

American Carbon Committee, Eighth Biennial Conference on Carbon,
Buffalo, New York, June 19 - 23, 1967

An Electron-Microscopic Investigation
of the Graphite-Water Reaction*

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The initial stages of oxidation of highly purified single crystals of natural graphite by water vapor at high temperatures are being studied by use of the etch-decoration technique developed by Gerhart Hennig.¹ Vacancies produced by electron irradiation of the crystals are enlarged to a known size by etching the surfaces of cleaved slices of the crystals with a standard chlorine-oxygen mixture. The crystal slices are then degassed in vacuo and the vacancies further expanded by passing a stream of helium, carrying a known concentration of water vapor as determined by a "moisture-monitor", over the slices at a rate of $150 \text{ cm}^3\text{-min}^{-1}$. The cleavage surfaces are then decorated with gold and the increase in diameter of the vacancy pits is measured from photographic plates of known magnification taken in an electron microscope. Catalytic effects were prominent on most of the earlier samples and statistical methods were used to insure that areas representative of non-catalytic oxidation were studied. These catalytic effects, which apparently were due to the entrainment of microscopic particles of mercury, have been minimized in recent experiments by a more efficient trapping procedure. Expansion of vacancies produced by what appears to be "puncture" of the cleavage surfaces during etching by water vapor further complicates observation.

The most complete set of data so far accumulated were taken with the helium stream saturated with water at room temperature to give a concentration of about 2×10^4 vpm. Runs made at 25 degree intervals in the range from 800°C to 950°C inclusive yield data points which fall on a fairly straight line with a slope corresponding to an activation energy of $68 \text{ kcal-mole}^{-1}$; however, when the probable error of the points is taken into consideration, it is found that the activation energy may be anywhere in the range $63\text{-}75 \text{ kcal-mole}^{-1}$.

Current experiments are being carried out at a water concentration of 2×10^3 vpm. The three data points obtained at 950°C , 975°C , and 1000°C fall on a straight line yielding an activation energy of $60 \text{ kcal-mole}^{-1}$; again, consideration of probable errors indicates a range of $60\text{-}65 \text{ kcal-mole}^{-1}$. Because of the overlap in the ranges of activation energy, it is impossible to determine, at present, if the activation

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

energy varies with concentration of water vapor; in addition, it should be emphasized that the data at the lower concentration are too sparse for any firm conclusions to be drawn. Comparison of the rates at 950°C gives an apparent order of reaction of 0.8 in good agreement with the result of Overholser and Blakely.²

This investigation will be extended over greater ranges of concentration and temperature in order to determine the influence of various parameters on the rate of reaction of graphite and water vapor.

- (1) G. R. Hennig, Chemistry and Physics of Carbon 2, 1 (1966)
- (2) L. G. Overholser and J. P. Blakely, Carbon 2, 385 (1965)