

TABLE V. Mixed conversion particle parameter b for $E1+M2$ mixture.

$Z \backslash k$	0.3	0.5	1.0	1.8	3.0	5.0
30	-0.2069	-0.3293	-0.5550	-0.7463	-0.8649	-0.9336
40	-0.2032	-0.3237	-0.5410	-0.7268	-0.8431	-0.9159
54	-0.1980	-0.3146	-0.5195	-0.6913	-0.8043	-0.8796
64	-0.1939	-0.3089	-0.5042	-0.6651	-0.7739	-0.8476
72	-0.1903	-0.3045	-0.4919	-0.6436	-0.7467	-0.8177
78	-0.1872	-0.3015	-0.4832	-0.6273	-0.7254	-0.7927
83		-0.2992	-0.4762	-0.6139	-0.7073	-0.7715
88		-0.2968	-0.4695	-0.6004	-0.6889	-0.7489
92		-0.2949	-0.4644	-0.5898	-0.6739	-0.7303
96		-0.2929	-0.4595	-0.5793	-0.6589	-0.7112

Calculations of b for the $E1+M2$ mixed transition were performed by the method outlined by Biedenharn and Rose.^{24,40,41} As a check of the results, we also calculated the b_2^e for $E1$, b_2^m for $M2$, and some b values for a $E2+M1$ mixture. The results obtained agree well with those of Biedenharn and Rose within 0.1%. Numerical values of b for the $E1+M2$ mixed transition are given in Table V.

⁴⁰ J. Matsumoto and H. Ikegami (to be published).

⁴¹ The factor $-i^{2l(\omega)}$ has been omitted from Eq. (82) of reference 24. Recently, the misprint was also corrected by Church *et al.* [E. Church, M. Rose and J. Weneser, Phys. Rev. **109**, 1299 (1958)].

L/K -Capture Ratio and E_L/E_K for $\text{Ar}^{37\ddagger,*}$

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The L/K capture ratio of Ar^{37} has been determined to be 0.103 ± 0.003 in a high-pressure, multiwire proportional counter. This value is in excellent agreement with the theoretical value of 0.100. The average energy of the L peak was found to be 273 ± 6 ev. When a new value of 265 ± 5 ev is obtained for the critical L absorption energy of Cl by interpolation and the effect of the Auger process is considered, it is concluded that the energy to produce an ion pair in Ar at 0.2 kev is 0.98 ± 0.04 times the value at 2.8 kev.

INTRODUCTION

IF the correlations between the positions of the electrons are neglected, the theoretical L/K capture ratio for Ar^{37} is 0.082.¹ The theoretical ratio is increased to 0.100 when the Pauli correlations are introduced, although the ratio would probably be somewhat larger if all the correlations were considered.²

In the relatively low Z region the L/K -capture ratio, R , can be determined in a proportional counter by use of the relation

$$R = R'(1 - P\omega_K) - P\omega_K k, \quad (1)$$

in which R' is the observed ratio of the two peak areas in the pulse-height spectrum; P , the probability of a K_α x ray escaping the counter; ω_K , the K -fluorescence yield; and k , the fraction of K_α x rays in the K series. It is best to perform the experiment with P equal to zero because of the uncertainties in the values of ω_K and k .³ Pontecorvo *et al.*⁴ obtained an L/K capture ratio of 0.087 for Ar^{37} in a Xe-filled proportional counter

in which P was 0.13. A value of 0.092 ± 0.010 or -0.005 was obtained by Langevin and Radvanyi⁵ in a Xe filled counter in which P was 0.026. Their error was estimated from the uncertainty introduced in the extrapolation of the L peak to zero energy. Kiser and Johnston⁶ obtained 0.102 ± 0.008 . However, P varied from 1–0.4, and a longer extrapolation of the L peak was required. Values of 0.108 (± 0.016) for the ω_K ⁷ and 1.0 for the k of Cl were used in Eq. (1). If the new value⁸ for ω_K of 0.093 ± 0.003 is used, the capture ratio is increased to 0.116 ± 0.011 (standard deviation). In the present investigation a more accurate value for the L/K -capture ratio has been determined which can be compared to the theoretical value which has been corrected for the Pauli correlations only.

Recently the low-energy region of the tritium spectrum was examined in a proportional counter using P -10 gas (9 Ar/CH₄) and found to deviate from theory.⁹ It was noted that the deviation could have been caused by an increase in the energy to produce an ion pair, w , of 4–6% in the energy interval 1.2–0.25 kev. Most of the electron beam investigations have shown w to be

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* Taken in part from the doctoral dissertation of Augusto G. Santos-Ocampo.

¹ H. Brysk and M. E. Rose, Revs. Modern Phys. **30**, 1169 (1959).

² S. Odier and R. Daudel, J. phys. radium **17**, 60 (1956).

³ B. L. Robinson and R. W. Fink, Revs. Modern Phys. **32**, 117 (1960).

⁴ B. Pontecorvo, D. H. W. Kirkwood, and G. C. Hanna, Phys. Rev. **75**, 982, 985 (1949).

⁵ M. Langevin and P. Radvanyi, Compt. rend. **241**, 33 (1955).

⁶ R. W. Kiser and W. H. Johnston, J. Am. Chem. Soc. **81**, 1810 (1959).

⁷ M. Haas, Ann. Physik **16**, 473 (1933).

⁸ F. Bertrand, G. Charpak, and F. Suzor, J. phys. radium **20**, 956 (1959).

⁹ D. C. Conway and W. H. Johnston, Phys. Rev. **116**, 1544 (1959).

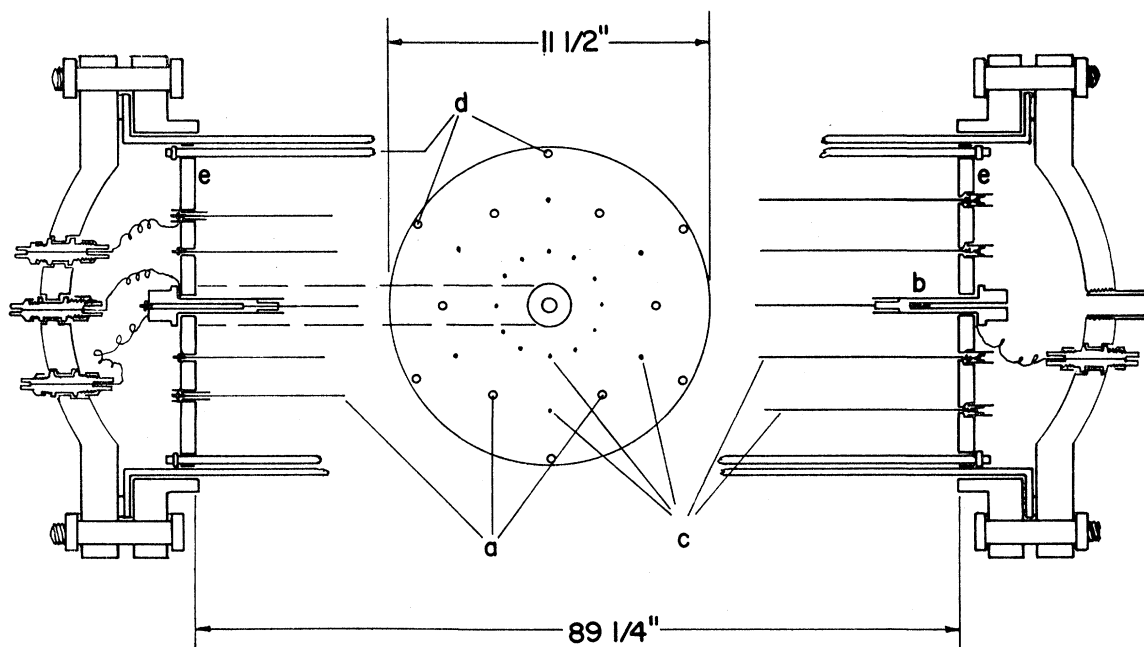


FIG. 1. General construction of the multiwire counter. (a) Ring counter anodes. (b) Field adjusting electrode with Teflon insulator. (c) Cathode wires. (d) Steel spacers. (e) Araldite end plate.

constant down to about 70–100 ev and to increase at lower energies, but there are no accurate results for Ar or Xe over the region of interest. The literature on w is reviewed by Valentine and Curran.¹⁰

Another method for measuring the variation in w over this region is to calculate E_L , the average energy of the L peak, from the experimental ratio of E_K/E_L for Ar^{37} . Since it is a $2s$ electron which is captured in L capture, it has been assumed that E_L should equal the critical L_I absorption energy of Cl, E_{L_I} , if w is constant. Pontecorvo *et al.*^{4,11} found E_L to be 220 ev in the Xe filled counter, but this measurement may not be very accurate as the statement was made that this proves that w at about 250 ev is at the most 20% greater than w at 2.8 kev.¹² Langevin and Radvanyi's value for E_L was 275 ev, which they compared to the interpolated value for E_{L_I} of 238 ev.¹³ Because of the presence of the escape peak, the previous experiments in which Ar was used as a counting gas cannot be used to calculate the variation in w accurately for this gas.¹⁴ The apparatus to be described blocks out the escape peak electronically,

so it was decided to measure E_L/E_K for Ar^{37} in P -10 gas.¹⁵

APPARATUS

The proportional counter is a high pressure, multiwire type as described by Curran *et al.*¹⁶ (Fig. 1). The center counter is 4 in. in diameter and 82.6 in. in active length with 12 two-mil wolfram wires as the cathode. The 6 cathode wires in the ring counters are 9-mil stainless steel. All anodes are 2-mil wolfram, those of the ring counters being fitted with guard electrodes. The entire assembly fits inside a 12-in. i.d. steel chamber with a thin Al liner which will withstand 11 atm pressure. The electrical connections are made via springs through a high voltage (>10 kv) Teflon insulated vacuum seal. The springs and internal connections are shielded from electrical breakdown by Teflon wafers (not shown).

The pulses from the central counter are fed through a low-noise preamplifier to a dc-coupled amplifier¹⁷ which is dc-coupled to the RIDL Model 3300 100-

¹⁰ J. M. Valentine and S. C. Curran, *Reports of Progress in Physics* (The Physical Society, London, 1958), Vol. 21, pp. 1–29.

¹¹ B. Pontecorvo, *Suppl. Helv. Phys. Acta*, **23**, 97 (1950).

¹² These authors assumed E_{L_I} to be 280 ev.

¹³ R. D. Hill, E. L. Church, and J. W. Mihelich, *Rev. Sci. Instr.* **23**, 523 (1952).

¹⁴ In these experiments P was relatively large. Therefore, the expected energy of the L peak is rather uncertain as it is somewhere between the E_{L_I} of L capture and $E_{L_{II,III}}$ (198 ev) [Y. Cauchois, *J. phys. radium* **16**, 253 (1955)] left after the escape of the K_α x rays.

¹⁵ It should be noted that Valentine [Proc. Roy. Soc. (London) **A211**, 75 (1952)] assumes w is constant from 2.8–0.2 kev in Ar as it is expected to be from theory and because of previous experimental evidence. The present authors believe w could vary at least 10% within the limits of error for the experimental evidence.^{10,14} If w were proven constant, E_{L_I} for Cl could be calculated from E_L/E_K .

¹⁶ R. W. P. Drever, A. Moljk, and S. C. Curran, *Nuclear Instr.* **1**, 41 (1957); R. W. P. Drever and A. Moljk, *Phil. Mag.* **2**, 427 (1957); J. Scobie, R. B. Moler, and R. W. Fink, *Phys. Rev.* **116**, 657 (1959).

¹⁷ D. C. Conway and Roy M. Hayes (to be published).

channel analyzer.¹⁸ (See Fig. 2.) Pulses from the ring counters are amplified and fed into a pulse shaper with the gate set at 0.9 kev. The 15- μ sec delay ac (anticoincidence) pulse is fed into the delay ac gate of the analyzer. (The sample pulse is delayed 1 μ sec at this gate.) Hence if a K_{α} x ray escapes the center counter and is absorbed in a ring counter, the residual L pulse left in the center counter is canceled electronically. The 115- μ sec prompt ac pulse begins at the same time as the 15- μ sec pulse and is dc-coupled into a prompt ac gate (gate 1) and the live time gate for the A -268 live timer (i.e., into pin 7 of $V10B$ of the A -262 converter). Therefore, the live timer also corrects for the dead time caused by the ring counters. Since two separate spectra were taken for the L and K peaks, they could thereby be corrected to the same live time. The pulse shaper is reset by each pulse so there is at least 100- μ sec blocking after every pulse to block out the positive overshoot pulses from the pulses of opposite sign induced in the center counter by the discharges in the ring counters. (Drever and Moljk¹⁶ point out the companion problem, the induced pulses on the ring counter anodes.)

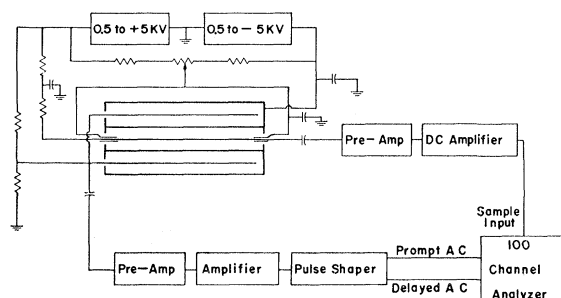


FIG. 2. Block diagram of the electronics.

EXPERIMENTAL PROCEDURE

Each time the counter was exposed to air, it was degassed for 10 hours at 80°C and pumped out to a residual pressure of 2 microns. A trace of Oak Ridge National Laboratory Ar^{37} was added to a 50 liter mixing tank. Then P -10 gas was passed into the mixing tank through a Ca purifier at 300°C and a dry ice trap. (The valley to the left of the L peak is "washed out" at 5 atm if the P -10 is not purified.) The gases were then expanded into the counter. (When pre-mixing was not used, a varying count rate showed the activity was not thoroughly mixed. Although the peaks could be compared at the same time by interpolation, the specific activity must be constant throughout the counter so that the number of K x rays which escape from the central counter and are absorbed in the ring counters will exactly equal the number from the ring counters that are absorbed in the central counter.)

¹⁸ Radiation Instrument Development Laboratory, 61 East North Avenue, Northlake, Illinois.

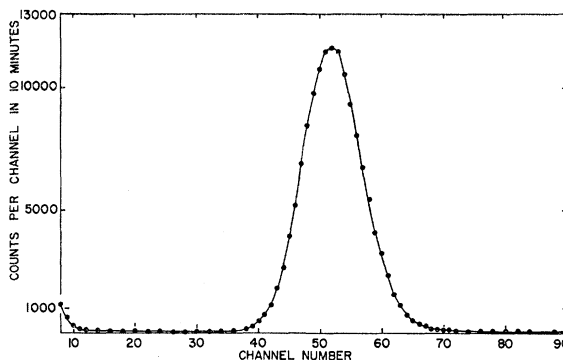


FIG. 3. Ar^{37} K peak from the central counter in anticoincidence with the ring counters. The natural background has not been subtracted, but it is too low to be shown.

L/K -CAPTURE RESULTS

The typical K and L peaks observed with the counter design described above are shown in Figs. 3 and 4, respectively. The K -peak resolutions in the center and ring counters were 23% and 25%, respectively. After the background was subtracted, there remained an activity between the L and K peaks which had a height equal to 2% of the L -peak height. By linearly extrapolating this baseline under both peaks, it was estimated that 3-4% of the activity was under this baseline from 0-5 kev. Therefore, the baseline is too high to be caused by the internal bremsstrahlung accompanying electron capture.¹⁹ Most of the baseline activity is below 5 kev and must be due to degraded K pulses. The same percent of the L peak should be lost to the left of the L peak, so no correction was made for the effect of the baseline other than to simply subtract the extrapolated baselines from the peaks as has been done previously.⁵ Thus the activity in the L peak was determined by subtracting the background and residual baseline and adding the integrated counts in the

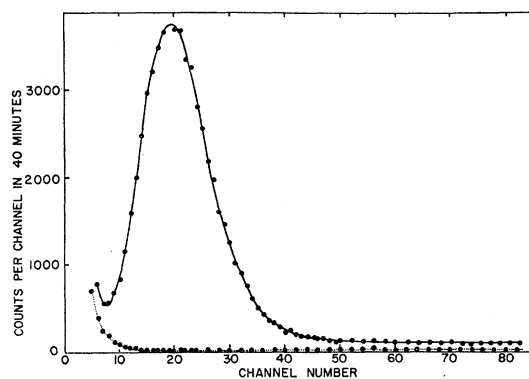


FIG. 4. Ar^{37} L peak from the central counter in anticoincidence with the ring counters. The natural background has not been subtracted and is shown by the dotted line.

¹⁹ C. S. Wu, *Beta- and Gamma-Ray Spectroscopy*, edited by Kai Siegbahn (Interscience Publishers, Inc., New York, 1955), pp. 656-659.

TABLE I. L/K-capture ratios of Ar³⁷.

Pressure (atm)	$P_1 \times 10^3$	$(P_2+P_3) \times 10^3$	R'	R	Comments
1			0.1013		Resolution in ring counters about 40% because of faulty counter construction
1			0.1007		
2			0.1006		
3			0.1007		
1	6.6	3.0	0.1035	0.1025	Final counter design. P-10 gas purified over Ca
3	2.1	0.2	0.1034	0.1032	
5	1.3	0.1	0.1040	0.1039	
5	1.3	0.1	0.1036	0.1035	
Average			0.1033 \pm 0.003		

extrapolated region of the L peak to the sum of the counts above this region.

Drever and Moljk¹⁶ derived a slightly different form of Eq. (1) for a multiwire counter with field adjusting electrodes:

$$R = R'[1 - (P_2 + P_3)\omega_K] - (P_1 + P_2 + P_3)\omega_K k. \quad (1')$$

Here P_1 is the probability that a K_α x ray will escape the center counter through the ends; P_2 , that the x ray will escape the center counter and hit a cathode wire; and P_3 , that the x ray will escape the center counter and pass through the ring counters without being absorbed. These authors also discuss the calculation of these probabilities. The experimental value⁸ of 0.093 for ω_K and an assumed value of 1.0 for k were used to calculate the ratios given in Table I. Because the first set of data were taken with unpurified P-10 when the resolution in the ring counters was poor, only the second set were used in calculating the average ratio.

The following facts were considered in estimating the limits of error: (1) The average value for two early determinations of the L/K ratio, made before the counter was fitted with field adjusting electrodes so that the baseline was 4 times as high, is 0.103 ± 0.007 . (2) Considering the fact that the L/K ratio did not change with a twofold change in the activity, the error due to the dead time correction is less than 0.5%. (3) The L activity in the extrapolated region amounted to about 2% of the total L activity. (4) The standard deviation in the ratio due to the counting error amounted to about 0.6%.

VARIATION IN w FROM 2.8-0.2 kev

At a pressure of 5 atm the position of the K peak at two gains on the expanded (0.16 v/channel) scale was used to calculate the zero-energy channel. The L peak was fitted to a Poisson distribution with m equal to 10.0, and the average pulse height determined from the curve. From these measurements E_L/E_K was

TABLE II. Apparent L -capture energies for Ar³⁷.

Counter voltage (v)	5500	5300	5300	5100	5100	5010
E_L (ev)	310	278	283	275	264	279

calculated with an estimated accuracy of 2%. This procedure gave the same results within 1% as that obtained by calibrating the pulse heights with a precision pulse generator. It was assumed that E_K is 2.819 kev²⁰ in calculating E_L (Table II). It is seen that at 5500 v the counter was no longer in the proportional region as the gas gain was less for the K peak than the L peak²¹ which caused the calculated E_L to be too high. The K peak is certainly in the proportional region at the lowest two voltages from which E_L is calculated and compared to the previous results in Table III. It is to be noted that the previous results in Ar are low because of the presence of the escape peak,¹⁴ and that the results of Pontecorvo *et al.*⁴ are in disagreement with the later results and are, therefore, presumed to be in error.

A value of 238 ev was obtained for the E_{LI} of Cl¹³ by an interpolation between the well-known E_{LI} values at higher Z and the rather uncertain values for Al (87 ev) and Mg (63 ev).²² However, the "accepted" value for Al is now 117 ev^{20,23} which will increase the inter-

TABLE III. Experimental values for the average L -peak energies of Ar³⁷.

Counter gas		Reference
Xe	Ar	
220	200	4
275		5
	245	6
	273 \pm 6	Present work

polated value for Cl. Apparently the earlier E_{LI} values for Mg and Al were derived from the absorption spectra observed by Skinner and Johnston.²⁴ However, Tomboulou and Pell²⁵ showed that the absorption dip at about 96 ev in Al was due to a surface phenomenon, i.e., absorption by several hundred angstroms of metal-substrate "interface." Tomboulou felt the Mg absorption peak was probably also due to the same sort of phenomenon. Further, he postulated that certain lines in the emission spectra of Na-Al²⁴ and S²⁶ are due to $L_I \rightarrow L_{III}$ transitions. Since the L_{III} levels are well-known, the energies of the L_I levels for these elements were calculated from these lines. Then by use of the screening-doublet law, which can be expressed in the

²⁰ Y. Cauchois, J. phys. radium **16**, 253 (1955).

²¹ D. West, *Progress in Nuclear Physics*, edited by O. R. Frisch (Academic Press, Inc., New York, 1953), Vol. III, p. 24.

²² Y. Cauchois and H. Hulubei, *Tables de Constantes et Données Numériques. 1. Longueurs d'Onde des Émissions X et des Discontinuités d'Absorption X*. (Herman et Cie, Paris, 1947), Plate 1.

²³ K. Sagel, *Tabellen zur Röntgen-Emissionen-Und Absorptions-Analyse* (Springer-Verlag, Berlin, 1959), p. 37.

²⁴ H. W. B. Skinner, Phil. Trans. Roy. Soc. (London) **239**, 95 (1940); J. E. Johnston, Proc. Cambridge Phil. Soc. **35**, 108 (1939); H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) **A161**, 420 (1937).

²⁵ D. H. Tomboulou and E. M. Pell, Phys. Rev. **83**, 1196 (1951).

²⁶ D. H. Tomboulou, Phys. Rev. **74**, 1887 (1948).

TABLE IV. Calculation of the L_I absorption energies in ev.

Atomic number	Element	E_{L_I}	$E_{L_{II}}$	$(E_{L_I})^{\frac{1}{2}} - (E_{L_{II}})^{\frac{1}{2}}$
10	Ne	4 _s ^a	2 _s ^a	2.24
11	Na	6 _s ^b	3 _s ^c	2.43
12	Mg	8 _s ^b	4 _s	2.39
13	Al	11 _s ^b	7 _s	2.14
14	Si	(14 _s) ^d	9 _s	
15	P	(18 _s)	12 _s	
16	S	22 _s ^b	16 _s	2.16
17	Cl	(26 _s)	19 _s	
18	Ar	(32 _s)	24 _s	
19	K	(37 _s)	29 _s	
20	Ca	(43 _s)	35 _s	
21	Sc	(50 _s)	41 _s	
22	Ti	(55 _s)	45 _s	
23	V	(62 _s)	51 _s	
24-30	Cr-Zn	Average \pm standard deviation 2.17 \pm 0.17		

^a S. Fine and C. F. Hendee, *Nucleonics* **13**, 36 (1955).^b Calculated from the $L_I \rightarrow L_{III}$ transition energy. (See text.)^c Unless otherwise noted, the values come from reference 20.^d Values in parentheses calculated by interpolation using Eq. (2) with $C = 2.17$.

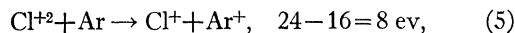
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$$(E_{L_I})^{\frac{1}{2}} - (E_{L_{II}})^{\frac{1}{2}} = C \quad (2)$$

the E_{L_I} values for the intervening elements were

Process	Energy of Auger electron
$L_I \rightarrow L_{II,III} M_{II,III}$	$(\mathcal{E}_{L_I})_{Cl} - (\mathcal{E}_{L_{II,III}})_{Cl} - (\mathcal{E}_{M_{II,III}})_{Ar} = 269 - 202 - 16 = 51 \text{ ev}$ (3)
$L_{II,III} \rightarrow M_{II,III} M_{II,III}$	$(\mathcal{E}_{L_{II,III}})_{Cl} - (\mathcal{E}_{M_{II,III}})_{Cl} - (\mathcal{E}_{M_{II,III}})_{Cl^+} = 202 - 13 - 24 = 165 \text{ ev}$ (4)

in which $(\mathcal{E}_{M_{II,III}})_{Cl^+}$ represents the second ionization potential of Cl. The reaction which follows,



probably is not exothermic enough to produce further ionization. Therefore, the total "energy" release is 216 ev plus two Auger electrons which are worth 54 ev ($w = 27 \text{ ev/electron}$) or 270 ev. Thus it can be seen that the Auger process makes electrons cheaply, causing E_L to be greater than the expected $(\mathcal{E}_{L_I})_{Cl} - (\mathcal{E}_{M_{II,III}})_{Ar}$. If the various more probable Auger processes are considered as above, the average value of \mathcal{E}_L (weighted by the probability for each process³⁰) is calculated to be

²⁷ D. H. Tomboulion and W. M. Cady, *Phys. Rev.* **59**, 422 (1941).²⁸ E. H. S. Burhop, *The Auger Effect and Other Radiationless Transitions* (Cambridge University Press, Cambridge, 1952), p. 55.²⁹ *Ibid.*, pp. 50-72.³⁰ It seemed reasonable to assume that each 2s vacancy was filled from the 2p subshell and that each 3p electron was transferred with $\frac{2}{3}$ the probability of a 3s electron.²⁹

calculated.²⁷ This calculation has been repeated with modern data (Table IV). The value of C is relatively constant through Al and appears to increase at lower atomic numbers where the 3s subshell is being filled. From the uncertainty in C , E_{L_I} for Cl is taken to be $265 \pm 5 \text{ ev}$.

The expected value for E_L is not really E_{L_I} , but the energy obtained in the $L_I \rightarrow M_{II,III}$ transition for Cl. Because a 2s electron is absent, the energy to remove a 3p electron to infinity, $\mathcal{E}_{M_{II,III}}$, is the ionization potential of Ar, 16 ev. Since \mathcal{E}_{L_I} is the energy required to remove a 2s electron by an allowed transition to the nearest unfilled shell, i.e., the N shell,¹³ \mathcal{E}_{L_I} is larger by approximately the ionization potential of K or 4 ev. Therefore, the energy available in $Ar^{37} L$ capture is $253 \pm 5 \text{ ev}$.

It is seen by extrapolation that after the 2s electron is captured, the Cl atom de-excites by the Auger process.²⁸ From the theoretical expression for the Auger transition rate together with a qualitative idea of the radial parts of the wave functions and relative numbers of electrons involved,²⁹ the most probable de-excitation mechanism is the following:

about $268 \pm 6 \text{ ev}$ or $268 \pm 8 \text{ ev}$ if the uncertainty in E_{L_I} is included. So for P -10 gas

$$w(0.2 \text{ kev}) = \frac{(268 \pm 8)}{(273 \pm 6)} w(2.8 \text{ kev}) \\ = (0.98 \pm 0.04) w(2.8 \text{ kev}). \quad (6)$$

Although w appears to be constant from 2.8-0.2 kev, a 5-6% increase in w is not impossible within the accuracy of the experimental results.

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