

Thermodynamic properties and melting of solid helium

By J. S. DUGDALE* AND F. E. SIMON, F.R.S.

Clarendon Laboratory, University of Oxford

(Received 6 February 1953)

The melting properties and thermodynamic functions of solid helium have been determined at temperatures from 4 to 26°K and at pressures up to 3000 atm. The upper temperature corresponds to about five times the critical temperature of helium; it was therefore possible to measure properties of the solid state in a range which has not yet been attained for any other substance. The melting curve shows no signs of an approach to a solid-fluid critical point; in fact, the difference between the phases becomes more pronounced at higher melting temperatures.

The internal energy at 0°K was calculated from the experimental data and was found to be in good agreement with the theoretical values based on the Slater-Kirkwood potential, using $\frac{3}{2}R\theta$ as an estimate of the zero-point energy (θ being the Debye characteristic temperature).

A first-order transition in the solid was revealed; its equilibrium line cuts the melting curve at 14.9°K and moves to higher temperatures at higher densities. The heat of transition is very small, about 0.08 cal/mole. The transition is assumed to correspond to a change of crystal structure from hexagonal to cubic close-packed.

At the highest pressure solid helium is compressed to less than half its volume under equilibrium conditions at absolute zero, and the Debye θ is increased five times. It was hence possible to test the Lindemann melting formula for a single substance over a very wide range. The formula was found to fit the experimental data satisfactorily, although the value of the constant in it differed somewhat from the classical value.

INTRODUCTION

Because its interatomic forces are so weak, solid helium is the most compressible of all solids, and quite moderate pressures give rise to changes in volume far in excess of those obtained with ordinary substances. Measurements of the thermal properties of solid helium over a relatively small pressure range can therefore provide data on the solid state over a wide range of volumes, and this data may help to elucidate a number of questions arising in the theory of the solid state. Of course, it must be remembered that quantum effects, such as zero-point energy (Simon 1934), play a major part in determining the properties of helium at low temperatures, and therefore helium cannot be regarded as a perfect model substance. Nevertheless, for some purposes these quantum effects can be adequately taken into account and general conclusions drawn; in other cases an analysis of the differences between the behaviour of classical substances and helium can be illuminating.

One problem in which helium can, at least in some respects, serve as a model substance is the behaviour of the melting curve at high pressures. The equilibrium curve between liquid and vapour ends in a critical point above which the discontinuity between these phases disappears, and a good deal of discussion has centred around the question whether the equilibrium curve between solid and fluid behaves similarly or not. Much of the earlier speculation on the problem was

* Now at National Research Council, Ottawa.

based on the extrapolation of limited experimental data, and in an attempt to provide a more fundamental approach one of the present writers attempted to find a reduced melting formula which would apply to all substances, and in which the reducing parameters could be related to definite physical properties of the individual substances. The formula proposed was (see Simon 1937)

$$\frac{p}{a} = \left(\frac{T}{T_0}\right)^c - 1, \quad (1)$$

where T_0 is the normal melting-point of the substance, a the internal pressure, and c a constant whose value was about 2 for most substances (except for metals). This formula was found to fit all the existing experimental data quite accurately; for helium the quantity T_0 needed reinterpretation, but the use of the internal pressure a as a parameter automatically took account of the quantum effects. Recent experimental work has confirmed this formula over a very much wider range than that for which data were available when it was proposed (Holland, Huggill, Jones & Simon 1950; Holland, Huggill & Jones 1951). At this point we would like to correct a statement erroneously attributed to one of us in the literature (e.g. Bridgman 1935) 'that the melting curve will end in a critical point'. Our statement actually was that the reasons brought forward for the impossibility of a critical point did not seem conclusive; a decision could only be given by experiments and the best chance of success would, according to relation (1), be with the low boiling-point gases.

Recently, equation (1) has also received some theoretical justification for substances in the classical region. Domb (1951) has shown that by a reinterpretation of the Lennard-Jones & Devonshire theory of melting, a formula similar to (1) can be derived for high pressures, the constant c being related to the intermolecular potential energy. De Boer (1952) has completed the derivation by showing that the internal pressure does in fact enter the formula in the way suggested by Simon. (See also Note added in proof, p. 309).

We feel, therefore, that the 'reduced' formula for the 'temperature dependence of the melting pressure has the same kind of validity as that of the 'reduced' vapour-pressure formula, even in the case of substances in which quantum effects play a role; hence the fact that helium can be solidified at temperatures of about fifty times the 'normal' melting temperature by exerting pressures of about five hundred times the internal pressure may be taken to apply to other substances under similar conditions (Simon 1952). This statement naturally is only valid if the particular conditions of pressure and temperature do not produce changes on a subatomic scale (e.g. changes in electronic configuration), for such changes cannot of course be taken care of by our formula.

The experiments mentioned so far were solely concerned with the position of the melting-point at different pressures and were not concerned with other thermodynamic properties along the melting curve. But there is another property of helium which is of great consequence when making thermal measurements. The heat capacities of all the materials used in constructing the apparatus are very much smaller at low temperatures than those of helium, and it is therefore

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.

The layout of the apparatus is shown in figure 1. Helium at about 100 atm was introduced into the transmitter, *E*, through the high-pressure valve, *G*. *E* consisted of a steel U-tube containing mercury and was used to transmit to the helium the pressure generated in oil by the high-pressure pump, *F*. Details of the design of this transmitter have already been given in a recent paper (Holland *et al.* 1951).

After compression in the right-hand limb of *E*, the helium was transmitted to the calorimeter, *I*, in the cryostat, *L*, through a capillary tube of 18/8 austenitic

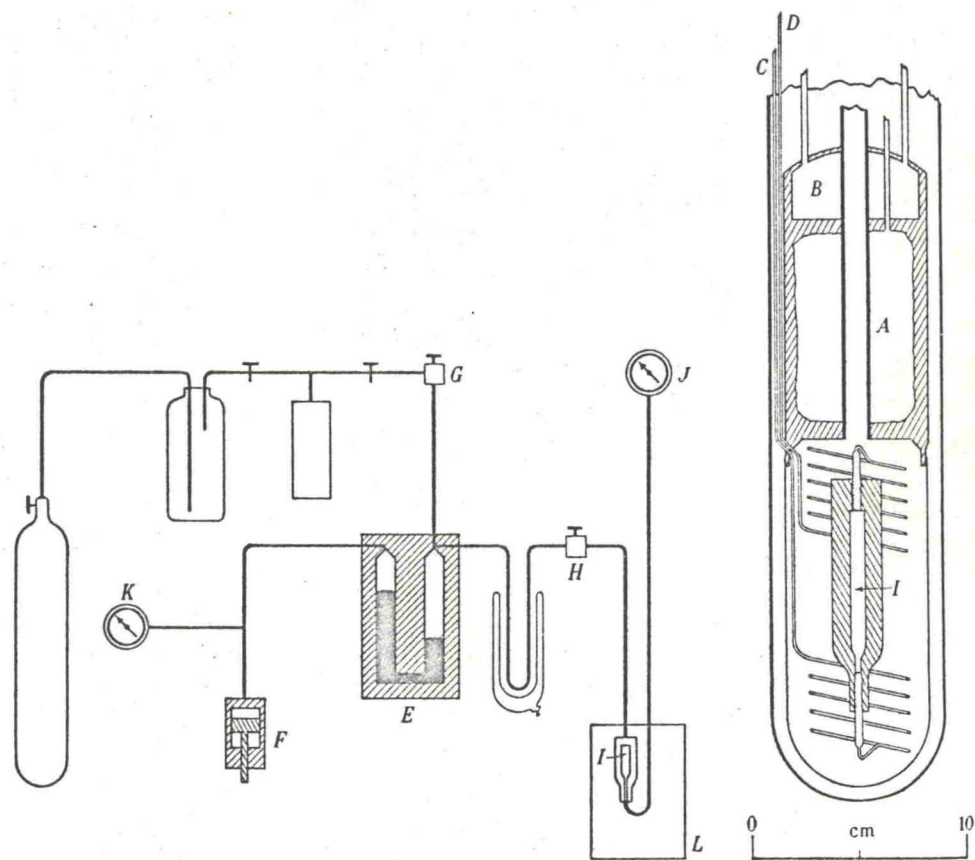


FIGURE 1. Lay-out of the apparatus.

FIGURE 2. The calorimeter and cryostat.

stainless steel. This tube was interrupted at *H* by a second high-pressure valve so that the calorimeter, once filled to a suitable density, could be isolated from the rest of the high-pressure circuit.

A second stainless steel capillary connected the other end of the calorimeter to a Bourdon gauge, *J*. This, in conjunction with that on the pump, *K*, could be used to ensure that the pressure was actually transmitted to the calorimeter. The gauge, *J*, was filled with mercury so that its dead volume was very small.

The calorimeter and cryostat are shown in detail in figure 2. *A* is the expansion chamber of the liquefier and *B* the hydrogen chamber. The calorimeter *I* is

1. Helium at about 100 atm high-pressure valve, *G*. *E* con- was used to transmit to the pressure pump, *F*. Details of the in a recent paper (Holland *et al.*

the helium was transmitted to capillary tube of 18/8 austenitic

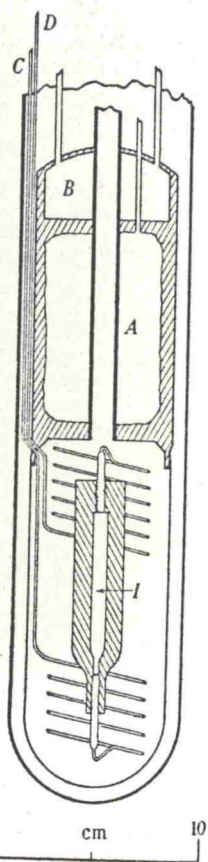


FIGURE 2. The calorimeter and cryostat.

a second high-pressure valve ty, could be isolated from the

her end of the calorimeter to n the pump, *K*, could be used o the calorimeter. The gauge, as very small.

figure 2. *A* is the expansion mber. The calorimeter *I* is

suspended in a vacuum chamber attached to *A*, while outside this and enclosing both *A* and *B* is a second vacuum space. Exchange gas could be introduced into either vacuum space.

The calorimeter was made from a solid cylinder of 'Vibrac' steel (diameter 2.1 cm and length 12 cm) in which was drilled an axial hole of 0.7 cm diameter to within 1.8 cm of the end. The open end was then swaged down for a length of about 2 cm until the inner diameter of this part was reduced to less than 1.5 mm. Both ends were then drilled and tapped to receive the capillary tubes. The volume of the calorimeter at room temperature, after having been tested to 4000 atm pressure was 2.69 cm³ as determined by filling with mercury. Over the greater part of their length the dimensions of the capillaries leading to the calorimeter were: outer diameter 1 mm and inner diameter approximately 0.1 mm. At about 2 cm from the calorimeter the outer diameter increased to 2.5 mm and the inner to about 0.5 mm. The wider part of the capillary could then be threaded and hard-soldered into the calorimeter. (These 'pipette' type tubes were originally developed for the experiments on the melting curve of helium of Holland *et al.* 1951.)

Although this is not shown in the figure, the capillaries *C* and *D* were soldered in half-loops to the sides of the expansion chamber. The length of each capillary touching the walls of the chamber was about 15 cm, and good thermal contact was thus assured. This was essential not only for the purpose of reducing heat flow along the capillaries to the calorimeter from the external hydrogen bath but also because these half-loops in the capillaries were used to 'freeze off' the helium in the calorimeter and had therefore to attain the temperature of the helium chamber to be effective. Provided that the pressure in the helium was always maintained at a value higher than the freezing pressure corresponding to the temperature of the chamber, solid helium remained in the capillaries and held the helium in the calorimeter accurately at constant volume.

Around the calorimeter a jacket of 0.25 mm copper foil was soldered in order to reduce the time of reaching temperature equilibrium after an application of heat during an experiment. On top of this were wound the resistance thermometer and the heater.

The resistance thermometer was of 47 s.w.g. constantan (490 ohms at the hydrogen boiling-point) fastened around the outside of the calorimeter in a zigzag path parallel to the axis to avoid any strain on the wire due to pressure inside the calorimeter. The thermometer was calibrated against the vapour pressure of hydrogen in the range of temperatures between 14 and 27°K. In the helium region it was calibrated against the vapour pressure of helium, and the calibration in the intervening region was obtained by interpolation on the basis of the known behaviour of samples of the same constantan wire.

The heater (approximately 800 ohms) was also of constantan. It was fitted with extra leads so that the potential could be measured directly. The time of each heating period was determined by a stop-watch (calibrated against a crystal-controlled clock) which was automatically operated in synchronism with the current switch.

The quantity of helium in the calorimeter was determined after each experiment by releasing the helium contained in it and the associated 'dead' volume into an evacuated vessel of known capacity. This 'dead' volume consisted of the gauge, *J*, the capillaries leading to the calorimeter and the high-pressure valve, *H*. Effectively all the gas in it was at room temperature. Under the conditions of the experiments, the gas in the 'dead' volume constituted about 7% of the total. Its quantity was determined directly by connecting the gauge to the valve by a capillary equal in volume to those on the apparatus and measuring the helium contained in this system as a function of pressure.

RESULTS

(a) Melting

(i) Entropy

The general information obtained from the experiments is summarized in figures 3 and 4. Figure 3 shows the entropy of solid helium along the melting curve and the entropy of fluid helium along the solidification curve. Four lines of constant volume are drawn, and for completeness the diagram is extended into the liquid-solid equilibrium region. Below 4°K the entropy of the solid is taken from the measurements of Keesom & Keesom (1936) and the entropy of melting from the measurements of Swenson (1950, 1951). Extrapolation of the values of the melting entropy found in these experiments agreed with those due to Swenson rather than those reported earlier by Keesom & Keesom (1936). The values of the melting entropy are estimated to be accurate to 3%.

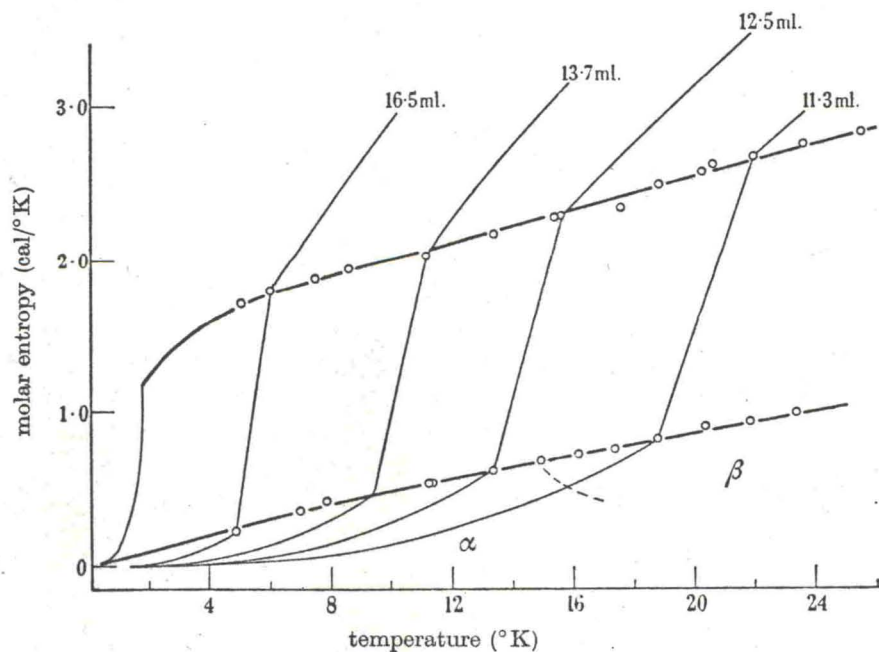
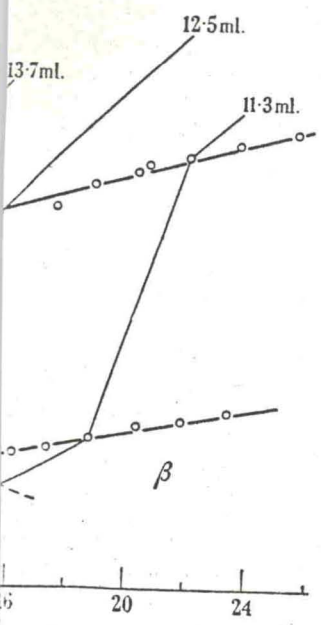


FIGURE 3. The entropy of helium on melting and solidification. — (fine lines), lines of constant volume; ----, transition line in the solid.

s determined after each experi-
 d the associated 'dead' volume
 s 'dead' volume consisted of the
 and the high-pressure valve, *H*.
 ature. Under the conditions of
 nstituted about 7% of the total.
 ing the gauge to the valve by a
 atus and measuring the helium
 e.

experiments is summarized in
 solid helium along the melting
 solidification curve. Four lines
 nness the diagram is extended
 °K the entropy of the solid is
 som (1936) and the entropy of
 o, 1951). Extrapolation of the
 eriments agreed with those due
 by Keesom & Keesom (1936).
 o be accurate to 3%.



solidification. — (fine lines),
 a line in the solid.

In the course of the experiments a transition was discovered in solid helium. The transition line is indicated on the entropy diagram; further details of the transition are given below.

The significance of our results will be discussed in a later paragraph.

(ii) Molar volumes along the melting curve

Figure 4 shows the molar volumes of helium along the melting and solidification curves. Values below 4°K are due to Keesom & Keesom (1936) and to Swenson (1950). The transition line in solid helium is also shown in the figure.

The consistency of corresponding measurements of the melting entropy ΔS and the change of volume on melting ΔV may be tested using the Clausius-Clapeyron equation, provided that the slope of the melting curve is known. Keesom (1926) had measured the melting curve of helium below 4°K and Simon, Ruhemann & Edwards (1929*b*) from 12 to 42°K. The apparatus of the present experiments was used to establish the curve between 4 and 12°K, using the blocked capillary technique. The results showed that the melting curve could be represented, within the experimental accuracy (± 3 atm, $\pm 0.1^\circ$ K), by the equation

$$\frac{p}{16.45} = \left(\frac{T}{0.992} \right)^{1.554} - 1, \quad (2)$$

where p is the pressure in atmospheres and T the absolute temperature. This is the equation originally established by Simon *et al.* (1929*b*). Using this equation

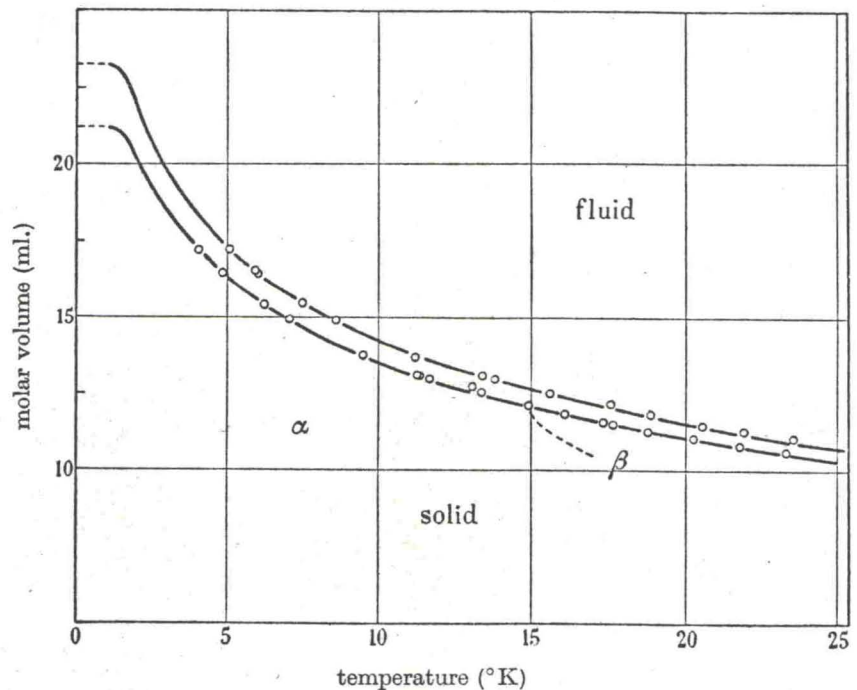


FIGURE 4. The molar volume of helium on melting and solidification. —, transition line in the solid.

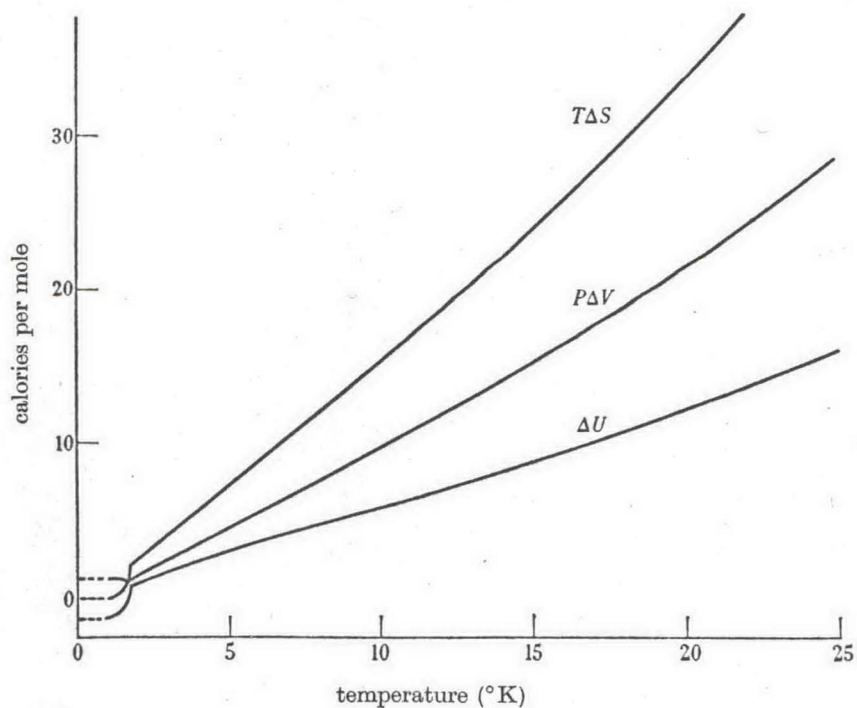
TABLE 1. THE HELIUM MELTING CURVE BETWEEN 4.2 AND 12° K

T (°K)	p (atm)	T (°K)	p (atm)
4.23	141	8.20	423
5.20	202	8.75	469
6.00	255	9.70	550
6.50	285	10.17	590
6.88	314	10.78	652
7.46	358	11.20	695
7.91	400	12.07	779

TABLE 2. SMOOTHED VALUES OF THE ENTROPIES AND VOLUMES ALONG THE MELTING LINE

Entropies in cal/°C per mole, volumes in ml/mole. (The volumes are given to a higher accuracy than is warranted by the experiments in order to give ΔV correctly.)

T (°K)	S_{solid}	S_{fluid}	V_{solid}	V_{fluid}
4	0.18	1.60	17.25	18.25
6	0.29	1.79	15.53	16.42
8	0.39	1.90	14.34	15.10
10	0.48	2.00	13.45	14.13
12	0.56	2.11	12.82	13.45
14	0.63	2.21	12.30	12.88
16	0.70	2.31	11.87	12.42
18	0.78	2.42	11.42	11.95
20	0.86	2.54	11.10	11.61
22	0.94	2.66	10.75	11.24
24	1.01	2.77	10.40	10.88
26	1.08	2.88	10.10	10.57

FIGURE 5. $T\Delta S$, $P\Delta V$ and ΔU for helium on melting.

BETWEEN 4.2 AND 12° K

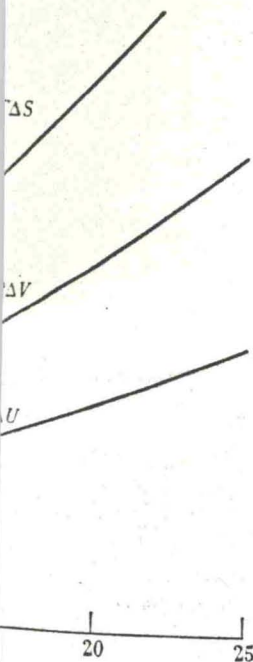
T (K)	p (atm)
4.2	423
5	469
7	550
7	590
8	652
10	695
12	779

PROPERTIES AND VOLUMES

NE

The volumes are given to a higher order to give ΔV correctly.)

V_{solid}	V_{fluid}
17.25	18.25
15.53	16.42
14.34	15.10
13.45	14.13
12.82	13.45
12.30	12.88
11.87	12.42
11.42	11.95
11.10	11.61
10.75	11.24
10.40	10.88
10.10	10.57



on melting.

to determine the slope of the melting curve, the consistency of the ΔS and ΔV measurements was demonstrated.

As the experimental data have only been shown in the form of diagrams it may be useful to give smoothed numerical values for entropy and volume at a few temperatures along the melting line.

(iii) Energy relations

To concentrate attention more specifically on the change in properties on melting, the latent heat of melting $T\Delta S$, the change in internal energy ΔU , and the product $p\Delta V$ have been plotted as functions of temperature in figure 5. The values of ΔV used here were calculated from the Clausius-Clapeyron equation, since they are more accurate than the values derived directly from the volume measurements. Again, values below 4° K, taken from Swenson (1950), have been included for completeness. At the highest temperature to which measurements extended the latent heat of melting was almost 50 cal/mole, more than three times the latent heat of vaporization at absolute zero.

(b) The thermodynamic properties of solid helium

We shall now discuss the data on the molar heat at constant volume of solid helium which have been obtained as a function both of molar volume (from 17 to 10.6 ml.) and of temperature (from 5 to 26° K). Altogether measurements were made at twelve different densities, the whole temperature range was not covered at every density; as will be explained, certain temperature regions were examined more closely than others.

These data, together with one p, V, T relationship which covers the complete range of variation of temperature and volume, are then sufficient to determine all the thermodynamic properties of the solid in the region of the measurements. Such a p, V, T relationship was obtained from the melting curve (equation (2) above) together with the volume of the solid on melting.

(i) The specific heats, entropy and internal energy

In figure 6, the results of specific-heat measurements at four densities are shown, while in figure 7 the variation of Debye θ with temperature is shown for the same four densities. Although the molar heats follow only approximate Debye curves, all the results for different densities may be represented in a reduced form simply by a change of scale of the temperature axis. That is, the molar heats may be represented by

$$C_v = f(T/\phi),$$

where f is always the same function and ϕ is a parameter depending only on the volume. This is illustrated in figure 8 in which are shown the curves of figure 6 plotted as a function of T/ϕ . In this figure there have been included two Debye curves for comparison.

To avoid confusion the points in the figure are representative of only four densities, but by choosing suitable values of ϕ (see table 3) it is possible to reduce all our present results on to this curve. Hence in our range of measurement C_v

may be expressed as a function of T/ϕ only. It is also possible to treat the results of Keesom & Keesom (1936) at much lower densities and temperatures so that they too lie on this curve, although in this case the fit is not so good. Such discrepancy as occurs is associated with the fact that for values of $T/\phi < 0.10$ our Debye θ values are almost independent of temperature while Keesom & Keesom's values

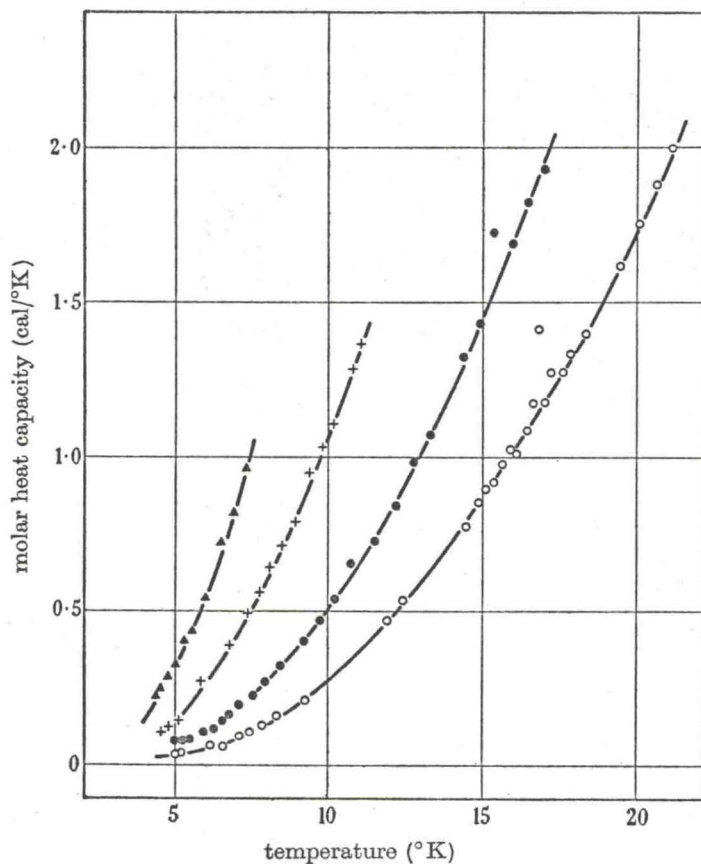


FIGURE 6. The molar-heat capacities of solid helium. \circ , 10.6 ml.; \bullet , 11.7 ml.; +, 13.0 ml.; \blacktriangle , 14.4 ml.

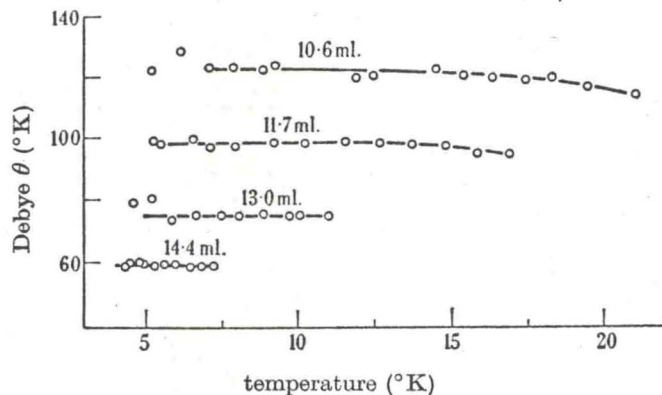
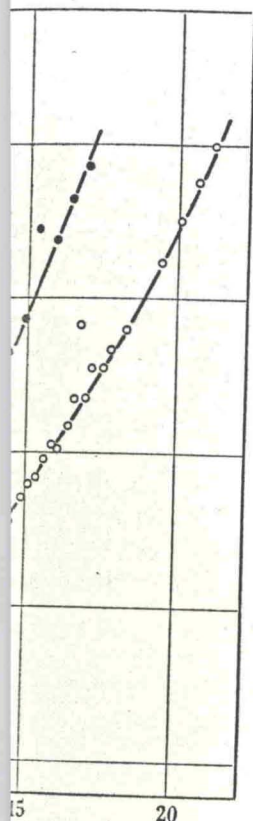
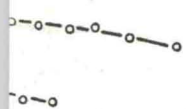


FIGURE 7. The Debye θ 's of solid helium at four molar volumes.

is also possible to treat the results at various pressures and temperatures so that they are not so good. Such discrepancy between our values of $T/\phi < 0.10$ and our Debye θ values while Keesom & Keesom's values



of solid helium.
ml.; \blacktriangle , 14.4 ml.



20

four molar volumes.

increase with falling temperature. We may notice that Webb, Wilkinson & Wilks (1952) have also observed this effect.

In view of this relationship it is convenient to present certain thermodynamic properties of the solid in terms of T/ϕ and table 4 gives C_v , S and $(U - U_0)/T$ as

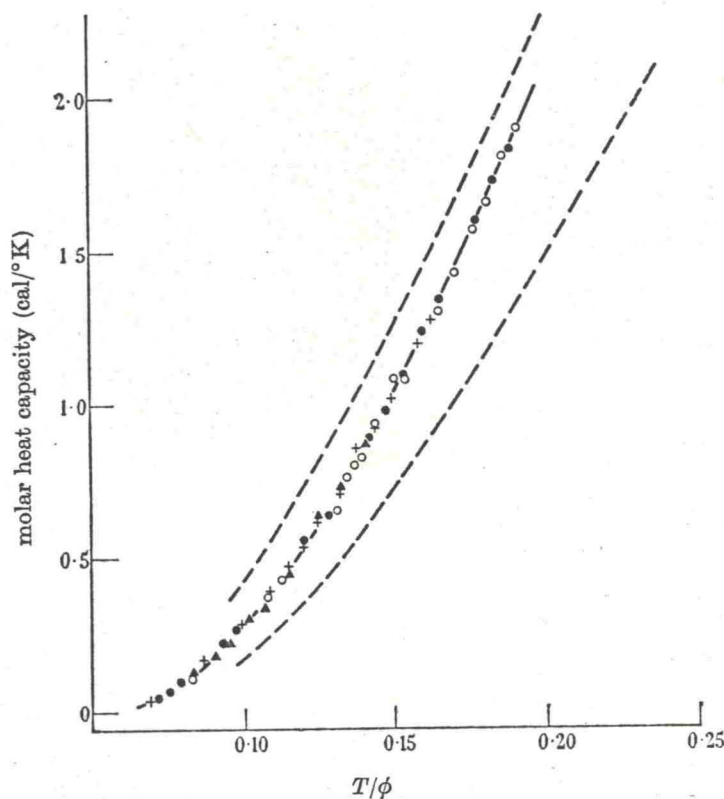


FIGURE 8. The molar-heat capacities of figure 6 plotted against the reduced temperature T/ϕ .
 \circ , 10.6 ml.; \bullet , 11.7 ml.; $+$, 13.0 ml.; \blacktriangle , 14.4 ml.

TABLE 3. SMOOTHED VALUES OF THE PARAMETER ϕ AS A FUNCTION OF VOLUME

V (ml.)	ϕ	V (ml.)	ϕ
10.5	113	15	48.5
11	101.5	16	41.4
12	83.2	17	35.7
13	68.7	18	31.1
14	57.4	19	27.2
		20	24.2

functions of T/ϕ . (The units of ϕ are arbitrary; they have, however, been chosen so as to be similar in magnitude to the Debye θ 's.) These values depend on an extrapolation of the specific heats to 0°K . This extrapolation entails some uncertainty owing to the above-mentioned discrepancy between our results and those of Keesom & Keesom. As, however, the maximum error will only be of the order of 0.01 entropy unit, it is quite immaterial for our purposes. For a fuller discussion of this point we refer to a paper by Webb & Wilks (1953).

From the relationship between ϕ and V , one can derive the quantity

$$\gamma = -\frac{d \ln \phi}{d \ln V}.$$

For values of the volume greater than 13 ml. γ is approximately constant and equal to 2.4. At lower volumes γ begins to diminish slowly, but this may be within the limits of accuracy.

TABLE 4. C_v , S AND $(U - U_0)/T$ AS A FUNCTION OF T/ϕ

(All in cal/°C per mole)			
T/ϕ	C_v	S	$(U - U_0)/T$
0.04	0.02	0.008	0.010
0.06	0.08	0.023	0.017
0.08	0.19	0.060	0.043
0.10	0.38	0.121	0.091
0.12	0.64	0.213	0.158
0.14	0.96	0.333	0.248
0.16	1.33	0.483	0.359
0.18	1.73	0.662	0.491
0.20	2.21	0.870	0.645

(ii) *The isochores*

It is now possible to calculate the isochores by integrating the relationship

$$\left(\frac{\delta p}{\delta T}\right)_V = \gamma \frac{C_v}{V}, \quad (3)$$

which is valid if C_v is a function only of T/ϕ , and ϕ depends only on volume. The integration constants were determined from the p , V , T values on the melting curve. The isochores at eight densities are shown in figure 9, together with the equilibrium line between the two solid modifications.

(iii) *The isotherms and compressibilities*

As may be seen from figure 9 the isochores may be extrapolated to 0°K with considerable accuracy, and in this way the p , V relationship at absolute zero can be derived. Figure 10 shows this relationship. From this in turn the compressibility at 0°K as a function of volume may be found and is shown in table 5. Isotherms and compressibilities at other temperatures may also be obtained.

TABLE 5. THE COMPRESSIBILITY OF SOLID HELIUM AT 0°K

volume (ml.)	pressure (atm)	$10^5 \beta$ (atm ⁻¹)	volume (ml.)	pressure (atm)	$10^5 \beta$ (atm ⁻¹)
10.5	2170	10	15.0	295	54
11.0	1660	12	16.0	200	76
12.0	1070	17	17.0	136	103
13.0	695	26	18.0	88	140
14.0	460	38	19.0	50	190

can derive the quantity

is approximately constant and
 slowly, but this may be within

FUNCTION OF T/ϕ

$$(U - U_0)/T$$

- 0.010
- 0.017
- 0.043
- 0.091
- 0.158
- 0.248
- 0.359
- 0.491
- 0.645

integrating the relationship

(3)

depends only on volume. The
 p, V, T values on the melting
 in figure 9, together with the
 as.

be extrapolated to 0°K with
 relationship at absolute zero can
 from this in turn the compressi-
 und and is shown in table 5.
 res may also be obtained.

HELIUM AT 0°K

pressure (atm)	$10^5 \beta$ (atm^{-1})
295	54
200	76
136	103
88	140
50	190

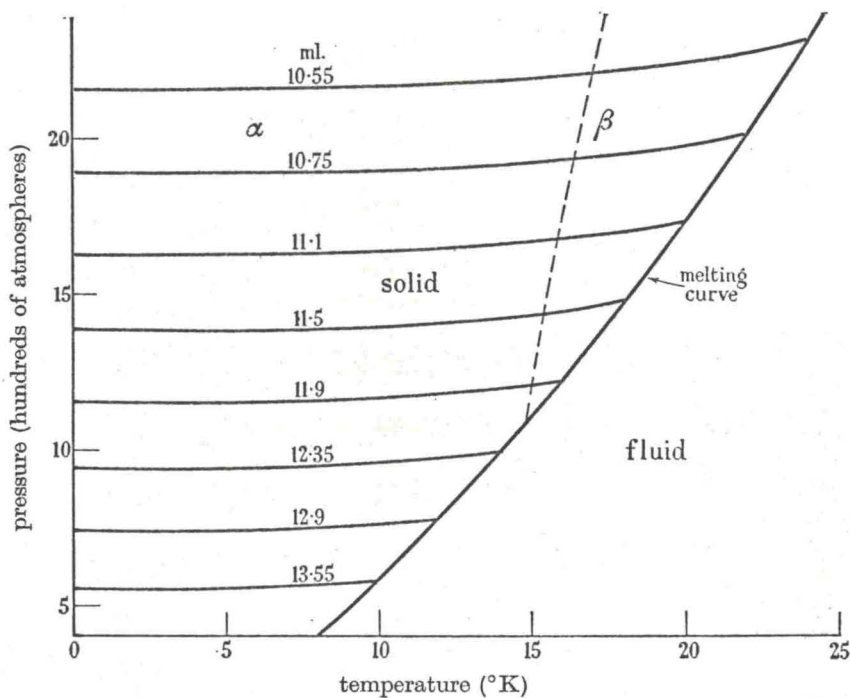


FIGURE 9. The isochores of solid helium at eight molar volumes.
 -----, transition line in the solid.

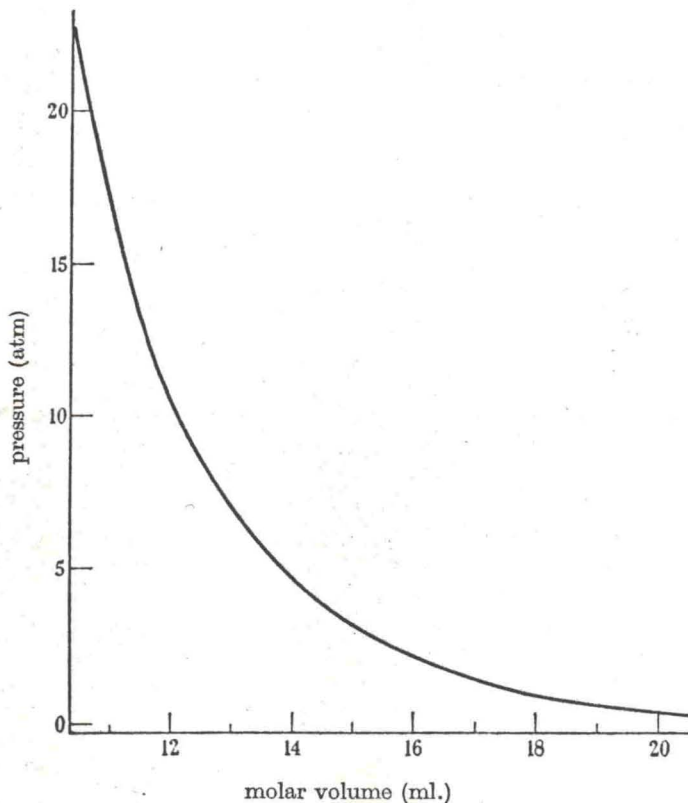


FIGURE 10. The pressure-volume relation in solid helium at 0°K .

(iv) *The thermal expansion*

From the relationship (3) and from the compressibility the volume thermal expansion coefficient, α , can be derived. Table 6 shows the variation of the expansion coefficient with temperature at three different densities.

TABLE 6. THE THERMAL EXPANSION OF SOLID HELIUM; THE VOLUME EXPANSION COEFFICIENT AS A FUNCTION OF TEMPERATURE

T ($^{\circ}\text{K}$)	10.6 ml. $10^4\alpha$	12 ml. $10^4\alpha$	15 ml. $10^4\alpha$
0	0	0	0
2	—	—	1.05
4	0.09	0.48	10.2
8	0.93	4.9	—
12	3.4	14.6	—
16	7.3	—	—
20	12.6	—	—

(v) *The internal energy at 0°K and the lattice energy*

By integrating the p, V relationship at 0°K the internal energy at absolute zero, U_0 , can be obtained as a function of volume. In this calculation, the value of U_0 at 25 atm pressure is taken as -11.9 cal/mole (Simon & Swenson 1950;

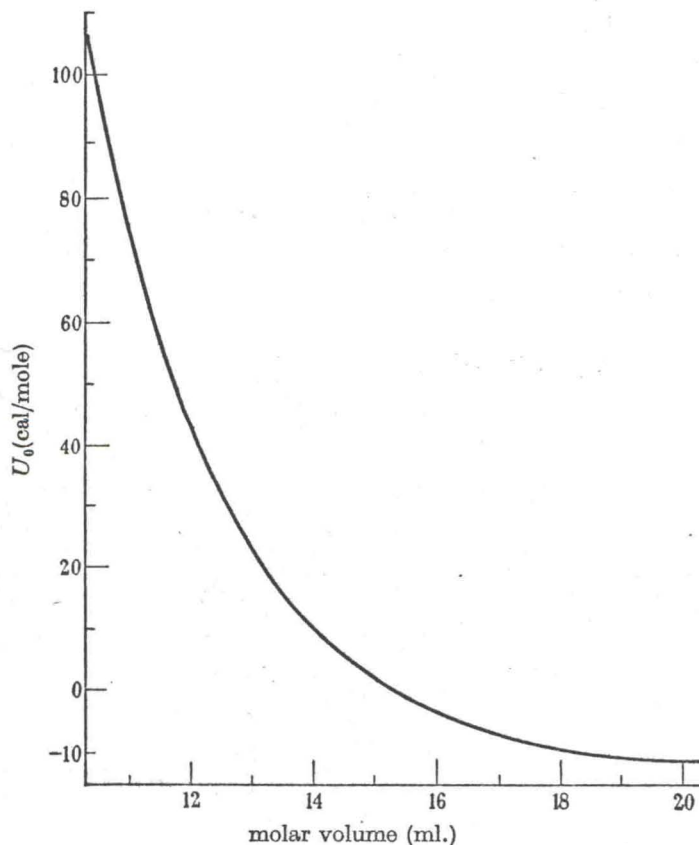


FIGURE 11. The internal energy of solid helium at 0°K as a function of volume.

compressibility the volume thermal expansion shows the variation of the expansion coefficients at different densities.

SOLID HELIUM; THE VOLUME EXPANSION COEFFICIENT AS A FUNCTION OF TEMPERATURE

- 15 ml.
- $10^4 \alpha$
- 0
- 1.05
- 10.2
-
-
-
-

the internal energy at absolute zero. In this calculation, the value of the lattice energy per mole (Simon & Swenson 1950;

Swenson 1950). The resulting values of U_0 are estimated to be accurate to 2% and are shown in figure 11.

To obtain the lattice energy from the internal energy at absolute zero it is necessary to subtract from it the zero-point energy. The latter may be approximately evaluated, assuming a Debye model for the solid, as $\frac{3}{8}R\theta_D$, where the θ_D values are those appropriate to the absolute zero.

From the experiments of Webb *et al.* (1952) which, of all the measurements on solid helium, have extended to the lowest values of T/ϕ , the θ_D for a molar volume of 20.6 ml. was taken as 22.7°K at absolute zero. On the basis of these assumptions, the lattice energy of solid helium was derived and the results are shown in figure 12.

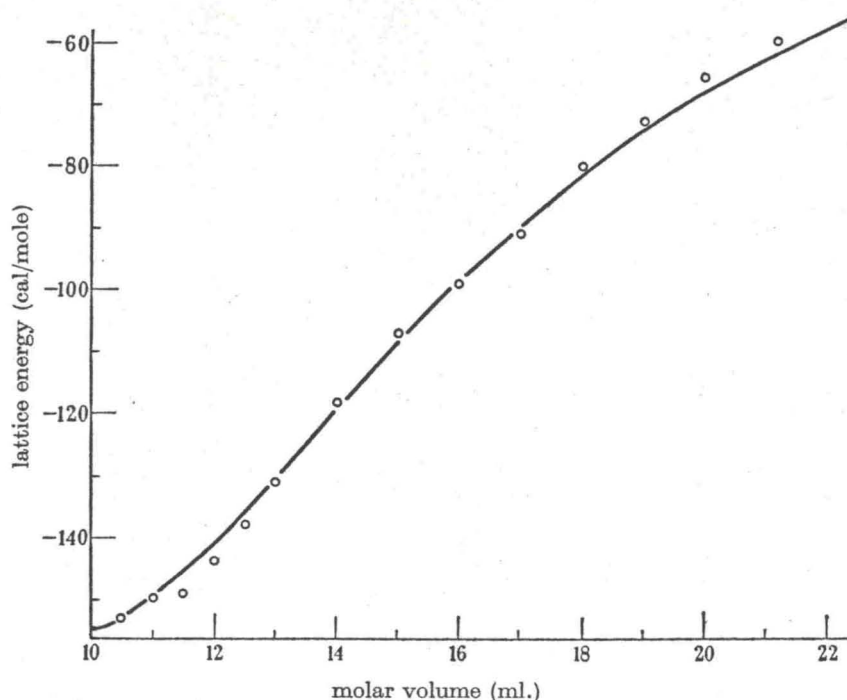
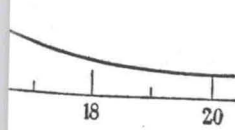


FIGURE 12. The lattice energy of solid helium as a function of volume. O, derived from experimental measurements; —, calculated by London.

London (1936) has calculated this lattice energy as a function of volume for a close-packed structure assuming the Slater-Kirkwood intermolecular potential for two helium atoms, and his values are represented by the continuous line in figure 12. Considering the inaccuracies involved in (a) the Debye model, (b) the extrapolation of the Debye θ to 0°K, and (c) the lattice energy calculated from the Slater-Kirkwood potential, it must be concluded that the very close agreement is accidental. It may be mentioned that the recent work of Yntema & Schneider (1950) has shown that the Slater-Kirkwood potential reproduces quite well the variation of the second virial coefficient with temperature over a wide range of temperatures, and is, indeed, more successful than the more refined expression due to Margenau.



0°K as a function of volume.

(vi) Specific heat of the fluid

The heat-capacity measurements were extended slightly into the fluid region, and it was found that at the higher densities and temperatures the specific heats of the fluid at all densities were very close to, though slightly less than, the classical value for a gas, i.e. $\frac{3}{2}R$. This rather surprising result is now being investigated in more detail by experiments over a wider temperature region.

(c) A transition in solid helium

In the course of the determination of the specific heats of solid helium, a series of anomalously high values was obtained in the region between 15 and 17°K, the actual temperature depending on the volume. In order to fix more exactly the position of the anomalies, a number of specific heat runs were made at different densities in this particular temperature region. The specific heat was measured at every $\frac{1}{10}^\circ\text{K}$ for a number of different densities and showed that the anomalous region was confined to less than $\frac{1}{10}^\circ\text{K}$ for each density.

Then a series of heating curves was made in the same temperature region. The calorimeter, filled to a suitable density, was supplied with heat at a constant rate while the temperature was measured as a function of time. The anomaly showed as a well-defined step in the heating curve.

In order to verify that the transition was reversible, cooling curves were also determined. It was concluded that the transition was reversible and, from the shape of the curves, that it was a first-order transition separating two modifications of solid helium. The low-temperature modification was labelled α and the high-temperature modification β .

The equilibrium line of the two modifications has already been shown in figures 3, 4 and 9. It cuts the melting curve at 14.9°K. In addition, the experiments showed that the entropy change associated with the transition was about 5×10^{-3} entropy units, corresponding to a heat of transition of 0.08 cal/mole. The corresponding volume change derived on the basis of the Clausius-Clapeyron equation is 4×10^{-4} ml. Furthermore, when the transition takes place at constant volume, the change in pressure is less than half an atmosphere. Since these qualities are all relatively small, the effect of the transition has been neglected in the derivation of the thermodynamic properties of the solid.

Since substances with short-range forces of the van der Waals type are stable only in close-packed lattices, the most probable conclusion is that the transition is from a close-packed hexagonal structure to a close-packed cubic structure. The very small heat of transition is consistent with this interpretation. The experiments of Keesom & Taconis (1938) indicate that the modification stable at lower temperatures (our α modification) is the hexagonal structure.

(d) The Lindemann melting formula

It is now of interest to see if, on the basis of the Lindemann formula (Lindemann 1910), there is any correlation between the Debye θ 's, the molar volume, V , and the melting temperature, T_m , since here for the first time there exist the data for

ded slightly into the fluid region, and temperatures the specific heats, though slightly less than, the classical result is now being investigated in the temperature region.

Helium

Specific heats of solid helium, a series in the region between 15 and 17°K, are. In order to fix more exactly the specific heat runs were made at different densities and showed that the θ_D for each density.

In the same temperature region. The heat was applied with heat at a constant rate of time. The anomaly showed

reversible, cooling curves were also reversible and, from the transition separating two modifications was labelled α and the high-

ions has already been shown in 4.9°K. In addition, the experiment with the transition was about transition of 0.08 cal/mole. The basis of the Clausius-Clapeyron transition takes place at constant pressure of an atmosphere. Since these transition has been neglected in the solid.

van der Waals type are stable conclusion is that the transition is a close-packed cubic structure. with this interpretation. The fact that the modification stable at hexagonal structure.

Formula

Lindemann formula (Lindemann θ_D 's, the molar volume, V , and at time there exist the data for

such a comparison over a substantial region of the melting curve of one single substance.

According to the Lindemann melting formula,

$$\theta_D = c \sqrt{\frac{T_m}{MV^{\frac{2}{3}}}}$$

where M is the molecular weight of the substance, and c is a constant. Table 7 gives the values of c for helium at different temperatures, and it is seen that the values are indeed very nearly constant. A comparison of the value of c for helium with those of the other inert gases is made in table 8. It is evident that neon and helium deviate considerably from the behaviour of the heavier elements.

TABLE 7. APPLICATION OF THE LINDEMANN MELTING FORMULA TO HELIUM

θ_D (°K)	T_m (°K)	V (ml.)	c
110	23.3	10.6	101
92	17.3	11.6	100
72	11.3	13.1	102
55	7.9	14.4	95
32	3.1	18.3	96

TABLE 8. APPLICATION OF THE LINDEMANN MELTING FORMULA TO THE INERT GASES

substance	c	source of data
He	99	present experiments
Ne	140	Clusius (1936)
A	162	Clusius (1936)
Kr	163.5	Clusius (1936)
Xe	164	Clusius (1936)

In a recent paper Domb (1952) has used the results of the present experiments to estimate the mean amplitudes of vibration of the atoms of the lattice at the melting-point. It appears that this amplitude decreases with rising melting temperature, its value at the lowest temperatures being three times its classical value. Hence it is clear that the original semi-empirical argument of Lindemann breaks down for solid helium, even though the melting formula itself remains valid with a somewhat different value for the constant c . Domb interprets this as showing that zero-point energy makes little contribution towards melting, since most of its energy is concentrated in the short-wave region.

DISCUSSION OF THE ENTROPY DIAGRAM

We wish now to discuss the significance of our results in respect of the entropy of the solid and fluid phases in equilibrium, and to compare these results with those of former experiments on substances with much higher melting points. In doing this we have to realize two things: first, these earlier experiments could give only the values of the *change* of entropy and not the entropies of the two phases themselves (for the reasons mentioned in the introduction); and secondly, these experiments refer only to a very much smaller temperature range. Hardly any of them

reach up to temperatures as high as the ordinary critical temperature, while ours only start in this region and extend to five times its value. On the other hand, our data are at least partly influenced by quantum effects.

Turning first to compare the values of the entropy change on melting, we find that our values are rather less than R , the gas constant, i.e. they are of the usual order of magnitude, although only about one-half of the values observed for the other inert gases at their normal melting-points (see table 9). The falling trend towards neon and helium indicates the onset of quantum effects.

TABLE 9. COMPARISON OF THE MELTING ENTROPIES OF THE INERT GASES

substance	T ($^{\circ}\text{K}$)	ΔS melting (cal/deg/mole)	source of data
He	10.0	1.52	present experiments
	20.0	1.68	present experiments
Ne	24.6	3.26	Clusius (1936)
A	83.9	3.35	Clusius (1936)
K	116.0	3.36	Clusius (1936)
Xe	161.3	3.40	Clusius & Riccoboni (1937)

Passing on now to the temperature dependence of the entropy of melting it is clear that our experiments on helium show no indication of any approach to a hypothetical 'critical point' between the solid and fluid phases. Although in ordinary substances the entropy change can be traced only over a relatively small temperature interval, the existing data indicate that to a first approximation the heat of melting remains constant. This implies that the entropy of melting *falls* in inverse proportion to the temperature; for helium, however, a slight *rise* is observed. Of course, one could say that the entropy difference is bound to be zero at absolute zero and therefore must initially increase with rising temperature. This steep initial rise, however, seems more or less to have finished on reaching the λ -point, in agreement with the general observation that all the abnormal properties of liquid helium end abruptly at this particular temperature. It is true that the solid is still very degenerate even at the higher temperatures, but, on the other hand, the specific heat of the fluid has more or less the classical value of a gas at all volumes. It is not easy to see how this behaviour of the two phases should in itself lead to a tendency of the entropy difference to increase with rising temperature. It seems that for a better understanding of this point we will have to wait for the more comprehensive measurements of the thermal properties of the fluid which are at present under preparation in this laboratory.

We have now to discuss the *absolute values of the entropy* of the two phases in equilibrium. The only data so far available are results of calculations (Simon 1937) carried out for potassium, sodium and argon, making use of the change of θ derived from the Lindemann formula, the compressibility, and the thermal expansion. These calculations naturally cannot compete in accuracy with the direct measurements, but such measurements are only possible with helium and perhaps one or two other substances of low boiling temperature. The calculation shows that the entropies of the fluid and solid phases approach a mean value, so that the entropy of the fluid falls and that of the solid rises with increasing temperature.

These results agree with our present measurements on helium in so far as the entropy of the solid always rises along the melting curve with increasing temperature. There would, of course, be no objection from the thermodynamic point of view to this curve *falling* with rising temperature, and the result is therefore not trivial. It indicates that the effect of the rising temperature on the entropy surpasses the effect of the rise in Debye θ associated with the increase of pressure; in other words, the temperature of the solid, measured in terms of the characteristic temperature, rises along the melting curve. Now with helium, the entropy obviously cannot fall below its value at absolute zero. It is also obvious that as the melting pressure remains practically constant up to about the λ point the entropy is bound to rise in this region. There is no reason, however, why the curve should not from then onwards approach the zero line again. The fact that it does not do so seems to be just as valid an indication that T/θ (and therefore the entropy) rises along the melting curve as if it were happening in the 'classical' region—all the more so as the rise continues over such an enormous temperature range.

These experiments therefore lend additional strong support to a tentative statement proffered by one of us (Simon 1937) for normal substances (and according to Bridgman all substances tend towards normal behaviour at very high pressures), namely, that it is impossible to melt a substance by adiabatic, reversible compression, as such a compression would lead further into the range of stability of the solid. This statement may be of some interest in astrophysical and geophysical considerations.

Note added in proof, 28 May 1953. Since this paper was submitted, Mr L. Salter of the Clarendon Laboratory has succeeded in establishing equation (1) theoretically under more general conditions; no particular model of the melting process is needed, the substances are not assumed to be classical, and the range of validity is not restricted to high pressures. The basic assumptions are that the substance obeys the Grüneisen equation of state, that is, $C_v = f(T/\theta)$, $\theta = \phi(V)$, and that the Lindemann melting formula is obeyed along the melting curve, a fact proved by the present experiments. The derivation relates the parameter c in equation (1) to Grüneisen's γ ,

$$\gamma \equiv -\frac{d \ln \theta}{d \ln V} = -\left(\frac{\partial \ln T}{\partial \ln V}\right)_s.$$

These results allow us to determine the condition for $\frac{d}{dT} \left(\frac{T_m}{\theta}\right) > 0$ in terms of γ ; for substances which satisfy the two restrictions underlying Salter's derivation, the condition is simply $\gamma > \frac{2}{3}$. This value, it may be recalled, is the theoretical limiting value of γ as $V \rightarrow \infty$, i.e. for a gas; experimentally, γ values for regular crystals are found to lie between 1.5 and 2.5. These considerations, then, give theoretical support for the contention that melting cannot be achieved solely by reversible adiabatic compression.

We wish to express our thanks to Dr G. O. Jones (now at Queen Mary College, London) for his collaboration in the first year of these experiments; to him was due much of the design of the high-pressure equipment. We also wish to thank

E. Simon

critical temperature, while ours is its value. On the other hand, our effects.

entropy change on melting, we find constant, i.e. they are of the usual kind of the values observed for the (see table 9). The falling trend is due to quantum effects.

PROPERTIES OF THE INERT GASES

source of data

- present experiments
- present experiments
- Clusius (1936)
- Clusius (1936)
- Clusius (1936)
- Clusius & Riccoboni (1937)

of the entropy of melting it is an indication of any approach to a solid and fluid phases. Although in helium only over a relatively small range of temperature to a first approximation the entropy of melting falls for helium, however, a slight rise in entropy difference is bound to be observed with rising temperature. It is possible to have finished on reaching a temperature that all the abnormal behaviour is due to a particular temperature. It is at the higher temperatures, but, the entropy difference is more or less the classical value. This behaviour of the two phases is due to the difference to increase with rising temperature. On reaching of this point we will have reached the thermal properties of helium in this laboratory.

The entropy of the two phases in helium is the result of calculations (Simon 1937), making use of the change of θ with temperature, and the thermal expansion coefficient in accuracy with the direct measurements possible with helium and perhaps with other substances. The calculation shows that the entropy difference approaches a mean value, so that the entropy difference increases with increasing temperature.

Dr C. Domb (now at Cambridge), for many interesting discussions. We are indebted to Mr A. B. Charters of the Clarendon Laboratory for building the cryostats and to Mr A. T. Croxon for his help in taking the readings.

Imperial Chemical Industries, Limited, have been most generous in financial help, in the supply of high-pressure equipment and in valuable advice. In particular we would like to thank Dr J. Ferguson, Dr E. Hunter and Mr G. A. Shephard of I.C.I. (Alkali), Limited, and Mr W. R. D. Manning of I.C.I. (Plastics), Limited.

This work was made possible for one of us by the award of a Department of Scientific and Industrial Research maintenance grant.

REFERENCES

- Bridgman, P. W. 1935 *Proc. Amer. Acad. Arts Sci.* 70, 1.
Clusius, K. 1936 *Z. phys. Chem. B*, 31, 459.
Clusius, K. & Riccoboni, L. 1937 *Z. phys. Chem. B*, 38, 81.
De Boer, J. 1952 *Proc. Roy. Soc. A*, 215, 4.
Domb, C. 1951 *Phil. Mag.* 42, 1316.
Domb, C. 1952 *Proceedings of the International Conference on Phase Transitions, Paris*.
Holland, F. A., Huggill, J. A. W. & Jones, G. O. 1951 *Proc. Roy. Soc. A*, 207, 268.
Holland, F. A., Huggill, J. A. W., Jones, G. O. & Simon, F. E. 1950 *Nature, Lond.*, 165, 147.
Keesom, W. H. 1926 *Commun. Phys. Lab. Univ. Leiden*, no. 184b.
Keesom, W. H. & Keesom, A. P. 1936 *Commun. Phys. Lab. Univ. Leiden*, no. 240b.
Keesom, W. H. & Taconis, K. W. 1938 *Commun. Phys. Lab. Univ. Leiden*, no. 250e.
Lindemann, F. A. 1910 *Phys. Z.* 11, 609.
London, F. 1936 *Proc. Roy. Soc. A*, 153, 576.
Simon, F. E. 1934 *Nature, Lond.*, 133, 529.
Simon, F. E. 1937 *Trans. Faraday Soc.* 33, 65.
Simon, F. E. 1952 *L. Farkas Memorial Volume*, p. 37. Research Council of Israel Special Publication, no. 1. Jerusalem.
Simon, F. E. 1952 *Comptes rendus de la 2e. Reunion de Chimie-Physique*, 2-7 juin, Paris.
Simon, F. E., Ruhemann, M. & Edwards, W. A. M. 1929a *Z. phys. Chem.* 2, 340.
Simon, F. E., Ruhemann, M. & Edwards, W. A. M. 1929b *Z. phys. Chem.* 6, 62.
Simon, F. E., Ruhemann, M. & Edwards, W. A. M. 1930 *Z. phys. Chem.* 6, 331.
Simon, F. E. & Swenson, C. A. 1950 *Nature, Lond.*, 165, 829.
Swenson, C. A. 1950 *Phys. Rev.* 79, 626.
Swenson, C. A. 1951 *Proceedings of the Oxford Low Temperature Conference*, p. 27.
Webb, F. J. & Wilks, J. 1953 *Phil. Mag.* 44, 664.
Webb, F. J., Wilkinson, K. R. & Wilks, J. 1952 *Proc. Roy. Soc. A*, 214, 546.
Wilkinson, K. & Wilks, J. 1951 *Proceedings of the Oxford Low Temperature Conference*, p. 33.
Yntema, J. L. & Schneider, W. G. 1950 *J. Chem. Phys.* 18, 646.