

ORNL
MASTER COPY

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION



ORNL-TM- 71

COPY NO. - 4

DATE - December 5, 1961

A Proposed Experimental Program for Study of the Kinetics of the Mass Transfer of Carbon in a Gas-Cooled Reactor

C. D. Scott
J. C. Giddath

ABSTRACT

An experimental program is proposed for study of the kinetics of the mass transport of carbon from the graphite in a gas-cooled reactor core to cooler portions of the reactor system. This will involve study of the dynamic kinetics of the two reactions: (1) $C + CO_2 \rightarrow 2 CO$ and (wall)
(2) $2 CO \rightarrow C + CO_2$. Anticipated experimental equipment and man power needs are presented.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

RELEASE APPROVED
BY PATENT BRANCH

12-8-61
DATE SIGNATURE

1.0 INTRODUCTION

A problem in gas-cooled reactor design is loss of graphite from the reactor core by reaction with oxidizing gases in the coolant. This problem can be further compounded by the reversible nature of one of these reactions:



The forward reaction is favorable at high temperatures¹ while at low temperatures the reverse reaction may become favorable and it is catalyzed by solid surface area. This change can be shown by considering the equilibrium constant for the reaction, $CO_2 + C \rightarrow 2 CO$ (see Fig. 1). The equilibrium constant for the forward reaction becomes less than unity at approximately 970°K, thus, indicating that the reverse reaction, $2 CO \rightarrow CO_2 + C$, would be more favorable at temperatures less than 970°K. The reverse reaction^{3,4} has been known for some time in the water gas reaction and in steel making^{3,4} and it has been studied to some extent in relation to gas-cooled reactors.^{5,6} These two reactions make possible a carbon transport loop which could be set up in a gas-cooled reactor where graphite would react with CO_2 in the hot core and carbon would be deposited in the coolant heat exchanger while generating CO_2 which would be sent back to the reactor core (see Fig. 2).

If the reaction rates were high enough, a significant quantity of graphite could be removed from the reactor and deposited in the heat exchanger. This could cause change in criticality condition in the core and excessive pressure drop in the heat exchanger. Therefore, it is desirable to know the kinetics of the reactions involved so that adequate design limits can be placed on CO_2 contamination, etc. Some work has been done in this field,^{5,6,7,8} but it was mainly empirical in nature, and it covers specific materials and operating conditions not necessarily usable in our GCR program. As a result, the published literature proves to be contradictory when more general use of it is attempted.

The previous work with direct GCR application is that of Antill and Peakall^{5,6} who did some work for the British HTGCR. In their work, the forward reaction ($CO_2 + C \rightarrow 2 CO$) was tested with several types of graphite at 1 atm with an argon diluent. The reverse reaction ($2 CO \rightarrow C + CO_2$) was also studied at fairly high CO concentrations. Antill and Peakall noted that the reaction rates were influenced by temperature, flow rate, concentration, and type of graphite. However, they did not establish the reaction mechanism and their resulting empirical relationships have limited application.

It would be desirable to have kinetic information of more general use such as mechanisms of reactions. If this is not possible, the empirical correlations for the kinetics of the two reactions of interest should cover the range of operating conditions anticipated in future GCR systems.

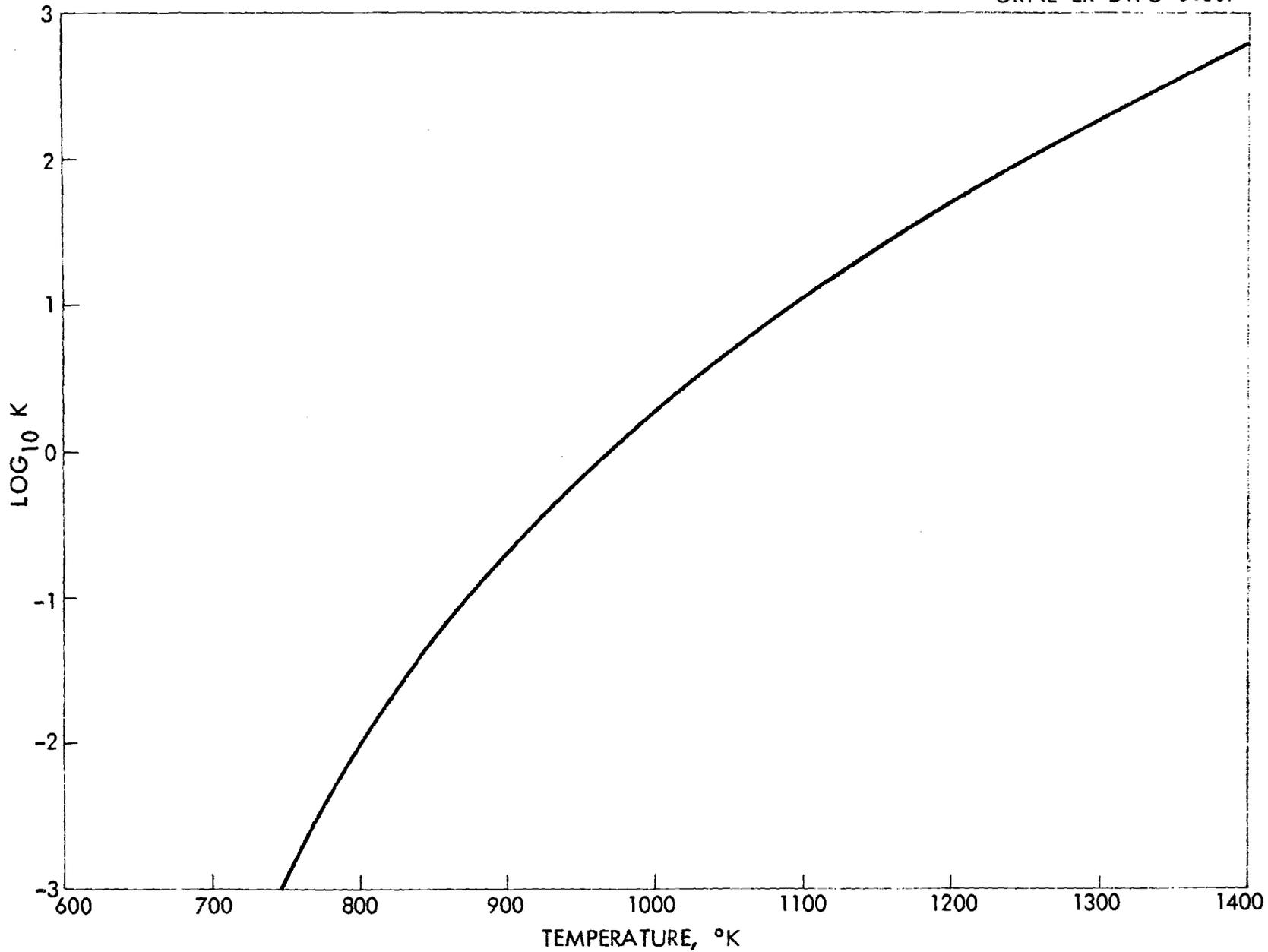


Fig. 1. Reaction equilibrium constant for the reactor, $\text{CO}_2 + \text{C} = 2\text{CO}^{(1, 2)}$.

2.0 PROPOSED PROGRAM

It is proposed that the Unit Operations Section of the Chemical Technology Division initiates a program in which a study is made on the dynamic kinetics of the two reactions:



The experimental program should have application over the range of operating conditions anticipated in present and future gas-cooled reactor concepts in which helium is used for the coolant. The range of operating conditions should be:

Temperature of CO_2 reaction - 400 - 1000°C
Temperature of CO reaction - 20 - 400°C
Pressure - 1 - 60 atm
CO and CO_2 concentrations - 1 - 1000 ppm by vol
Reynold's Number of total gas flow - 50 - 50,000

Various types of graphite should be tested during the program. The two reactions should be investigated separately and together in a closed loop if possible.

It should be desirable to determine effects of radiation on the kinetics of the reactions by utilizing an existing reactor loop for some check tests.

3.0 EXPERIMENTAL FACILITY

Some components of the Helium Purification Test Facility presently in use in Building 4505 could be used for the experimental portion of this program; however, some additional equipment would have to be fabricated and installed to ensure testing over the entire range of proposed conditions. The experimental apparatus would include (1) provisions for continuously measuring weight change of various graphite shapes in an enclosed, heated vessel through which the synthesized contaminated coolant could be metered, (2) a similar vessel in which the continuous weight change of various amounts of metal turnings of known surface area can be determined, (3) a gas adsorption chromatograph for accurately measuring the CO and CO_2 content of the gas stream at any point in the system, and (4) necessary gas blower, metering device, and gas heater and coolers (see Fig. 3).

4.0 MAN POWER LEVEL AND PROGRAM PROGRESS

It is anticipated that a total man power level of three men would be adequate for this program for FY 1962. The following program schedule could be followed during the remainder of FY 1962:

September-November - Literature survey and equipment design
December-January - Literature survey and equipment fabrication
and installation
February-June - Shakedown of experimental facility and
experimental work

REFERENCES

1. MGCR Staff, "Evaluation of Coolants and Moderators for the Maritime Gas-Cooled Reactor (MGCR)," TID-4500 (1958).
2. O. A. Hougen and K. M. Watson, "Chemical Process Principles," Vol. II, p. 712, John Wiley and Sons, New York (1943).
3. J. H. Perry, Editor, "Chemical Engineers Handbook," 3rd Edition, p. 1579, McGraw-Hill Book Co., New York (1950).
4. P. H. Emmett, "Catalysis," Vol. IV, p. 388-417, Reinhold, New York (1956).
5. J. E. Antill, K. A. Peakall, "Coolant Purity in the HTGCR," AERE-R-3070 (1959).
6. J. E. Antill, K. A. Peakall, "Removal of Graphite by Gaseous Impurities in the HTGCR," AERE M/M 201 (1958).
7. J. W. Pradas, "Estimation of Reaction and Heat Release Rates for Graphite Oxidation," ORNL CF 60-10-131 (1960).
8. D. D. Eley, P. W. Selwood, and P. B. Weisz, Editors, "Advances in Catalysis and Related Subjects," Vol. XI, p. 133-221, Academic Press, New York (1959).

-8-

Distribution

- 1-3. DTIE, AEC
4. M. J. Skinner