

FIG. 2. Distribution of the proton and α -particle pulses during the day.

and Table II. The proton flux was constant within statistics throughout the day.

Further experiments are now in progress with high resolution equipment which will be flown at a latitude of 30° N.

TABLE II. Frequencies of pulses vs time.

Time	Frequency of pulses of magnitude greater than 16 times the average proton pulse (pulses/min)	Frequency of proton pulses (pulses/min)
10:30 to 12:20 A.M. 12:20 to 1:20 P.M. 1:20 to 3:30 P.M.	$1.8 \pm 0.13 \\ 2.4 \pm 0.2 \\ 2.6 \pm 0.14$	78 ± 0.8 76.5 ± 1.4 79 ± 0.8

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Non-Equilibrium Thermodynamics of **Two-Fluid Models**

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WO-FLUID models have been proposed for the explanation of the properties of liquid helium II and for superconducting metals.¹ In both cases the existence of two kinds of particles has been assumed: in liquid helium II normal (n) and superfluid (s) atoms, and in superconducting metals normal (n) and superconductive (s) electrons. It is supposed that the "chemical reaction" $n \rightleftharpoons s$ is possible. In these systems occur further the phenomena of heat conduction, diffusion of electrical conduction, and various cross-effects.

The thermodynamics of irreversible processes, based on the Onsager reciprocal relations,² can be used to treat these models mentioned above by means of the general methods, including the entropy balance equation, the phenomenological relations, and the theory of stationary states.³

Among the results for helium⁴ we note a connection between the fountain effect and the mechano-caloric effect. The fountain effect is the pressure difference, $\Delta P,$ which arises in the stationary state when a fixed temperature difference, ΔT , exists between two reservoirs, containing liquid He II, which are connected by a capillary. The mechano-caloric effect is the heat, Q transferred by the unit of mass from one reservoir to the other in the state of fixed ΔP and $\Delta T = 0$ (uniform temperature). An application of

the Onsager relations gives the connection

$$v\Delta P/\Delta T = -O^*/T.$$

Between the two effects (v is the specific volume) we can derive Gorter's relation

$$O^* = -T_x (\partial s / \partial x)_{PT}, \tag{2}$$

(1)

(with x is the fraction of normal atoms and s the specific entropy) as a special case, if we accept the following assumptions, which are generally made for He II: first, immediate "chemical equilibrium" of the reaction $n \rightleftharpoons s$ under all circumstances, and second, only superfluid atoms can pass through a sufficiently narrow capillary.

In a recent work,⁵ I. Prigogine and one of the authors (P. M.) have obtained Gorter's equation of motion for the normal- and the super-fluid, by deriving a new set of "hydrothermodynamical" equations for systems of several components, with the assumption of a negligible transfer of impulse between the components, and by applying these equations to the two-fluid model by liquid helium II.

For superconductive metals, work is still in progress, but it already can be said that new terms arise in the expression for heat conductivity and probably also in the expression for the thermoelectric homogeneous effect, as compared with the results for ordinary metals.

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Field Variation of Superconducting Penetration Depth

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N a recent article of the same title, Pippard¹ has shown that there is only a small dependence of penetration depth, λ , on the applied magnetic field. Pippard's observations are based on changes of the reactive component of the skin impedance of superconducting tin at 3.2 cm with applied field. The over-all change in λ is no more than 3 percent at the critical field strength. From an application of the Gorter-Casimir two fluid theory, he estimates the size of the regions over which order must exist.

Pippard's argument is briefly as follows. With an increase in applied field, one might expect a decrease in concentration of superconducting electrons near the surface so as to increase the penetration depth and decrease the magnetic energy. The fact that this occurs only to a small degree-indicates that the size of the regions over which order exists and which must be considered as a unit in the transition must be at least as large as 10^{-4} cm. The very sharp resistance transition in pure tin is given as further evidence of an order existing over regions of this size. This result appeared to be difficult to reconcile with observations on thin films^{2,3} and on colloidal mercury⁴ that there is very little change in transition temperature with dimensions, even when the film thickness or particle size is as small as 5×10^{-6} cm; i.e., less than the penetration depth.

These apparently contradictory results both follow from the lattice-vibration theory⁵ of superconductivity and may be taken as evidence that the general approach, which is the one anticipated by London, is along the correct lines. London⁶ had previously shown that the phenomenological equations follow if it is assumed that the wave functions of the electrons are not changed very much by the magnetic field. The fact that the penetration depth is independent of field is good evidence that the wave functions are not altered; for if they were, one would expect the penetration to change.

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In our theory, the wave functions, Ψ_k , of the superconducting electrons are taken to be linear combinations of Bloch functions, ψ_k , which have energies near the Fermi surface. One consequence of a very small effective mass of the superconducting electrons is that the wave functions are not altered very much by an applied field, so that the London equations follow. We wish to point out here as a second consequence that the wave functions must extend over distances of at least 10⁻⁴ cm, in accord with Pippard's results. A small effective mass corresponds to the fact that it takes considerable energy to confine the wave function to a small region, as would be required to change the concentration near the surface. A localized superconducting electron can be described by a wave function of the form $U(x)\Psi_k(x)$, where U(x) represents the envelope and Ψ_k extends through the crystal with uniform amplitude. The effective mass can be used to estimate the energy change which comes from the variation of U(x). To confine the wave function to a distance $\pi/\Delta k$ requires an energy of the order of

$\Delta E = \hbar^2 (\Delta k)^2 / 2m_s,$

where m_s is the effective mass. We have shown that $m_s \sim 10^{-4}$ m, so that $\Delta E \sim 5 \times 10^{-16}$ erg for $\Delta k \sim 10^4$ cm⁻¹. This corresponds to thermal energy for a few degrees absolute and is the order of the magnetic energy, $H_c^2/8\pi$, per superconducting electron.

In case the size of the wave function is limited by the dimensions of the crystal, as it is in thin films and in colloidal particles, one can take U(x) = constant. The Bloch functions of the normal metal from which the linear combinations are formed are localized and satisfy the boundary conditions at the surface. No additional energy is required to localize the electrons in the superconducting state. As the dimensions are made smaller there are fewer terms in the sum over the Bloch states. One would not expect much change in transition temperature as long as the number of terms is sufficient to give a good approximation to the integral obtained as a limit for large volumes.

There is some question concerning the wavelengths of the vibrational waves which interact most strongly with the electrons. The low energies involved in the transition suggest that perhaps long wavelengths are most important. The fact that there is little change in T_c for dimensions of 5×10^{-6} cm shows that the important wavelengths are no more than, say, one-tenth of this, or less than 5×10^{-7} cm. If all wavelengths are involved, there are around 10 terms in the sum for a volume of 10^{-18} cm³, so that one might, in any case, expect changes in T_c for dimensions of $\sim 10^{-6}$ cm or less.⁷ A measurement of the way in which T_c changes with film thickness or particle sizes hould provide information about the important vibrational wavelengths.

The application of the effective mass concept to the calculation of the surface energy between normal and superconducting phases will be given in a subsequent communication.

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Magic Numbers and the Missing Elements **Technetium and Promethium**

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I N order to find an explanation for the absence of β -stable isotopes of the elements T = 1.2 isotopes of the elements Tc and Pm,1-3 a more general abnormality in the region following the closing of the 50- and 82neutron shell should be taken into consideration. This abnormality can be recognized from the differences of the binding energies of pairs of isobars as found from β -decay schemes. These show that



FIG. 1. Differences in the binding energies of the ground states of isobars as derived from beta-decay schemes.

in these regions the binding energies of the even Z, odd N nuclei (in their ground states) do not lie on the same energy surface as those of the odd Z, even N nuclei.

To illustrate this, the β -decay energies for nuclei with a given isotopic number I=N-Z may be plotted versus A=N+Z. Figure 1 shows such plots for I=13 and I=23 as examples. Following the general rule of the equivalence of odd N and odd Z nuclei with respect to their binding energies, both kinds of odd mass numbered nuclei with N < 50 or 82 lie close to a common line intersecting the zero line of decay energy at a point where the isobar stability changes to the next higher value of I. After the filling of the 50- and 82-neutron shell, an upward shift in the β^{-} decay energies occurs equivalent to the drop in the binding energy of the last neutron. This shift is somewhat larger, however, for the odd Z than for the odd N nuclei, indicating that the drop is not equal for paired and for unpaired neutrons. The general trend in this region can be represented by two different lines: the lower one representing the trend in the decay energies of the odd N, the higher one that of the odd Z nuclei. Thus, for a given I, the isobars with odd numbers of neutrons become stable at a lower mass number than those with an odd number of protons. This difference is large enough to cause the β -instability of all nuclei with a certain odd number of protons, incidentally those of Z = 43 and 61.

In Fig. 1 the value for Zr⁹³ is omitted, because it seems uncertain whether the low decay energy as reported by Steinberg and



FIG. 2. Energy parabolas for mass number 89, illustrating the proposed split in the energy surface for odd N and odd Z nuclei in the region N > 50.