PHYSICAL REVIEW VOLUME 101, NUMBER 4 FEBRUARY 15, 1956

Melting Curves of H_2, D_2, and T_2 up to 3500 kg/cm^2*

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(Received November 2, 1955)

The melting pressure-temperature relationship of the three hydrogen isotopes has been determined accurately to 3500 kg/cm² by the blocked-capillary method. The data were fitted with fair success to the Simon-type equation, $P=a+bT^c$. The melting curves of H_2, D_2, and T_2 are displaced downward on the pressure axis in that order and, at identical temperatures, exhibit approximately equal slopes.

A PREVIOUS paper[1] discussed the failures, under high-pressure hydrogen, of a coiled Bourdon gauge used in melting-point measurements. In order to avoid this difficulty, we substituted a manganin resistance gauge with the essential characteristics of small volume, high sensitivity, and high strength, regardless of the gas enclosed. The manganin resistance gauge was housed in the Type 303 stainless steel vessel shown in Fig. 1. A stainless steel electrode was sealed through the cap by conventional Bridgman unsupported area packing which ultilized mica washers and Neoprene packing. Initially the packing was tightened by pulling on the electrode with a micarta thumb screw. The coil itself was wound of No. 36 double nylon-covered manganin wire soldered at one end to the insulated electrode and at the other to the coned capillary adapter tube. Nominal resistance of the manganin gauge was 60 ohms and its measured sensitivity was 13.93×10^{-5} ohm/kg/cm². With a suitable bridge current, pressure changes of 0.3 kg/cm² could be detected by galvanometer deflection. Drifting of the zero-pressure resistance was of no consequence since the gauge was used only to indicate sudden pressure changes.

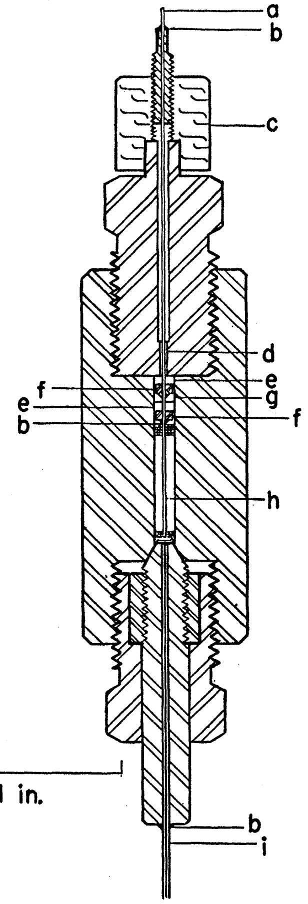

FIG. 1. Manganin pressure gauge. (a) electrode; (b) silver solder; (c) micarta; (d) glass sleeve; (e) mica washers; (f) steel; (g) rubber; (h) manganin coil (fills entire space); (i) steel capillary.

The present results were obtained by the same blocked-capillary technique as described previously.[1] The present measurements from 1277 kg/cm² (38°K) to 3700 kg/cm² (65°K) employed the same H_2 as was used in the previous measurements, which extended only to 1920 kg/cm². The old and new results joined together smoothly.

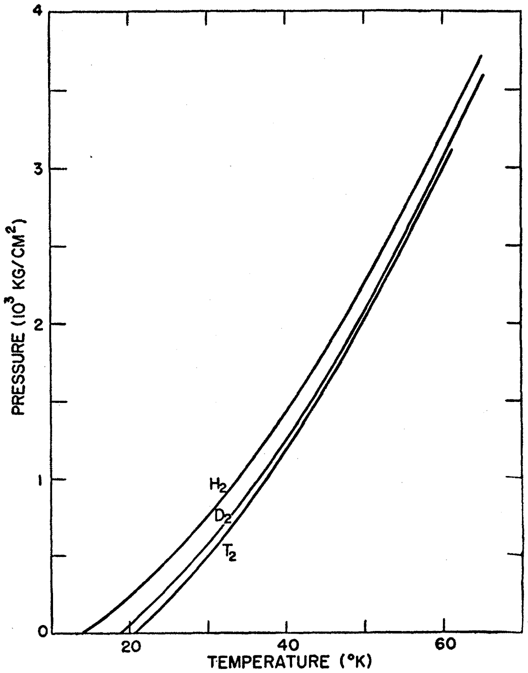

FIG. 2. Melting curves of the hydrogen isotopes.

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

[1] R. L. Mills and E. R. Grilly, Phys. Rev. 99, 480 (1955).

TABLE I. Constants in the Simon melting equation, $P_{\mathrm{Eq.}}=a+bT^c$.

	a	b	c	P_{range} kg/cm²	$\left[\frac{\Sigma(P-P_{\mathrm{Eq.}})^2}{n}\right]^{\frac{1}{2}}$	n
H_2	−279.63	2.749629	1.744070	0–3700	5.98	27
D_2	−438.15	2.312026	1.787213	0–3600	4.19	24
T_2	−540.39	2.581294	1.764179	0–3100	2.90	16

The D_2 used in the new measurements was somewhat purer than that used previously: a different tank, from the same source but containing more gas per unit surface area, was used, and its contents were shown, by mass spectrometer, to be 0.85 (+0.00−0.11)% HD, <0.06% H_2, <0.09% N_2, and <0.02% O_2. Although this indicates only a slight improvement over the previous D_2, we feel that there was a significant change in purity of the D_2 in the melting-point apparatus as a result of the improved method of handling. Previously the gas was liquefied in the cryogenic pump, then the liquid was vaporized into the melting-point apparatus until the proper high pressure was obtained there; the fractionation in this process undoubtedly raised the H concentration. In the present work, the D_2 was never liquefied outside the melting-point tube; instead the proper pressure was obtained by mechanically compressing the low-pressure gas (from 35 kg/cm²), a process causing no fractionation. As a result, the composition of the D_2 in the melting-point apparatus could be definitely known. (The only uncertainty remaining was the slight composition change arising from the fractionation caused by solidification during the melting-point measurement itself.) For this reason and because the present measurements extend over a wider range with the same D_2, the present data are preferred over the old data, which showed somewhat higher melting pressures.

The measurements on T_2 were complicated by both the original impurities and those picked up in handling. Tritium decays to He^3 at the rate of ~0.9% per month; in our storage tank, the He^3 had built up to ~4%. For elimination of this, the solidified T_2 in the cryogenic pump was fractionated, by pumping, vaporizing, refreezing, and pumping until the He^3 content was below mass spectrometer detection; the process also eliminated some H (mostly as HT). From the effective removal of He^3, one can infer the removal of any He^4 which might have been present originally. The second difficulty resulted from the H growth in the melting-point apparatus, the exchange being accelerated by the relatively large surface area. This effect was minimized by letting T_2 stand in the apparatus for a few days, removing it, and replacing it with fresh T_2, then making the melting-point measurements rapidly. Gas samples for analysis were taken before and after the measurements to ensure knowledge of the gas composition. Fortunately the composition proved to be constant for each charge of T_2. The three T_2 charges had the following HT concentrations in the indicated pressure ranges of the measurements: 0.90% for 58 to 290 kg/cm²; 0.56% for 440 to 961 kg/cm²; 0.73% for 1195 to 3109 kg/cm². The slightly different HT concentrations apparently caused no discontinuities in the melting curve. All of the T_2 charges contained <0.05% H_2, <0.05% DT, <0.05% He^3, <0.02% N_2, and <0.001% O_2. Since failures of the capillary tubing still occurred occasionally when filled to high pressure with hydrogen, the melting curve of T_2 was measured only up to 3100 kg/cm².

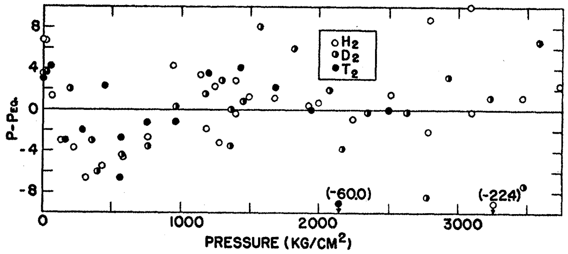

FIG. 3. Deviations of observed melting pressures from Simon equation.

The melting points of H_2 D_2, and T_2 were fitted to the empirical form of the Simon melting equation,[2] $P=a+bT^c$, by the method of least squares, minimizing $\sum(\Delta P)^2$. Table I gives the constants, the pressure range of application, the root-mean-square deviation, and the number of points fitted. Figure 2 shows the general character of the curves, and Fig. 3 gives the difference between measured and equation pressures as a function of pressure.[3]

Previously, Chester and Dugdale[4] showed that there is a constant pressure difference between the melting curves of H_2 and D_2 amounting to 170±6 kg/cm² over the temperature range 25–57°K. The present work agrees with their results up to 50°, but then it shows that the difference drops off to 135 kg/cm² at 65°K. In addition, the present results indicate that the T_2 melting curve is lower than the H_2 curve by 250±5 kg/cm² between 20 and 40°K and that then the differential drops to 185 kg/cm² at 60°K. These results mean that at identical temperatures the melting curves of H_2, D_2, and T_2 have approximately the same slopes, which in turn indicates that the ratio of the entropy or heat of melting to the volume change on melting is independent of the isotope.

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

[3] The −60 difference for T_2 at $P=2142$ kg/cm² was not used in computing the equation constants.

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