES

Source strengths of about a millicurie are required for convenient photon counting rates. There are rather stringent requirements on the isotopic and chemical purity of the sources for two reasons:

(1) Absorption of Cl K photons in the source. If the S^{35} atoms are distributed uniformly through a disk of S^{32} atoms $200 \mu g/cm^2$ thick, then, since the absorption coefficient of sulfur for Cl $K\alpha$ photons

(2.63 kev) is³ $1800 \text{ cm}^2/g$, some 25 percent of the Cl radiations will be absorbed in the source.

(2) Excitation of atoms in the source by beta particles. Any isotopic or chemical contaminant in a source is under beta bombardment, and so may be excited to x-ray emission. If the contaminant is sulfur or chlorine, the cross section for ejecting a K electron from a contaminant atom by an incident beta of 65-kev energy (\sim the mean energy of a S^{35} beta) is about 1200 barns, as computed from a theoretical formula deduced by Bethe.⁴ The corresponding total cross section for a disk of contaminant $200 \mu g/cm^2$ thick is about 10^{-3} cm^2 , i.e., the probability, per beta, of creating a K hole in some disk atom is $\sim 10^{-3}$. Since 10^{-3} is also the order of magnitude of the probability that a S^{35} decay results in a Cl^{35} with a K hole (see Sec VI below), the K x-ray spectrum from such a contaminated source consists of a superposition of Cl K x-rays from S^{35} decay and contaminant K x-rays from excitation by betas, the intensities of the two being approximately equal. Indeed, this is just what we have observed with a 5-mC S^{35} source containing 1000 S^{32} atoms per S^{35} atom, and 0.5 cm^2 in area.⁵

S^{35} sources of adequate strength and purity were prepared as follows: Mallinckrodt Reagent Grade KCl which, according to its label, contains less than 20 parts per million of sulfate, was recrystallized twice from doubly distilled water, and then volatilized in vacuum at 1050° (quartz tube). This treatment reduced the sulfate content by a factor of at least 30, as shown by the use of S^{35} tracer. The purified KCl was ground finely in a Pyrex mortar, and a 5-gram quantity of it, in an atmosphere of 5 cm of O_2 , was sealed into a quartz ampoule provided with a breakseal.⁶ Two such ampoules were made, one of which was irradiated for five days, and the other for ten days, at the center of the Brookhaven reactor. An irradiated ampoule was placed in a quartz tube on a vacuum line, and opened

* Research carried out under the auspices of the U. S. Atomic Energy Commission.

† Present address: University of California Radiation Laboratory, Livermore, California.

¹ W. Rubinson and W. Bernstein, Phys. Rev. **86**, 545 (1952).

² J. A. Miskel and M. L. Perlman, Phys. Rev. **94**, 1683 (1954).

³ Interpolation of data tabulated in A. H. Compton and S. K. Allison, *X-rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1935).

⁴ See N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (The Clarendon Press, Oxford, 1949), second edition, p. 243.

⁵ Before realizing the magnitude of this effect, we permitted quotation (references 14 and 16) of measurements that were high by a factor of 2.

⁶ W. Koski and V. W. Cohen gave us the essentials of this recipe for extracting S^{35} from neutron-irradiated KCl .

in vacuo by means of a magnetic hammer sealed in quartz. The tube was then heated at about 1050° for several hours, under which treatment the KCl volatilizes out of the ampoule to deposit on a six-inch section of the tube immediately above the furnace, while the S^{35} compound of unknown composition (perhaps SO_2 or $SOCl_2$) diffuses through some three feet of glass tubing wound into a coil of three turns, and is finally caught in a U tube at liquid-air temperature. The U tube was then sealed off the vacuum line, and its invisible contents were taken up in 2 ml of 1N HNO_3 (prepared with doubly distilled water). This constituted a S^{35} stock solution containing about 20 mC, or about 10^{-8} mol, of S^{35} (about half the S^{35} initially in the irradiated KCl). When an aliquot of stock solution was evaporated to dryness to prepare a source, traces of impurity in the solvent sufficed to provide the necessary cations.

Stock solutions were assayed by evaporating 10 λ of a 10^4 dilution on a backing of aluminized "Mylar" 700 $\mu g/cm^2$ thick, and counting in a 4π counter.⁷

A source was prepared by evaporating under a heat lamp a 100 λ pipette-full (~ 1.5 mC of S^{35}) of the stock solution plus a pipette-full of 1N HNO_3 wash in a clean, polished polystyrene cup $\frac{3}{8}$ inch in diameter and $\frac{1}{8}$ inch deep.

III. EXPERIMENTAL ARRANGEMENT

This is shown schematically in Fig. 1. The source sits at the bottom of a well in a polystyrene block in a 3000-gauss magnetic field, where the radius of curvature of a maximum energy S^{35} beta (167 keV) is ~ 5 mm. The geometry for photon detection is defined by a hole of $\frac{1}{4}$ -inch diameter in a diaphragm of $\frac{1}{32}$ -inch thick aluminum located 1.70 inches above the source. The photons pass into the counter through an 18 mg/cm^2 Be window, in which about half the Cl K photons are absorbed. Since 70 percent of Cl K photons are absorbed in a 1.70-inch air path, the space between source and

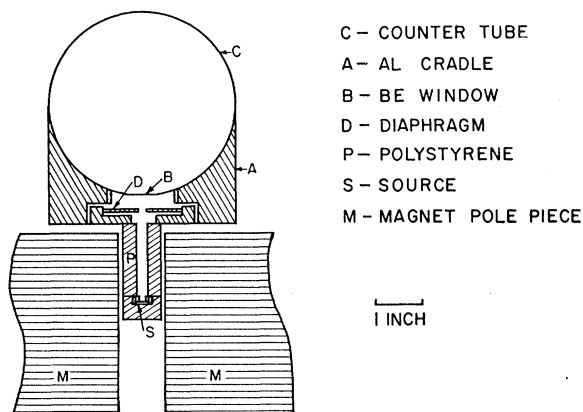


FIG. 1. Experimental arrangement.

⁷ 4π counting of S^{35} on a 700 $\mu g/cm^2$ backing requires a 12 percent correction for absorption of betas in the backing, according to R. C. Hawkings of Chalk River (private communication).

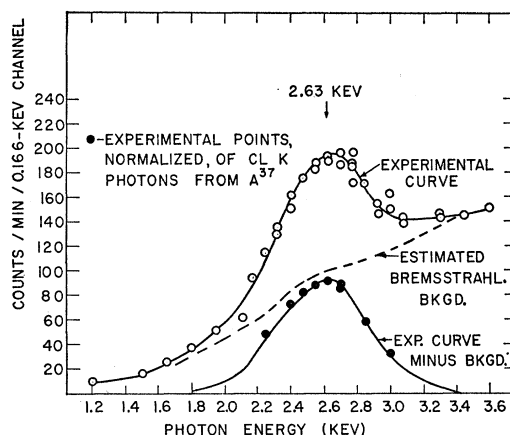


FIG. 2. Photons from S^{35} .

counter window was kept filled with helium. The counter gas for these experiments consisted of 9 parts of Kr and 1 part of CH_4 at a total pressure of 1 atmosphere. The counter pulses were amplified to about 30 volts, and a channel-width of 1.55 volts was used for the pulse-height analysis.

IV. PROOF THAT THE PHOTONS ARE K X-RAYS OF CHLORINE

One of our experimental curves, obtained with a S^{35} source of strength 3.9×10^9 dis/min, is shown in Fig. 2. The dotted line is an estimated bremsstrahlung background (see below). The difference peak obtained by subtracting the estimated bremsstrahlung background from the experimental curve coincides in energy with the Cl $K\alpha$ peak from an A^{37} (K -capture) source,⁸ as shown in Fig. 2, where the counting rates observed with the A^{37} source, normalized to have the same peak-maximum rate as the difference peak, are entered as black circles. Now, the energy coordinate of the difference peak is very insensitive to the particular bremsstrahlung background one assumes, so long as the latter is not completely fantastic. For instance, by making extreme assumptions about the shape of the bremsstrahlung background one can vary the height of the difference peak by a factor of three without changing the energy coordinate by as much as one percent. This, together with the fact that the K x-ray energies of elements adjacent to Cl differ from the K x-ray energy of Cl by more than 10 percent, suffices to establish that the photons under study are Cl K photons.

The possibility that these photons arose from excitation under beta bombardment of Cl impurity in the source or source mount is eliminated by the following considerations.

In view of the method of source preparation, any chloride in the source would be accompanied by at least

⁸ We are indebted to J. A. Miskel and M. L. Perlman who prepared the A^{37} for us by the method described in reference 2.

an equivalent amount of potassium, which would give rise to potassium x-rays. No significant intensity of the latter was observed. In the preparation of the second of our two stock solutions, the S^{35} was subjected to an additional distillation, at about 200° , before being taken up in HNO_3 . The sources made from this second stock solution gave spectra which did not differ significantly from those of the first. A source prepared by deliberately adding $50\text{ }\mu\text{g}$ of potassium chloride to an aliquot of S^{35} stock solution before evaporation gave a potassium x-ray intensity at least as great as, and a chlorine x-ray intensity little greater than, the chlorine x-ray intensity from a clean S^{35} source. From the slightly increased chlorine x-ray intensity shown by the source with the added KCl we can infer that in the preparation of this source about 80 percent of the added chloride was fumed off (as HCl) by the HNO_3 of the S^{35} stock solution. By comparing the magnitude of the potassium x-ray intensity of this source with that from the clean sources we can estimate that the clean sources certainly contained less than $5\text{ }\mu\text{g}$ of potassium and therefore, in view of chloride fume-off, less than one microgram of chloride. By Bethe's theory (see reference 4) we compute that such a small quantity of chloride would make a completely negligible contribution to the observed chlorine photon intensity.

The possibility of chlorine in the polystyrene of the source mount is eliminated by the fact that no chlorine photons were observed when the S^{35} sources were replaced by an identically mounted source of C^{14} (as Li_2CO_3 , 20 mg/cm^2 thick), which has a beta energy about the same as that of S^{35} .

Thus, all the Cl K photons from our S^{35} sources must be attributed to K holes in the Cl daughter atoms of S^{35} decay.

V. MEASUREMENT OF THE PHOTON YIELD

The computed intensity of Cl K photons depends very sensitively, of course, upon the estimate of bremsstrahlung background. Now, in the case of both internal⁹ and external¹⁰ bremsstrahlung the photon intensity per unit range of photon energy increases somewhat faster than the inverse of the photon energy. The mass absorption coefficients of polystyrene and the Be window increase exponentially as the photon energy decreases. For the photon energy range of concern here, in the neighborhood of 2.5 kev, both bremsstrahlung intensity and photon absorption increase very rapidly with decrease of photon energy, and it would be an exceedingly tedious task to make an accurate theoretical calculation of the resultant bremsstrahlung spectrum seen by the counter. We have made rough calculations of this kind which serve as a rough verification of our estimated bremsstrahlung

spectrum, and have avoided an accurate computation by the following empirical approach.

The bremsstrahlung background must be such that on subtracting it from the experimental curve the resulting difference peak has the same shape as the clean Cl peak observed with an A^{37} source. This single consideration serves to fix the bremsstrahlung background with considerable accuracy, because the half-width and the symmetry of the difference peak are very sensitive to the shape and magnitude of the bremsstrahlung background assumed. Thus, to analyze an experimental curve one needs only to try different background curves until a Cl peak of correct shape is obtained. The agreement between a Cl peak obtained in this way and a clean Cl peak from A^{37} can be seen in Fig. 2.

The five sources used in our measurements, including those prepared from the same stock solution, gave experimental curves whose background intensities at energies above 2.8 kev differed as much as 30 percent, though the curves were essentially superposable at lower energies. We cannot explain this. However, with the method of estimating bremsstrahlung background described above, the Cl x-ray intensities obtained with the different sources were all in reasonable agreement (see Table I).

TABLE I. Photon yield in S^{35} decay.

Source	Date	Photon rate (photons/min)	Source strength dis/min	Photon yield
<i>I-B</i>	1 June 54	1.12×10^6	4.04×10^9	2.77×10^{-4}
<i>I-A</i>	3 June	0.93	3.98	2.34
<i>I-D</i>	8 June	1.23	4.37	2.81
<i>II-A</i>	31 May	0.79	3.90	2.03
<i>II-A</i>	3 June	0.815	3.81	2.14
<i>II-B</i>	14 June	0.96	3.49	2.75
				Mean = 2.47×10^{-4}

This method of subtracting the bremsstrahlung background may be compared to another in which the bremsstrahlung spectrum was taken to be that obtained with the thick C^{14} source mentioned above, normalized to the S^{35} curve at 3.4 kev. Account must be taken of the fact that the observed C^{14} bremsstrahlung curve is considerably distorted, particularly in the low energy portion, by absorption in the source. In the case of several of the S^{35} sources, the shape of the Cl x-ray peak obtained by subtracting this background from the experimental curve showed unacceptable deviations from the known shape as obtained with an A^{37} source, and the Cl x-ray intensities computed from these peaks were, on the average, about 20 percent higher than those obtained by the previous method. We consider the previous method to be much the more accurate of the two. However, the C^{14} bremsstrahlung curve was of considerable help in finding the correct background curve. It was the C^{14} curve that suggested

⁹ See, e.g., J. K. Knipp and G. E. Uhlenbeck, *Physica* **3**, 425 (1936).

¹⁰ W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, London, 1944), p. 166.

the bremsstrahlung hump in the neighborhood of the chlorine peak (see Fig. 2).

Table I shows the data and results of six runs with five different S^{35} sources made from two independently prepared and assayed S^{35} stock solutions. The geometry for photon detection, as defined by a $\frac{1}{4}$ -inch diameter hole located 1.70 inches from an effectively point source, was 1.35×10^{-3} , and 0.517 of the Cl photons were absorbed in the Be window. Thus, the total photon rate was 1.43×10^3 times the observed rate. Reproducibility of results with a single source can be seen from the two runs with source II-A, made on different days, which agree to better than 5 percent.

The mean photon yield computed from the six runs is: Cl K photons/beta = 2.47×10^{-4} . The standard deviation of a single measurement is 14 percent of the mean, so that the 99:1 probable error is about 25 percent of the mean. The spread of the results is 31.6 percent of the mean.

The measured¹¹ fluorescence yield of a Cl K hole is 0.108, with limits of error stated as 15–20 percent. Thus, the probability of K -hole production in S^{35} decay is: K holes/beta = 2.29×10^{-3} , with an extreme error of about 32 percent.

VI. COMPARISON WITH THEORY

The theory of the process involved here has been the subject of fairly extensive study,^{12–17} and is well understood. In the act of β decay, the nuclear charge increases by one unit in a time that is short compared to the orbital periods of the bound electrons if (as is true of S^{35}) the orbital electron speed is very much smaller than the beta speed. In this case, the decay act is a “sudden” perturbation on the electronic eigenfunctions, so that the probability for transition of an electron from a given bound state of the parent atom to a given bound or continuum state of the daughter atom is, by standard theory, simply the square of the overlap integral of the eigenfunctions of the two states. Then the total probability of ejection of an electron from a given initial state can be obtained by computing the distribution of probability over all final states,

and summing. But if, as is the case in our experiments, the distribution of ejected electrons over the final states is of no interest, the probability of creation of a hole in a shell is much more easily computed by way of the completeness theorem, as is done by both Levinger¹⁴ and Schwartz,¹⁵ whose results obtained with the use of non-relativistic hydrogenic wave functions are identical.¹⁸ In this method one computes the probability, P_0 , that an electron initially in, say, a $1s$ state of the parent atom remains a $1s$ electron of the daughter atom. Then the probability that the electron does *not* remain a $1s$ electron, i.e., the probability of K -hole creation, is $1 - P_0$ minus the sum of the probabilities of transitions to otherwise allowed states that are excluded by the Pauli principle.

Taking account of the fact that the $2s$ and $3s$ states in Cl are occupied and of the existence of two $1s$ electrons in the initial state of S^{35} , we get from tables in the cited papers:

$$(K \text{ holes/beta})_{\text{theor}} = 0.78/Z^2,$$

where Z is an effective nuclear charge appropriate to the hydrogenic wave functions used.

The theory does not distinguish between the nuclear charges of the parent and daughter nuclei. As the appropriate nuclear charge we choose $Z = 16.2$, which is the mean nuclear charge of S and Cl, minus the shielding effect of 0.3 unit charge that K electrons have for each other. With this choice, the theoretical probability of K -hole creation in S^{35} decay is

$$(K \text{ holes/beta})_{\text{theor}} = 2.97 \times 10^{-3},$$

about 30 percent higher than our experimental value, 2.29×10^{-3} . The agreement between experiment and theory is quite satisfactory since the experimental error is about 35 percent, and since the use of hydrogenic wave functions in the theory may be expected to introduce an error of about the same magnitude.

We point out that the probability of K -hole production in P^{32} decay (1.7-Mev maximum beta energy), which should be about the same as that in S^{35} decay, has been found by Renard¹⁹ to be 4.23×10^{-3} , about 25 percent higher than the theoretical value computed in the above manner.

¹⁸ We do not use the results that Levinger (reference 14) has obtained with Hartree functions, since he believes them to be in error.

¹⁹ G.-A. Renard, Compt. rend. **238**, 1991 (1954).

¹¹ A. Haas, Ann. Physik **16**, 473 (1933).

¹² E. L. Feinberg, J. Phys. (U.S.S.R.) **4**, 423 (1941).

¹³ A. Migdal, J. Phys. (U.S.S.R.) **4**, 449 (1941).

¹⁴ J. S. Levinger, Phys. Rev. **90**, 11 (1953).

¹⁵ H. M. Schwartz, J. Chem. Phys. **21**, 45 (1953).

¹⁶ H. Primakoff and F. T. Porter, Phys. Rev. **89**, 930 (1953).

¹⁷ P. Benoist-Gueutal, Ann. phys. **8**, 593 (1953).