[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Radioactivity of Argon-37[1,2]

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Proportional counter spectroscopy has been utilized in the investigation of the electron capture processes of radioactive argon-37. From quantitative measurements of the K- and L-capture of argon-37 in various counters using a number of different gases, the L/K-capture ratio of argon-37 has been determined to be 0.102 ± 0.008. Recent results which might indicate that the argon-37 L/K-capture ratio might be significantly greater than 0.10 are discussed. Measurements show that double K-vacancies occur to the extent of $(3.7 \pm 0.9) \times 10^{-4}$ of K-capture events. The half-life of argon-37 against decay was observed to be 34.30 ± 0.14 days.

Introduction

Argon-37 was first shown to decay by the process of orbital electron capture by Weimer, Kurbatov and Pool.[4,5] They[4,5] gave a half-life against decay of 34.1 days. More recent determinations by Miskel and Perlman[6] using ionization chamber and proportional counter techniques give the half-life as 35.5 days and 35.0 ± 0.4 days, respectively. Marshak,[7,8] Segre[9] and Bouchez, Daudel, Daudel and Muxart[10] predicted from theoretical bases the existence of the phenomenon of L-capture, and it was first shown by Kirkwood, Pontecorvo and Hanna[11] that such L-capture could be observed experimentally in argon-37.

Pontecorvo, Kirkwood and Hanna[12] found the ratio of L-capture to K-capture to be 0.08 to 0.09, using proportional counter spectrometry. Langevin and Radvanyi,[13] also using proportional spectrometry, determined the L/K-ratio to be 0.092 $+ 0.010$ or -0.005. However, Rubenstein and Snyder[14] pointed out that the charge spectrum of the recoil chlorine-37 ions resulting from the orbital electron capture in argon, as measured by Kofoed–Hansen,[15] was not consistent with the measured L/K-capture ratio of 0.09. Winther[16] attempted to show that the charge spectrum of recoil chlorine-37 ions could be explained if about 25% of the orbital electron capture was L-capture.

Primakoff and Porter[17] first calculated from theoretical bases the probability of orbital electron capture accompanied by atomic excitation and ionization. These authors gave the probability for a double K-vacancy per K-capture event in argon-37 to be 2.8×10^{-4}. Wolfsberg[18] later showed that by inclusion of terms neglected by Primakoff and Porter, the theoretical value is 3.9×10^{-4}. Levinger[19] also calculated theoretically the probability of double K-vacancies in argon-37, arriving at the value of 4.9×10^{-4}. Miskel and Perlman[20,21] are the only workers to have experimentally observed these double K-vacancies in argon-37, although Langevin[22,23] has experimentally determined the double K-vacancy occurrence in germanium-71. Miskel and Perlman gave $(3.9 \pm 0.7) \times 10^{-4}$ as the occurrence per K-capture event in the decay of argon-37.

In view of the apparently contradictory results of the experimentally-determined L/K-capture ratios, the relatively large error in the reported values of the half-life, and that only one determination has been made of the double K-vacancies in argon-37 decay, we subjected argon-37 to further investigation in our laboratories. Making use of the techniques of proportional counter spectrometry and using a number of different counters and counting gases, we have obtained a value for the L/K-capture ratio of argon-37 of 0.102 ± 0.008. The details of the investigation and the results are given below and an explanation is offered for the apparent conflict with recoil charge spectrum measurements. The occurrence of double K-vacancies per K-capture event was determined to be $(3.7 \pm 0.9) \times 10^{-4}$ and the half-life was found to be 34.30 ± 0.14 days.

Experimental

The techniques of proportional counter spectrometry have been employed in this investigation. The proportional counter, integrating the fast cascade of X-rays and Auger K-electrons which result from each L-capture event, gives a sharp "K-peak" in the pulse height–distribution spectrum. Any K-capture event which is followed by escape of the chlorine K-X-rays from the sensitive volume, thereby producing L-radiation, as well as the capture of the L_1-electron and the Auger L-electrons, gives rise to an "L-peak."

In our determination of the L/K-capture ratios, the intensities of the L-peak, L, and of the K-peak, K, were measured by integral counting using a 100-channel pulse height analyzer. Letting F be the K-fluorescence yield of chlorine and E the escape probability for the K-X-ray, we obtain

$$(L/K)_{\text{true}} = (L/K)_{\text{meas}} - EF[1 + (L/K)_{\text{meas}}]$$

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[2] Taken in part from a thesis submitted by Robert W. Kiser to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1958.

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[8] R. E. Marshak, *ibid.*, **61**, 431 (1942).

[9] E. Segre, *ibid.*, **71**, 274 (1947).

[10] R. Bouchez, R. Daudel, P. Daudel and R. Muxart, *J. phys. radium*, [8] **8**, 336 (1947).

[11] D. H. W. Kirkwood, B. Pontecorvo and G. C. Hanna, *Phys. Rev.*, **74**, 497 (1948).

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[13] M. Langevin and P. Radvanyi, *Compt. rend.*, **241**, 33 (1955).

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[15] O. Kofoed-Hansen, *ibid.*, **96**, 1045 (1954).

[16] A. Winther, *J. phys. radium*, [8] **16**, 562 (1955).

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[18] M. Wolfsberg, *ibid.*, **96**, 1712 (1954).

[19] J. S. Levinger, *ibid.*, **90**, 11 (1953).

[20] J. A. Miskel and M. L. Perlman, *ibid.*, **94**, 1683 (1954).

[21] J. A. Miskel and M. L. Perlman, *ibid.*, **95**, 612 (1954).

[22] M. Langevin, *Compt. rend.*, **245**, 664 (1957).

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The assumption made here (since no reliably accurate information could be found in the literature), that the fraction of Kα-X-rays in the K-series is unity, will not seriously affect the L/K-ratio results; a change of 10% in this value affects the results by approximately the error which is quoted, and it should be noted that such a change would cause the value of $(L/K)_{true}$ to become larger and not smaller.

Variation of the counter sizes and the counting gases will cause variations in the amount of escape of the chlorine X-ray. Since the L-X-rays and the L-Auger electrons are completely absorbed, the variations in the counter size and the counter gas will not affect the L-capture portion of the "L-peak." The correction for K-X-ray escape in the "L-peak" may be made from a knowledge of the counter size, counting gas, filling pressure, X-ray absorption coefficients and K-fluorescence yield. These are two ways that elimination of some uncertainty in the calculation of the amount of escape may be accomplished: (a) allow no escape or (b) allow 100% escape. It will be noted in the tabular presentation of the results that method (b) has been used in all but three cases. The three cases which were not 100% escape, but which had escape factors ranging between zero and unity were carried out to check the validity of the method of escape calculations for values between zero and unity; the method appears satisfactory.

We have used the value of 0.108 for the K-fluorescence yield of chlorine, as given by Haas.[24] (See also Broyles, Thomas and Haynes.[25]) By means of the tables and "universal" functions given by Henke, White and Lundberg,[26] we have obtained, for use in the above-mentioned corrections, the following mass absorption coefficients for a 2.82 kev. X-ray: carbon, 102 ± 2 cm.^{2}/g., oxygen, 260 ± 4 cm.^{2}/g., and argon, 208 ± 2 cm.^{2}/g.

In the calculation of the path lengths to be used in calculating the escape probabilities, we have used the model designed by Lind.[27] The path length d is related to the radius R of a spherical volume by the equation

$$d = 0.75R$$

This is taken to hold, as shown by Lind, as approximately true for cylindrical volumes. In this case, however, the volume of the cylinder is first converted to a spherical volume and then R is calculated. Since the validity of the approximation varies, depending roughly on the length to diameter ratio, slightly different values of the constant, selected on such bases, are given along with the values of the L/K-capture ratios for individual counters. An error of 15% in the d/R ratio will affect the results by approximately 1% when the escape probability approaches unity, thus making the technique of measurement of the L/K-capture ratio at or near an escape probability of unity even more attractive.

The escape probabilities were calculated according to the equation

$$\ln(1/E) = (\mu/\rho)\rho d$$

where (μ/ρ) is the mass absorption coefficient and ρ is the density.

The double K-vacancies should exhibit a "peak" at approximately 5.7 kev. By integration of the peak between 4.0 and 9.0 kev. and by subtraction of the background, any double K-vacancies may be observed, after correction for chance coincidences and counter dead time.

For the purposes of this investigation, we had need for a stable high voltage supply. The high voltage for operation of the proportional counters was obtained from a Fluke model 400-BDA power supply.[28] This supply had an output variable from 500 to 5100 v. d.c., positive or negative, at a current drain of 0 to 1 ma., and the stability was better than 0.01% per hour. The ripple was less than 5 mv. at any output voltage and current, and the voltage resolution was 50 mv. at any output voltage.

We employed a Bay amplifier[29] for amplification of the proportional pulses. The unit consisted of a preamplifier stage close to the counter and the final amplification stages removed a short distance from the counter. The maximum electronic gain attainable was 215,000. Excellent linearity of response of the amplifier for the proportional pulses was established experimentally.

A 100-channel pulse height analyzer, RIDL model 3300,[30] was used for measuring and recording the pulse height-distribution spectra. The excellent linearity of response of the analyzer was shown both by pulse-generator calibrations and by proportional counter calibrations involving the use of argon-37 and iron-55.

The physical characteristics of the counters employed in this investigation are given in Table I. Details of the effects of changes of counter parameters on counter characteristics will appear shortly in publication. It will be noted, however, that counters III and XV are Maze-type[31] counters.

TABLE I

PHYSICAL CHARACTERISTICS OF COUNTERS

Counter no.	Shell	Cathode	Center wire	Internal shell radius (in.)	Center wire radius (in.)	Counter length (in.)[b]
III	Pyrex	External[a]	W	0.51	0.0010	8.3
XV	Soda	External[a]	W	1.00	.0010	15.0
2182	Brass	Brass	Pt	0.94	.0125	10.5
3151	Copper	Copper	W	0.94	.0010	15.6

[a] A silver layer placed on the external wall of the counter shell. The silver layer was prepared by painting the shell surface with Silver Print Paint (General Cement Manufacturing Co., Rockford, Illinois). [b] Length of actual body of the counters.

All gases used were obtained from Matheson.[32] Methane was C.P. grade, stated to be 99.0% pure; ethane was stated to be 95% purity; and argon was stated to have a minimum purity of 99.9%. The carbon dioxide used was of "Bone dry" grade and was stated to have a minimum purity of 99.8%. These gases were not further purified when withdrawn from the cylinders in which they were furnished.

Results and Discussion

Typical proportional counter spectra of argon-37 are shown in Figs. 1 and 2. It will be noted that the resolution, 1/2 $\Gamma_{1/2}$, is 12.6% for the "K-peak" and is 50% for the "L-peak." It may be further

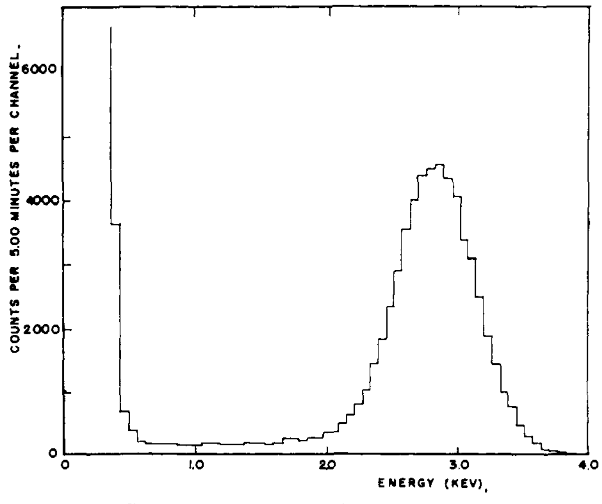

Fig. 1.—K-Capture distribution in the decay of argon-37.

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(27) S. C. Lind, "The Chemical Effects of Alpha Particles and Electrons," A.C.S. Monograph, No. 2, Chemical Catalog Co., New York, N. Y., 1928, pp. 92–94.

(28) John Fluke Manufacturing Co., Inc., 1111 W. Nickerson Street, Seattle 99, Washington.

(29) Bay Engineering Company, Chicago, Illinois.

(30) Radiation Instrument Development Laboratory, 5737 South Halstead Street, Chicago, Illinois.

(31) R. Maze, *J. phys. radium*, [8] **7**, 164 (1946).

(32) The Matheson Company, East Rutherford, New Jersey.

TABLE II

L/K CAPTURE RATIO OF ARGON-37

Counter	Gas mixture	Total pressure (mm.)	(d/R)	Apparent (L/K)	True (L/K)
III	99.9% CH_4-0.1% A	357	0.65	0.235	0.107
III	99.9% CH_4-0.1% A	357	.65	.216	.091
III	4.7% CO_2-95.3% A	574	.65	.214	.103
XV	99.9% C_2H_6-0.1% A	355	.65	.224	.110
XV	7.4% CH_4-92.6% A	530	.65	.140	.089
XV	7.4% CH_4-92.6% A	530	.65	.158	.106
2182	9.1% CH_4-90.9% A	451	.70	.167	.104
3151	99.9% C_3H_8-0.1% A	143	.65	.234	.110

Average ± std. dev. = 0.102 ± 0.008

seen that the 50% resolution will not allow separation of the 200 e.v. escape peak (L_{II} and L_{III}) from the 240 e.v. L_I-capture electrons.[33]

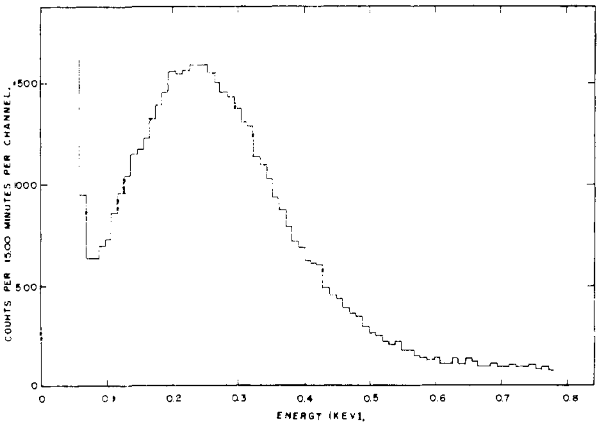

Fig. 2.—L-Capture and "escape" distribution in the decay of argon-37.

1. **The L/K-Capture Ratio.**—The results of the determinations are given in Table II. The average value, with its standard deviation, is 0.102 ± 0.008, in excellent agreement with Langevin and Radvanyi.[13] This further appears to contradict the results from charge distribution of chlorine-37 in recoil measurements. However, recent measurements of such charge distribution by Snell and Pleasonton[34,35] satisfactorily agree with the results by proportional counter spectrometry.

Table III summarizes the theoretical and experimental results on charge distribution measurements. It may be seen from this that if the theoretical calculations also include some small contributions from double K-vacancies and by use of the revised value of the L/K-capture ratio of 0.102 ± 0.008, agreement between our proportional counter spectrometric measurements of the L/K-capture ratio of argon-37 and of the charge distribution measurements of the chlorine-37 recoil ions made by Snell and Pleasonton is quite good.

From an examination of Table III it is seen that one of the possibilities included by Rubenstein and Snyder[14] was that of 75% K-capture, 8% L_I-capture and 17% L_{II}- and L_{III}-capture. From an examination of the theoretical treatments given by Radvanyi,[36] Brysk and Rose,[37] and Odiot and

TABLE III

CHARGE DISTRIBUTION OF CHLORINE-37 IONS RESULTING FROM ELECTRON CAPTURE OF ARGON-37

Charge on final ion	Theoretical[a] 0.75K 0.25L	0.75K 0.08L_I 0.171$L_{II,III}$	0.92K 0.08L	0.907K 0.093L[b]	Experimental A[c]	B[d]	C[e]	D[f,g]
1	0.10	0.27	0.11	0.10	..	..	0.26	0.062
2	.31	.13	.16	.15	..	..	.13	.157
3	.39	.39	.49	.48	..	..	.38	.392
4	.15	.15	.18	.20	..	..	.18	.267
5	.04	.04	.05	.06	..	..	.04	.100
6	.00	.00	.00	.01	..	..	.01	.018
7	..	..	..	..	..	..	..	.004
Av. charge	2.69	2.50	2.87	3.03	3.85	3.41	2.64	3.26

[a] With the exception of the last column under this heading, these values have been quoted from work listed in reference 14. [b] Calculations by these authors. [c] See reference 6. [d] M. L. Perlman and J. A. Miskel, *Phys. Rev.*, **91**, 899 (1953). [e] See reference 15. [f] See reference 34. [g] See reference 35.

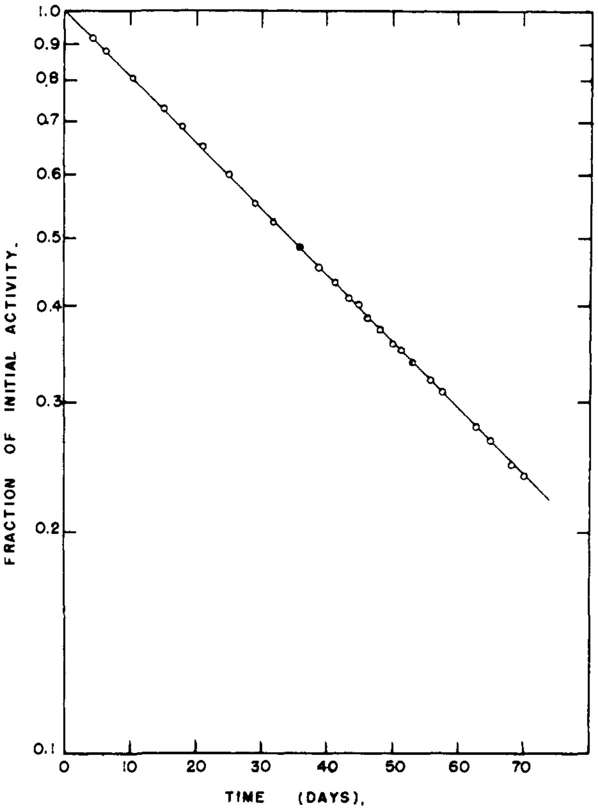

Fig. 3.—The decay and half-life of argon-37.

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Daudel,[38] it is evident that 17% L_{II}- and L_{III}-capture is not at all probable here; the inclusion of the data in Table III has been made only for the purposes of comparison.

The L/K-capture ratio is established from this work as being 0.102 ± 0.008 and is in fair agreement with the value of 0.091 calculated from the theoretically-derived formula given by Bouchez, Daudel, Daudel and Muxart.[10] It is, however, significantly different from the results of Brysk and Rose[37] and Hoff and Rasmussen.[39] Further, our experimental results completely verify the use of the Pauli correlation in taking account of the effect of positron–electron correlation, as done recently by Odiot and Daudel[38] in extending the simplified theory of orbital electron-capture previously used. Odiot and Daudel calculated $(L/K)_{\text{true}}$ for argon-37 to be equal to 0.100.

2. **Occurrence of Double K-Vacancies.**—We made two determinations of the occurrence of double K-vacancies. A high-energy "tail" was observed in these spectra, as was also noted by Miskel and Perlman,[20] who showed the peak as occurring over the region of 4.5 to 10 kev. The average result of the two determinations was $(3.7 \pm 0.9) \times 10^{-4}$, which agrees very well with the data of Miskel and Perlman[20,21] and with the theoretical value given by Wolfsberg.[18]

3. **Half-life Determinations.**—The half-life of argon-37 was determined by integral counting over the region 0.75 to 5.2 kev. The study of the argon-37 decay was continued for seventy days. The results are shown in Fig. 3. From a least squares treatment of the data shown, the half-life is found to be 34.30 ± 0.14 days, the statistics here being given for a 95% confidence level. This result agrees within the quoted errors with the early result of Weimer, Kurbatov and Pool.[5]

Acknowledgment.—The authors wish to thank Professor D. C. Conway for his helpful comments.

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[CONTRIBUTION FROM THE ISOTOPE DEPARTMENT, THE WEIZMANN INSTITUTE OF SCIENCE]

The Isotopic Exchange between Hypohalites and Halide Ions. I. The Exchange between Hypobromous Acid and Bromide Ion

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The isotopic exchange of bromine between hypobromite and bromide ions has been studied in concentrated alkaline solutions. The reaction was found to involve a molecule of HOBr and a Br^- ion in the activated complex. The specific rate constant was found as $k = 7.6 \times 10^5$ l. mole^{-1} min.$^{-1}$ at 25°. Contrary to the case of hypobromite–water–oxygen exchange, there is no catalytic effect of chloride ions on the bromine exchange.

Introduction

The reactions of the hypohalous acids and their derivatives with nucleophilic reagents have been studied extensively up to date. The interaction of hypochlorous esters with various anions[1] points to the positive nature of the chlorine in the hypochlorous molecule and suggested the existence of intermediates of the type ACl, wherein chlorine is of a positive character. The study of halogenation of aromatic compounds by hypohalous acids[2] suggested the formation of H_2OX^+ or X^+ as the active species. The reduction of hypochlorous acid by bromide ions[3] provided kinetic information on an irreversible nucleophilic attack on a hypohalous acid; extending this study to hypobromous acid and to iodide ions provided additional information.[4] The last mentioned reactions may be compared to the interaction of hypochlorous with hypobromous acid[5] and with the interaction of hypohalous acids with nitrite ions.[6] The study of the interaction of hypochlorous and hypobromous acids with water by following the rate of oxygen exchange between these species, as well as the catalytic effects of halide ions on this exchange,[6] provided additional basic information on the character of the hypohalite reactions.

The purpose of the present work was to elucidate some points in the halide catalysis of the oxygen exchange reaction and to provide a mechanism for the interaction of hypohalites with the corresponding halide ions. These results will be compared with the reactions of hypohalites with other nucleophilic reagents. In this first paper we shall discuss the hypobromite–bromide reaction. The analogous reactions between hypochlorous acid and chloride ions and between hypochlorous esters and chloride ions will be presented in the following paper.[7]

Experimental

Reagents.—Sodium hypobromite, bromate free, has been prepared by dissolving bromine in ice-cooled 1 molar sodium hydroxide solution, afterwards adding freshly prepared silver oxide, and thereby precipitating the bromide as silver bromide. The silver bromide and the excess of silver oxide were separated by centrifuge as soon as possible. The concentration of the sodium hypobromite solution was determined by reduction with excess of a standardized arsenite solution at *p*H 5, and afterwards the excess arsenite was titrated with a standardized iodine solution. Another aliquot was treated with acid iodide and titrated with a standardized

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