Daunt, unlike the other two theories, predicts a negative heat of mixing. In this case the He^3 component is degenerate in the pure state as well as in a mixture while the He^4 component, which is degenerate in the pure state, becomes nondegenerate (except for very low temperatures) in solution. For this case we have

$$\Delta U=\frac{3}{2}N_4kT\left\{1-0.514\left(\frac{T}{T_0}\right)^{\frac{3}{2}}-0.462\left(\frac{T_\lambda}{T}\right)^{\frac{3}{2}}-0.0225\left(\frac{T_\lambda}{T}\right)^{3}-\cdots\right\}-\frac{2}{5}\pi\left(\frac{3}{4\pi}\right)^{\frac{3}{3}}\frac{v_4^0}{v_3^0}N_4kT^*, \quad (4)$$

where T^* is the degeneracy temperature in the pure He^3 case. From Eq. (4) we can obtain the temperature at which the heat of mixing changes sign. If the observed temperature variation of ΔU for dilute and concentrated solutions turns out to be similar in character to that predicted in Eqs. (2a), (2b), and (4), the relevance of statistics to the problem of liquid helium would be more firmly established.

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Range Measurement of Low-Voltage Electrons*†‡

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Determinations of the ranges of electrons between the energies of 600 and 2000 volts are difficult to perform since the short ranges of the particles cannot be detected by the usual physical methods. A biologically active molecule such as an enzyme can be used as detector in this energy region, the amount of inactivation in uniform layers of the enzyme being a function of the range of the electron. The ranges of the very low energy electrons determined in this manner were found to be considerably less than those predicted by the Bethe formula for energy loss if no allowance for scattering and straggling is made. If about 40 percent loss of range due to this is assumed, then theory and experiment are in fair agreement. Alternatively, a constant correction of 100A to be subtracted from the calculated range brings theory and experiment into agreement.

INTRODUCTION

THE measurement of the ranges of electrons in solids is difficult due to the statistical fluctuation of energy loss and to the multiple scattering which electrons suffer in each collision. In the low-energy region, between 600 and 2000 volts, the ranges of electrons are so small that the usual physical methods of measurement are not applicable. The use of absorbing foils is no longer feasible; the ranges are also too small to allow use of cloud chamber methods to any degree of accuracy even at 2000 volts. Since the use of low-voltage electrons as penetration probes into various kinds of structure is attractive, an experimental determination of the range of low-voltage electrons in solid material is of interest. The quantum-mechanical theory of energy loss as developed by Bethe[1] using the Born approximation assumes the interaction between the incident electron and the nucleus of the absorber atom to be weak and the probability of an electron undergoing more than one scattering process while traversing this field to be infinitely small. However, when the velocity of the particle is such that these conditions no longer hold, higher-order approximations to the solution must be used. The transition from the region where the theory of energy loss, as developed by Bethe, holds to regions where it is no longer applicable will be gradual.

In the low-energy region, the high sensitivity of biological materials to radiation can be utilized as a means of detection of the ranges of the electrons. In the present experiment, a layer of an enzyme of thickness greater than the range of the incident electrons was used as an absorber. When a uniform layer of the dry enzyme is irradiated with a sufficiently large number of electrons, all the enzyme molecules within the range of the electrons are inactivated; the enzyme beyond the range of the electrons is unaffected by the radiation. After irradiation, the material is dissolved off the cover-slip, and assayed for the activity remaining. Since the amount of enzyme originally in the sample is known, the weight of the enzyme equivalent to the fraction inactivated is easily found. The surface area of the enzyme exposed to the electron bombardment is known from the area of the cover-slip; from the

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‡ Assisted by the U. S. Atomic Energy Commission.

[1] H. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, No. 1, p. 491.

amount of the material affected by the radiation, the surface area exposed, and the density of the material, taken as 1.3 g/cm³, the range of the electron is found. Since the range is calculated in the region where additional radiation of a given voltage causes no further inactivation, the range as found by this method is the distance which the electron travels in the forward direction.

EXPERIMENTAL PROCEDURE

The enzyme invertase was used in these experiments because of its stability after drying and exposure to high vacuum, and the high degree of accuracy of the assay. The assay was that of Sumner and Howell.[2] This enzyme catalyzes the hydrolysis of sugar into monosaccharides, and follows first-order reaction kinetics as long as the substrate is in excess. By providing a large excess of sugar and allowing the reaction to proceed over a long period of time, the presence of very small amounts of active enzyme can be detected with high precision. A change in activity of a few percent from a total of five micrograms of material can be measured in this manner. Under the experimental conditions used, range differences of the order of ten angstroms could be detected.

The enzyme, melabiase free, from Nutritional Biochemicals Inc., was dried down from quartz distilled water in 0.05-ml amounts onto stainless steel cover-slips, great care being taken to insure even spreading of the solution over the surface of the cover-slip. Various methods of drying were tried in order to get a uniform layer over the surface. The most consistently uniform results were found when the samples were freeze-dried. A fine crystalline network could be seen on the surface of the cover-slip. The dry samples were irradiated in vacuum (10^{-5} mm Hg pressure) by a simple electron gun consisting of a heated tungsten filament and accelerating grid. The energy of the accelerating potential measured between the filament and the irradiation plate was read on a standardized voltmeter. The amount of irradiation given to the samples in electrons/cm² was measured from the known area of electron beam and from the product of the electron current picked up on the irradiation plate times the time of irradiation. The samples dried down on the stainless steel cover-slips were placed on a metal bombardment plate in the irradiation chamber and exposed to the electrons by successively rotating the samples into the beam.

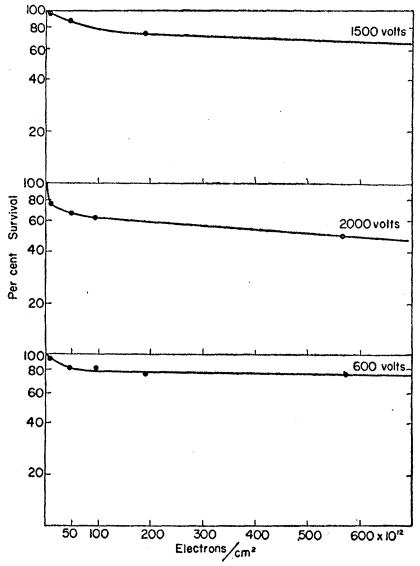

FIG. 1. Logarithm of surviving activity of invertase as a function of electrons/cm² and electron energy.

EXPERIMENTAL RESULTS

The fraction of the enzyme surviving the irradiation was investigated as a function of the number of electrons incident. Two distinct regions are apparent in the resulting curves (see Fig. 1). The initial slope is due to the inactivation of the enzyme within the range of the electrons; this trails off into a region which becomes nearly horizontal when all the molecules within the range of the electrons have been inactivated. The slight slope of this horizontal portion is presumably due to inhomogeneities in the invertase layer and to photons generated by the electron beam. The fraction which is not affected directly by the electrons can be found by extrapolating the almost horizontal part back to zero dose; this is equal to that portion of the enzyme beyond the range of the electron. From the amount inactivated, the range can be calculated by the method explained above.

Ranges were determined in this manner for electrons of energies of 100 to 2000 volts. Five micrograms of enzyme were irradiated in the 600-volt sample while 50 micrograms were used in the 1500- and 2000-volt determinations. A greater amount of scatter was found in the data at the higher energies when large amounts of enzyme were dried down on the cover-slips.

Figure 2 shows the results of the range measurements plotted against energy; the dotted line represents the ranges as calculated by Lea[3] from the Bethe theory of energy loss, assuming the validity of the extrapolation of the expression down to low energies. The values have been corrected for ranges in material of the density of protein. The constant range found experimentally from 100 to 600 volts represents the thickness of one invertase molecule. The smallest unit which can be affected corresponds to the single molecule, 90A thick. Deuteron and high-energy electron data on invertase[4] have shown the sensitive unit to be a cylinder of radius of 24A and length 83A; this corre-

[2] J. B. Sumner and S. F. Howell, J. Biol. Chem. **108**, 58 (1935).

[3] D. E. Lea, *The Action of Radiation on Living Cells* (Cambridge University Press, Cambridge, 1947), p. 23.

[4] Pollard, Powell, and Reaume, Proc. Natl. Acad. Sci. (U.S.) **38**, 173 (1952).

sponds to a molecular weight for the enzyme which is in good agreement with the value found from diffusion experiments. The present data provide further evidence that the single enzyme molecule acts as an active unit of uniform sensitivity throughout. The amount of inactivation remains constant until the incident electron has enough energy to penetrate beyond the top layer of molecules. At 600 volts the measured range of 90A can be compared with 200A, that predicted by theory. At energies greater than 600 volts, the range increases smoothly with energy. As can be seen from Table I, the difference between theory and experiment becomes less pronounced with increased energy; at 1500 and 2000 volts the discrepancy observed is a small fraction of the total range. At lower energies, the distance that the electron travels is less than the figures given by Lea. A large part of this discrepancy is probably due to scattering of the electrons. Williams[5] estimates that the penetration range is less than the path length range by about 40 percent, which would give fair agreement. The constantly decreasing discrepancy shown in the last column of Table I indicates other factors may enter, such as a constant correction the order of 100A which is to be subtracted from the calculated range. This correction could easily be due to failure of the underlying assumptions of the theory at very low electron energies.

TABLE I. Predicted and observed values of ranges of low energy electrons.

Energy of electron (volts)	Range in angstroms		Percent deviation from theory[b] (probably due to scattering)
	Theory (Bethe)	Observed[a]	
600	195	90±10	54
900	350	230±40	34
1200	545	400±80	30
1500	770	620±120	19
2000	1300	1130±225	13

[a] These values were obtained by drawing a smooth curve to fit the data shown in Fig. 2.
[b] The percentage deviation of the experimentally observed values of the range of an electron of a given energy from that predicted by theory decreases with increasing energy.

DISCUSSION

In traversing an absorber, the average electron travels a tortuous path, and it is only a rare particle that penetrates the absorber completely in the forward direction, undeviated from its original direction of motion. The range of initially monoenergetic electrons is not a clearly defined quantity as has been shown by White and Millington[6] in their measurements of the energy distribution of electrons after penetration of mica foils of various thicknesses. For a given initial energy, the number of electrons which emerge after the penetration of a foil of a given thickness steadily decreases as the thickness of the foil increases. A thickness can be found which reduces the number of electrons which penetrates to zero. This thickness is a measure of the true maximum range that is measured in the present experiment. The point where no further inactivation of the enzyme is seen for an increase in electrons incident on the enzyme can be taken as corresponding to the foil thickness that effectively stops all electrons of that energy. It has been shown by Hereford and Swann[7] that the error in range determinations in foil measurements increases with increasing energy due to the greater statistical fluctuation in energy loss per collision with electrons of higher energies.

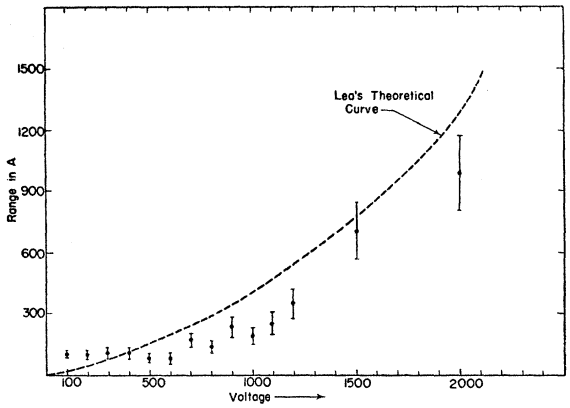

FIG. 2. Experimentally determined ranges of low energy electrons compared with theoretical values calculated by Lea from the Bethe theory of energy loss.

CONCLUSIONS

The values of ranges as determined here represent the distance which the electron travels in the forward direction. If the electron scatters in such a way that the penetration range is about 40 percent less than the path length range, the results are in fair agreement with theory. Alternatively, it may be assumed that a constant correction the order of 100A must be subtracted from the calculated ranges for electrons over 600 ev in energy.

ACKNOWLEDGMENTS

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[5] E. J. Williams, Proc. Roy. Soc. (London) **A130**, 310 (1930).
[6] P. White and G. Millington, Proc. Roy. Soc. (London) **A128**, 701 (1928).
[7] F. L. Hereford and C. P. Swann, Phys. Rev. **78**, 727 (1950).