References and Notes

1. G. H. Pettengill and R. B. Dyce, *Nature* **206**, 1240 (1965).
2. G. Columbo and I. I. Shapiro, *Astrophys. J.* **145**, 296 (1966).
3. S. J. Peale, *Astron. J.* **74** (3), 483 (1969).
4. This report presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under NASA contract No. NAS 7-100.

23 January 1970

Superheated Ice Formed by the Freezing of Superheated Water

Abstract. *Water, superheated with respect to the vapor phase, has been made to freeze, thus forming ice that is also superheated with respect to the vapor. This phase transformation occurred at the extension of the melting curve below the triple point pressure.*

The possibility that a superheated liquid could undergo a phase change to form a superheated solid has been suggested by Pippard (*1*). We have succeeded in demonstrating that this phase transformation between metastable states can indeed take place.

In order to understand this phenomenon let us consider a simple substance which exhibits the three phases solid, liquid, and vapor, characterized by the thermodynamic variables pressure *p*, temperature *T*, and the Gibbs function per unit mass *g*. The phase diagram for the stable or equilibrium states of the substance (Fig. 1a) is the projection of the intersections of the surfaces of minimum *g*. These intersections define three lines: *S-L*, *L-V*, and *V-S* at which transitions between the stable phases occur. These lines, which correspond to the melting, evaporation, and sublimation curves, respectively, intersect at the triple point.

The fact that metastable states of a substance exist makes it appropriate to continue the *g*-surface for each phase beyond those values of *p* and *T* delineated by the equilibrium phase diagram. Thus phase diagrams for the metastable states (Fig. 1, b and c) may be constructed from the projections of the intersections of the surfaces having intermediate and maximum values of *g*, denoted by subscripts I and II, respectively (*2*). These metastable phase diagrams suggest that phase transitions between metastable states and "stability transitions" between stable and metastable states of the same phase could, in principle, occur. A summary of both known and hypothetical phase and stability transitions is given in Table 1. In the experiment reported here, we describe the first observations of the phase transitions: (i) $L_{II} \rightarrow S_I$, the formation of a superheated solid by the freezing of a superheated liquid; (ii) either $S_I \rightarrow V$ or $S_I \rightarrow V_I$, the sublimation of a superheated solid to produce either a stable or a supercooled vapor; and (iii) the stability transition $L_I \rightarrow L_{II}$, the supercooling of superheated liquid at pressures below the triple point.

When the chamber pressure of a vacuum chamber containing a beaker of water falls to the vapor pressure of the water, as determined by its temperature, the water will begin to boil and then to cool, and the system will follow the vapor pressure curve as the pressure is reduced further. At the triple point pressure, a layer of ice will rapidly form at the water surface. However, the behavior of water subjected to such diminishing pressure will be quite different if the water has no free surface. In the experiment reported here the free surface of the water was removed by covering the water with a layer of triethylbenzene $C_6H_3(C_2H_5)_3$. This clear, colorless liquid is insoluble in water and has a specific gravity of 0.87 and a low vapor pressure.

The experimental apparatus is sketched in Fig. 2. The thermocouple (accurate to within 0.1°C) was located just below the triethylbenzene-water interface. Special care was taken to ensure that the thermocouple did not make contact with the beaker walls in the water, as such contacts serve as nucleation points for violent boiling which would prevent reduction of the pressure to less than that of the triple point. The weight per unit area of the triethylbenzene layer is 0.64 mm-Hg and the weight per unit area of a layer of H_2O 2.5 cm thick is 1.84 mm-Hg. At the bottom of the water the pressure is the sum of the chamber pressure and 2.48 mm-Hg. The entire apparatus was placed in a vacuum glass bell jar 45.5 by 76 cm with the oil bath resting on a plate cooled by liquid nitrogen. The heat capacity of the oil bath prevents the water from experiencing sudden changes in its thermal environment.

Before the water was covered with the triethylbenzene, it was thoroughly degassed. The degassing was accomplished by placing the water in the vacuum chamber and slowly reducing the pressure until ice formed on the water surface. After the ice had been removed and the water had been covered with degassed triethylbenzene (the oil was also degassed by exposure to

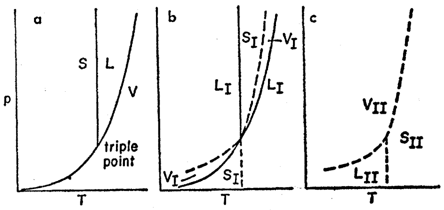

Fig. 1. Phase diagrams for a simple substance exhibiting the three phases solid, liquid, and vapor. (a) Equilibrium phase diagram. (b) Projection of intersections of surfaces having intermediate values of *g*, that is, the phase diagram for the first metastable state. (c) Projection of intersections of surfaces having maximum *g*-values, that is, the phase diagram for the second metastable state.

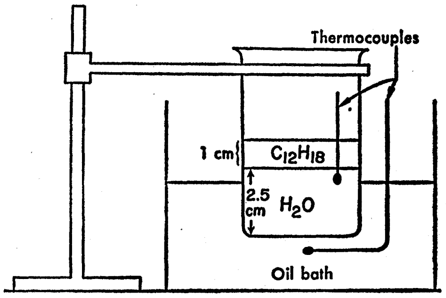

Fig. 2. Schematic of the experimental apparatus.

Table 1. Possible phase and stability transitions for a substance exhibiting the three phases solid, liquid, and vapor.

Type of transition	*S-L* line	*L-V* line	*V-S* line
	Pressures above the triple point pressure		
Phase	$S \rightleftharpoons L$, $S \rightleftharpoons L_I$,	$L \rightleftharpoons V$, $L \rightleftharpoons V_I$,	$S_I \rightleftharpoons V_I$, $S_I \rightleftharpoons V_{II}$,
Phase	$S_I \rightleftharpoons L$, $S_I \rightleftharpoons L_I$	$L_I \rightleftharpoons V$, $L_I \rightleftharpoons V_I$	$S_{II} \rightleftharpoons V_I$, $S_{II} \rightleftharpoons V_{II}$
Stability	$S \rightleftharpoons S_I$, $L \rightleftharpoons L_I$	$L \rightleftharpoons L_I$, $V \rightleftharpoons V_I$	$S_I \rightleftharpoons S_{II}$, $V_I \rightleftharpoons V_{II}$
	Pressures below the triple point pressure		
Phase	$S_I \rightleftharpoons L_I$, $S_I \rightleftharpoons L_{II}$,	$L_I \rightleftharpoons V_I$, $L_I \rightleftharpoons V_{II}$,	$V \rightleftharpoons S$, $V \rightleftharpoons S_I$,
Phase	$S_{II} \rightleftharpoons L_I$, $S_{II} \rightleftharpoons L_{II}$	$L_{II} \rightleftharpoons V_I$, $L_{II} \rightleftharpoons V_{II}$	$V_I \rightleftharpoons S$, $V_I \rightleftharpoons S_I$
Stability	$S_I \rightleftharpoons S_{II}$, $L_I \rightleftharpoons L_{II}$	$L_I \rightleftharpoons L_{II}$, $V_I \rightleftharpoons V_{II}$	$V \rightleftharpoons V_I$, $S \rightleftharpoons S_I$

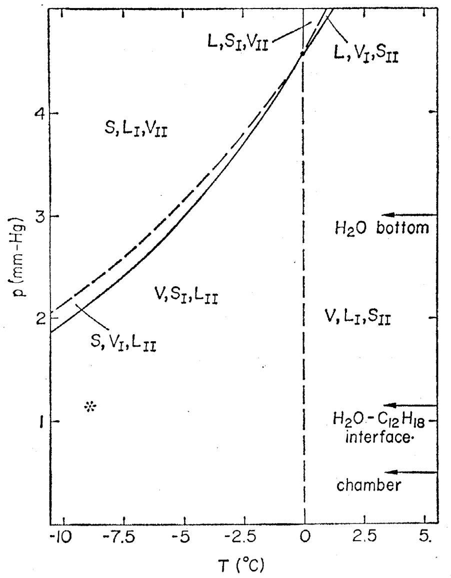

Fig. 3. Phase diagram showing significant system locations. The asterisk indicates the state of the system at the H_2O-$C_6H_3(C_2H_5)_3$ interface at the onset of freezing.

low pressures), the chamber pressure was reduced to 0.5 mm-Hg. At this time the water and oil were at temperatures of 16.7°C and 17.8°C, respectively. The pressure in the water at the water-triethylbenzene interface was only 1.1 mm-Hg, and at the bottom of the beaker the pressure was only 3.0 mm-Hg; both of these values are well below the triple point pressure of 4.6 mm-Hg. The water was in state L_I, superheated with respect to the equilibrium vapor phase (Fig. 1b). Throughout the rest of the experiment the chamber pressure was maintained at 0.5 mm-Hg.

The temperatures of the water and the oil were slowly reduced. The water did not freeze at 0°C; instead it went through the stability transition $L_I \rightarrow L_{II}$ (Fig. 1b) and continued to cool to −9.4°C where rapid freezing commenced at the water-triethylbenzene interface and at the beaker walls. The temperature of the ice-water mixture rose abruptly (within 6 seconds) to −2.8°C (Fig. 3). Subsequent freezing farther from the interface proceeded more slowly and the temperature increased to −0.6°C in about 3 minutes, during which time the oil temperature rose from −15°C to −7.8°C (*3*). Some 3 minutes after freezing commenced ice-encrusted bubbles began to grow in the water-ice mixture near the bottom of the beaker, and this volumetric expansion caused the water to break through the thin ice crust at the water-triethylbenzene interface. These bubbles were held in the ice-water matrix near the bottom of the beaker and their growth was sufficiently slow so that the water was able to rise gradually above the ice crust at the original water-triethylbenzene interface and to displace the triethylbenzene upward without disrupting it. This upward displacement of the triethylbenzene is evidence that the ice which formed at the water-triethylbenzene interface did not pressurize the system above the chamber pressure. The experiment was terminated when the water had risen 1 cm above its original level. After pressurization of the system, the bubbles collapsed and the water returned to near its original position (some bubbles frozen into the coherent ice mass that had formed at the bottom of the beaker remained after pressurization).

Ice, formed at the triethylbenzene-water interface, was in state S_I, superheated with respect to the equilibrium vapor, whereas the liquid that remained was in state L_{II} (Fig. 1c), supercooled with respect to the ice in state S_I but also superheated with respect to vapor in state V. Vapor either in state V or V_I was contained in the ice-encrusted bubbles that formed subsequent to the freezing. We believe that in the experiment reported here a superheated liquid L_{II} has been made to freeze to the superheated solid S_I, a hitherto unobserved phase transformation.

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References and Notes

1. A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge Univ. Press, London, 1960), p. 115.
2. The construction of the phase diagrams for the metastable states is facilitated if one recognizes that around a triple point there is only one metastable line in each region (*1*). It is not claimed that a *g*-surface exists for all phases at all values of *p* and *T*.
3. The use of the glass bell jar vacuum chamber allowed us to observe the system throughout the course of the experiment. Thus, even though there was only a single thermocouple below the H_2O-$C_6H_3(C_2H_5)_3$ interface, the growth of ice in different parts of the system could be seen.
4. We thank the staff of the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, for the use of their vacuum equipment. We thank D. Ross, J. Stoker, W. Andrews, P. Miller, and L. Short of the Environmental Test Laboratory of the Jet Propulsion Laboratory for their invaluable aid and cooperation. Supported in part by NSF grant Ga-10167. Publication No. 810, Institute of Geophysics and Planetary Physics, University of California, Los Angeles.

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Shock Synthesis of Amino Acids in Simulated Primitive Environments

Abstract. *A mixture of gases roughly simulating the primitive terrestrial atmosphere has been subjected to shock heating followed by a rapid thermal quench. Under strictly homogeneous conditions there is a very high efficiency of 5 × 10^{10} molecules per erg of shock-injected energy for production of alpha-amino acids. Calculations suggest that rapid quenching bypasses the usual thermochemical barrier. The product of energy flux and efficiency implies the unexpected conclusion that shocks occurring on atmospheric entry of cometary meteors and micrometeorites and from thunder may have been the principal energy sources for prebiological organic synthesis on the primitive earth.*

A wide variety of energy sources are effective in generating α-amino acids (among many other organic compounds) from simulated primitive environments; the atmosphere of precursor gases may apparently have any composition, provided only that it is reducing and that the atoms H, N, O, and C are present (*1, 2*). There has heretofore been no report of simulated prebiological organic synthesis in shock tubes. Such syntheses may be of importance because (i) the composition and temperature of the gas mixture, the duration of activation, and the rate of quenching can be controlled; (ii) the significant kinetic reactions occur under strictly homogeneous conditions, since the sample is heated gas dynamically while the tube walls are cold; and (iii) as discussed below, the product of energy available from shock sources on the primitive earth and the efficiency of synthesis suggests that shock excitation may have been a major source of primordial organic molecules.

The single-pulse shock tube used for these experiments consisted of a Pyrex low-pressure (driven) section of uniform bore, 2.5 cm in inner diameter and 175 cm long, and a brass high-pressure (driver) section, 2.5 cm in inner diameter and 45 cm long. These were separated by 3-mil Mylar diaphragms which were burst (thus initiating the shock) when the helium driver gas pressure was raised to about 8.1 atm (*3*). Pressure traces were recorded with a dual-beam oscilloscope with one beam operating at a total scan time of 100 μsec and the other at a total scan time