masked by the resonance of single As impurities. Thus the central *satellite* should be twice as large as the outer satellites.

As the concentration increases, we would have resonances coming from clusters of more than two, but we might expect such clusters to be rather infrequent in the concentration range in which clusters of two are rare. The extreme case is the one in which the exchange coupling is so strong that we have a metal with completely nonlocalized electrons. Thus our case of interacting pairs is simply the first step in the process of turning the sample into a metal.

We note, finally, that if $A\sim kT$ or larger, there should be a temperature dependence of the satellite intensity of $\exp(-2A/kT)$, assuming the triplet states are higher in energy. The presence of satellites should also be a function of concentration (approximately proportional to c for low concentrations) and possibly of the mechanical treatment of the material if it causes the distribution of As in the lattice to be appreciably altered.

The predicted greater intensity of the central satellite for As is confirmed experimentally. The weakness of the lines makes it difficult to check the intensity ratio accurately, although Dr. Fletcher states that the experimental values scatter in the vicinity of the theoretical prediction

The author wishes to thank Dr. Fletcher for interesting conversations. This paper grew out of discussions on another problem with Professor David Pines and Professor John Bardeen. The author is indebted to them for numerous stimulating conversations and helpful comments.

PHYSICAL REVIEW VOLUME 99, NUMBER 2 JULY 15, 1955

Melting Curves of He^3, He^4, H_2, D_2, Ne, N_2, and O_2 up to 3500 kg/cm^2*

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(Received April 13, 1955)

New and more accurate measurements were made on the melting pressure-temperature relationship of seven substances below 120°K and up to 3500 kg/cm^2. New regions were covered for He^3 and O_2. The blocked-capillary method was used. The data were fitted to the Simon-type equation, $P=a+bT^c$, with more success than to a quadratic, $P=A+BT+CT^2$. Rather straightforward shifts were obtained in the melting curves of the isotope pairs, He^3-He^4 and H_2-D_2. Superpressuring in the O_2 measurements was unusually great.

1. INTRODUCTION

OUTSIDE of the pioneering work of Simon and his collaborators,[1,2] there is a surprisingly small amount of data on melting[3] temperatures as a function of pressure over a wide range and in the region below 100°K. They covered He, H_2, Ne, N_2, and A up to about 5000 kg/cm^2 using the blocked capillary technique first used by Kamerlingh Onnes and van Gulik.[4] Bridgman[5] also determined the the melting curves of N_2 and A to about 6000 kg/cm^2 but used the discontinuity in the specific volume as the criterion of melting. His P–T curves lay below those of Simon *et al.*; he felt that their data were in error as a result of the shear stress in the capillary plug. Recently, Robinson,[6] using the freedom of a pellet as the criterion of melting, measured A and N_2 to about 9400 kg/cm^2; his P–T curve for A lay below those of both Simon[2] and Bridgman,[5] while his N_2 curve lay between those of Simon and Bridgman (if one believes Robinson's actual data rather than his conclusions).

Helium has been studied in the 4000–7300 atmos (35–50°K) region by Holland, Huggill, and Jones[7] and in the 140–780 atmos (4–12°K) region by Dugdale and Simon.[8] All of these He data agree substantially with those of Simon.[1,2]

An interesting isotopic comparison resulted from the observations of Chester and Dugdale[9] on H_2 and D_2. They found the D_2 P–T curve to be consistently 170 kg/cm^2 lower than the H_2 curve up to their maximum pressure of 2800 kg/cm^2. However, their quantitative results were expressed only as the difference between the two isotopes and are therefore inadequate for general use.

One of the most debated points concerning solid-gas equilibria is the maximum temperature at which solid exists.[10–13] According to Simon,[10] the substance most

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* Work done under the auspices of the U. S. Atomic Energy Commission.

[1] F. Simon, Z. physik. Chem. **B2**, 340 (1929).

[2] Simon, Ruhemann, and Edwards, Z. physik. Chem. **B6**, 62 (1929); **B6**, 331 (1930).

[3] Used in its most general sense: solid to either fluid phase, liquid or gas.

[4] H. Kamerlingh Onnes and W. van Gulik, Leiden Comm. 184a (1926).

[5] P. W. Bridgman, Phys. Rev. **46**, 930 (1934); Proc. Am. Acad. Arts Sci. **70**, 1–32 (1935).

[6] D. W. Robinson, Proc. Roy. Soc. (London) **A225**, 393 (1954).

[7] Holland, Huggill, and Jones, Proc. Roy. Soc. (London) **A207**, 268 (1951).

[8] J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

[9] P. F. Chester and J. S. Dugdale, Phys. Rev. **95**, 278 (1954).

[10] F. E. Simon, Z. Elektrochem. **35**, 618 (1929); Trans. Faraday Soc. **33**, 65 (1937); Proc. Roy. Soc. (London) **A218**, 291 (1953).

likely to show this phenomenon, if it exists at all, is He. Since He^4 has not yet shown the effect, it seems that measurements on He^3 will provide the last chance for an experimental test. Up to now the only melting point measurements on He^3 have been those below 1.5° K and 56 atmos by Osborne, Abraham, and Weinstock.[14]

A review of the melting curves measured heretofore indicates their deficiencies in both extent and accuracy. Greater accuracy or, at least, internal consistency is especially desirable for deriving thermodynamic quantities from the slope of the melting curve. Therefore, we felt that there was a need for a comprehensive program of measurements, repetitive as well as new. We report here the results of the first phase: melting curves to 3500 kg/cm² for He^3, He^4, Ne, N_2, and O_2 and to 1800 kg/cm² for H_2 and D_2.

2. APPARATUS

A. General

The apparatus is shown schematically in Fig. 1. Here the gas source is a metal tank containing the gas at low pressures, from 1 to 150 atmos. The cryogenic pump is a heavy-walled steel vessel into which is condensed the gas when the pump is cooled by an appropriate bath. When the pump is warmed, the resulting high-pressure gas is sent into the steel capillary tubing, the mercury pusher, and the coil gauge. The process is repeated, if necessary, until the system is loaded to $\sim$1000 kg/cm² with the mercury in the right leg of the pusher at a minimum. From the left leg of the pusher, an oil line leads to a free-piston gauge and its manually operated oil injector. The capillary of Type 347 stainless steel, 0.69 mm o.d., by 0.25 mm i.d., is bent into a long, narrow loop, the tip of which can be cooled to any temperature down to 1.9°K. On the other side of the cold loop is a Bourdon helical coil gauge whose degree of uncoil, a measure of pressure, is observed by means of mirror, telescope, and scale.

The following procedure was used in making a melting-point measurement. The cold loop was adjusted to an appropriate temperature. The piston gauge was loaded stepwise with weights, and the oil injector was adjusted accordingly, thus increasing the pressure in the capillary until no movement of the coil gauge was observed, which indicated plugging in the cold capillary loop. Removal of weights caused unplugging. The initial freezing and melting pressures were usually within 1 percent of each other but, at times, differed by 10 percent. (In some cases, the temperature was varied at constant pressure; the supercooling found was approximately equivalent to the superpressuring.) If, during the melting transition, a weight was immediately added, freezing could be induced at a pressure lower than the initial freezing pressure. By successive freezings and meltings, we approached a pressure which needed smaller and smaller changes in weight to cause a freezing or melting. When melting and freezing were caused within $\sim\pm 1$ kg/cm², the point was taken as our "melting point."

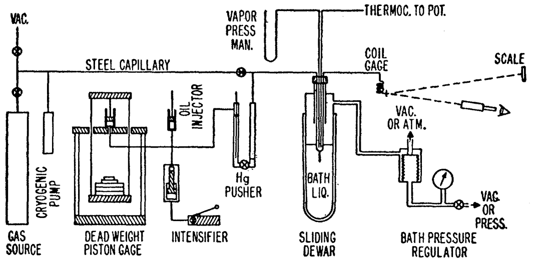

FIG.1. Schematic diagram of the melting point apparatus.

B. Source and Purity of Gases Used

All the gases used in the melting-point determinations, and in the vapor pressure thermometer, were analyzed in our mass spectrometer, which generally is sensitive to $\sim$0.05 percent for each impurity. However, considerable discretion must be used if impurities are indicated; many of these indications are false because of residues in the instrument.

(*a*) The helium-3 was obtained from the radioactive disintegration of tritium (T or H^3); the T was kept as UT_3, which has a negligible chemical decomposition pressure at 300°K, therefore the He^3 could be simply pumped off. Our analysis showed the He^3 to contain: <0.10 percent He^4, <0.01 percent H_2, <0.06 percent DT, <0.03 percent T_2, <0.03 percent N_2. The 4, 5, 6 masses are probably residues of HT, DT, and T_2 in in the spectrometer.

(*b*) The helium-4 was obtained directly from an AEC helium cylinder which had been filled by the Bureau of Mines. The Bureau's precautions are generally adequate to allow it to quote a purity of 99.99 percent in the filled cylinder. Our analysis showed <0.02 percent H_2, <0.01 percent Ne, <0.05 percent N_2.

(*c*) The hydrogen was produced through water electrolysis by the National Cylinder Gas Company. The more condensable gases were removed by adsorption on silica gel at 77°K. Our analysis showed <0.02 percent N_2 and <0.01 percent O_2 on the mass spectrometer and <1 ppm O_2 on a Beckman magnetic susceptibility analyzer.

(*d*) The deuterium was produced through heavy water electrolysis by the Stuart Oxygen Company, who claimed >99.5 percent purity. Our analysis showed 1.10 ($+0.00$ or -0.37) percent HD, <0.02 percent H_2, <0.12 percent N_2, and 0.01 percent O_2.

(*e*) The neon was produced through air distillation by the Linde Air Products Company, who designated it "spectroscopically pure." Our analysis showed 0.09 ($+0.00$ or -0.05) percent He, <0.05 percent H_2,

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[11] P. W. Bridgman, Revs. Modern Phys. **7**, 1 (1935).

[12] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A170**, 464 (1939).

[13] J. de Boer, Proc. Roy. Soc. (London) **A215**, 4 (1952).

[14] Osborne, Abraham, and Weinstock, Phys. Rev. **82**, 263 (1951); **85**, 158 (1952).

<0.05 percent N_2, 0.28 percent Ne^{21}, and 10.0 percent Ne^{22}. The adopted value of Ne^{22} content is 8.82 percent, but several observers have obtained 9.72 percent.[15]

(*f*) The nitrogen was produced through air distillation by Linde Air Products Company, who claimed a minimum purity of 99.7 percent and the impurities to be <0.3 percent O_2 and traces of Ne, A, Xe. Our analysis showed 0.11 (±0.01) percent O_2, 0.06 (±0.01) percent A, <0.06 percent Ne, <0.03 percent He, <0.04 percent H_2.

(*g*) Melting measurements were made on three kinds of oxygen: (1) Air distillation oxygen by Linde Air Products Company, who claimed >99.5 percent purity with <0.5 percent N_2 and traces of Ne, A, and CO_2. Our analysis showed 0.14 (±0.01) percent A, <0.05 percent He, <0.03 percent H_2. Mass spectrometric observations on N_2 and Ne were meaningless because of interference from other molecules. (2) Electrolytic oxygen by Stuart Oxygen Company labeled "Medical grade." Our analysis showed 0.30 (±0.03) percent H_2, <0.05 percent He, 0.03 (±0.01) percent A (the presence of A is difficult to explain). (3) The same as (2) but with the H_2 removed by distillation of the liquid. The resulting liquid showed a vapor pressure independent of amount evaporated. Our analysis of the gas showed <0.03 percent H_2, 0.03 (±0.01) percent A. This is the only O_2 that we consider gave reliable results.

C. Temperature Control and Measurement

The capillary cold loop, wherein freezing and melting occurred, went through a small copper block, 6 mm diam and 10 mm long, which had been split open and shaped to receive the tube and a thermocouple. All these parts were soldered together with "Cerrobend" (an alloy melting at ~70°C). Into the top of the copper block was drilled a hole to act as a vapor pressure thermometer well. This was connected to a manometer by means of steel capillary tubing. The vapor pressure thermometer system could be loaded with an appropriate gas: He, Ne, H_2, N_2, or O_2. Into the bottom of the copper block was soldered a steel rod whose purpose was to bridge the gaps between those temperatures obtained directly with liquid baths. This was accomplished by adjusting the bath level below the copper block until the temperature gradient was suitable to get the desired temperature at the block. This technique was aided by use of a Dewar with a sliding seal at top. The Dewar, 4 cm diam and 35 cm long on the inside, was of double construction, so that liquid nitrogen could be used as a shield, and had unsilvered strips for windows. The Dewar sat on a screw-type leveling ring so that its height could be adjusted closely with minimum effort on the part of the observer.

The liquid baths used were He, H_2, N_2, O_2, and CH_4; they were thermally stirred to promote temperature uniformity. With each, various temperatures could be chosen by adjustment of its vapor pressure from several to 2000 mm Hg. The bath pressure was controlled to the equivalent of 0.02° by a valve which was actuated by the difference between control and controlled pressures across a metal bellows.

The melting temperatures were determined by the vapor pressure thermometer wherever possible, otherwise by a thermocouple. Both were in intimate contact with the coldest point of the high pressure capillary. Where it was advantageous, a platinum resistance thermometer suspended in the bath was also used, but this was not entirely reliable in liquids like air, O_2, and N_2, which often have large temperature gradients. The thermocouple was made of Cu and an alloy of Cu containing 0.015 wt percent Fe, both wires being ~0.005 in. in diameter. The alloy, suggested by the work of Borelius,[16] was mixed, drawn, and annealed in this laboratory. The sensitivity in μv/deg was 10 at 5°K and 14 at 15° to 30°K, then dropped off to 5.5 at 60°K and finally to 1 at the ice point, which was used as the reference junction.[17]

Table I gives the thermometers used in various temperature ranges.

Wherever possible, concurrent comparisons were made between temperatures from vapor pressure, resistance thermometer, and thermocouple so that the last would have maximum interpolation value. In general, the vapor pressure thermometer was considered most reliable. In another type of apparatus, a similar resistance thermometer had been compared with vapor pressures of the gases used in this research; a maximum deviation of $T_{RT}-T_{VP}=0.08°$ was obtained at 75°K with N_2. Simultaneously emf *vs* T data

TABLE I. Thermometers used in various temperature ranges.

T range, °K	Thermometer used	Reference
1.9–5.2	v.p. He	a
5.2–12; 31–55	Cu–Cu Fe thermoc.	This research
12–24.5	v.p. $n-H_2$	b
24.5–31	v.p. Ne	c
55–78	v.p. N_2	d
75–101	v.p. O_2	e
14–24.5; 58–121	Pt resis. therm.	f

[a] The 1948 agreement at Amsterdam, and published by the Royal Society Mond Laboratory, Cambridge, in 1949, up to 4.2°; R. Berman and C. A. Swenson, Phys. Rev. **95**, 311 (1954) for 4.2–5.2°.

[b] Woolley, Scott, and Brickwedde, J. Research Natl. Bur. Standards **41**, 379 (1948) for 12–20°; E. R. Grilly, J. Am. Chem. Soc. **73**, 843 (1951) for 20–24.5°.

[c] F. Henning and J. Otto, Physik Z. **37**, 633 (1936) for 24.5–27.5°; E. R. Grilly (unpublished) for 24.5–31°.

[d] F. Henning and J. Otto, Physik Z. **37**, 633 (1936) for 66–78°; W. F. Giauque and J. O. Clayton, J. Am. Chem. Soc. **55**, 4880 (1933) for 55–66°.

[e] H. J. Hoge, J. Research Natl. Bur. Standards **44**, 321 (1950).

[f] Leeds & Northrup Company, serial No. 1008495, calibrated at the international fixed points and in the region 10–91° by the National Bureau of Standards against a gas thermometer.

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[15] K. T. Bainbridge and A. O. Nier, "Relative Isotopic Abundance of the Elements," Preliminary Report No. 9, Nuclear Science Series, Div. of Math. and Physical Sciences, National Research Council, Washington, D. C. (unpublished).

[16] G. Borelius, Physica **19**, 807 (1953).

[17] An alloy of Cu and 0.008 wt percent Sn, suggested by the work of Dauphinee, MacDonald, and Pearson [J. Sci. Instr. **30**, 399 (1953)], was also made up and tried, but it failed to give the proper sensitivity. Perhaps the mixture was not of uniform composition.

were obtained for two other Cu—Cu Fe thermocouples; these two and the thermocouple used for the present melting points gave parallel and only slightly separated calibration curves. In view of the various checks on the thermometry, it is estimated that the greatest possible error in melting temperature was 0.1°, which applied to the midpoints of the 5.2–12° and 31–55° regions, where interpolation by thermocouple was necessary; in other regions, the possible errors probably averaged about 0.03°.

The temperature control and measurement system used here was simple in principle and construction. Besides doing its main job of accurately measuring the melting temperature, it provided a means of rapidly changing the temperature whenever desired. This proved useful when melting points obtained in the normal way were checked by keeping the pressure constant and varying the temperature. Operation of the system was more tedious than that of the conventional system whereby the cold point is isolated from the bath by vacuum after reaching the lowest temperature desired. Whether the advantage was worth this is not readily discernible.

D. Pressure Measurements

On one side of the cold loop, high pressures were established and measured precisely with a free-piston gauge. Pressure changes on the other side of the loop were observed by means of a highly sensitive Bourdon helix. The two pressure devices will be described separately.

(*a*) *Free-Piston Gauge*

In the range of 350 to 3500 kg/cm^2, pressures were measured with a controlled-clearance free-piston gauge. The advantages of a controlled-clearance gauge, i.e., high sensitivity, manageable leakage of fluid past piston, and knowledge of effective area, have been discussed by its inventors, Johnson and Newhall.[18] Our instrument, shown in Fig. 2, was similar to theirs with minor modifications.

The jacket was designed to cover the range 0–3500 kg/cm^2 although the inner components could be pressured somewhat higher. The inner cylinder was machined from a manganese tool steel, hardened to Rockwell C-65, and then ground and lapped. The cylinder bore, nominally 0.0646 cm^2 in cross-sectional area, was 3.56 cm long.

The piston was made from a rod of Kennametal,[19] 2.5 cm long and 0.32 cm in diameter, brazed to a larger steel support. The piston was ground with a diamond wheel and lapped with diamond dust until it slipped into the cylinder without interference. In the completed assembly, the piston was free to move 5 mm, the tip moving 2.5 mm above and below the center of the cylinder bore. The piston was rotated at 24 rpm after the method of Myers and Jessup.[20] A height gauge of calibrated spring tension was firmly mounted to follow the travel of the piston. In practice the piston was floated to within ±0.012 mm of its center position with a manually operated oil injector.

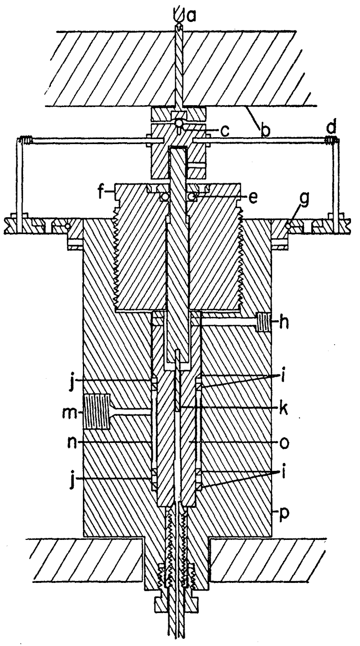

FIG. 2 The controlled-clearance free piston gauge. (*a*) height gauge; (*b*) yoke; (*c*) tungsten carbide insert and hardened ball; (*d*) light spring; (*e*) ball bearing guide; (*f*) packing nut; (*g*) ball bearing for rotating pulley; (*h*) oil overflow; (*i*) steel rings; (*j*) lead washer; (*k*) tungsten carbide piston; (*m*) jacket inlet; (*n*) thrust sleeve; (*o*) inner cylinder; (*p*) outer cylinder.

The hydraulic fluid employed was an aviation instrument oil. Oil pressure was developed with a hand pump and a 10-to-1 intensifier. The outer jacket of the free-pistion gauge was pressured with oil from the same intensifier. Its pressure was read on a 0–1400 kg/cm^2 (0–20 000 psi) Heise[21] gauge of guaranteed 0.1 percent accuracy.

The piston gauge is a primary pressure standard in its own right if careful attention is given the measurement of force and effective area. The force exerted by the various pan loadings was calculated as the product of the masses, calibrated to 0.001 percent and corrected for air buoyancy, times the gravitational acceleration, determined at our location to the same accuracy. Slight corrections for the spring force of the height indicator gauge and for piston buoyancy in oil were made. The effective area of a free piston gauge is the mean of the cylinder and piston areas. Our piston area was calculated from an average diameter measured with an electrolimit gauge to a few microinches. The result at 20°C was 0.064570 cm^2. Direct measurement of a bore

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[18] D. P. Johnson and D. H. Newhall, Trans. Am. Soc. Mech. Engrs. **75**, 301 (1953).

[19] Trade name of a tungsten carbide-cobalt mixture manufactured by Kennametal Inc., Latrobe, Pennsylvania.

[20] C. H. Myers and R. H. Jessup, J. Research Natl. Bur. Standards **6**, 1061 (1931).

[21] Heise Bourdon Tube Company, Newtown, Connecticut.

diameter of corresponding size, however, suffers in accuracy by several orders of magnitude. The expedient was used of determining the clearance between piston and cylinder. This was calculated from direct observation of the flux of *n*-propyl alcohol[22] through the crevice at various measured pressures and with various jacket pressures surrounding the cylinder. The clearance at atmospheric pressure was found to be $5.64 \pm 0.08 \times 10^{-5}$ cm. Piston and cylinder diameters at the different experimental pressures were computed by substituting values of the jacket pressure and approximate experimental pressure into well-known elastic equations.[23] The effective area at 3500 kg/cm^2 was less than 0.2 percent larger than the piston area quoted above.

All indicated pressures obtained by dividing force by effective area were converted to absolute values by addition of the barometric pressure. It is estimated that the controlled-clearance free-pistion gauge gave pressures accurate to ±0.05 percent, although its observed sensitivity was 1 part in 100 000.

In the pressure range 3.5–350 kg/cm^2, a commercial[24] free-piston gauge was used. The platform weights were calibrated by weighing and the effective area, 0.080640 cm^2 at 35.5445 kg/cm^2, was determined by balancing the gauge against a pressure standard, the vapor pressure of pure CO_2 at 0°C.[25] Effective areas at other pressures were calculated from elastic theory. Pressures measured with this gauge were accurate to within 0.05 percent. A comparison of the commercial pistion gauge with the controlled-clearance gauge at 350 kg/cm^2 showed no significant deviation.

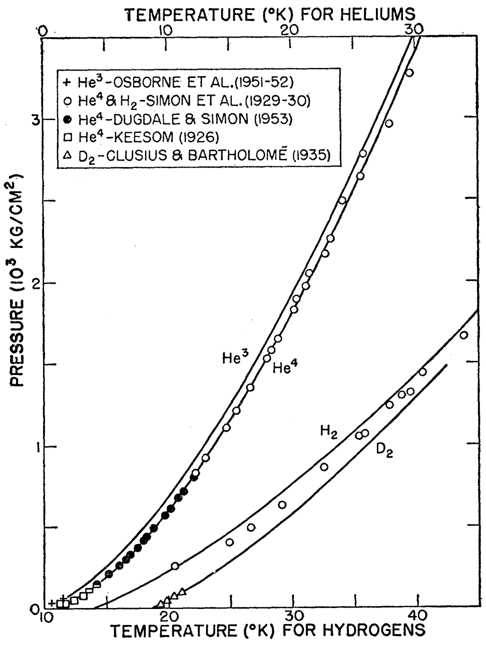

FIG. 3. Melting curves of helium and hydrogen isotopes. Present measurements are represented by the curves (no deviations are visible on this scale).

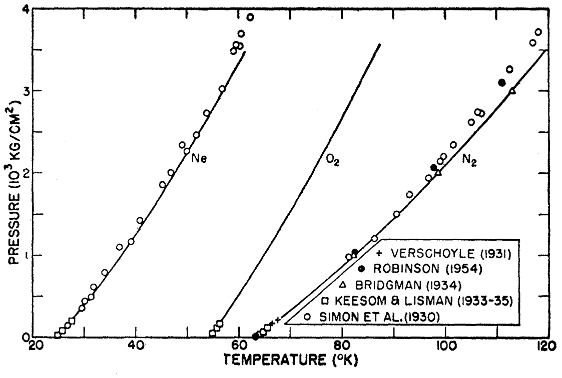

FIG. 4. Melting curves of Ne, O_2, and N_2. Present measurements are represented by the curves (no deviations are visible on this scale).

(*b*) *Bourdon Helix Gauge*

A 45-cm length of 0.69-mm o.d. by 0.25-mm i.d., Type 347, stainless steel capillary tubing was flattened by rolling until its major diameter was 1.5 times the minor diameter. The flattened tubing was then soldered shut at one end and coiled into a 2-cm diameter helix. The helix was fixed to a support just above the flattened section so that the closed end was free to describe angular rotation as a function of pressure. Such rotation was observed by means of a mirror, telescope, and scale. Scale deflections could be read to 0.1 mm which corresponded to a 0.2- or 0.3-kg/cm^2 pressure change in the helix gauge. This fixed the limit of resolution for all freezing- and melting-pressure determinations.

The helix gauge was initially pressure-seasoned at 3900 kg/cm^2, then calibrated *in situ* with He against the free-piston gauge. The calibration changed somewhat with time due to zero shifts, but the helix gauge was used to approximate absolute pressures only when the high-pressure system was charged initially from the cryogenic pump or subsequently bled to a lower range of pressures. Its primary function was that of sensing small pressure changes.

Response of the Bourdon helix gauge to pressure changes in the piston gauge became noticeably slower at low pressures. This was caused by the smaller density and larger compressibility of communicating gases in the capillary loop and resulted in somewhat more uncertain melting- and freezing-pressure determinations in the low-pressure region. At pressures greater than 350 kg/cm^2, the response was essentially instantaneous.

3. RESULTS

Putting 240 melting points into tabular form seemed impracticable; therefore, the measurements are given

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[22] The viscosity of *n*-propyl alcohol as a function of pressure has been determined by P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1949), pp. 330–356.

[23] See for example R. J. Roark, *Formulas for Stress and Strain* (McGraw-Hill Book Company, Inc., New York, 1943), p. 264.

[24] Ashcroft Gauge Tester 1312–50, Manning, Maxwell and Moore, Inc., Stratford, Connecticut.

[25] O. C. Bridgeman, J. Am. Chem. Soc. 49, 1174 (1927).

herein graphically and analytically. Figures 3 and 4 show the character of the melting curves in general and the comparison of our data (represented without visible deviations by the drawn curves) with those of other observers. Table II gives the results of fitting by least squares our measured pressures and temperatures to the melting equation advocated by Simon[1] and to be discussed later as Eq. (2): the constants, the pressure range of application, the root-mean-square deviation, and the number of points fitted. Figures 5 and 6 show the difference between measured and equation-computed pressures as a function of pressure. Of the three types of O_2 measured, only the results for the purest are reported in the table and figures.

Following the suggestion of Bridgman[5] that there should occur a transition point in solid N_2 in the 110–700 kg/cm² region, we measured melting points in this region at about every 30 kg/cm². We found no discontinuity in the slope of the melting curve.

4. DISCUSSION

A. Isotopic Effects

In each pair of isotopes observed here, He^3-He^4 and H_2-D_2, there is an approximate parallelism shown in Fig. 3 with the heavier isotopes displaced to lower pressures. The difference between the helium curves appears to increase from 40 to 120 kg/cm² over the range 2 to 30°K. Between the H_2 and D_2 curves there is a slight decrease in the difference, 170 to 140 kg/cm², in going from 19° to 43°K. The melting data of Clusius and Bartholomé[26] on D_2 up to 100 kg/cm² (21°K) first indicated a constant pressure (but not temperature) difference of ~170 kg/cm² between the H_2 and D_2 curves. Chester and Dugdale[9] reported a constant difference of 170±6 kg/cm² over the 25 to 57°K range. (Since they gave no absolute values, their results do not appear on our graph.) Unfortunately, we could not extend our measurements on H_2 and D_2 to 3500 kg/cm², nor include T_2, both of which were our intentions.[27]

TABLE II. Constants in the Simon melting equation, $P_{eq}=a+bT^c$.

	a	b	c	P range kg/cm²	$\left[\frac{\Sigma(P-P_{eq})^2}{n}\right]^{\frac{1}{2}}$	n [a]
He^3	25.16	20.08201	1.517083	76–3500	2.68	61
He^4	−17.80	17.31457	1.555414	37–3500	3.87	68
H_2	−270.52	2.534870	1.764739	0–1920	3.57	17
D_2	−418.29	1.812821	1.855812	0–1530	2.58	14
Ne	−1057.99	6.289415	1.599916	0–3500	4.91	37
N_2	−1638.30	0.976780	1.791000	0–3600	1.75	26
O_2	−2786.83	2.635754	1.742594	0–3600	5.09	17

[a] n = number of fitted points.

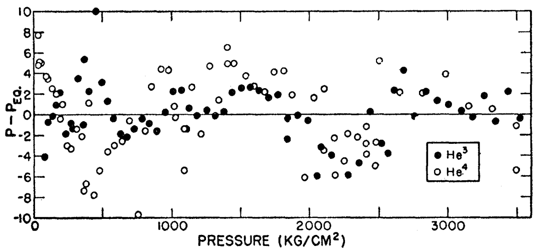

FIG. 5. Deviations of observed melting pressures from Simon equation.

B. Comparison of Present Measurements with Those of Other Observers

Also shown in Figs. 3 and 4 are results of other observers. The data of Simon, Ruhemann, and Edwards[1,2] show fair agreement with our He^4 results, less with our H_2 and Ne data, and give distinctly higher pressures than our N_2 curve. The recent work of Dugdale and and Simon[8] on He^4 up to 800 kg/cm² agrees with ours within ±5 kg/cm². Other observations, up to ~200 kg/cm², on He^4 by Keesom,[28] on Ne, O_2, and N_2 by Keesom and Lisman,[29] and on N_2 by Verschoyle,[30] also agree with ours. The only previous measurements on He^3, by Osborne, Abraham, and Weinstock,[14] covered 0.5 to 1.5°K. Below 0.5°, their melting curve approached 29.3 atmos. corresponding to the constant pressure reached by He^4 at somewhat higher temperatures. As well as we can presently determine, our data, down to 1.9°, meet theirs smoothly.

Since both Bridgman[5] and Robinson[6] gave their published results on N_2 as smoothed, we cannot examine the reliability of the individual measurements but must be content with the trends shown by their measurements. The status of the N_2 melting curve is now as follows: Simon *et al.*,[2] using the blocked-capillary technique, and Robinson,[6] using the moving-pellet method, agree with each other and give pressures 8 percent higher than the results of Bridgman,[5] using the volume-discontinuity criterion, and of our observations, using the blocked-capillary technique. Bridgman's smoothed data agree with ours to 5 kg/cm², thereby negating his objection to the blocked-capillary technique.

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[26] K. Clusius and E. Bartholomé, Z. physik. Chem. **B30**, 237 (1935).

[27] Among the readily available metals, we could not find any which would contain H_2 above 2000 kg/cm² in the Bourdon helical coil of rolled capillary necessary for determining small pressure changes. The capillary tubing used throughout to contain the high-pressure gases was Type 347 stainless steel, supposedly resistant to H_2 embrittlement. In other apparatus, the unrolled and uncoiled capillary withstood H_2 pressures of 3200 kg/cm² for at least a day and 2500 kg/cm² for at least a month. But in rolled and coiled form the capillary burst within a few minutes at H_2 pressures slightly greater than 2000 kg/cm². A similar effect resulted from using a capillary of the same steel but with heavier wall (0.79 mm o.d., 0.15 mm i.d.). A hard-drawn *K*-monel capillary (0.79 mm o.d., 0.33 mm i.d., manufacturer's specification of 3200 kg/cm² working pressure) also failed at 2300 kg/cm², probably purely the result of insufficient strength. Therefore, further measurements on the hydrogens will have to be delayed until we find a suitable substitute for the present coil gage.

[28] W. H. Keesom, Leiden Comm. No. 184b (1926).

[29] W. H. Keesom and J. H. C. Lisman, Physica **1**, 735 (1934) and **2**, 839, 901 (1935); Proc. Acad. Sci. Amsterdam **36**, 378 (1933) and **38**, 808 (1935).

[30] T. T. H. Verschoyle, Trans. Roy. Soc. (London) **A230**, 200 (1931).

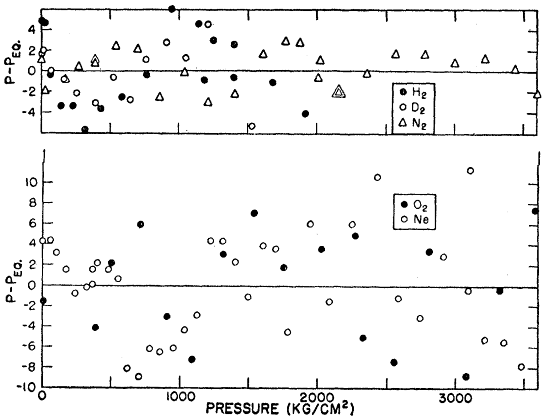

FIG. 6. Deviations of observed melting pressures from Simon equation.

C. Simon Melting Equation

Simon,[1,2,8,10] Lennard-Jones and Devonshire,[12] de Boer,[13] Domb,[31] and Salter[32] have advocated, on empirical and theoretical grounds, a universal melting formula

$$P/a = (T/T_0)^c - 1, \qquad (1)$$

in which a is related to the "internal pressure" of the solid, T_0 to the triple-point temperature, and c to the intermolecular potential. The formula has, indeed, been successful in expressing all the measurements made on the low-boiling elements. We undertook fitting our data by the method of least squares, minimizing $\sum(P-P_{\mathrm{eq}})^2$, to the empirical form of Eq. (1)

$$P = a + bT^c, \qquad (2)$$

and to a simple quadratic

$$P = A + BT + CT^2. \qquad (3)$$

Compared with Eq. (3), Eq. (2) gave a much better fit for He^3 and He^4, moderately better for H_2, D_2 and Ne, and about equally as good for N_2 and O_2. As shown in Figs. 5 and 6, the deviations of our data from Eq. (2) show some definite oscillations, indicating that minor corrections should be made to the equation. In the case of the heliums, the different characters of the deviation plots at low pressures reflect the different temperatures at which the pressures level off to constant values.

In spite of the generally good agreement between measurement and Eq. (2), we cannot consider any one set of the constants a, b, and c unique. With proper compensation between terms, we could vary the constants considerably without affecting $\sum(P-P_{\mathrm{eq}})^2$ appreciably, and with different sets of data we could get significant variations in the best-fitting constants. Therefore, we cannot attach much quantitative significance to the relations between the empirical constants and the fundamental properties noted in Eq. (1). On the other hand, it is difficult to disregard the positive value of a for He^3, which would mean, on the basis of Eq. (1), that the "internal pressure" is negative or that the isothermal increase of volume causes a decrease in the internal energy of the solid.

D. Unusual Melting-Freezing Transition in O_2

A rather speculative conclusion we reach is that there must be something unique in the melting-freezing transition in O_2. For all the other substances observed, we found the initial freezing pressure to be within 1 percent of the melting pressure and could easily bring the two to within 1 kg/cm² by the previously described procedure. But for O_2, the initial freezing pressure was usually 10 percent higher than the melting pressure, which remained fairly constant with alternate meltings and freezings; then only by considerable manipulation could the superpressuring be removed. It does not seem possible to blame this effect entirely on impurities. For example, the Ne and N_2 were more impure than some of the other substances (see 2-B) yet gave no anomalous reversibility; in fact the N_2 was remarkable in its overall reproducibility and adherence to the Simon melting equation. Moreover, the three types of O_2 that we observed showed no definite variation in reversibility although they gave three different melting curves.[33] We surmise there is some connection between the melting-freezing characteristics as observed in the present work and the behavior of the N_2 and O_2 impurities in a hydrogen liquefier. As is often observed in the liquefier, solid N_2 readily blows through the expansion valve while solid O_2 usually plugs the valve.

5. ACKNOWLEDGMENTS

We wish to thank the following persons who contributed to this research: Frederick J. Edeskuty for his large part in the development of the controlled-clearance piston gauge and for assistance in observations; Robert Chrisman for his skilful fabrication of the piston gauge; Isaac Valdez and Guadalupe Garcia for assistance in observations; and Max Goldstein for assistance in computations.

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[31] C. Domb, Phil. Mag. 42, 1316 (1951).

[32] L. Salter, Phil. Mag. 45, 369 (1954).

[33] The O_2 and 0.3 percent H_2 curve was 1 to 2 percent higher in pressure, while the O_2 and 0.14 percent. A curve was ½ percent lower in pressure than the curve of the purest O_2. This result is fairly consistent with the expected types of solid phase: single component and solid solution with H_2 and A, respectively.