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J.T. Price, N.J. Ramey and D.A. Reeve

Canadian Metallurgical Fuel Research Laboratory

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# A METHOD FOR ASSESSING THE REACTIVITY OF CARBON MATERIALS

by

J.T. Price[*], N.J. Ramey[**] and D.A. Reeve[***]

The following reaction of carbon materials with carbon dioxide to form carbon monoxide is of special interest to iron makers.

$$CO_2 + C \rightarrow 2CO \qquad (1)$$

The rate of this reaction (reactivity) for metallurgical cokes may affect the efficiency and performance of blast furnaces. Miyazu[1] and co-workers have suggested that a coke's reactivity (as measured in the laboratory) does influence the coke rate in the blast furnace. However, Schenck and Wenzel[2] have concluded that the reaction of carbon dioxide with carbon in laboratory experiments proceeds along different lines than in the blast furnace.

Recently, interest has been renewed in coke reactivity by studies done at the Bethlehem Steel Corporation[3] which found relationships between coke reactivity and the petrographic compositions of individually coked high- and low-volatile coals.

Various laboratory methods have been used for establishing reactivity indices of cokes. They include direct methods such as gas analyses[4,5] and weight loss methods[6] as well as indirect methods such as electrical conductivity[7].

This report describes a new and relatively simple way to monitor the reactivity of various cokes to carbon dioxide by measuring the oxygen potential of the gaseous product using a galvanic cell consisting of a lime stabilized zirconia solid electrolyte between two platinum electrodes. Air is used at the reference electrode. Systems involving solid oxide electrolytes have been used extensively in metallurgical processes and several reviews have been written upon the subject[8,9,10]. The open circuit voltage across a solid electrolyte can be represented mathematically by:

$$E = \frac{RT}{2NF} \int_{p^{1}_{O_2}}^{p^{11}_{O_2}} t \, d \ln p_{O_2} \qquad (2)$$

*Research Scientist, **Senior Technologist and ***Assistant Manager, Canadian Metallurgical Fuel Research Laboratory, CANMET, Department of Energy, Mines and Resources, Ottawa, Canada.

where $N$ is the charge transferred, $R$ is the gas constant, $T$ is the temperature in $^\circ K$, $t$ is the ionic transference number, and $p_{0_2}^{1}$ and $p_{0_2}^{11}$ are the partial oxygen pressures at the two electrodes, and $F$ is Faraday's constant. From the thermodynamic data[11] for the equilibrium:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (3)$$

the partial pressure of oxygen can be calculated for any $CO/CO_2$ mixture at a given temperature:

$$p_{0_2} = e^{\frac{2\Delta G}{RT}} \cdot \left(\frac{p_{CO_2}}{p_{CO}}\right)^2 \qquad (4)$$

where $\Delta G$ is the standard free energy of equation (3). Conversely, from equation (2) and (4) the $CO_2/CO$ ratio can be calculated from the EMF measured across a solid electrolyte.

If $f$ is the rate of flow of $CO_2$ into the reaction vessel and $y$ is the rate at which carbon reacts with the $CO_2$, then the product gases will flow at a rate of $f-y$ moles of $CO_2$ plus $2y$ moles of $CO$. From equation (1), the total flow of the gaseous reaction products is $f + y$ moles/min. The ratio of $CO_2/CO$ is:

$$\frac{p_{CO_2}}{p_{CO}} = \frac{f-y}{2y} \qquad (5)$$

If the flow rate of the carbon dioxide is known and maintained constant and the $CO_2/CO$ ratio is calculated from the EMF, then $y$, the rate of carbon loss, and the total carbon loss can be calculated with respect to time. With the aid of a simple calculator program, weight loss curves were obtained for several carbon materials by measuring the oxygen potential of the reaction products on a chart recorder and by knowing (a) the flow of $CO_2$ into the reactor and (b) the temperature of the solid electrolytic cell.

EXPERIMENTAL

(a) Apparatus

The zirconia tube ($0.85\ ZrO_2 - 0.15\ CaO$) was supplied by the Zirconia Corporation of America and was 310 mm long and 9 mm in diameter with a wall thickness of 1 mm. The closed end of the tube was platinized by applying a 1:1 mixture of ten percent solution of platinic chloride and formaldehyde and heating to a temperature of $850^\circ C$. Platinum wire fused to platinum foil served as the

sample electrode and ensured good electrical contact with the electrolyte. A small cylindrical platinum cup attached to a platinum-platinum 13% rhodium thermocouple was placed inside the tube to ensure a good electrical contact and serve as the reference electrode. The two legs of the thermocouple were insulated by a length of four bore alumina tube. The cell was attached by a Teflon ferrule to a brass adapter plate and supported vertically within an alumina reaction tube. A platinum mesh basket, supported by a heavy guage platinum wire served as a container for the one gram sample. Carbon dioxide entered the reaction vessel as indicated in Figure 1. Heating was achieved by utilizing a Lindberg Hevi-duty Globar furnace.

A platinum-platinum 13% rhodium thermocouple was placed within the carbon sample to determine the temperature at the reaction site. This temperature was found to be slightly different from the temperature at the galvanic cell. While the cell temperature was used for calculations involving equations (2) and (4), the sample temperature was used in calculations involving the reaction of carbon dioxide with carbon.

(b) Procedure

Crushed coke samples were heated to 1050$^{\circ}$C under nitrogen for one hour, then cooled and sized to -0.83 mm and +0.5 mm. The carefully weighed samples were loaded into the reaction tube as shown in Figure 1 and heated to temperature under a flow of dried nitrogen. When the EMF from the cell appeared constant, pure dried carbon dioxide was introduced at the rate of 1200 ml/min. At the end of the experiment the tube was cooled under nitrogen and the sample weighed.

As a method of checking the accuracy of the measurement of reaction rates between carbon and carbon dioxide using the galvanic cell, reaction rates at similar temperatures were also determined using a loss in weight technique. A Cahn RH-100 Electrobalance was utilized for these experiments, the platinum sample holder being suspended below the balance.

## RESULTS AND DISCUSSION

The reaction of carbon dioxide with carbon has been the subject of many mechanistic studies due to its important role in a number of industrial applications. The majority of studies[12,13,14] indicate the reaction occurs in two stages. The first involves a reversible oxygen exchange between carbon dioxide and the carbon surface which is followed by the rate determining step, the gasification of the carbon and adsorbed oxygen in the form of carbon monoxide.

Excessive amounts of carbon monoxide can reverse the first oxygen exchange reaction and slow down the overall gasification reaction. The overall rate expression used in this study can be expressed by:

$$-\frac{1}{W}\frac{dW}{dt} = \rho \qquad (6)$$

where $W$ is the weight of carbon and $\rho$ is proportional to the specific rate constant[15].

However, the purpose of this study was not to determine the mechanism involved in these reactions but to find a reliable and inexpensive means of measuring the relative reactivities of cokes to carbon dioxide. The most commonly used method[7] reports a loss in the percent weight of carbon after being reacted with carbon dioxide for a fixed period of time. Other methods involve gas analysis. One method[5] reports reactivity as the value of the $CO_2/(CO+CO_2)$ ratio of exit gas with a constant inlet flow rate of carbon dioxide. Another gas analysis method[6] reports reactivity as the flow rate of carbon dioxide necessary to produce 20 percent by volume of carbon monoxide in the exit gas.

The method utilizing a solid state electrolyte is essentially a gas analysis method and the experiments can be made to report reactivity in any desired manner. The advantage of this gas analysis method is that it is continuous and analyzes the gaseous products close to the reaction site. As a result it should be more reliable than other methods which require that the exit gases be cooled. The analyses can be easily converted to a continuous weight loss method by calculations using equations (2), (4) and (5).

Experiments were done on several coke samples at $1050^{\circ}$C with carbon dioxide flows of 1.2 l/min. This flow was found from loss-in-weight experiments at this temperature to be slightly in excess of the critical flow rate. The flow of 1.2 l/min. was used in all experiments and should be sufficient to avoid segregation of $CO_2$ and CO in the reaction zone. Weight loss curves were plotted with respect to time. From the integration of equation (6), it can be seen that a plot of $ln\ w_i/w_t$ with respect to time, will yield a slope proportional to the specific rate constant of the reaction. The initial weight and the weight at time $t$ are represented by $w_i$ and $w_t$ respectively. The slopes ($\rho$) of the plots for all cokes studied approach linearity, and the results are listed in Table 1. It appears that the petroleum coke and electrode graphite are slightly less reactive than the foundry and metallurgical cokes. The formed

coke and lignite char were much more reactive with the latter being about 50
times more reactive than the western Canadian coke at 1050°C.

TABLE 1

| Coke Type | Slope ($\rho$ min.$^{-1}$) | *Area (M$^2$/mg) | $\rho$/A |
|---|---|---|---|
| 1. W. Canadian Coke | $6.8 \times 10^{-3}$ | .0069 | 0.99 |
| 2. Petroleum Coke | $7.2 \times 10^{-3}$ | .0035 | 2.10 |
| 3. Electrode Graphite | $8.0 \times 10^{-3}$ | .0033 | 2.42 |
| 4. Foundry Coke | $8.7 \times 10^{-3}$ | .0124 | 0.70 |
| 5. Metallurgical Coke | $9.5 \times 10^{-3}$ | .0015 | 6.33 |
| 6. Wharton Preheat | $21.2 \times 10^{-3}$ | .0097 | 2.19 |
| 7. Formed Coke | $30.5 \times 10^{-3}$ | .08 | 0.38 |
| 8. Lignite Char | $316. \times 10^{-3}$ | 0.282 | 1.12 |

The reliability of the test method was examined by comparing the
reactivity of the metallurgical coke to that determined using the Cahn
balance. Weight loss curves were obtained at temperatures of 970, 1058,
and 1100°C. The loss in weight of coke was also calculated from the oxygen
potential method for experiments made at 967, 983, 1012, 1061, 1093, and 1141°C.
The loss in weight curves for this coke approached linearity for the first 30
minutes of reaction.

The effective rate constants, $\rho$, obtained from the plots of $w_i/w_t$
against time, are listed in Table 2 for various temperatures. The rate constants
for the determinations from the cell and balance differ slightly at temperatures
near 970°C but are nearly equivalent at temperatures near 1060 and 1100°C. When
$ln$ $\rho$ was plotted against the reciprocal of the absolute temperature the results
from the balance and the cell formed one straight line (Figure 2). From the slope
of this line, the pseudo-activation energy for the metallurgical coke was found to
be 255 kJ/mole. This is less than the activation energies (293, 360 kJ/mole)
found by other workers[15,16] for graphite. It is slightly more, however, than the
203, 237 kJ/mole found for petroleum coke[15].

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*Surface areas were determined by the BET Method

TABLE 2

| Method | Temp $^{\circ}C$ | $\rho$ | $\ln \rho$ |
|--------|--------|--------|--------|
| Cell | 967 | $1.56 \times 10^{-3}$ | -6.46 |
| Balance | 970 | $2.37 \times 10^{-3}$ | -6.05 |
| Cell | 983 | $2.35 \times 10^{-3}$ | -6.05 |
| Cell | 1012 | $4.31 \times 10^{-3}$ | -5.45 |
| Balance | 1058 | $10.42 \times 10^{-3}$ | -4.56 |
| Cell | 1061 | $9.93 \times 10^{-3}$ | -4.61 |
| Cell | 1093 | $17.45 \times 10^{-3}$ | -4.04 |
| Balance | 1100 | $18.98 \times 10^{-3}$ | -3.96 |
| Cell | 1141 | $39.52 \times 10^{-3}$ | -3.23 |

CONCLUSIONS

Galvanic cells consisting of a solid zirconia-lime electrolyte can be used to measure the oxygen potential and hence the reactivity of carbon to $CO_2$. Since the method is essentially a gas analysis method, the results could be expressed as the $CO/CO_2$ ratio of the exit gas for a fixed flow or as the flow of carbon dioxide required to produce exit gas consisting of 20 percent carbon monoxide. In this study, the results were used to calculate weight losses of carbon during reaction. The reactivities of several carbon materials were compared using this method. The results from the reactivities of a metallurgical coke measured at several temperatures compared favourably with results from a thermogravimetric method.

The EMF of the galvanic cell continuously monitors the reaction of carbon dioxide and carbon and is desirable because it allows for gas analysis at the temperatures of the reaction and at the reaction site. The apparatus is relatively inexpensive and easy to assemble. The apparatus can be modified so that sample loading can be done through the bottom of the equipment so that the zirconia tube does not need to be cooled after each experiment. Such an arrangement would allow for a quick and convenient laboratory method for continuous reactivity measurements.

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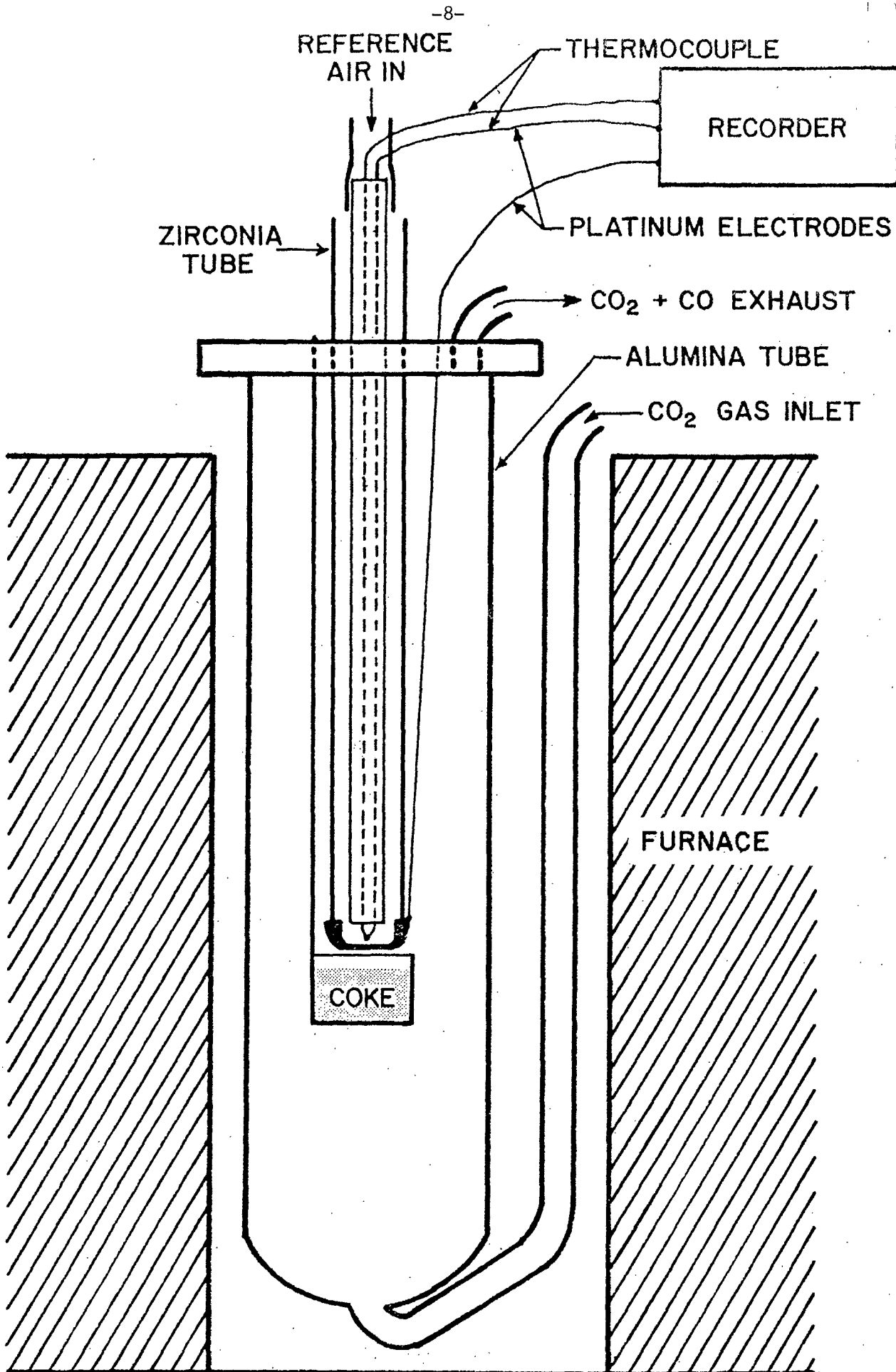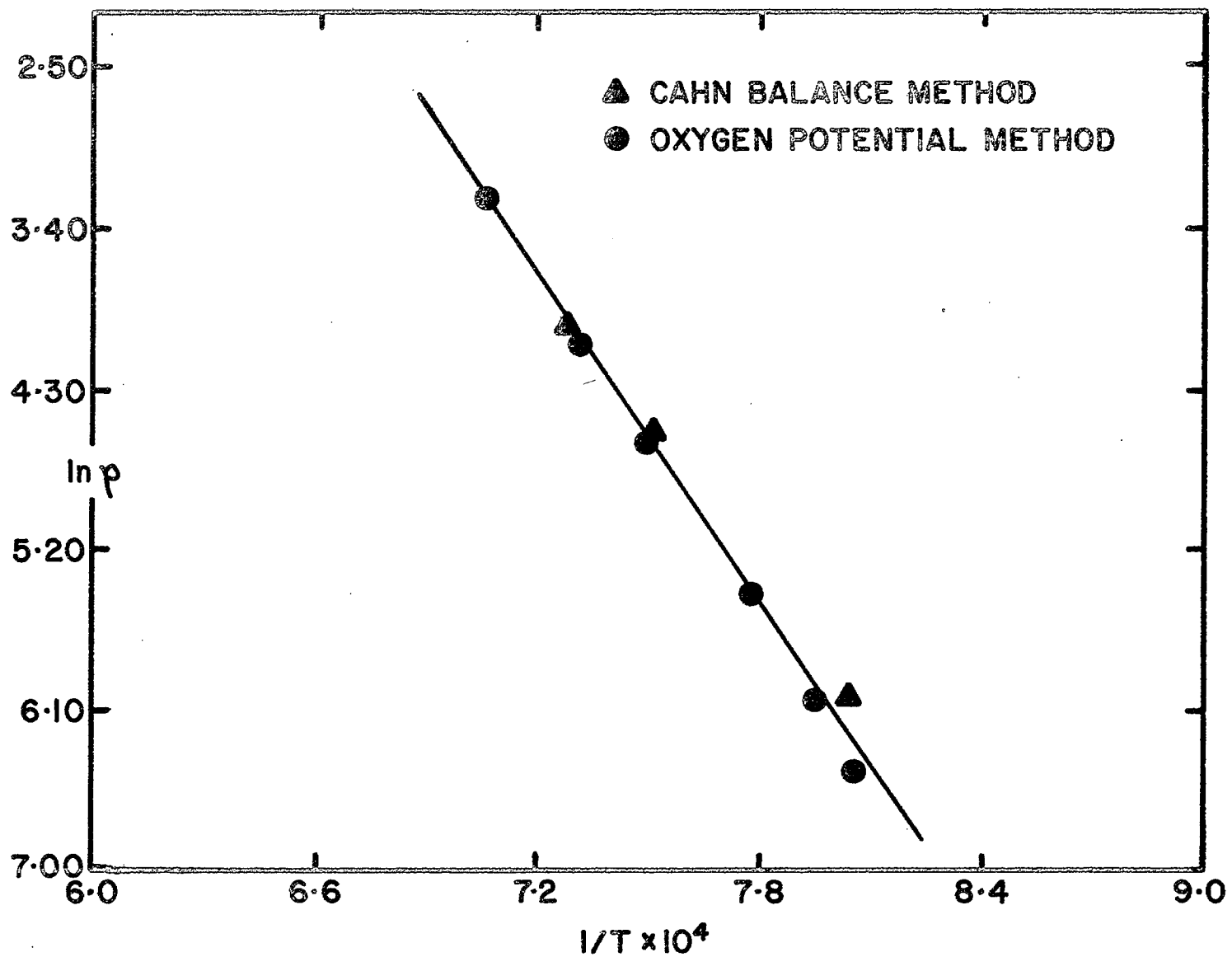
FIGURE 2. Arrhenius plot for metallurgical coke.