Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 48, No. 1, 526–527, 1 January 1968
Printed in U. S. A.

Solidification of *n*-Pentane at High Hydrostatic Pressure

S. H. GELLES
Ledgemont Laboratory, Kennecott Copper Corporation, Lexington, Massachusetts

(Received 5 July 1967)

n-Pentane, isopentane, and mixtures of the two have been extensively used as high hydrostatic pressure media since they were thought to have among the highest solidification pressures at room temperature. Bridgman has claimed that *n*-pentane or a mixture of *n*- and *i*-pentane[1,2] do not solidify even at 30 000 kg/cm^2.

Reeves, Scott, and Babb[3] in tracing the melting points of *n*-pentane to 10 kbar, found them to range between ~ -130°C at atmospheric pressure and -30°C at 10 kbar. Using a Simon representation for their data, they have computed the extrapolated melting pressure of *n*-pentane at 25°C as 15 kbar. There has been no experimental confirmation of the solidification pressure at room temperature. In fact evidence has recently been presented[4] that high shear stresses are absent in *n*-pentane subjected to 60 kbar pressure indicating that solidification did not occur even at this high pressure.

In some current studies[5] observations led to the suspicion that either *n*-pentane was freezing or that the previously reported transformation in 18-8 stainless steel[6] was being encountered at 18 kbar. A series of experiments was therefore carried out to determine whether the transformation was occurring in the *n*-pentane or in the stainless steel.

The experiments were conducted at room temperature in a Bridgman–Birch 30-kbar apparatus[7] using the piston discontinuity method for detecting the phase transition and measuring ΔV, the volume discontinuity at transformation. Pressure was measured with a calibrated manganin gage and is accurate to ± 500 bar.

Three different fluids were investigated: (1) Eastman *n*-pentane, practical grade; 97.2 vol % pure. (2) A 50–50 vol % mixture of the Eastman *n*-pentane and Eastman isopentane (practical grade). (3) Phillips Petroleum Company Research Grade *n*-pentane, 99.87 mole % pure. Two solids were used in these experiments: 18-8 stainless steel and Ferrovac E iron. (Iron does not transform in the pressure range under investigation.[8])

The volume of liquid V was calculated as a function of pressure from the dimensions of the pressure vessel and the piston displacement. The number of moles of *n*-pentane was calculated from the density–temperature relationship.[9]

Six experiments have been conducted embracing the combinations of the three pressure media and two solids. Transformations were seen only in the runs in which *n*-pentane (either Eastman or Phillips) was used as the pressure medium. The mixture of pentanes with either the stainless steel or iron sample showed no evidence of transformation up to the highest pressure reached (25–27 kbar).

From these experiments it is concluded that a solid–liquid transformation is taking place in *n*-pentane at a pressure of 17.55 ± 0.67 kbar at $23.3° \pm 0.3°$C. The thermodynamic melting parameters listed in Table I were computed by use of the Clapeyron equation.

The results presented are in direct conflict with statements made by Bridgman[1] that pentane does not solidify at room temperature and 30 000 kg/cm^2. The results however are in reasonable agreement with those of Reeves *et al.*[3] (Fig. 1) although they differ with the extrapolated 25°C solidification pressure by $\sim 17\%$. This must be attributed to the uncertainty in extrapolating the Simon relationship. The higher-pressure data of Reeves *et al.*[3] and the melting point determined in the present study when graphed on a log–log plot appear to fall on a straight line (Fig. 1) in agreement

TABLE I. Values of thermodynamic melting parameters.

Pressure (bar)	Temp (°K)	ΔV_m (cm^3/mole)	ΔH_m (kcal/mole)	ΔS_m (eu/mole)	$\Delta V/V$%
1	143.5[a]	7.72	2.01[b]	0.0140	...
17 550	296.3	2.67	7.04	0.0238	4.1

[a] See Ref. 3.
[b] M. G. Broadhurst, J. Res. Natl. Bur. Std. A66, 241 (1962).

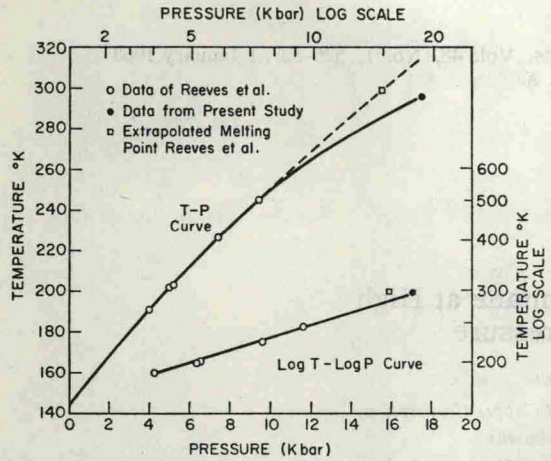

FIG. 1. T–P and log$T$–log$P$ representations of the melting curve of n-pentane (solid curves). Dashed curve represents Simon relation proposed by Reeves *et al.*[2]

with other representations of the melting relationship.[10,11]

The failure of Norris[4] to observe excessive shear stresses in n-pentane at 30 and 60 kbar and Bridgman's failure to observe solidification in this fluid lead to the probability that they were working with a superpressurized (supercooled) fluid. This is further confirmed by the experience of Reeves *et al.*[3] that subcooling in n-pentane was an experimental problem and Bridgman's observation[12] that it is possible to bypass solidification completely in some organic liquids with a sufficiently high pressurization rate.

The following is a summary of the results:

(1) n-Pentane undergoes a liquid–solid transformation at a pressure of 17.55±0.67 kbar at 23.3°±0.3°C in general agreement with the results of Reeves *et al.*,[3] but in apparent conflict with the results of Bridgman[1] and Norris,[4] who were probably working with a superpressurized fluid.

(2) No evidence of transformations was detected in a 50–50 vol % mixture of n-pentane and isopentane nor in 18-8 stainless steel up to pressures of 25 kbar at 22.5±0.5°C.

[1] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **77**, 117 (1949).
[2] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1958), p. 399.
[3] L. E. Reeves, G. J. Scott, and S. E. Babb, Jr., J. Chem. Phys. **40**, 3662 (1964).
[4] D. I. R. Norris, Brit. J. Appl. Phys. **16**, 709 (1965).
[5] S. H. Gelles (work in progress).
[6] C. M. Fowler, I. S. Minshall, and E. G. Zukas, *Response of Metals to High Velocity Deformation* (Interscience Publishers, Inc., New York, 1960), p. 290.
[7] F. Birch, E. C. Robertson, and S. P. Clark, Jr., Ind. Eng. Chem. **49**, 1965 (1957).
[8] W. Klement, Jr., and A. Jayaraman, *Progress in Solid State Chemistry* (Pergamon Press, Ltd., Oxford, England, 1967), Vol. 3, pp. 316–317.
[9] *International Critical Tables* (McGraw-Hill Book Co., Inc., New York, 1928), Vol. 3, p. 29.
[10] H. C. Longuet-Higgins and B. Widom, Mol. Phys. **8**, 549 (1964).
[11] J. S. Rowlinson, Mol. Phys. **8**, 107 (1964).
[12] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **74**, 399 (1942).