[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Supercooling of Liquid Phosphorus

BY J. H. HILDEBRAND AND G. J. ROTARIU

Phosphorus can be kept in liquid form indefinitely at room temperature, despite the fact that crystallization involves only minimal changes in entropy (R cal./deg.) density and number of nearest neighbors. We have succeeded in cooling drops of 1 mm. diameter or less to −71.3°, which is 115.6° below its melting point. There was no evidence of glass formation. This suggests that it is not altogether realistic to regard the structure of the liquid as that of a quasi solid lattice with occasional holes.

The freezing of liquid phosphorus is a process that would seem to involve, for a polyatomic molecule, a minimum of structural rearrangement. The solid is cubic, and Sugawara, Sakamoto and Kanda[1] have recently published evidence that it is body-centered cubic. Each P_4 molecule accordingly has 8 nearest neighbors. This is the number of nearest neighbors in the liquid as determined by Thomas and Gingrich.[2] The loss of entropy on freezing, according to Young and Hildebrand,[3] is 1.895 entropy units per mole of P_4 or 1.984, according to a doubtless more accurate determination, unpublished at this writing, kindly furnished by Professor Clark C. Stephenson. This is exactly the value of the gas constant, R, and seems to indicate clearly that the molecules, by virtue of their compact, tetrahedral structure, retain their rotational energy in the solid between the freezing point, 44.3°, and a transition[4] occurring at −76.9°. The crystallization process, therefore, is not hindered by any necessity for orientation. The contraction in volume on freezing is only 3.5% at the melting point, and 3.1% at 5°. In spite of these seemingly minor differences between solid and liquid, we have kept phosphorus in liquid form at room temperatures for months at a time. Thomas and Gingrich mentioned having had liquid phosphorus 50° below its melting point. These facts aroused our curiosity as to the degree of supercooling it might be possible to attain, and this we proceeded to investigate in the following manner.

Commercial C.P. white phosphorus was cleaned by melting it under dilute sulfuric acid–bichromate mixture, and letting it stand for several days in the dark at room temperature, where it almost invariably remains liquid. The initial milky appearance seems to be due to insoluble material that remains on the surface, and is, therefore, easily oxidizable by the chromic acid, because the liquid gradually becomes quite clear and colorless. This method of purification has long been employed by the senior author, and appears fully adequate for most purposes. For this experiment, however, we distilled the phosphorus after having submitted it to the above treatment.

Procedure.—About 0.5 ml. of liquid white phosphorus was pipetted into an evacuated glass tube (1.2 cm. diameter, 18 cm. long) which was connected to a vacuum line by means of a ball joint. The ball joint, lubricated with Dow-Corning High-Vacuum Silicone Grease, permitted rotation of the tube for inspection of the droplets formed later. After the trace of water was removed, the tube was evacuated to 10^{-5} mm., and the phosphorus was distilled onto the sides of the tube by heating it gently to 55°. Droplets of liquid white phosphorus were formed by warming the walls to 47°. The droplets were then cooled gradually by 2–5° intervals, allowed five minutes at each interval for temperature equilibrium, and inspected for solidification by aid of 5X magnifier.

In the case of the larger droplets, it was usually possible to distinguish the ones which had crystallized by their opacity and their obviously polygonal periphery, but the state of the smaller droplets could not be determined with certainty from their appearance alone, so a tiny, magnetic probe was introduced. This was a fine steel wire 2 mm. long, encased in a thin glass capillary, total length 5 mm. This probe could be moved about perpendicularly to the inner surface of the tube by an external Alnico magnet. A liquid drop, when touched with this probe, either smeared or crystallized, while a solid particle remained unchanged.

A water-bath was used down to 0°, water, ice and salt mixtures to −12° and carbon dioxide–methyl alcohol to −70°. When it was judged that the tube and its contents had reached the temperature of the bath, this was removed and drops which appeared to be liquid were investigated by aid of the probe. It was found that drops of 1 to 2 mm. diameter crystallized first, and were all solid at −4°, and the drops that remained liquid as the temperature was lowered further were successively the smaller and smaller ones. The lowest temperature at which any remained liquid was −71.3°. It is noteworthy that the drops surviving to the lowest temperatures were definitely liquid and not glass.

This supercooling is 115.6° below the melting point, and the ratio of our lowest temperature to the melting point, Kelvin, is 0.64. This is considerably less than the ratios varying between 0.75 and 0.87 for the numerous metals investigated by Turnbull,[5] despite his use of much smaller drops, which greatly favors supercooling.

The ability of the liquid to survive to such low temperatures may be explained in part by the comparatively small free energy of the process in the light of the small heat of fusion. But the fact that the pure liquid persists indefinitely at room temperatures shows that the barrier against crystallization is a very real and effective one, and seems to us to show the inadequacy of the assumption so often made in dealing with the liquid state that the structure is quasi-crystalline, being either that of a slightly mussed up close-packed solid or a regular lattice with holes here and there. One would think that phosphorus would not remain liquid so long if crystallization could be started simply by a few molecules moving into adjacent holes.

A good treatment of the liquid state should describe liquid structure as realistically as possible, and one should hardly expect the best results from a purely arbitrary lattice frame of reference. It is well understood that there is no general expression for crystal lattice energies, and that the most stable lattice structure can only be determined by assuming every probable one and calculating the energy of each. We suggest that, correspondingly, the energy of a liquid is likely to be most

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(1) T. Sugawara, Y. Sakamoto and E. Kanda, *Science Repts. Research Insts. Tohoku Univ. Ser. A*, 1, No. 1, 29–32 (1949).

(2) C. D. Thomas and N. S. Gingrich, *J. Chem. Phys.*, **6**, 659 (1938).

(3) F. W. Young and J. H. Hildebrand, THIS JOURNAL, **64**, 839 (1942).

(4) P. W. Bridgman, *Phys. Rev.*, **3**, 186 (1914).

(5) D. Turnbull, *J. Appl. Physics*, **21**, 1022 (1950).

closely approximated on the basis of that description of its structure which is nearest to actuality, and this is the continuous distribution function yielded by X-ray scattering and now, as well, by theoretical analysis such as that of Kirkwood and Boggs.[6]

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[6] J. G. Kirkwood and E. M. Boggs, *J. Chem. Phys.*, **10**, 394 (1942).

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Crystallization Velocity of Liquid Phosphorus[1]

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Strongly supercooled liquid phosphorus crystallizes with far higher linear velocities than those that have been reported for other substances, commonly in mm. per minute, therefore it seemed worthwhile to secure some quantitative data. Using an electronic circuit with photoelectric cells, and a liquid column 88 cm. long, velocities were measured at initial liquid temperatures from near the melting point down to 21.3°, where the velocity, v, was 210 cm./sec. The results are closely reproduced by the equation $(v\eta)^{1/2} = 1.01(44.1 - t)$, where η is the viscosity in centipoises, and t the temperature. A qualitative justification is given for this relation.

The amazing speed with which strongly supercooled liquid phosphorus crystallizes was made strikingly evident to the senior author by the sudden blackening upon crystallization of strongly supercooled solutions of mercury in phosphorus, described in another communication.[2] Since linear velocities of crystallization heretofore reported are commonly given in millimeters per minute,[3] it seemed worthwhile to obtain figures for this case of a velocity of an altogether different order of magnitude.

Our first observations of the crystallization velocity were made using a stopwatch and a 60 cm. length of phosphorus, under water in a somewhat longer U-tube of approximately 4 mm. internal diameter. The phosphorus was first melted by immersing the tube in a jar of water above the melting point; the tube was then transferred to a water-bath at some temperature below 44°, and, after waiting for temperature equilibrium, crystallization was started by touching the surface of the phosphorus in one limb with a copper wire that had been cooled in liquid nitrogen. The stopwatch was started at the same instant and was stopped when the wave of solidification had reached the other end of the phosphorus. The velocities corresponding to times as short as 2 seconds are, of course, subject to appreciable error, as shown by the scatter of the upper points for this run, therefore they are omitted from Table I.

In order to measure much shorter times with the desired accuracy, an electronic circuit was devised by one of us (Powell). A diagram of it is given in Fig. 3. As the wave of opacity travelled down one limb of the U-tube containing phosphorus, the light of a red lamp passing through the phosphorus and then through a small window to a photocell was interrupted and this started the charging of a condenser. As the wave passed up to near the top of the other limb, a second photocell stopped the charge, the amount of which gave the elapsed time. The total scale deflection could be set to correspond to 10, 1 or 0.1 second. The length of the phosphorus column was 88 cm.

There were two runs with this apparatus, using different samples of phosphorus; one which had been distilled in vacuum, the other cleaned till "water white" by being kept liquid for some hours under dilute sulfuric acid–bichromate solution. The two sets of points thus obtained are given in Table I. v is the velocity of crystallization in cm./second. Figure 1 plots the two sets of accurate points from Table I together with the earlier, less accurate, points for low velocities. It will be seen that the different runs agree quite satisfactorily. There is no evidence, moreover, that the velocity is approaching a maximum, such as demanded by well known theories and realized with many other substances.

TABLE I

LINEAR VELOCITY OF CRYSTALLIZATION OF PHOSPHORUS

Run	t, °C.	v, cm./sec.	η, centipoises	$(v\eta)^{1/2}/$ $44.1 - t$
2	37.9	23.3	1.84	1.06
2	35.1	45.5	1.90	1.03
2	33.4	63	1.95	1.04
2	32.2	79	1.99	1.05
2	29.8	102	2.05	1.01
2	29.3	108	2.06	1.01
2	25.8	153	2.16	0.99
2	23.3	181	2.19	0.98
3	25.0	161	2.26	0.97
3	22.0	210	2.30	0.99
3	21.4	210	2.32	0.97
			Mean	1.01

Many years ago, Gernez[4] measured the velocity of crystallization of phosphorus, using columns much narrower than ours—1 to 2 mm.—and some sort of special "chronometer." His points agree well with ours down to 33° but fall far below at the lower temperatures.

Turnbull and Cech,[5] in their investigation of the supercooling of liquid metals, have stated, however, that "With the exception of selenium, all of the droplets that had supercooled considerably solidi-

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[1] A brief preliminary report on this work was presented at the symposium on liquid structure of the American Chemical Society in Chicago, September 4, 1950.

[2] THIS JOURNAL, **73**, 2527 (1951).

[3] *Cf.*, G. Tammann, "States of Aggregation," D. Van Nostrand Co., Inc., New York, N. Y., 1925.

[4] Gernez, *Compt. rend.*, **95**, 1278 (1882).

[5] D. Turnbull and R. E. Cech, *J. Appl. Phys.*, **21**, 804 (1950); also D. Turnbull, *ibid.*, p. 1022.