

UNIVERSITY OF CALIFORNIA

DEPARTMENT OF CHEMISTRY
AND CHEMICAL ENGINEERING
BERKELEY 4, CALIFORNIA

July 6, 1956

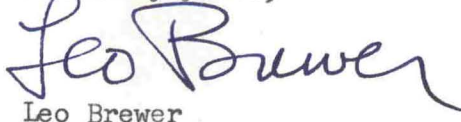
Professor H.T. Hall
Director of Research
Brigham Young University
Provo, Utah

Dear Professor Hall,

I am enclosing a reprint of my paper on the melting point of graphite. Reference 3 is the most important paper that I have seen on the question of melting graphite. I will have to review the recent data on C_3 and try to estimate the temperature at which the total vapor pressure in equilibrium with graphite reaches 100 atmospheres.

I enjoyed meeting you and talking with you at the Symposium. I would like to thank you for your very important contribution to the success of the Symposium. I hope that you will be visiting Berkeley again in the near future when I will have more time to talk with you.

Sincerely yours,


Leo Brewer

The Vapor Pressure and Melting Point of Graphite

LEO BREWER

Chemistry Department, University of California, Berkeley, California

September 24, 1948

IN a letter to this Journal, L. H. Long has listed four types of experimental data which he believes will not admit a value of 170 kilocalories for the heat of sublimation of graphite. Careful examination of these data indicate that they are not capable of contradicting a heat of sublimation of 170 kilocalories, an atmospheric sublimation point of around 4600°K, or a melting point of over 5000°K.

(i) At temperatures above 3400°K where the carbon partial pressure is above 1 mm, the smoke due to carbon gas condensing in the cooler portions of an apparatus invalidates direct observations of the temperature by an optical pyrometer. Thus the temperatures given by Ribaud and Begue,¹ Basset,² and others who have worked in this high temperature range are much too low. In addition, their degassing procedures were poor. Both these effects produce results which make carbon seem more volatile than it really is.

(ii) Long lists various values for the melting point of carbon. However, Steinle³ has clearly shown that these previous workers had not actually reached the melting point. The pressure work of Basset² and Steinle³ show that the triple point of carbon occurs above 100 atmospheres. From the vapor pressures given by Brewer, Gilles, and Jenkins,⁴ this must mean that carbon melts above 5000°K.

Carbon can be melted in contact with tantalum carbide at temperatures above 3300°C, but this is due to the eutectic between C and TaC as shown by Ellinger.⁵ A melting point over 5000°K for carbon is consistent with Steinle's work which showed that there was a large temperature gradient from the interior of the carbon rods, where melting

took place, to the exterior where a lower temperature was read.

(iii) At 4000°K, the partial pressure of carbon is almost 0.1 atmosphere which should be sufficient to maintain an arc.

(iv) The work of Mott⁶ only demonstrates that carbon is more volatile than tungsten. This is consistent with the boiling point of around 6000°K for tungsten which is given by Kelley.⁷ The volatilization which limited the thin carbon tube used by Brewer, Gilles, and Jenkins⁴ to a top temperature of 3000°K is consistent with the partial pressure of around 0.03 mm. As a result of faster vaporization from the hottest sections, these sections become thinner, which increases the electrical resistance and thus increases the temperature of these hot rings still further. Thus temperatures above 3000°K are reached, and these hot rings lose carbon rapidly enough to cause breaking of the tube at the weak ring which results after loss of a fraction of a mm thickness of carbon. These results are quite consistent with the vapor pressures given by Brewer, Gilles, and Jenkins.

The data discussed above and other data which present direct evidence on the vapor pressure of graphite have been carefully examined, and no experiments have been found that are capable of excluding 170 kilocalories as the heat of sublimation of graphite.

¹ G. Ribaud and J. Begue, *Comptes Rendus* 221, 73 (1945).

² J. Basset, *Brennstoff-Chemie* 23, 127 (1942).

³ H. Steinle, *Zeits. f. angew. Mineral.* 2, 28, 344 (1940).

⁴ L. Brewer, P. W. Gilles, and F. A. Jenkins, *J. Chem. Phys.* 16, 797 (1948).

⁵ F. H. Ellinger, *Trans. Am. Soc. Metals* 31, 89 (1943).

⁶ W. R. Mott, *Trans. Am. Electrochem. Soc.* 34, 255 (1918).

⁷ K. K. Kelley, *Bur. of Mines Bull.* 383 (1935).