these triplets, as calculated from these measurements, is 2.68 Mev and 2.66 Mev. This agrees with the 2.68 Mev gamma-ray from $Na^{24} \rightarrow Mg^{24}$ reported in the preceding paper. Momentum relations check well except for the x-component of triplet No. 2. In this case the discrepancy is about 4 percent of the total momentum and represents a not impossible experimental error.

In these studies two triplets were observed while 56 pairs were observed. The probability of ordinary pair production in the field of a nucleus is proportional to Z^2. Since a triplet is formed in the field of an electron the probability of triplet production in an atom should be proportional to Z, the number of electrons present in the atom. Thus the ratio of triplets to ordinary pairs observed should be of the order of $1/Z$. This should hold approximately at high energy but not near the threshold for the processes, since one threshold is at 2 mc^2 and the other at 4 mc^2. However, if it is assumed that, near the threshold, the shape of the triplet production curve is similar to the pair production curve, the relative probability of the two processes at low energy can be estimated roughly. The pair production probability at 2.7 Mev (5.3 mc^2), as given by Heitler is 0.79 in units of $Z^2r_0^2/137$. 5.3 mc^2 is 1.3 mc^2 above the threshold for triplet production. The pair probability at 1.3 mc^2 above the pair threshold is 0.225 in the same units as above. By assuming that this probability also applies to triplet formation at 1.3 mc^2 above the triplet threshold, the ratio of triplet production to pair production is 0.225/0.79 or 1/3.5. Since the triplets and pairs observed were formed in air in a cloud chamber, the above ratio must be reduced by $1/Z$, which for air is about 1/7.2. Thus, the ratio becomes 1/25. The observed ratio of 1/28 is in much better agreement with the estimated ratio than should be expected when so few triplets are observed.

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Atomic Distribution Function of Liquid Argon

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An atomic distribution curve for a simple monatomic liquid, such as argon, is generally characterized by a prominent first peak. This peak may be used to determine the elements of the first coordination shell, i.e., the radius of the shell and the number of nearest neighbors of an atom. Frequently this peak can be closely approximated by a simple polynomial involving a parameter σ. This parameter may be determined empirically by a process of fitting. In the case of liquid argon, where the force function between the atoms is known, it is possible to make a theoretical determination of σ provided the elements of the first coordination shell are given. This has been done for liquid argon at a temperature of 91.8°K and under a pressure of 1.8 atmos. The theoretical value of σ is compared with various empirical values obtained from the experimental distribution curve for liquid argon under these conditions as given by Eisenstein and Gingrich. It is found that the theoretical value is somewhat smaller than the empirical value of σ obtained by fitting and slightly larger than that obtained by the Coulson-Rushbrooke method. A possible interpretation of these results is given.

INTRODUCTION

ATOMIC distribution curves for liquid argon over a considerable range of temperatures and pressures have been obtained by Eisenstein and Gingrich[1] by an analysis of x-ray diffraction patterns of the liquid. Previous to this work, Rushbrooke[2] calculated the first peak of the distribution curve for liquid argon at 90°K by use of a general expression for liquid distribution

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[2] G. S. Rushbrooke, Proc. Roy. Soc. Edinburgh **60**, 182 (1940); J. G. Kirkwood and E. M. Boggs, J. Chem. Phys. **10**, 394 (1942).

functions derived by Coulson and Rushbrooke[3] and based upon the Lennard-Jones and Devonshire[4] cell model of liquids. In his paper[2] Rushbrooke showed that the polynomial expression given by Wall[5] for a distribution peak was in "quite remarkably close agreement" with his own calculated peak.

A comparison of Rushbrooke's theoretical peak with the Eisenstein and Gingrich experimental peak for liquid argon at approximately the same temperature and density shows that, although the two peaks have about the same shape, there is little agreement as to size and position. This is to be expected since Rushbrooke assumed N_1, the first coordination number, to be 12 as in the solid state, whereas Eisenstein and Gingrich found N_1 to be approximately 7. Also R_1, the radius of the first coordination shell, was taken as 4.077A by Rushbrooke, whereas Eisenstein and Gingrich found $R_1=3.8$A approximately.

It has been found that the polynomial expression closely approximates the first experimental peak for several different liquids.[5,6] It also appears to fit the Rushbrooke theoretical peak for liquid argon. The weakness of the polynomial expression lies in the fact that it involves a parameter σ which, heretofore, has had to be determined empirically. The purpose of this paper is to show how this parameter may be determined theoretically, and to give the results of such determination both for the hypothetical structure of liquid argon used by Rushbrooke and for the observed structure given by Eisenstein and Gingrich.

THEORETICAL DETERMINATION OF σ

The liquid distribution formula for a single peak, e.g., the first, given by Coulson and Rushbrooke[3] is

$$4\pi r\rho_1(r)=\frac{4\pi^2N_1}{R_1v^2}\int_0^\infty r_1e^{-\bar{\phi}/KT}\times\left[2r\psi(\infty)-\int_{|R_1-r_1|}^{|R_1+r_1|}\psi(|r-x|)dx\right]dr_1, \quad (1)$$

where

$$v=4\pi\int_0^\infty s^2e^{-\bar{\phi}/KT}ds, \quad (2)$$

$$\psi(r)=\int_0^r se^{-\bar{\phi}/KT}ds, \quad (3)$$

and N_1 and R_1 are respectively the number of atoms in and the radius of the first coordination shell of atoms. $\rho_1(r)$ is the density of atoms contributed by the first shell and $\bar{\phi}$ is the average potential energy of an atom as a function of its distance s from the center of its cell. For liquid argon $\bar{\phi}(s)$, as given by Lennard-Jones and Devonshire and modified by Corner,[7] is

$$\bar{\phi}(s)=\frac{N_1a}{2s}\left[\frac{\lambda}{(n-2)a^n}\left\{\left(1-\frac{s}{a}\right)^{-n+2}-\left(1+\frac{s}{a}\right)^{-n+2}\right\}-\frac{\mu}{(m-2)a^m}\left\{\left(1-\frac{s}{a}\right)^{-m+2}-\left(1+\frac{s}{a}\right)^{-m+2}\right\}\right]-C, \quad (4)$$

where $a\equiv R_1$, $\lambda=5.43\times10^{-99}$, $\mu=11.1\times10^{-59}$, $n=11.4$, $m=6$, and C is chosen so that $\bar{\phi}(0)=0$. All quantities in Eq. (4) are expressed in c.g.s. units. By use of Eqs. (1)–(4) it is clear that $\rho_1(r)$ may be determined provided N_1 and R_1 are given.

Wall's polynomial expression for $\rho_1(r)$ is a special case of Eq. (1) in which $\bar{\phi}=0$ for $s\leqq\sigma$, and $\bar{\phi}=\infty$ for $s>\sigma$, where σ is an unknown parameter. Equation (1), in this case, reduces to

$$y_1\equiv4\pi r\rho_1(r,\sigma)=\frac{3N_1}{5\sigma R_1}\left\{1-\frac{5(R_1-r)}{4\sigma^2}\times\left[1-\frac{|R_1-r|}{2\sigma}+\frac{|R_1-r|^3}{40\sigma^3}\right]\right\}, \quad (5)$$

for $|R_1-r|\leqq2\sigma$. Outside of this interval $\rho_1(r,\sigma)=0$. From the manner in which σ is defined, it is evident that its determination enables one to make an estimate of the free volume of the liquid. σ may be determined empirically by the process of fitting the right hand member of Eq. (5) to a given experimental liquid distribution peak.

There is, however, a theoretical method of determining σ which does not involve the use of

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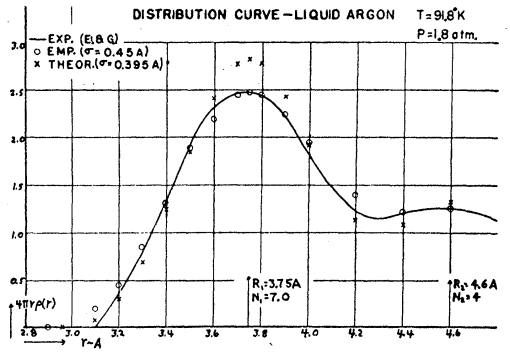

FIG. 1. The experimental distribution curve for liquid argon at a temperature of 91.8°K and a pressure of 1.8 atmos. Empirical and theoretical values of $4\pi r\rho(r)$ for various values of r are also shown for purposes of comparison.

Eq. (5) and which clearly reveals the significance of this parameter. It is evident that the procedure followed in obtaining Eq. (5) from Eq. (1) amounts to replacing the Lennard-Jones and Devonshire potential function for an atom in its cell by the simple but discontinuous function,

$$\bar{\phi}(s,\sigma)=\begin{cases}0 & \text{for } s\leqq\sigma\\ \infty & \text{for } s>\sigma\end{cases}. \tag{6}$$

This function defines a spherical cell of definite radius σ. Its precise relation to the Lennard-Jones and Devonshire function $\bar{\phi}(s)$ given in Eq. (4) is the crux of the matter. It seems reasonable to assume in this case that $\bar{\phi}(s,\sigma)$ must be so chosen that it yields the same average value of s as does the Lennard-Jones and Devonshire function. In other words, the average displacement of an atom from the center of its cell for the two potential functions should be the same. This leads at once to the relation,

$$\tfrac{3}{4}\sigma=\frac{\int_0^\infty s^3 e^{-\bar{\phi}(s)/KT}ds}{\int_0^\infty s^2 e^{-\bar{\phi}/KT}ds}. \tag{7}$$

The left member of Eq. (7) is just the average value of s for $\bar{\phi}(s,\sigma)$ while the right member is that for $\bar{\phi}(s)$. Once the function $\bar{\phi}(s)$ is given, the corresponding value of σ may be determined for any temperature T by means of Eq. (7).

RESULTS

The value of σ has been computed by means of Eqs. (4) and (7) for the case of liquid argon considered by Rushbrooke. The value obtained, *viz.*, $0.140R_1$ compares very favorably with the value, 0.141 R_1, given by Rushbrooke on the basis of matching maxima. This close agreement between the two values of σ makes it worth while to apply this method to another case of liquid argon experimentally studied by Eisenstein and Gingrich.

Distribution curve No. 2 for liquid argon in the paper of Eisenstein and Gingrich[1] was chosen for analysis, first, because the conditions of temperature and density were nearly the same as those postulated by Rushbrooke, and second, because Eisenstein and Gingrich state that they were especially careful in the determination of this curve. The forepart of this curve consisting of the first two peaks is shown in Fig. 1. It should be noted that $y\equiv 4\pi r\rho(r)$ is plotted against r since it is this function, rather than $4\pi r^2\rho(r)$, which is symmetrical about its maxima according to the Lennard-Jones and Devonshire liquid model.[3]

In order to compute σ for this case of liquid argon we make use of Eqs. (4) and (7) with the corresponding values of the constants for argon. The temperature is 91.8°K. The two parameters, N_1 and $R_1\equiv a$, are not given by theory but may be obtained from the experimental curve. We take $N_1=7.0$ and $R_1=3.75$A. The two integrals in Eq. (7) are evaluated by numerical integration by use of the Euler-Maclaurin formula. In this computation $x\equiv s/a$ is used as the argument and the integrands in Eq. (7) are tabulated for values of x running from 0 to 0.25 in steps of 0.01. At $x=0.21$ both integrands become negligibly small. A graph showing $\bar{\phi}/KT$ as a function of x for the state of liquid argon under consideration is given in Fig. 2. The net result of the computation gives a value of σ equal to 0.395A. By inspection of Table I it may be seen that this theoretical value compares very favorably with the various empirical estimates of σ made by direct analysis of the experimental curve.

The four empirical methods of obtaining the values of σ shown in Table I may be described as follows. In method one[5] the right-hand member

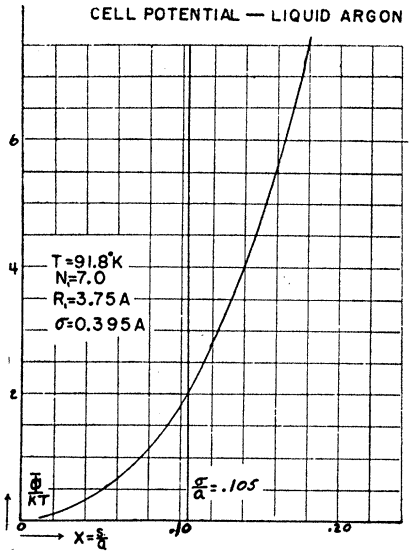

FIG. 2. $\bar{\phi}/KT$ as a function of s/a for liquid argon at a temperature of 91.8°K and a pressure of 1.8 atmos.

of Eq. (5) is fitted to the forepart of the first peak in the experimental curve. In method two[2] the maximum value of y_1, in Eq. (5), i.e., $3N_1/5\sigma R_1$, is made equal to the maximum ordinate of the first peak in the experimental curve. In method three one determines the half-width of the first peak for $y_1=\frac{11}{32}y_1(\max)$. This half-width just equals σ as is evident by inspection of Eq. (5). Method four, developed by Coulson and Rushbrooke,[3] requires a knowledge of R_1, R_2, $y_1(\max.)$ and $y_2(\max.)$ as well as the density of the liquid. Details of this method are given in their paper.

It will be observed from Table I that the first three empirical methods give values of $\sigma(\leqq 0.45\text{A})$ which are practically identical. It will also be observed from Fig. 1 that this value, when used in Eq. (5), reproduces the experimental curve very well. The theoretical value of $\sigma(=0.395\text{A})$ does not produce such a good fit nor does the empirical value of $\sigma(=0.37\text{A})$ given by method four. It is interesting to note, however, that these latter two values are fairly close together.

Whether or not the differences between the various values of σ are significant is difficult to determine. Perhaps two comments are in order on this score. In the first place, the theoretically computed value of σ is very sensitive to small changes in $R_1\equiv a$, since high powers of this quantity enter in the expression for $\bar{\phi}(s)$. Also, in computing σ, only the atoms in the first shell are considered. The effect of atoms outside this shell would tend to increase the value of σ slightly but probably not enough to raise its value to 0.45A.

In the second place, it has been tacitly assumed in this work that there exists a definite equilibrium distance R_1 for the atoms in liquid argon corresponding to a definite number of nearest neighbors N_1. This is not likely to be the case. One would certainly expect some spread in the values of R_1 and N_1. If there is a significant spread in values of R_1, then one would expect the first three empirical methods of determining σ to include this spread, whereas the theoretical method and also empirical method four would not include this spread. Hence, one would expect to get somewhat larger values of σ in the former three cases than in the latter two cases, the difference being dependent upon the spread in R_1 values.

TABLE I. σ for liquid argon ($T=91.8$°K, $P=1.8$ atmos.).

Method	σ in A	R_1 in A	y_1 (max.)	N_1	R_2 in A	y_2 (max.)
1 (emp.)	0.45	3.75	2.48			
2 (emp.)	0.45	3.75	2.48	7.0		
3 (emp.)	0.44	3.75	2.48			
4 (emp.)	0.37	3.75	2.48		4.62	1.26
5 (theor.)	0.395	3.75		7.0		