

al data, and in an attempt to present writers attempted to to all substances, and in which finite physical properties of the see Simon 1937)

(1)

ance, a the internal pressure, substances (except for metals). imental data quite accurately; a, but the use of the internal ount of the quantum effects. nula over a very much wider en it was proposed (Holland, Jones 1951). At this point we tributed to one of us in the ve will end in a critical point'. t forward for the impossibility sion could only be given by , according to relation (1), be

oretical justification for sub- wn that by a reinterpretation ing, a formula similar to (1) related to the intermolecular e derivation by showing that la in the way suggested by

the temperature dependence ity as that of the 'reduced' ces in which quantum effects ied at temperatures of about rting pressures of about five to apply to other substances ent naturally is only valid if e do not produce changes on ion), for such changes cannot

cerned with the position of not concerned with other But there is another property ing thermal measurements. ructing the apparatus are f helium, and it is therefore

possible to measure the specific heat of highly compressed helium with considerable accuracy in spite of the fact that it has to be enclosed in massive steel containers. We could therefore determine the specific heats over an extensive region including the solid and fluid phases on both sides of the melting curve between 4 and 26°K. Moreover, the rapid variation with temperature of the molar volume of helium along the melting and solidification lines makes possible both the measurements of melting at constant volume within a convenient temperature interval and the filling of the calorimeter with solid by freezing at constant volume.

By using available data for lower temperatures the complete thermodynamic properties of the substance may be deduced, and hence the volume and entropy changes along the melting curve; these properties may then provide useful additional information regarding the behaviour of the melting curve.

THE EXPERIMENTS

Starting with solid helium at the lowest available temperature, specific heat measurements at constant volume were made at successively increasing temperatures. This procedure was repeated at a number of different densities.

The temperature range of the experiments at each density included the melting region, which occupies a finite temperature interval when the melting takes place at constant volume. At temperatures below that at which melting begins, the measurements give the specific heat of the solid at constant volume. During melting, the energy supplied (a) heats the solid not yet melted, (b) furnishes the heat of melting, and (c) heats the fluid already formed. When melting is complete, it is the specific heat of the fluid at constant volume which is being measured. (The term 'fluid' is used in this paper to denote the non-solid phase, and the term melting describes the transition from solid to fluid.)

If C_v is the measured thermal capacity per mole for a given density, then the entropy at that density and at a temperature T may be evaluated according to Nernst's theorem:

$$S = \int_0^T \frac{C_v}{T} dT,$$

provided that a suitable extrapolation of C_v to 0°K can be made.

The entropy of helium at points on the melting and solidification lines can be determined in this way, and from these curves the entropy change during isothermal melting at any temperature within the experimental range can be found. From the temperatures at which melting begins and ends for different densities the specific volumes along the melting and solidification curves can also be deduced.

The apparatus

In the first set of experiments, only temperatures available with liquid hydrogen were used, but in the second set a Simon expansion liquefier was incorporated and the whole range of temperatures from 4 to 26°K was covered. Since the apparatuses used for the two sets of experiments were essentially the same except in the arrangement for producing the low temperatures, only the second apparatus will be described.