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**Carbon: The 129-Year Controversy Over the Solid
Liquid-Vapor Triple Point**

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22 August 1978

Interim Report

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Prepared for
SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009

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This interim report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-77-C-0078 with the Space and Missile Systems Organization, Deputy for Advanced Space Programs, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. C. Riley, Director, Materials Sciences Laboratory. Lieutenant A. G. Fernandez, SAMSO/YCPT, was the project officer for Advanced Space Programs.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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| 19 REPORT DOCUMENTATION PAGE | | READ INSTRUCTIONS BEFORE COMPLETING FORM |
|--|--|--|
| 1. REPORT NUMBER SAMSO-TR-78-121 | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) CARBON: THE 129-YEAR CONTROVERSY OVER THE SOLID-LIQUID-VAPOR TRIPLE POINT. | 5. TYPE OF REPORT & PERIOD COVERED Interim rept. | 6. PERFORMING ORG. REPORT NUMBER TR-0078(3950-03)-3 |
| 7. AUTHOR(s) A. Greenville/Whittaker | 8. CONTRACT OR GRANT NUMBER(s) F04701-77-C-0078 | 9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245 |
| 10. CONTROLLING OFFICE NAME AND ADDRESS Space and Missile Systems Organization Air Force Systems Command Los Angeles, Calif. 90009 | 11. REPORT DATE 22 August 1978 | 12. NUMBER OF PAGES 8 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | 15. SECURITY CLASS. (of this report) Unclassified | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |
| 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| 18. SUPPLEMENTARY NOTES | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carbon Phase Diagram Carbyne Forms of Carbon Carbon Solid-Liquid-Vapor Triple Point Carbon Melting | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The location of the solid-liquid-vapor triple point on the carbon phase diagram has been a subject for controversy for many years. A triple-point pressure of $\approx 10^7$ Pa has been favored for quite some time, but recent data indicate that the correct value is $\approx 10^5$ Pa. An effort is made to account for the high-pressure data on the basis of a recently proposed phase diagram. * approx. 409 944 1 atm | | |

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CARBON: THE 129-YEAR CONTROVERSY OVER THE
SOLID-LIQUID-VAPOR TRIPLE POINT

The controversy over the solid-liquid-vapor (S-L-V) triple point of carbon started in 1849¹. Since that time, investigators in this field have developed widely differing points of view. Some believe the triple-point pressure is $\sim 10^5$ Pa (~ 1 atm), whereas others believe it is $\sim 10^7$ Pa (~ 100 atm). Over the past approximately 40 years, the 10^7 Pa view has been dominant, but the evidence is not entirely convincing. In the past few years, new evidence has been obtained that appears to end the controversy at least from the standpoint of the proper order of magnitude of the pressure.

In any single-component phase diagram, the S-L-V triple point is located at the intersection of the solid-liquid (S-L) and solid-vapor (S-V) boundaries. These boundaries for carbon are shown in Fig. 1. The S-L boundary was obtained by an extrapolation of Bundy's high-pressure data, and the JANAF data gives the S-V boundary^{2, 3}. Even though Bundy's extrapolated data could be in error by one or two hundred degrees, these boundaries (Fig. 1) clearly indicate that the S-L-V triple-point pressure must be on the order of 10^5 Pa. However, the S-L-V triple point was believed to occur at $\sim 10^7$ Pa and 4200 K, and it was considered possible that the JANAF calculations above ~ 3000 K were in error. Thus, S-V boundaries, e.g., A in Fig. 1, were proposed, even though there was little experimental basis for doing so⁴. The question of whether or not the S-V boundary is correct can be answered by considering the results of several studies on the vapor pressure of carbon in the region of 4000 K.

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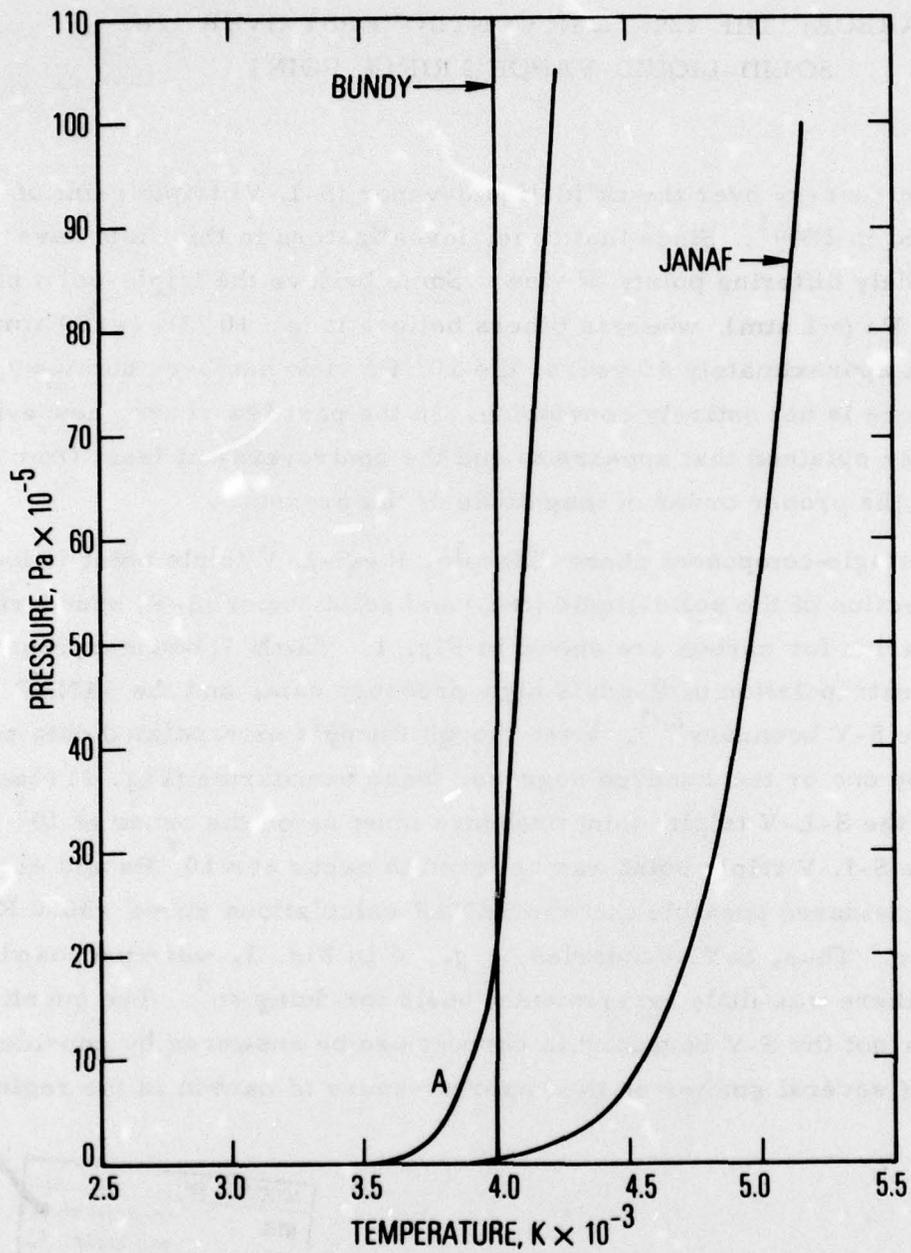


Figure 1. Solid-Liquid and Solid-Vapor Boundaries for the Low-Pressure Region of the Carbon Phase Diagram

A short time ago, Covington, Liu, and Lincoln⁵ and Lundell and Dickey⁶ obtained vapor pressure data that confirmed the JANAF data in the region of 10^5 to 10^7 Pa. Also, Maurer and co-workers⁷ obtained data at $\sim 10^4$ Pa that were in agreement with the JANAF curve. Data obtained several years ago by Whittaker and co-workers⁸⁻¹⁰ indicated that graphite transforms to the more stable carbyne forms of carbon above ~ 2600 K. Hence, the equilibrium S-V boundary must lie below the JANAF curve. All of these data are shown in Fig. 2 in the region of the S-L-V triple point. Recently, Whittaker¹¹ reported preliminary data on the rate of transformation of graphite into each of two of the carbyne forms¹¹. These data also show that the lowest transformation temperature is ~ 2600 K and further supports the conclusion that the equilibrium vapor pressure of carbon must be less than the JANAF values above this temperature. These rate data show that the transformation graphite \rightarrow carbyne is relatively slow up to 2800 K (first-order rate constant of $\sim 10^{-5}$ / sec at 2800 K). There is some evidence that the transformation rates increase with temperature as expected, but 2 or 3 sec are required for 80 to 90% conversion in the region of 3800 K. Therefore, the transformation did not have time to take place in the experiments of Covington, Liu, and Lincoln because their measurement time was on the order of 1 msec or less. Hence, it would be expected that their data would fall on the JANAF curve because it represents the vapor pressure that graphite would have if it were the stable form above ~ 2600 K. In the experiments of Lundell and Dickey, it is difficult to estimate the time required to heat and vaporize the carbon because the beam traversed through the sample at an appreciable rate. However, it appears that the time available for transformation of the carbon was well below 1 sec, especially at the higher power densities. Therefore, their data would be expected to fall on the JANAF curve. These five groups of data constitute a mutually consistent set that experimentally establishes the S-V curve in the region of 4000 K and rules out the possibility of an S-V curve as A in Fig. 1. With the S-V curve thus established, the only other way to get an S-L-V triple point at $\sim 10^7$ Pa would be for Bundy's data to be in error by > 1000 K, which is highly unlikely.

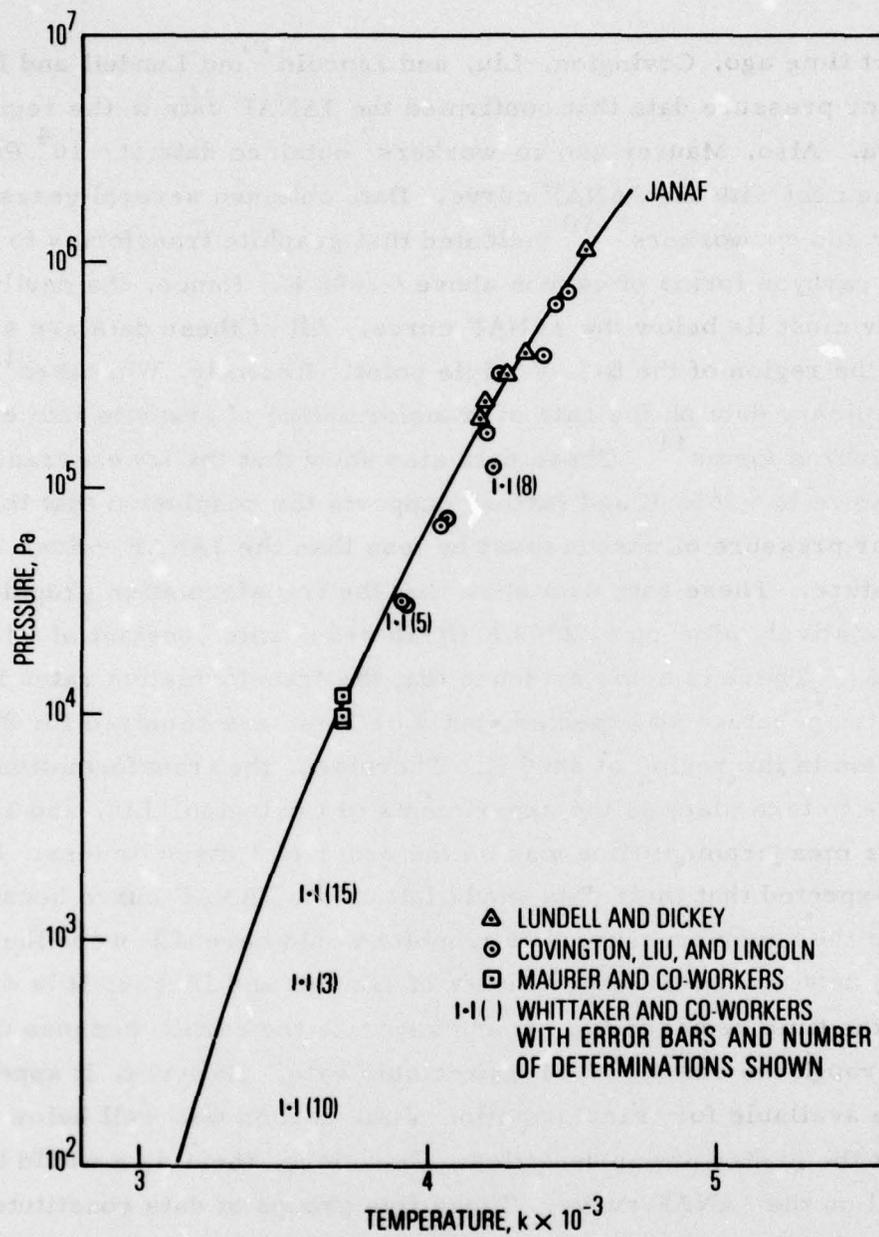


Figure 2. Vapor-Pressure Data for Carbon in the Region of the Solid-Liquid-Vapor Triple Point

If the S-L-V triple-point pressure of carbon occurs at $\sim 10^5$ Pa, then it is reasonable to question the significance of the results obtained at $\sim 10^7$ Pa. The pressures reported range from 1.01×10^7 to 1.22×10^7 Pa, but most values approximate 1.01 to 1.03×10^7 Pa. Temperatures range from ~ 3970 to 4390 K with no tendency to cluster about a particular value. All of these high-pressure results suffer from at least two major shortcomings: (1) In all cases, it was assumed that the carbon vapor pressure equilibrated with the pressurizing gas. This condition is not necessarily achieved, and some means must be provided to show that this equilibration has been achieved. Therefore, the pressures are suspect inasmuch as they are not really experimentally determined values but essentially assumed values. (2) No spectroscopy was carried out on the radiation that arrived at the pyrometer. It is necessary to assure that line or band emission is not causing spurious pyrometer readings and to show that the radiating gas surrounding the specimen is not optically dense. In the laser heating experiments of Whittaker and co-workers, much spectroscopy was carried out on the solid and gas phases. It was found that the carbon gas emits only Swan radiation. If impurities are present, additional lines or bands appear in the spectrum; hence, it is important to assure that the pyrometer uses a wave length range that is free of this radiation. Also, it was found that the optical density of the gas increases with pressure, and, at $\sim 10^6$ Pa, the effect of the optical density is no longer negligible. At 10^7 Pa, the optical density would be quite high. Hence, it is possible that a pyrometer may not be able to "see" the surface of the condensed phase at this pressure. In this case, the reported temperatures would have little meaning. Indeed, the effect of high optical density could account for the wide range of reported temperatures.

One possible reason why the high-pressure data clusters in a general region is that a solid-solid-liquid triple point could exist near 10^7 Pa at point P in the proposed phase diagram (Fig. 3)¹⁰. In this case, the solid phases would have to be carbyne forms of carbon. Since the equipment used in the high-pressure work was not designed to study condensed phase equilibria, the

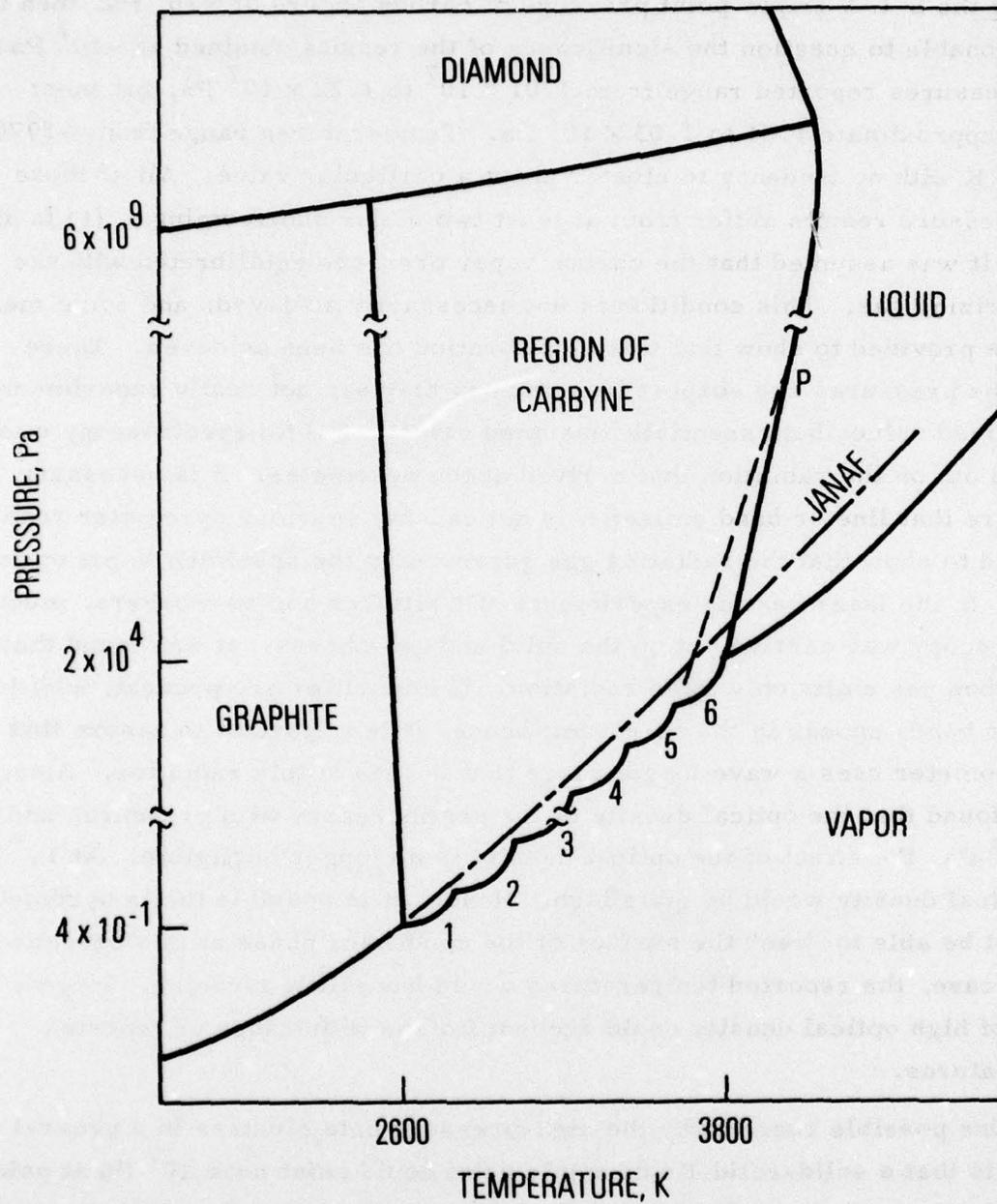


Figure 3. Proposed Carbon-Phase Diagram. From Ref. 10.

observed pressure and temperature would be some kind of average determined by the competition between the condensed-phase equilibrium and the liquid-vapor equilibrium attempting to coexist. This situation would result in a large scatter in reported temperatures and pressures because this competition would depend on the idiosyncrasies of each particular apparatus.

In view of the uncertainties discussed here, it is difficult to interpret the high-pressure results. However, the recent vapor-pressure data cited here, together with Bundy's high-pressure results, contribute to the inescapable conclusion that the S-L-V triple point of carbon occurs at a pressure on the order of 10^5 Pa, and that the reported results in the region of 10^7 Pa must refer to some other phenomenon.

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