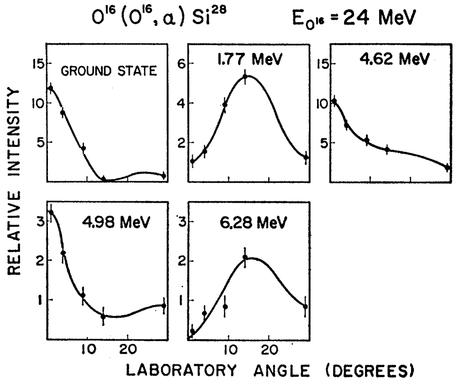

FIG. 7. Angular distributions (laboratory system) for alpha particles from the reaction $O^{16}(O^{16},\alpha)Si^{28}$ at an incident O^{16} energy of 24 MeV. The excitation energy in Si^{28} is indicated in each case.

able assumption that it is unlikely that zero yield at 0° will accidentally persist over a wide energy range.

The prominent fluctuations with energy of the excitation curves (Figs. 3 and 5) suggest that a compound nucleus process dominates in the reactions. Of course, excitation of "unnatural" parity states cannot come through a one-step direct-interaction process and the fact that such states are strongly excited is additional evidence for the compound-nucleus process. The measured widths average ~170 keV c.m. for the $O^{16}(C^{12},\alpha)Mg^{24}$ reaction and ~600 keV c.m. for the $O^{16}(O^{16},\alpha)Si^{28}$ reaction, corresponding to mean lifetimes of 3.5×10^{-21} and 1×10^{-21} sec for the compound systems, respectively. The sharp structure and forward peaking of the angular distributions indicate that compound states of high spin are involved. This is not surprising since at the energies used here the incident nuclei can readily interact with 8 or 10 units of $\hbar$ of angular momentum. It is noted that, although the resonance structure is clearly evident in individual channels, it averages out to give a smooth featureless energy dependence of the total cross section.[7] This behavior is different from that observed in the C^{12}–C^{12} system at low collision energies where the total-reaction cross section shows clear resonance behavior.[7]

ACKNOWLEDGMENT

The authors are indebted to Dr. A. J. Ferguson for a critical reading of the manuscript.

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L/K-Capture Ratio in Mn^{54}, Fe^{55}, Co^{57}, and Co^{58} Decays*

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The multiwire proportional counter method has been applied to measurements of the L and K radiations arising from orbital electron-capture in gaseous sources of 290-day Mn^{54}, 2.6-yr Fe^{55}, 270-day Co^{57}, and 72-day Co^{58}. The presence of gamma transitions and positrons in the decay of Mn^{54}, Co^{57}, and Co^{58} is shown not to interfere with an accurate measurement of the L/K-capture ratio. The experimental values of the L/K-capture ratio are 0.098 ± 0.006, 0.106 ± 0.005, 0.099 ± 0.011, and 0.108 ± 0.004 for Mn^{54}, Fe^{55}, Co^{57}, and Co^{58}, respectively. The result for Fe^{55} is in excellent agreement with the earlier value measured by Scobie, Moler, and Fink, although the present value has been corrected for counter escape somewhat more exactly. These values lie above the theoretical results of Brysk and Rose by some 9% for Mn^{54}, 9.3% for Fe^{55}, 7% for Co^{57}, and 17% for Co^{58}. These discrepancies are reduced by application of the exchange correction pointed out by Bahcall to the theoretical results of Brysk and Rose. This correction for the effect of exchange among the various electrons participating in the electron capture process apparently explains the well-established general discrepancy between the precision experimental values and the theory of Brysk and Rose. Remaining slight discrepancies probably can be traced to systematic experimental errors.

INTRODUCTION

EARLIER we reported[1] a precision measurement of the L/K-capture ratio in Fe^{55} decay using gaseous radioactive ferrocene in the counting gas (9:1 argon-methane) of a multiwire proportional counter. In the present work, Fe^{55} has been remeasured but with more exact corrections for counter escape, and the result is found to be in slightly closer agreement with theoretical results. In addition, L/K-capture ratios for 290-day Mn^{54}, 270-day Co^{57}, and 72-day Co^{58} have been measured by utilizing gaseous manganocene and cobaltocene as radioactive sources in the counter gas (see Appendix B).

A general discussion of experimental results on L/K-

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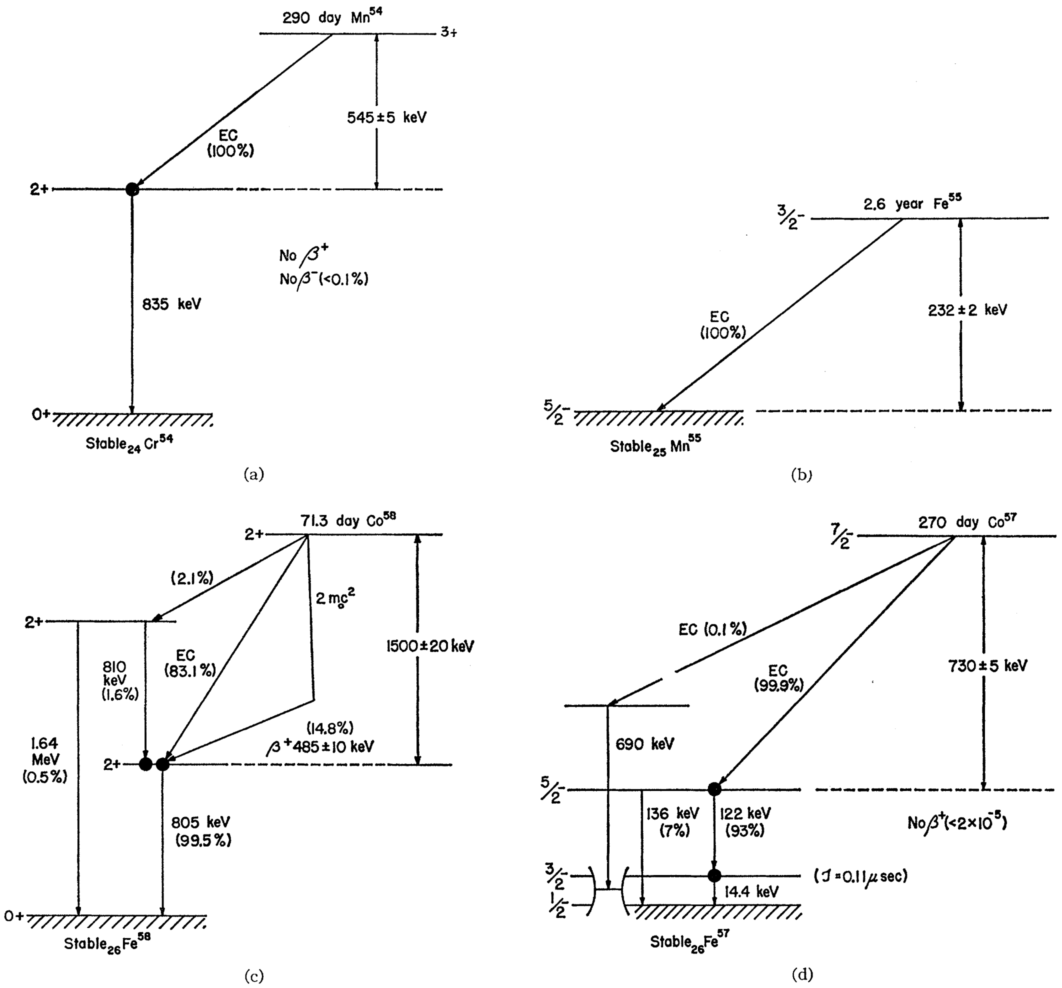

FIG. 1. Decay schemes of Mn^{54}, Fe^{55}, Co^{57}, and Co^{58} taken from the literature.

capture ratios and comparisons with theory[2] is contained in the reviews by Robinson and Fink[3] and Bouchez and Depommier.[4] Since these reviews, there have appeared a number of precision measurements of L/K-capture ratios using gaseous sources in multiwire counters. These are summarized in Appendix A and compared with theoretical results. The existence of a significant discrepancy between the experimental values and the theory of Brysk and Rose[2] seems now to be well established.

This discrepancy, typically about 10%, between experiment and theory apparently is removed when the exchange correction of Bahcall[5] is made (see Appendix A). Small remaining disagreements may lie in experimental systematic error. The effect of exchange among the bound electrons that participate in the electron capture process leads to a correction, as given by Bahcall,[5] of the form

$$\frac{P_L}{P_K}=\left(\frac{\lambda_{LI}}{\lambda_K}\right)^0\left[\frac{1-[2R_{1s}(0)/R_{2s}(0)]\langle 1s'|2s\rangle}{1-[2R_{2s}(0)/R_{1s}(0)]\langle 2s'|1s\rangle}\right], \qquad (1)$$

where $(\lambda_{L_I}/\lambda_K)^0$ is the usual L_I/K-capture ratio, $\langle 1s'|2s\rangle$ is the overlap integral between a $1s$ electron in the daughter atom and a $2s$ electron in the parent atom, and $R_{1s}(0)/R_{2s}(0)$ is the ratio of radial wave functions evaluated at the nuclear radius. The overlap integrals have been evaluated by Bahcall[5] using Hartree-Fock wave functions, and the ratio of radial wave functions come from the tables of Brysk and Rose.[2] The Bahcall exchange correction, X_{Th}, can be represented by the approximate expression, which is accurate to about 5%:

$$X_{\mathrm{Th}}\cong 1+(4\pm0.4)Z^{-1}, \qquad (2)$$

in the region of $17\lesssim Z\lesssim 33$.

The additional correlation correction proposed by

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Odiot and Daudel[6] arising from the use of Hylleraas wave functions has been shown to be spurious.[5]

The decay energy (545±5 keV) of Mn^{54} to the first excited state of Cr^{54} at 835 keV has been measured from (p,n) threshold measurements.[7,8] The decay scheme[9] is shown in Fig. 1(a). In the case of Fe^{55}, the decay energy is known accurately from several measurements of the inner bremsstrahlung end point,[10] and these results agree well with (p,n) threshold measurements.[11] The latter value (232±2 keV) was used in our calculations. The decay scheme[12] is shown in Fig. 1(b).

For Co^{57} the decay energy (730±5 keV) to the second excited state of Fe^{57} at 136 keV has been obtained from (p,n) threshold measurements.[8,13] There is no electron capture to the ground state of Fe^{57} and probably none ($<14\%$) to the 14.4 keV level.

A gamma ray at approximately 700 keV has been observed in this decay and confirmed in this lab. The energy was found to be 690±5 keV with an intensity of 0.1%. Coincidence experiments were carried out and no coincidences between this gamma and the 136, 123, or 14.4 keV gammas could be observed. Also no coincidences between the 700 keV gamma and the K x ray could be observed. The decay scheme is shown in Fig. 1(c).[14]

For Co^{58}, the principal mode of decay is by electron capture (85.5%) to the first excited state of Fe^{58} at 799 keV. There also is positron decay (14%) to this level, the end point of this spectrum being well measured[15] ($E_{\beta^+}=485\pm20$ keV, $Q_{\mathrm{EC}}=1.50\pm0.02$ MeV). The decay scheme is shown in Fig. 1(d).[16]

Previously, Moussa and Julliard[17] measured $P_{L+M+\ldots}/P_K$ for Co^{57} by a coincidence method involving solid sources; their rough value (0.20±0.13) cannot be compared critically with theory. Recently, Kramer[18] also made measurements for Mn^{54}, Co^{57}, and Zn^{65}, ($P_L/P_K=0.11\pm0.01$, 0.15 ± 0.01, and 0.14 ± 0.01, respectively) using solid sources in a double chamber proportional counter and taking (K x ray) (L Auger electron) coincidences. These and other experiments involving solid sources are subject to considerable experimental uncertainty and cannot, therefore, be compared critically with theory.

EXPERIMENTAL

The preparation of radioactive ferrocene was mentioned briefly in our earlier paper.[1] In the present work, reagent-grade $FeCl_26HO_2$ crystals were dissolved in pyridine, and the solution was evaporated until ferrous pyridyl chloride crystals began to appear. Cooling in an ice-water bath crystallized the greater part of the solute, which was filtered off, washed with pyridine, and dried.

The crystals were powered and heated to 200°C under vacuum for several hours to form powdery yellow-green ferrous chloride, which could be stored in a closed container for several weeks without absorbing enough moisture to affect the ferrocene yield. In the case of cobalt, anhydrous cobaltous chloride, made by heating the hydrated salt to 150–200°C under vacuum, must be used immediately since it absorbs moisture very rapidly. The radioactive Fe^{55} and Co^{58} were obtained from Oak Ridge National Laboratory as $FeCl_3$ and $CoCl_2$ in HCl solution containing negligible amounts of Co^{60} ($<10^{-2}$ mCi) impurity. Radioactive Co^{57} was obtained from $Fe(d,Xn)$ reactions through Nuclear Science and Engineering Corporation, Pittsburgh, Pennsylvania. A gamma-ray spectrum of the Co^{57} showed it to be quite pure ($>99.0\%$). The amount of Co^{56} was less than 0.5%, the remainder being Co^{60}.

Details of the synthesis of the metalocenes and a summary of their properties are gathered together from the literature and from our experience and constitute Appendix B.

The multiwire anticoincidence proportional counter has been described previously[1]; but in the present investigation, a more exact evaluation of counter escape corrections has been made. The L/K-capture ratio is

$$P_L/P_K=(N_L/N_K)(1-P\omega_K)-P\omega_K k, \qquad (3)$$

where (N_L/N_K) is the observed intensity ratio of the L and K peaks, ω_K is the K-fluorescence yield, values of which are known experimentally for chromium[18,19]

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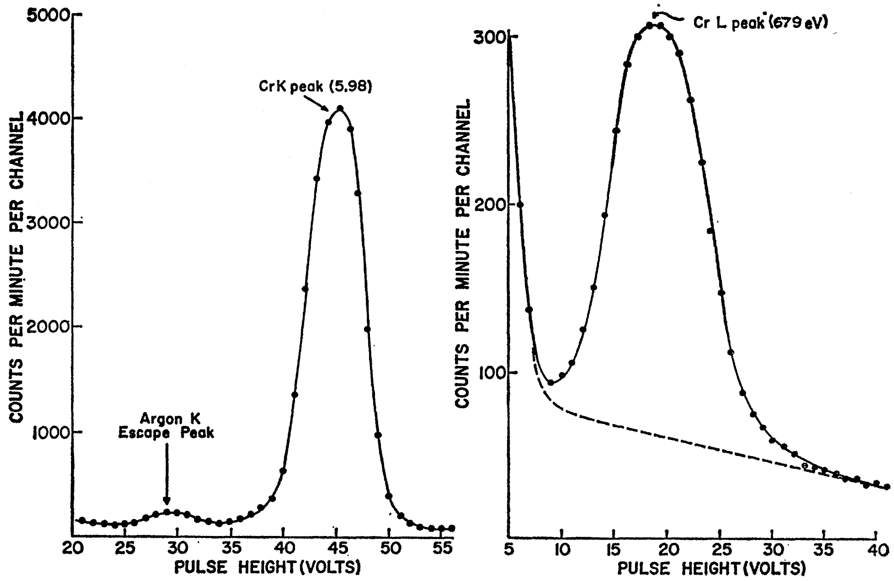

FIG. 2. K- and L-peak spectra of Mn^{54} from the center counter in anticoincidence with the ring counters. The natural background is shown as a dashed line but has not been subtracted. The resolutions for the K and L peaks are 15 and 50%, respectively.

manganese,[18,20,21] and iron,[19] and although the error limits on the fluorescence yields are still quite high, P_L/P_K is insensitive to these uncertainties because of the smallness of P, the K x-ray escape probability. Since k, the fraction of K_α x rays in the K x-rays series, is known,[22] it remains to evaluate P, which is the sum of three terms: P_1, the fraction of K x rays from the center counter which escape through the ends of the counter; P_2, the fraction of K x rays from the center counter which hit the wires defining the center counter and are not detected, and P_3, the fraction of K x rays from the center counter which escape and which also pass through the ring counters undetected.

From reactor theory,[23] it is shown that f_1, the fractional escape of radiation from the sides of an infinite disk source of thickness H, is expressed by

$$f_1 = (\lambda/H)[\tfrac{1}{2} - F_2(H/\lambda)], \tag{4}$$

where λ is the relaxation length given by $1/(\mu_m p)$, μ_m being the mass attenuation coefficient and p the density of the filling gas. The factor F_2 is the well-known exponential integral defined by

$$F_n(c) = c^n \int_{x=c}^{\infty} \left(\frac{e^{-x}}{x^{n+1}}\right) dx, \tag{5}$$

the tables of which are available.[24] In our case, the relation given above for f_1 is not even approximately valid. The best that can be done is to use the inequality

$$f_1 = P_1 \geq \frac{\lambda}{H}\left[\frac{1}{2} - F_2\left(\frac{H}{\lambda}\right)\right]\left[\frac{1}{1+2(\lambda/R)^2}\right], \tag{6}$$

and choose a value between the limits set by the inequality and the equality which is valid for small values of λ/R, where R is the radius of the center counter. In our case, the factor in the second bracket is roughly 0.6 and P_1 may vary some 20% to either side of the average of the limiting values. This makes little difference in P since P_1 contributes a relatively small amount to this sum.

If we define f_2 as the fraction of K x rays that escape from the surface of the center counter, it is seen that

$$P_2 = (nd/c) f_2, \tag{7}$$

where n is the number of wires in the defining ring, d is the diameter of each wire, and c is the circumference of the ring of wires. Again, from reactor theory, it is found that

$$f_2 = (\lambda/R)[\tfrac{1}{2} - F_2(R/\lambda)], \tag{8}$$

in the case of an infinitely long cylinder of radius R. This is a good approximation in our case.

The fraction P_3 can be calculated from reactor theory also, the result of a rather lengthy deviation being

$$P_3 = \frac{\lambda R_1}{(R_1 - R_2)^2}\left[F_2\left(\frac{R_2}{\lambda}\right) - F_2\left(\frac{R_1}{\lambda}\right)\right], \tag{9}$$

where R_1 is the radius of the counter including the ring counters and R_2 is the thickness of the ring counters. Numerical results for these quantities are given in Table I.

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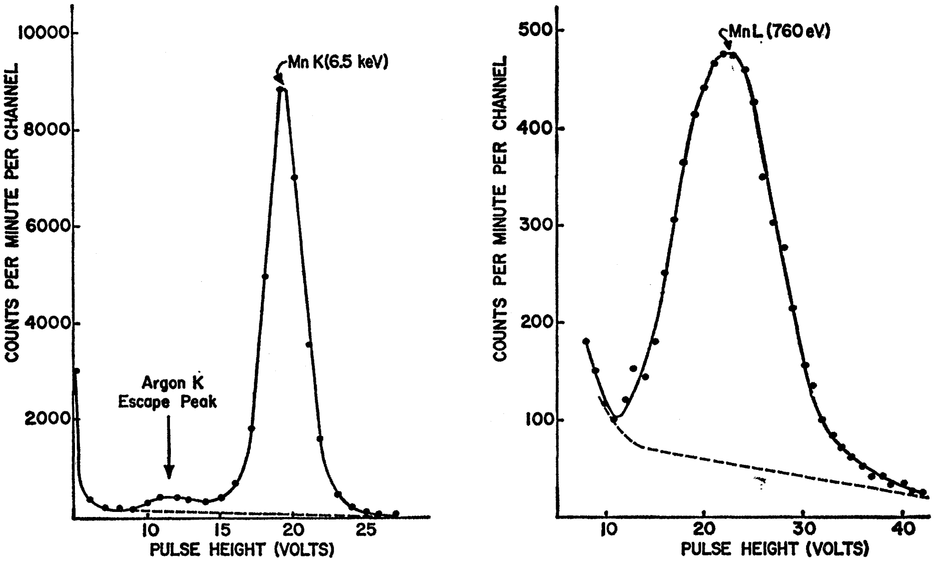

FIG. 3. *K*- and *L*-peak spectra of Fe^{55} from the center counter in anticoincidence with the ring counters. The natural background is shown as a dashed line but has not been subtracted. The resolutions for the *K* and *L* peaks are 15 and 50%, respectively.

The above calculations represent a significant improvement in the escape probability correction of the experimental *L*/*K*-capture ratio over that published by Scobie, Moler, and Fink.[1]

The counter has been described previously.[1] Calibration was accomplished by introducing a small quantity of Ar^{37} into the counting gas; the 2.8 keV *K* peak of chlorine exhibited a resolution of 30%. The best resolutions for the Cr^{54} *K* (5.98 keV) and *L* (679 eV) peaks obtained from the decay of Mn^{54} were 15 and 50%, respectively. For the Mn^{55} *K* (6.5 keV) and *L* (760 eV) peaks obtained from the decay of Fe^{55}, the best resolutions were 15 and 45%, respectively. In the case of Fe^{57} from the decay of Co^{57}, for the *K*-γ sum peak (21.45 keV) a resolution of 5% was observed and for the *L*-γ sum peak a resolution of 9% was found. For Fe^{58} from the decay of Co^{58}, the best resolutions obtained for the *K* (7.08 keV) and *L* (845 eV) peaks were 14 and 45%, respectively. Typical examples of these spectra are shown in Figs. 2–4. With ferrocene, runs were made many times at 0.5, 1, and 2 atm pressure. Above 1 atm, the variation in the observed ratio due to *K* x-ray escape through the anticoincidence ring counters is very small. All results reported in the present work were obtained with 2 atm pressure, and in some of the measurements on Fe^{55} at this pressure the counter was heated to 70°C. No change from the room temperature results was observed, and since the vapor pressure of ferrocene increases rapidly with temperature (see Appendix B), this indicates that none of the source had condensed on the counter walls. About 15 spectra were taken with 5 samples of ferrocene-Fe^{55} varying from less than 1 mg to about 5 mg distributed through the 10 liter volume of the counter. Some 10 spectra were measured with 4 samples of cobaltocene-Co^{58} ranging in weight from several hundred micrograms to about 2 mg. Similar efforts were made using two samples of manganocene-Mn^{54} of about 1 mg each. Integral-bias counting also was done as an independent check on the single-channel differential spectra. In the cases of the manganese and cobalt results, at the end of runs the counter was rapidly evacuated to a few mm of pressure and refilled with argon-methane (9:1). Spectra were taken immediately and again after waiting about 24 h to ascertain if there had been any sample condensed on the walls or wires of the counter. The observed background activity did not change appreciably for two observations, indicating no condensation of the source on the walls. For Co^{57}, only one run was made, and the result therefore is somewhat preliminary, as indicated by the rather larger error spread assigned (see Table II).

For the *K* peaks, the background was assumed to be linear; e.g., typically, it varied from 100 counts/min/channel at the low-energy end to 40 counts/min/channel at the high-energy end. The *L* peaks, however, offered more difficulty in that the background rose sharply at the low-energy end, the over-all gain setting for observations of the *L* peaks being about 4×10^4. Since the uncertainty in N_L is the largest source of error, the background being the critical factor, some additional measurements were made for cobalt in which the lower bias limit in the *L*-peak spectrum was varied some 10 V in

TABLE I. Numerical values of quantities in Eqs. (6)–(9) for the *K* x rays of chromium, manganese, and iron.

Element	K_α x-ray energy (keV)	Mass attenuation coefficient for argon	Relaxation length λ (cm)[a]	Calculated escape probabilities ($\times10^3$) P_1	P_2	P_3	$=P$
$_{24}Cr$	5.44	3.25×10^2	0.948	4.91	3.49	0.69	9.09
$_{25}Mn$	5.92	2.60×10^2	1.18	5.65	4.20	2.41	12.26
$_{26}Fe$	6.44	2.10×10^2	1.46	6.83	5.18	8.20	18.31

[a] The relaxation length λ is defined as $1/(\mu_m\rho)$ where ρ is the density of argon at 2 atm pressure and 27°C.

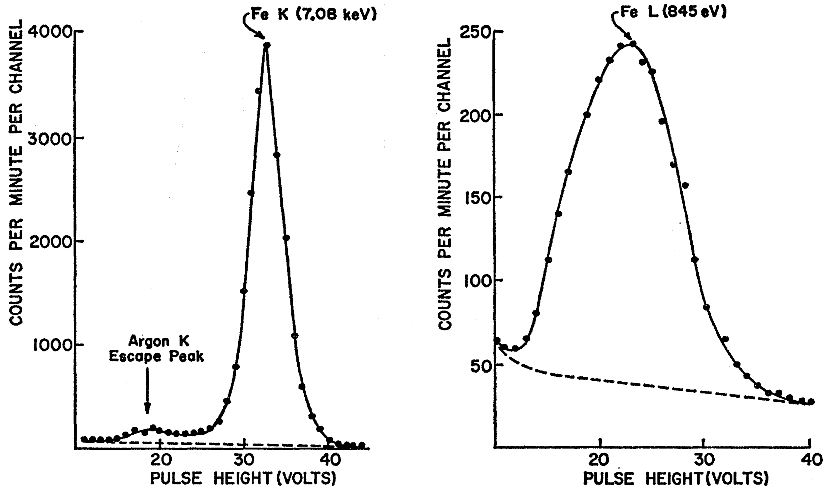

FIG. 4. K- and L-peak spectra of Co^{58} from the center counter in anticoincidence with the ring counters. The natural background is shown as a dashed line but has not been subtracted. The resolutions for the K and L peaks are 14 and 55%, respectively.

order to ascertain whether a systematic error was being introduced in N_L owing to uncertainties in the background. Values of N_L/N_K from such an experiment exhibited only random fluctuations, no trend being discernible. Table II presents the results of the present investigation in comparison with theoretical values.

Fe^{55} decays by orbital electron capture exclusively, so there is no source of error from positrons or gamma rays in the decay scheme (Fig. 1).

Co^{58} decays mainly by electron capture and positron emission to the first excited state of Fe^{58}, 0.805 MeV above the ground state (see Fig. 1). In addition, there is electron capture to the second excited state. Gamma rays of these energies (0.810 and 0.805 MeV) are not appreciably absorbed in the counting gas ($<0.01\%$), although they may, of course, produce Compton or photoelectrons on striking the wires or walls of the counter; such electrons simply add slightly to the observed background. Some 14% of the transitions occur by positron emission. In the pulse-height spectra, a slight rise at a pulse height corresponding to 20 keV was observed, but at 50 keV, this rise ceased. This was due presumably to the low-energy end of the positron spectrum. As the energy of the positrons increases, it becomes more probable that along with the pulse in the central counter, there occurs a pulse in the ring counters large enough to trigger the gate. This is due to the likelihood that two or more argon K x rays will escape from the center counter and be subsequently detected in the ring counters, triggering the gate. At 50 keV there is nearly always more than 3.5 keV of energy absorbed in the ring counters due to a positron emitted within the central or ring counters. Thus, the anticoincidence circuit becomes effective in eliminating the positron spectrum except at the very low energy end. Similar arguments apply to the experiments with Mn^{54}.

In the case of Co^{57}, 90% of EC events give rise to the 14.4 keV gamma transition, which is 90.6% converted.[14] Consequently, for K capture, the observed peak lies at 21.5 keV, the sum of the K x-ray and gamma-transition energy; for L capture, the peak is at 15.2 keV. There being no ground-state EC transition in Co^{57} decay, about 10% of EC events lead to the 136 keV cross-over transition in Fe^{57}. Those 136 keV transitions which are unconverted (about 12%) may escape, the remaining converted transitions being detected in the center counter. Thus at most, only about 1.2% of the total number of Co^{57} EC decays are lost. For the small number of 14.4 keV transitions which are not converted (9.4%) and which escape from the center counter, small

TABLE II. Comparison of the experimental ratio P_L/P_K to the theoretical values.

Nuclide	Mean observed intensity ratio N_L/N_K	Escape probability ($\times 10^3$) P	K-fluorescence yield ω_K	Ratio of K_α x rays to total K x rays[d] k	Corrected observed ratio[e] P_L/P_K	Theoretical ratio[f] P_L/P_K	Theoretical ratio[c] corrected for exchange P_L/P_K
$_{25}Mn^{54}$	0.101 ± 0.004	9.09	0.264 ± 0.002[a]	0.873	0.098 ± 0.006	0.0899	0.1043
$_{26}Fe^{55}$	0.111 ± 0.004	12.26	0.273 ± 0.003[b]	0.872	0.106 ± 0.005	0.0937	0.1078
$_{27}Co^{57}$	0.105 ± 0.010	18.31	0.324 ± 0.020[a]	0.889	0.099 ± 0.011	0.0916	0.1044
$_{27}Co^{58}$	0.114 ± 0.003	18.31	0.324 ± 0.020[a]	0.889	0.107 ± 0.004	0.0908	0.1035

[a] See Ref. 19. [b] See Ref. 18. [c] See Ref. 5 and discussion in text. [d] See Ref. 22.

[e] Error limits in the observed ratios correspond to twice the standard deviation from the mean, except for Co^{57}, the value for which is based on only one run.

[f] See Ref. 2.

peaks arise at 820 eV and 7 keV, from L and K x rays, respectively. The number of unconverted 14.4 keV transitions escaping, however, is extremely small. Thus, the effect of conversion in the gamma transitions following Co^{57} electron capture has a negligible effect on the P_L/P_K measurement.

Hence, the background for Fe^{55} arises from cosmic rays and other natural sources, whereas for Co^{57}, Co^{58}, and Mn^{54}, there is a slight addition to this natural background from gamma-produced electrons in the counter, so that the statistical spread in the intensity of the L peak and the variation in the background are the principal sources of error.

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APPENDIX A: RECENT PRECISION RESULTS FOR EXPERIMENTAL L/K-CAPTURE RATIOS

Since 1959 when we published a precision result for the L/K-capture ratio in Fe^{55} decay[1] and since the reviews by Robinson and Fink[3] and Bouchez and Depommier,[4] a number of precision results have appeared, based on measurements made with gaseous sources in multiwire proportional counters. In all cases, the experimental values lie above the theoretical values from Brysk and Rose[2] by some 5–10%, typically.

Table III lists these recent precision experiments together with the values from Brysk and Rose[2] and the theoretical values corrected for electron exchange after Bahcall.[5] Only multiwire proportional counter measurements are included for comparison.

In two cases, Cl^{36} and Zn^{65}, there seems to be an unexplained deviation even after the Bahcall exchange correction is made. This possibly could arise from some, as yet not fully understood, systematic error. In the case of Ar^{37} Manduchi and Zannoni[25] give the P_L/P_K ratio with a precision five times better than other workers have been able to obtain with the multiwire counter technique. (In the cases of Cr^{51}, Fe^{55}, and Ge^{71}, their reported error limits are between two and ten times better than others have achieved with this method.) It is questionable that such precision can be significant, but if so, then this result also deviates from the theoretical value listed in Table III.

TABLE III. Comparison of the L/K-capture ratios with theory.

Nuclide	Decay energy (keV)	Theoretical capture ratio[a] (P_L/P_K)	Exchange correction factor[b]	Corrected theoretical capture ratio (P_L/P_K)	Observed ratios[c] (P_L/P_K)	References
Cl^{36}	1138±6	0.0808	1.23[d]	0.0994	0.112 ±0.008	e
Ar^{37}	815±5	0.0820	1.22	0.100	0.102 ±0.008	f
					0.103 ±0.003	g
					0.102 ±0.004	h
					0.0971±0.0005	i
Cr^{51}	752±5	0.0885	1.17	0.1034	0.1026±0.0004	j
Mn^{54}	545±5	0.0899	1.16	0.1043	0.098 ±0.006	k
Fe^{55}	232±2	0.0937	1.15	0.1078	0.106 ±0.005	k
					0.106 ±0.003	l
Co^{57}	730±5	0.0916	1.14	0.1044	0.099 ±0.011	k
Co^{58}	1500±20	0.0908	1.14	0.1035	0.107 ±0.004	k
Zn^{65}	234, 1347	0.0965 (av.)	1.13	0.1090	0.119 ±0.007	m
Ge^{71}	231±3	0.1032	1.12	0.1156	0.116 ±0.005	n
					0.1187±0.0008	l
Kr^{79}	$\begin{Bmatrix} 1620\pm5 \\ 1372\pm20 \end{Bmatrix}$	0.102(av.)	1.09	0.111	0.108 ±0.005	n

[a] See Ref. 2.
[b] See Ref. 5.
[c] Only precision results obtained with gaseous sources in multiwire counters are listed.
[d] Although the decay of Cl^{36} is first-forbidden nonunique ($\Delta J=2$, $n0$), the exchange correction has been calculated from the theory for an allowed transition. No theory exists at present of exchange effects for forbidden transitions, although it is currently being developed [J. N. Bahcall (private communication)].
[e] P. W. Dougan, K. W. D. Ledingham, and R. W. P. Drever, Phil. Mag. **7**, 1223 (1962).
[f] R. W. Kiser and W. H. Johnson, J. Am. Chem. Soc. **81**, 1810 (1959).
[g] A. G. Santos–Ocampo and D. C. Conway, Phys. Rev. **130**, 2196 (1960).
[h] P. W. Dougan, K. W. D. Ledingham, and R. W. P. Drever, Phil. Mag. **7**, 475 (1962).
[i] See reference 25.
[j] V. Fasoli, C. Manduchi, and G. Zannoni, Nuovo Cimento **23**, 1126 (1962).
[k] This paper.
[l] See the second part of Ref. 26.
[m] A. G. Santos–Ocampo and D. C. Conway, Phys. Rev. **128**, 258 (1962).
[n] R. W. P. Drever and A. Moljk, Phil. Mag. **2**, 427 (1957); revised value, R. W. P. Drever (private communication).

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[25] C. Manduchi and G. Zannoni, Nuovo Cimento **22**, 462 (1961).

TABLE IV. Exchange integrals calculated from measured L/K-capture ratios.

Nuclide	X_{exp}	$\langle 1S' \| 2S \rangle$
Cl^{36}	1.39	0.055[a]
Ar^{37}	1.25	0.036
	1.18	0.026
Cr^{51}	1.16	0.024
Mn^{54}	1.09	0.013
Fe^{55}	1.12	0.018
Co^{57}	1.08	0.009
Co^{58}	1.18	0.027
Zn^{65}	1.29	0.044
Ge^{71}	1.12	0.018

[a] See footnote d in Table III regarding the forbidden decay of Cl^{36}.

In this connection, Manduchi and Zannoni[26] have determined the M/L intensity ratio in Ge^{71} decay (0.141 ± 0.010) with a gaseous source in a multiwire proportional counter. Assuming no escape correction, this is just the M/L-capture ratio.[27]

It is of interest to note that one can compute with the aid of Eq. (1) the exchange overlap integral $\langle 1S' | 2S \rangle$. The values of this quantity computed from experimental P_L/P_K ratios are shown in Table IV. It can be seen that the experimental values show rather wide variations. Since the exchange corrections factors in Table III were obtained by extrapolating Eq. (2) from $Z=20$ to $Z=32$, it would be valuable to have Hartree-Fock calculations of this quantity for atomic number outside the range of $Z=16$ to 20. We are informed that this is currently being done.[28]

APPENDIX B: PREPARATION AND PROPERTIES OF METALOCENES

The method of synthesis of the metalocenes is based on that used by Wilkinson and Cotton,[29] namely

$$2C_5H_5Na + MX_2 \rightarrow (C_5H_5)_2M + 2NaX.$$

Except for ferrocene, this preparation must be carried out under water-free and oxygen-free conditions. The preparation of cobaltocene is described below as a typical example. We have synthesized all of the nonradioactive metalocenes listed in Table I in the preliminary studies prior to making the radioactive compounds for use in multiwire counter experiments.

Bicyclopentadiene (boiling point 170°C) was refluxed through a Vigreux column which served to crack the dimer, the monomer distilling over. The purity of the monomer was checked by observing its boiling point which was always within one degree of 42.5°C, the accepted boiling point. The yield of the monomer was 50–75% depending on the length of time the dimer was refluxed. The boiling point rose to beyond 170°C after approximately 50% of the volume had been distilled, indicating that higher polymers were present. The distillation was discontinued when the temperature reached 200°C. On cooling, the remaining polymer sometimes solidified into a yellow waxy mass.

Two solvents were used in these preparations with similar success; namely, tetrahydrofurane and 1,2-dimethoxyethane. It was necessary to purify these further to remove water. This was done by passing the solvent through columns of Linde Air molecular sieves $\frac{1}{16}$ in. in diameter or by distillation over lithium aluminum hydride. The first method is the simpler and gives moderate purity. The second is preferable if complete freedom from water, alcohols, and similar impurities is desired.

The next step in the synthesis is the preparation of sodium cyclopentadienide. A small block of sodium metal was cleaned while submerged in toluene. It was transformed to a container of boiling toluene and stirred until it was thoroughly dispersed. When the sodium had solidified, the toluene was replaced by the solvent. Cyclopentadiene was then dropped slowly into the solvent containing dispersed sodium. This was done in a container (Fig. 5) having only a small exit for argon and hydrogen released in the reaction, the former being passed through the solution to prevent air from entering. Magnetic stirring was continued until the reaction was complete. The resulting solution of sodium cyclopentadienide was clear to pale yellow if the system had been kept free of air and water, and was red to purple if air or water were present.

The anhydrous cobaltous chloride was dispersed in approximately 100 ml of the solvent and added to the solution of sodium cyclopentadienide. This mixture was stirred for from 6 to 8 h, under an Ar atmosphere. The solvent was then removed by distillation at reduced pressure. The vapor pressure of the metalocenes is small enough at 15–20°C, the temperature at which the distillation was carried out, to keep the loss of product small.

The residue after distillation contained a small amount of solvent, excess sodium cyclopentadienide,

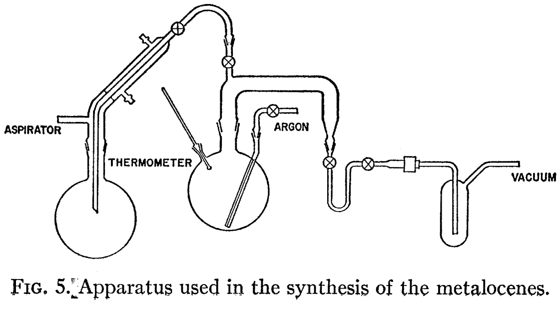

FIG. 5. Apparatus used in the synthesis of the metalocenes.

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[26] C. Manduchi and G. Zannoni, Nuovo Cimento **24**, 181 (1962); C. Manduchi and G. Zannoni, Nucl. Phys. **36**, 497 (1962).

[27] We are presently attempting the measurement of the M/L capture ratio for 30 million yr Pb^{205}. B. L. Robinson (private communication), has computed values of the M/L ratios from the relativistic M-shell electron wave functions of H. R. Brewer, D. S. Harmer, and D. H. Hay [Phys. Rev. Letters **7**, 319 (1961)]. A preliminary report of this work is given in Bull. Am. Phys. Soc. **8**, 130 (1963).

[28] J. N. Bahcall (private communication).

[29] G. Wilkinson and F. A. Cotton, Chem. Ind. (London) **32**, 307(1954).

TABLE V. Some physical and chemical properties of the metalocenes.

Compound	Color	Melting point (°C)	Chemical reactivity	Reference
$Ni(C_5H_5)_2$	green	171–173	Oxidized by O_2 and HNO_3 to $(Ni^+)(C_5H_5)_2$. Stable in H_2O.	a,b,c
$Co(C_5H_5)_2$	black	171–173	Oxidized by O_2 and other oxidizers. Hydrolyzed by H_2O.	a,b,d
$Fe(C_2H_5)_2$	orange	172–173	Stable. Can be steam distilled. Strong oxidizers form $(Fe^+)(C_2H_5)_2$.	a,b,d,e,f
$Mn(C_2H_5)_2$	brown-pink	172–173	Hydrolyzed by H_2O. Oxidized explosively by O_2.	b
$Cr(C_5H_5)_2$	scarlet	170–172	Hydrolyzed by H^+. Pyrophoric. Oxidative decomposition by oxidizers.	b,g
$V(C_5H_5)_2$	purple	167–168	Oxidized to $(V^+)(C_5H_5)_2$. Pyrophoric.	b,h
$Ti(C_5H_5)_2$	green	decomposes at 130°C	Hydrolyzed by H_2O. Oxidative decomposition by oxidizers. Pyrophoric.	i
$Ru(C_5H_5)_2$[j]	brown	195.5	Oxidized by O_2 and other oxidizers.	d

[a] See Ref. 32.
[b] See Ref. 31.
[c] G. Wilkinson, P. L. Paulson, J. M. Birmingham, and F. A. Cotton, J. Am. Chem. Soc. **75**, 1011 (1953).
[d] C. Wilkinson, J. Am. Chem. Soc. **74**, 6146 (1952).
[e] See Ref. 30.
[f] G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. R. Woodward, J. Am. Chem. Soc. **74**, 2125 (1952).
[g] G. Wilkinson, J. Am. Chem. Soc. **76**, 209 (1954).
[h] See Ref. 29.
[i] A. K. Fischer and G. Wilkinson, J. Inorg. Nucl. Chem. **2**, 149 (1956).
[j] Ruthonocene was added to the list although it is not among the first transition group of elements. It is of interest because it is analogous to ferrocene and has an appreciable vapor pressure. Its use as a gaseous source is contemplated.

sodium chloride, cobaltacene, and perhaps other substances of unknown composition as well. The last traces of solvent was removed by vacuum pumping and the system evacuated to a few tenths of a millimeter of pressure. The temperature was allowed to rise to 70°C during this operation.

The radioactive cobaltocene was collected by vacuum sublimation. A *U* tube connected between the flask containing the crude product and the vacuum system was immersed in a dry ice acetone mixture. As the flask and delivery tube were heated and a slow stream of argon passed through the system, the cobaltocene condensed on the cold walls of the *U* tube. Heating of the flask and the glass tube had to be carried out as close to the *U* tube as possible, lest the cobaltocene sublime and recondense on the walls and collect only slowly in the *U* tube. After collection was completed, the *U* tube was closed at both ends and connected to the vacuum line used for filling the counter.

Properties of Metalocenes

To be of value in this work the metalocenes must meet certain specifications. They must be stable in an argon-methane atmosphere; they must not act as a quench gas in the counter, and they must have a suitable vapor pressure.

For solid ferrocene, the vapor pressure[30] is given by

$$\log_{10}P(\text{mm}) = 10.27 - 3680/T_K. \qquad \text{(B1)}$$

At 27°C, the vapor pressure of ferrocene is 0.01 mm and at 73°C, it is 0.36 mm. A similar equation found for manganocene[31] is

$$\log_{10}P(\text{mm}) = 10.58 - 3780/T_K. \qquad \text{(B2)}$$

The vapor pressure of manganocene is 0.01 mm at 27°C and 0.36 mm at 70°C. No data are available for the vapor pressure of nickelocene and cobaltocene, but the known physical properties of all the metalocenes of the first transition series are surprisingly similar. These include nickel, cobalt, iron, manganese, chromium, vanadium, and titanium. The melting points of the metalocenes of all these except titanium and vanadium lie between 170–172°C. Titanocene decomposes at 130°C. The ease with which they may be oxidized is similar to that of the parent substance. Thus, ferrocene is oxidized in solution by mercuric chloride to the blue ferricinium ion and reduced to ferrocene by stannous chloride with 100% recovery, whereas chromocene is pyrophoric and must be carefully protected from contact with air. Infrared spectra have been taken on ferrocene,[30,31] nickelocene,[31] and manganocene.[32] The spectra are all very similar. The evidence indicates that the vapor pressures of these compounds are similar. Table V compares some of the known physical and chemical properties of the metalocenes.

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[30] L. Kaplan, W. L. Kester, and J. J. Katz, J. Am. Chem. Soc. **74**, 5531 (1952).

[31] G. G. Wilkinson, P. L. Paulson, and F. A. Cotton, J. Am. Chem. Soc. **76**, 1970 (1954).

[32] G. Wilkinson, F. A. Cotton, and J. M. Birmingham, J. Inorg. Nucl. Chem. **2**, 95 (1956).