Carbon, 1976, Vol. 14, pp. 83–84. Pergamon Press. Printed in Great Britain

LETTERS TO THE EDITOR

Kinetics of the carbon–carbon dioxide reaction under a continuous linear temperature increase

First order kinetics hold for the depletion of CO_2 during the gasification of carbon at sufficiently low CO_2 pressures[1]. Thus the depletion can be written as

$$dP_{CO_2}/dt = AP_{CO_2}\exp(-E/RT). \quad (1)$$

A is a function of the carbon being reacted but is normally considered to show little dependence on temperature compared to that shown by the exponential term.

If there is a linear temperature rise, $dT/dt = b$; substituting for dt in eqn (1) gives

$$dP_{CO_2}/dT = (A/b)P_{CO_2}\exp(-E/RT). \quad (2)$$

Rearranging and taking logarithms,

$$2{\cdot}3\log(d\log P_{CO_2}/dT) = \ln(A/b) - E/RT. \quad (3)$$

Therefore a graph of $\log(d\log P_{CO_2}/dT)$ vs $1/T$ should be a straight line, from the slope of which the activation energy of the reaction can be calculated.

The carbon reacted was a sample of Graphon[2] of 0·22 g weight, which had previously been subjected to a burn-off of 27% in O_2 at 600°C. The surface of the sample was cleaned at 950°C *in vacuo* and the temperature was subsequently reduced to 600°C. The sample was exposed to 2.27 mtorr of pure CO_2 in a 6·3 l system (most of which was at room temperature) connected to a mass spectrometer. The temperature was raised at either 3 or 10°C/min to 950°C. At frequent intervals, measurements were made of the partial pressures of CO and CO_2 in the system.

Material balances showed that no measurable stable complex was formed on the surface. Figures 1 and 2 show the depletion of CO_2 in the two experiments. For both experiments, values of $d\log P_{CO_2}/dT$ were calculated for various temperatures, from the slope of the curves. Since the partial pressures of the gaseous components were measured effectively at room temperature (298°K), instead of at reaction temperatures, it was necessary to standardize values of $d\log P_{CO_2}/dT$ by multiplying by the factor $T_R/298$, where T_R is the reaction temperature in °K.

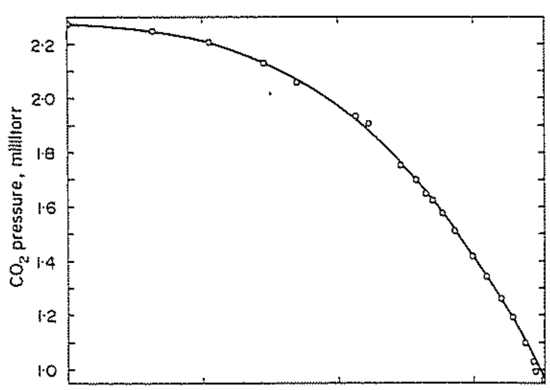

Fig. 1. Decrease in CO_2 pressure as a result of its reaction with Graphon during a linear 3°C/min rise in temperature between 600 and 950°C.

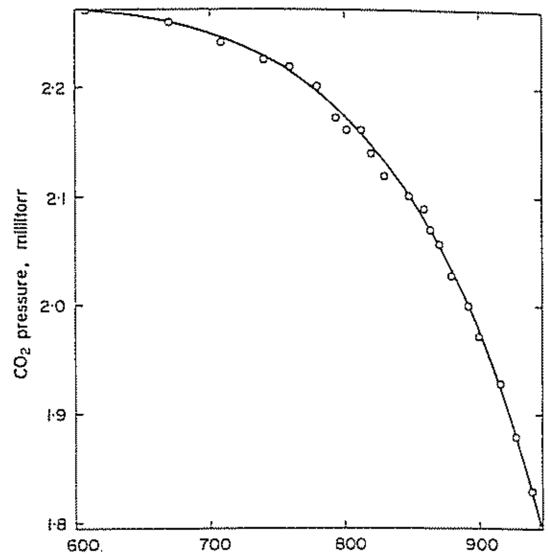

Fig. 2. Decrease in CO_2 pressure as a result of its reaction with Graphon during a linear 10°C/min rise in temperature between 600 and 950°C.

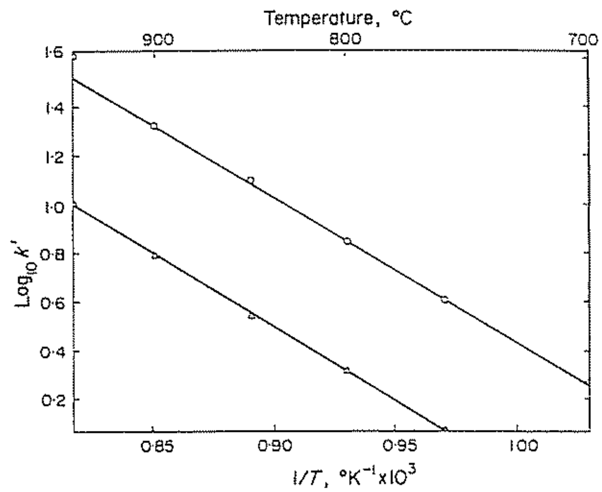

Fig. 3. Arrhenius plots for reaction of Graphon with CO_2 during linear rises in temperature: ○, 3°C/min; △, 10°C/min.

Figure 3 shows graphs of $\log[(1000/298)\,d\log P_{CO_2}/d\log T)]$ (called $Log_{10}\,k'$) plotted against $1/T$. It is seen that straight lines are obtained, parallel to each other and separated by an amount Log_{10} 10/3. The value of E calculated from the gradient of the lines is 27 kcal/mole. This value is at variance with values of E in eqn (1) calculated from rates measured at a series of fixed temperatures (isothermal reactions) for the carbon–carbon dioxide reaction—that is 85–103 kcal/mole[1, 3, 4]. This major difference in E is not understood at this time.

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Carbon, 1976, Vol. 14, pp. 84–86. Pergamon Press. Printed in Great Britain