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]

The support of this investigation by the Atomic Energy Commission is gratefully acknowledged.

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

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

Crystallization Velocity of Liquid Phosphorus[1]

BY R. E. POWELL, T. S. GILMAN AND J. H. HILDEBRAND

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.

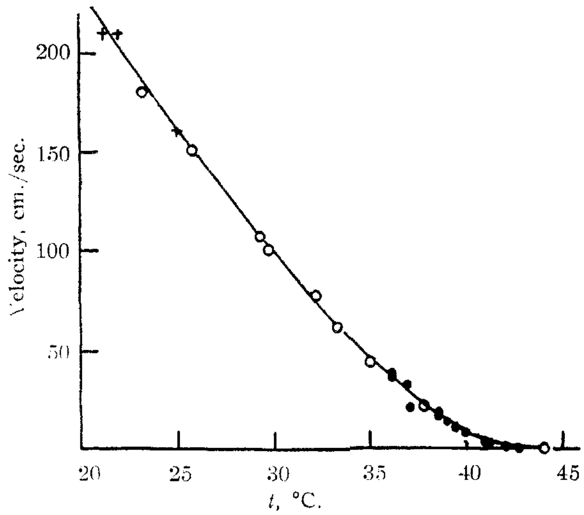

Fig. 1.—Velocity of crystallization of supercooled phosphorus.

fied in a time too short to estimate, even to an order of magnitude, after a nucleus had formed. From these observations it can only be maintained that the linear growth rates were greater than 1 mm./sec."

A plot of velocity against the square of the degrees of supercooling showed a small curvature, but the product of the velocity by viscosity, η gives a linear relation, as shown in Fig. 2, where $(v\eta)^{1/2}$ is plotted against temperature.

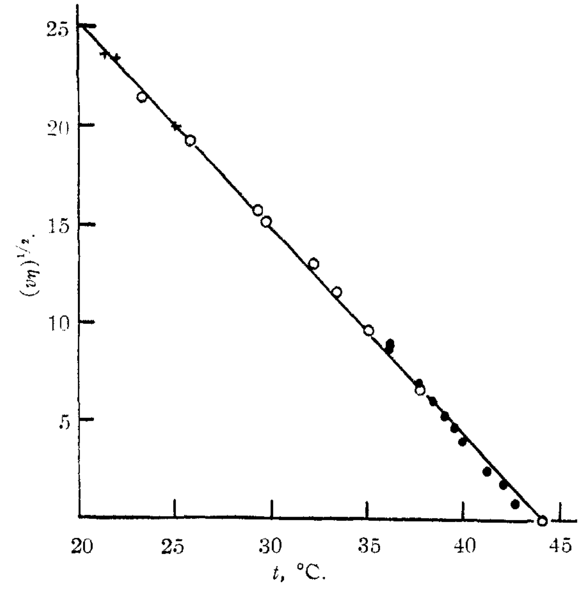

Fig. 2.—Velocity of crystallization of supercooled phosphorus. Test of relation $(v\eta)^{1/2} = K(44.1 - t)$

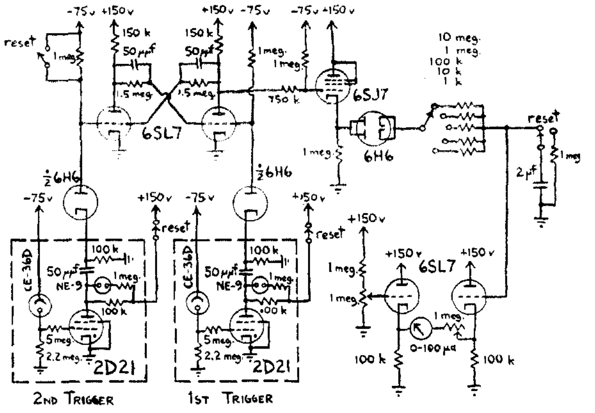

Fig. 3.—Circuit for measurement of crystallization velocity.

The viscosity of phosphorus has been reported by Dobinski[6] and by Campbell and Katz.[7] We have plotted their points as log η *vs.* $1/T$, and drawn the best straight line through them in the temperature range 25–50°. (The scatter of the points for higher temperatures is such as to make rather doubtful the curvature claimed by Campbell.) The values of η given in the table were taken from this line.

It is evident that crystallization occurring at such high velocities in a poor thermal conductor is far from an isothermal process. The heat of fusion is small, 601 cal./mole, but the solid is initially at a higher temperature than the liquid from which it forms. It seems probable, however, that the sleeve of solid next to the glass is formed at nearly the bath temperature and that the wave of crystallization in the center of the tube advances more slowly.

In order to construct a quantitative theory of this process one would need knowledge concerning such factors as heat conductivity and interfacial surface tension, which we do not have. We content ourselves, accordingly, merely with trying to account for the constancy shown by the relation in the last column of Table I. The dependence of the rate upon the *square* of the degree of supercooling may be explained by saying that the rate depends, first, upon the free energy of the process, and, second, upon the initial temperature of the wall of the tube which absorbs the heat of crystallization. The inverse relation between velocity and viscosity seems quite reasonable since viscosity is an obstacle to the adjustment of structure involved in going from liquid to solid.

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[6] S. Dobinski, *Bull. internat. acad. Polonaise des sci. et des lettres, Cl. des sci. math. et naturelles*, Ser. A, p. 103 (1934–1939).

[7] A. N. Campbell and S. Katz, THIS JOURNAL, **57**, 2051 (1935).