

L-Shell Fluorescence Yields in Elements Between $Z=40$ and 51^*

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The partial L -shell fluorescence yields of eight elements between $Z=40$ and 51 have been determined using a coincidence counting method. Vacancies are created in the K shell by the photoelectric absorption of suitable radiations. The coincidence rate between the K and L x rays emitted subsequent to the ionizing event determines the partial L -shell fluorescence yield ω_{KL} . The L x rays were observed with a proportional counter and the K x rays with a scintillation counter. The following values were obtained for ω_{KL} : zirconium, 0.034 ± 0.010 ; niobium, 0.036 ± 0.010 ; palladium, 0.047 ± 0.010 ; silver, 0.054 ± 0.007 ; cadmium, 0.055 ± 0.012 ; indium, 0.065 ± 0.012 ; tin, 0.064 ± 0.012 ; and antimony, 0.070 ± 0.013 .

1. INTRODUCTION

IN recent measurements of L -shell fluorescence yields,^{1,2} a coincidence method has been employed in which the coincidence rate between K and L x rays following K -shell ionization is measured. This coincidence rate depends on the partial L -shell fluorescence yield ω_{KL} as follows:

$$\omega_{KL} = (N_C/N_K)(1/aE_L A_L \Omega_L), \quad (1)$$

where N_C is the L -to- K x-ray coincidence rate, N_K is the K x-ray count rate, Ω_L is the geometric factor of the L x-ray counter, A_L is the transmission factor for the L x rays between the source and the counter, and E_L is the efficiency of the L counter. The factor a is the ratio of the number of counts due to K_α x rays to the total number of counts observed in the K x-ray peak. It must be included in the formula because the scintillation counter employed to observe the K x rays cannot resolve the K_α and K_β components and therefore does not distinguish between K x rays which leave L -shell vacancies and those which do not.

The major difference between the present measurements and those described in Ref. 1 is that a proportional counter was employed to observe the L x rays. This was necessary because the scintillation counter used in Ref. 1 could not be operated in the quantum energy region between 2 and 4 keV, which covers the L x rays between $Z=40$ and 51 . It was also necessary to place the target foil in a vacuum box to reduce the air absorption of the soft L x rays. The target foils used in these experiments were somewhat thinner than those used in Ref. 1 to minimize the self-absorption of L x rays in the foil.

2. EXPERIMENTAL PROCEDURE

Figure 1 shows the counter arrangement used to measure the K -to- L x-ray coincidences. A strong I^{125} source was used to provide the radiation to cause K -

shell ionization in the target materials. (I^{125} emits characteristic tellurium K x rays and a weaker 35-keV gamma ray.) The radiations were collimated and passed through a thin window into a small vacuum chamber. The target foil ($\frac{5}{8} \times \frac{5}{8}$ in.) was mounted inside the chamber on an aluminum frame and was suspended in the center of the frame by very thin nylon fibers. The K x-ray counter used was the same as the one described in Ref. 1 and was mounted next to a window in the vacuum chamber through which the K x rays leave the box. The proportional counter was mounted on the opposite side of the vacuum box. A 5-mil beryllium window was used to separate the evacuated region from the active volume of the counter. The proportional counter itself has a cylindrical active volume $3\frac{3}{8}$ in. in diameter and 9 in. long. The window was mounted approximately $\frac{1}{2}$ in. away from the cylindrical counter volume so that the distortion of the electric field caused by the window well was not severe. A 3-mil stainless-steel wire was employed as the center electrode. The counter was operated using a neon (90%)-methane (10%) mixture at atmospheric pressure. The center wire was held at a potential of 2150 V. All the vacuum seals on the counter tube were either metal-to-metal or metal-to-ceramic seals to prevent poisoning of the counter gas. In addition, great care was taken to eliminate high-voltage breakdown so that few background pulses due to this source were recorded.

An important problem which was encountered in

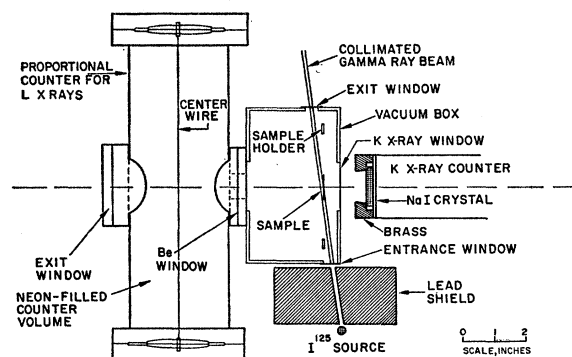


FIG. 1. Counter arrangement.

* Work done under the auspices of the U. S. Atomic Energy Commission.

¹ R. C. Jopson, Hans Mark, C. D. Swift, and M. A. Williamson, *Phys. Rev.* **131**, 1165 (1963).

² K. Hohmuth, G. Muller, and S. Schintmeister, *Nucl. Phys.* **48**, 209 (1963).

using proportional counters in these experiments is the time delay between the ionization caused by the x ray in the counter volume and the appearance of the electrical signal at the center wire. The time distribution of the pulses in the proportional counter was measured with a time-to-height converter connected to a pulse-height analyzer. The arrival time of the K x ray in the scintillation counter was employed as a trigger signal. With the neon-methane mixture under normal operating conditions, the longest delay times observed were about $1.25 \mu\text{sec}$. The resolving time of the coincidence circuit was set at $2.5 \mu\text{sec}$ to insure that no real coincidence events are lost. Argon and xenon mixed with methane were also considered as counter gases. Argon was ruled out because its K edge is at 3.203 keV , which is just in the middle of the energy region of the L x rays considered here. In some preliminary experiments, it was discovered that this led to some difficulties, probably caused by differential absorption effects. Xenon was found to be unsuitable because much longer delay times were measured when it was used as a counter gas. The efficiency of the neon counter was calculated using mass-absorption coefficients listed in Ref. 3. An appropriately weighted average of the prominent L x-ray components (L_{α_1} , L_{α_2} , L_{β_1} , L_{β_2} , and L_{γ_1}) was used for the x-ray energy.⁴ The relative intensity measurements of the L x-ray components were made using silver targets and electron bombardment to ionize the L shell. These intensity ratios are somewhat different from those expected if only the L_{II} and L_{III} shells are ionized as in the present experiments. However, in view of Coster-Kronig transitions, over 95% of the transitions go to the L_{II} and L_{III} shells in the electron bombardment experiments. The L_{II} to L_{III} vacancy ratios are also roughly the same in each case $L_{II}:L_{III} = 1:2$. Therefore, the experimental intensity ratios for this region of the periodic table quoted in Ref. 4 were used ($L_{\alpha_1}:L_{\alpha_2}:L_{\beta_1}:L_{\beta_2}:L_{\gamma_1} \approx 100:9:49:12:5$). The efficiency values resulting from this calculation are listed in Table I. The efficiency computation was checked by remeasuring ω_{KL} for dysprosium which was previously determined using scintillation counters.¹ The results obtained were in good agreement with each other. The efficiency calculations made in this way were accurate to $\pm 5\%$ for all the elements studied.

All the target materials used in these experiments were prepared in the form of thin metallic foils. The impurity content was less than 0.1% in all cases. No oxide targets of the type described in Ref. 1 were employed in these experiments. The targets ranged in thickness from 0.5 – 3.0 mg/cm^2 . A very important factor which had to be computed for each target was the self-absorption of L x rays in the foil. This is necessary to obtain one term of the transmission factor A_L in Eq. (1).

³ Rosemary T. McGinnies, Natl. Bur. Std. (U. S.) Circ. No. 583 (1959); Norelco Reporter, May–June 1962 (unpublished).

⁴ L. G. Parratt, Phys. Rev. 54, 99 (1938).

TABLE I. Transmission and efficiency factors to be used in Eq. (1).

Element	Target thickness (mg/cm ²)	L x-ray transmission factor in target foil	L x-ray transmission factor in Be counter window	Efficiency of neon counter
Zirconium	1.88	0.538	0.170	0.989
Niobium	1.91	0.539	0.235	0.975
Palladium	2.00	0.609	0.544	0.919
Silver	0.47	0.884	0.605	0.888
	1.10	0.769	0.605	0.888
	2.88	0.519	0.605	0.888
Cadmium	1.50	0.719	0.680	0.849
	2.80	0.533	0.680	0.849
Indium	2.19	0.634	0.704	0.808
Tin	2.40	0.635	0.730	0.761
Antimony	2.10	0.671	0.755	0.711

The intensities of the five most prominent L x-ray lines were estimated using the same procedure outlined in the description of the counter efficiency calculation. The average energy of the L x rays was calculated using these intensities as a weighting factor. The mass-absorption coefficients near the L shell of these elements for the average x-ray energies were taken from a number of standard sources.³ To estimate the appropriate coefficients, an "average curve" of the L -absorption edge for each of the elements was drawn using the available data. The computation of the self-absorption included the fact that K -shell ionizations were not uniformly distributed throughout the foil. The I^{125} x rays are incident on the foil at a relatively small angle (see Fig. 1) so that the effective thickness of the target foil may be quite large. The effect of source x-ray absorption in the foil was as high as 4% in some cases. In addition to estimating the mass-absorption coefficients of the materials the foil thickness also had to be determined. This was done by weighing the foils with a good chemical balance and was confirmed in the case of one of the thicker foils by measuring the energy loss of Am^{241} α particles in passing through the foil. The absorption coefficient and the thickness were both determined to $\pm 10\%$ so that the values of the self-absorption listed in Table I are accurate to roughly $\pm 15\%$. The estimate of the self-absorption in the foil was checked by measuring ω_{KL} for several targets of differing thicknesses. The results are shown in Table II. The measurements are

TABLE II. Target thickness effects on ω_{KL} measurements.

Element	Target foil thickness (mg/cm ²)	ω_{KL}
Silver	0.47	0.0554
	1.10	0.0533
	2.88	0.0543
	Cd ¹⁰⁹ source	0.0570
Cadmium	1.50	0.0548
	2.80	0.0553

in good agreement with each other indicating that the calculations are reliable. Unfortunately it was not possible to perform these measurements for all the targets used in these experiments because of the difficulties encountered in making target foils with controlled thicknesses. Thus a rather large error in estimating the self-absorption is unavoidable.

Another factor which had to be included in the calculation of the transmission factor A_L is the absorption coefficient for the L x rays in the 5-mil beryllium window. The intensities of the various components of the L x rays were assumed to be the same as those employed in the calculation of the self-absorption of the foil. It was found that the modification of the relative intensities by the self-absorption in the target foil could be safely ignored in computing the beryllium window absorption. Table I also shows the transmission factors for beryllium used for each of the targets. The attenuation in a 5-mil beryllium window of silver characteristic x rays emitted by a Cd^{109} source was measured and the result was found to be in good agreement with the calculated value. The calculated beryllium transmission factors are accurate to $\pm 5\%$ for the heavier elements. For the lighter elements, the calculations are much less reliable because of the large attenuation in the window. For zirconium, the calculation of the beryllium absorption is accurate to about $\pm 15\%$.

Using the geometry shown in Fig. 1, the observed K x-ray counting rate was between 1500 and 15 000 counts per minute and a coincidence rate of between $\frac{1}{10}$ and 1 count per minute. To obtain more than 1000 coincidences in each case, running times of the order of 50–150 h were required. This was done to keep the statistical deviation below 3%. Indium, tin, and antimony required much longer runs than the other materials because their K -absorption edges are above the energies of the K_α x rays emitted by the I^{125} source. Thus the ionizations can only be produced by the K_β x rays from the source so that the counting rates observed were roughly one-quarter of those obtained for cadmium and

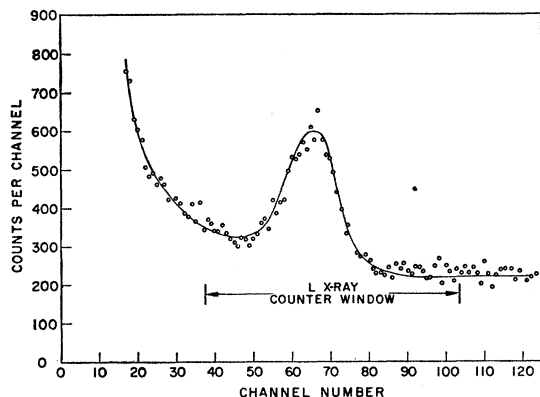


FIG. 2. Cadmium L x rays observed with proportional counter (2.88-mg/cm^2 Cd target).

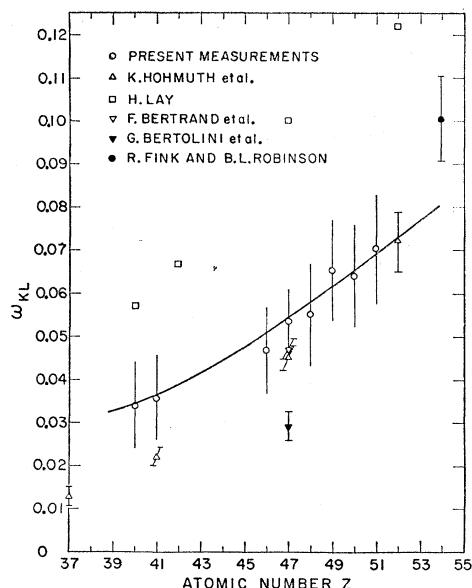
the other, lower Z elements. In order to insure that the counting components of the system remain stable over the long periods required for one experiment, the whole system was installed in a temperature controlled box. The solid angle subtended by the L counter was calculated assuming that the foil was a point source. This approximation is valid because the distance from the L counter to the foil is much larger than the dimension of the target foil itself. The geometry calculation was accurate to $\pm 5\%$. Since it is not necessary to know the K -counter geometry, the counting rate was made as large as possible by placing the K counter as close to the foil as possible. The pulse-height spectrum of cadmium L x rays observed with the proportional counter is shown in Fig. 2. The electronic window used in the coincidence experiment is also indicated in the figure. It can be seen that the window is quite wide. The reason for this is that it is necessary to make certain that all the pulses due to L x rays are counted if Eq. (1) is to be used to compute ω_{KL} . Fortunately, the high background rate does not affect the result other than to slightly change the random coincidence rate which must be subtracted from the observed coincidence rate.

In order to calculate the background corrections for the coincidence counting rate N_C and the K x-ray counting rate N_K , two background runs were made for each foil. One background run was made with no foil in place. The counting rates observed were used to determine the background from cosmic rays and local radiation near the counter. Another background measurement was made with a 10.8-mg/cm^2 Cu foil mounted on the target holder. The data from this background run were used to determine the background contributions to the counting rates from all causes other than K -shell ionization. Among these are Compton scattering and a number of smaller effects. For tin, antimony, and indium, the measured K x-ray background is less than 4%, and it is observed to be less than 1% for the other five elements. The real (i.e., cosmic rays, etc.) coincidence background measured was less than 3% in all cases. The random coincidence rate was of the order of 15% for the two lowest Z elements and 3% for the six highest Z elements studied in these experiments.

Another interesting result shown in Table II is the value of ω_{KL} obtained using a Cd^{109} source. In this case, the K shell of silver is ionized by the electron capture decay of Cd^{109} and also the possible K conversion of the 88-keV metastable (39.2-sec) level in the decay product Ag^{109} . The coincidence measurements between L and K x rays can be performed just as in the case of photoelectric ionization and the resulting value of ω_{KL} is in reasonably good agreement with those obtained by the other method.

3. DISCUSSION OF RESULTS

The results obtained in this series of measurements are shown in Fig. 3. Other measurements which have

FIG. 3. ω_{KL} as a function of Z .

been made previously are also shown and all these values are given numerically in Table II. When comparing measurements of various L -shell fluorescence yields, care must be taken to make certain that the same average L -shell yields are used. It has already been pointed out¹ that ω_{KL} is a linear combination of the L_{II} and L_{III} subshell fluorescence yields $\omega_{L_{II}}$ and $\omega_{L_{III}}$. The coefficients of the linear combination are determined by the ratio of the number of primary vacancies in the L_{II} and L_{III} shells. Assuming that there are no radiationless (Coster-Kronig) transitions between the L_{II} and L_{III} shell, the ratio of primary vacancies is one to two, reflecting the fact that there are twice as many transitions from the L_{III} shell as from the L_{II} shell in filling a K -shell vacancy. Thus,

$$\omega_{KL} \approx 0.33\omega_{L_{II}} + 0.67\omega_{L_{III}}. \quad (2)$$

When other methods are employed to create the primary L -shell vacancies, the ratios may be quite different. The number of primary vacancies, $n_1:n_2:n_3$, are shown in Table III next to the quoted "average"

TABLE III. Summary of results.

Element	Z	ω_{KL}	$\bar{\omega}_L$ (Lay) ($n_1:n_2:n_3=1:2:3$)	Other measurements of $\bar{\omega}_L$
Zirconium	40	0.034 ± 0.010	0.057	
Niobium	41	0.036 ± 0.010		$0.022(\omega_{KL})^a$
Palladium	46	0.047 ± 0.010		
Silver	47	0.054 ± 0.007	0.100	$0.045 \pm 0.003(1:1.8:2.8)^a$ $0.047 \pm 0.002(1:2:3)^b$ $0.029 \pm 0.003(1:1.8:2.8)^c$
Cadmium	48	0.055 ± 0.012		
Indium	49	0.065 ± 0.012		
Tin	50	0.064 ± 0.012		
Antimony	51	0.070 ± 0.013	0.119	

^a Reference 2.^b F. Bertrand, G. Charpak, and F. Suzor, J. Phys. Radium 20, 462, 956 (1959).^c Reference 8.

L -shell fluorescence yields $\bar{\omega}_L$. In this region of the periodic table, $\omega_{L_{II}}$ and $\omega_{L_{III}}$ should be quite close together⁵ in value because the binding energies of the L_{II} and the L_{III} shells differ by less than they do at higher values of Z . The same is not true of ω_{L_I} since this subshell is relatively more tightly bound as Z is decreased. Thus, ω_{L_I} should stay substantially larger than $\omega_{L_{II}}$ and $\omega_{L_{III}}$ (and hence ω_{KL}) over the range of Z values covered by these experiments. Therefore, if an average fluorescence yield $\bar{\omega}_L$ is measured for which there are a substantial number of vacancies in the L_I shell, it should always be larger than ω_{KL} . The existence of Coster-Kronig transitions modifies this conclusion because some of the L_I shell vacancies can be moved to the L_{III} shell. For $Z < 50$, Coster-Kronig transitions $L_I \rightarrow L_{III}(M_{IV,V})$ are energetically possible⁶ and these tend to change the vacancy ratio in such a way that L_{III} shell vacancies are increased at the expense of L_I shell vacancies. The net effect of these Coster-Kronig transitions is to bring the numerical value of $\bar{\omega}_L$ closer to ω_{KL} . However, $\bar{\omega}_L$ will always be somewhat larger than ω_{KL} unless the Coster-Kronig yield, $f_{L_I L_{III}}$, is unity, in which case the two fluorescence yields $\bar{\omega}_L$ and ω_{KL} will be equal.

Unfortunately, no conclusions can be drawn from the comparison in Table III which are consistent with the ideas outlined in the previous paragraph. The average fluorescence yields measured by Lay⁷ are very much larger than the ω_{KL} values given in the present work. (The error limit on Lay's numbers is $\pm 10\%$.) The difference is so large that it is very unlikely that it can be explained in terms of Coster-Kronig transitions. In the case of more recent measurements, the situation is equally confusing. The measurements of Hohmuth *et al.*² are smaller in the region of $Z=40$ and are in reasonably good agreement around $Z=50$. The values for silver ($Z=47$) given in Refs. 7 and 8 differ substantially and, in view of the present measurement, it is probable that the number given in Ref. 8 is too small.

The estimated standard errors given for the values of ω_{KL} in Table III are quite large. The primary error source is the uncertainty introduced in the computation of A_L and E_L as described in Sec. 2. The efficiency of the counter E_L can be computed to $\pm 5\%$ for the heaviest elements in the series. The calculation for the lighter elements is actually somewhat more accurate because the efficiency is larger. The reverse is true for the transmission factor A_L . This quantity is most accurately ($\pm 16\%$) known for the heavier elements because the L x-ray energy is largest for these cases. This means that the transmission factors are large and

⁵ R. C. Jopson, J. M. Khan, Hans Mark, C. D. Swift, and M. A. Williamson, Phys. Rev. 133, A381 (1964).⁶ A. H. Wapstra, G. J. Nijgh, and R. Van Lieshout, *Nuclear Spectroscopy Tables* (North-Holland Publishing Company, Amsterdam, 1959).⁷ H. Lay, Z. Physik 91, 533 (1935).⁸ G. Bertolini, A. Bisi, E. Lazarrini, and L. Zappa, Nuovo Cimento 11, 539 (1954).

therefore easy to estimate with reasonable accuracy. In the case of the lighter elements considered, the errors in the computation of the transmission factors may be as large as $\pm 25\%$. Statistical counting errors and systematic errors introduced in the background subtraction procedure constitute another 5%. The cumulative standard errors quoted in Table III were computed in the usual manner assuming that the errors from each of the sources listed are statistically independent. They range from about $\pm 20\%$ in the heavy elements to $\pm 30\%$ in the lighter ones. The error quoted for the silver measurement is smaller because many measurements were made in this case with differing thicknesses. In addition, the results obtained using the Cd^{109} source were included in calculating the final ω_{KL} value for silver. In spite of the large experimental uncertainties, the comparison with previous measurements is meaningful since many of the other measurements differ from the present results (and from each other) by more than the quoted errors. In any event, it is safe to say that

some of the error estimates on previous measurements may have been optimistic. Furthermore, there is also little question that more accurate measurements of fluorescence yields would be desirable.

The behavior of ω_{KL} as a function of Z is in good accord with theoretical expectations.⁹ The magnitude of ω_{KL} should decrease slowly as a function of Z . In this region of the periodic table the change in ω_{KL} as a function of Z is considerably smaller than in the region considered in Ref. 1. This is not surprising, because the change in quantum energy of the L x rays as a function of Z is smaller in this region than for higher values of Z .

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⁹ M. A. Listengarten, *Izv. Akad. Nauk SSSR Ser. Fiz.* **24**, 1041 (1960); **25**, 792 (1962); **26**, 182 (1962).

Double Excitation of Helium by Electron Impact

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This study is devoted to the theory and calculation of cross sections for the electron-impact excitation of doubly-excited states in helium which are stable to autoionization. The cross sections are found to exhibit sharp peaks just above the threshold energies for excitation and to decrease rapidly with further increase of energy. The maximum value of the Born-Oppenheimer cross section for excitation of the $(2p)^2\ ^3P_o$ state is about 6×10^{-4} (a_o)² and occurs at approximately 11 eV above threshold. The cross sections for excitation of the $2p3p\ ^1P_o$, $2p3d\ ^3D_u$, and $2p3d\ ^1D_u$ states are all less than 35 b. The cross section for the $(2p)^2\ ^3P_o$ state has been calculated according to the Born-Oppenheimer, distorted-wave, and two-state strong-coupling approximations. In all of these cases the maximum amplitude of the scattered beam occurs at right angles to the direction of the incident electrons. The cross sections of the potential-and-exchange-distortion method (DEW) and of the complete two-state strong-coupling approximation are virtually identical. The Born-Oppenheimer approximation produces remarkably similar results. Rigorous upper bounds to the energies of the $2p3p\ ^1P_o$, $2p3d\ ^3D_u$, and $2p3d\ ^1D_u$ states of helium are reported. Finally, the cross sections are calculated in Born-Oppenheimer approximation for electron-impact excitation of the $(1s)^2(2p)^2\ ^3P_o$ and $(1s)^22p3p\ ^3P_o$ states of beryllium. The peak values of these cross sections are $12(a_o)^2$ and $2(a_o)^2$, respectively.

I. INTRODUCTION

ALTHOUGH there is considerable evidence of discrete atomic states with energies which lie within the continuum for single ionization, until very recently little attention had been directed to the properties of these states. Indeed, their very existence often comes as a surprise to those who have been schooled in the doctrine that beyond the ionization potential all is chaos. The persistence of such highly energetic states for periods of as much as a microsecond

invariably can be traced to the selection rules for autoionization, that is, the selection rules for the internal conversion process whereby an electron is shed from the atom. Our own interest in these states has grown from an initial conjecture that they may be involved in the formation of the diatomic ions HeA^+ and NeXe^+ . Thus, Munson *et al.*¹ have reported appearance potentials for these ions which lie above the lowest ionization potential of A and Xe, but below the lowest excited states of He and Ne, respectively. While it is certainly possible that the helium and neon negative

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¹ M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.* **67**, 1 (1963).