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# On the Rate of Reaction in Carbon Dioxide-Coke System

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By

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## 1. Introduction

The reaction $C + CO_2 = 2CO$ is essential in the manufacture of producer gas. Especially for thick fuel beds this reaction becomes most important when we consider the combustion process of solid fuels.

Boudouard [1] was the first to study the equilibrium in a temperature ranging from 450° to 1000°C, and the reaction is called as "Boudouard reaction." The physical chemistry of this reaction was also discussed by Clement and coworkers. [2] It was pointed out by the latter that chemical reaction rate is the controlling factor in this reaction and the effect of diffusion is of secondary importance.

Since 1930 the determination of the velocity of the reaction at different temperature has been advanced materially. Dubinsky [3] studied this reaction at the temperature ranging from 950° to 1100°C and expressed the reaction rate $\frac{d(CO)}{dt}$ as $K_1(CO_2) - K_2(CO)^2$ considering the importance of the influence of the reverse reaction.

An elaborate study concerning this reaction was made by Mayers. [4] The observed reaction rate $A$ could be represented by two straight lines which intercept at about 950°, indicating that the reaction rate increased at the higher temperatures than 950°. The two equations were as follows: Below 950°C (850° to 950°), $\log A = 3.40 - \frac{32,360}{4.575 T}$. Above 950°C (950° to 1300°) $\log A = 5.07 - \frac{38,700}{4.575 T}$. The discontinuity was attributed to a change in nature of the CxOy complex. Moreover it was suggested that the diffusion is also seriously important.

In this paper a quantitative formulation of the rate of reaction in carbon dioxide and coke system was attempted in the case when the influence of diffusion and at the same time the influence of chemical reaction must be considered.

## 2. Derivation of Formulas.

When a piece of coke briquette reacts with carbon dioxide which flows around

the sample, the gradients of the partial pressure of carbon dioxide and carbon must be established in the boundary layer between the coke surface and gas and also in the layer of ash as shown in Fig. 1. In this case it is assumed that carbon monoxide is formed at the reaction surface. The carbon monoxide diffuses outwards through the layer of ash and then boundary film. At the same time carbon dioxide reaches to the fresh carbon surface diffusing the layers in the opposite direction.
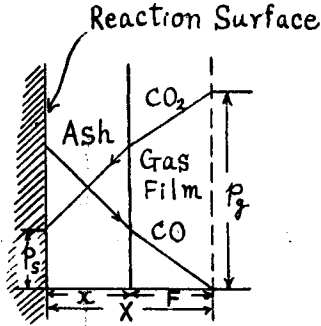


Fig. 1 The Partial Pressure Gradients in the Layers Overlying the Coke.

The specific rate $K$ of reaction $C + CO_2 = 2CO$ can be represented by

$$K = kp_s = \frac{C}{\sqrt{T_s}} e^{-\frac{E}{RT_s}}, \tag{1}$$

in which $c$ is constant, $E$ the energy of activation, $p_s$ the partial pressure of carbon dioxide at the reaction surface, $k$ the coefficent of reaction rate and $T_s$ the temperature at the reaction surface.

For diffusion of carbon dioxide into carbon monoxide, the following equation may be written: [5]

$$-\frac{dp}{dx} = \frac{RT}{D} \left( N_{CO_2} - \frac{p}{P} N_{CO_2} - \frac{p}{P} N_{CO} \right), \tag{2}$$

where $D$ is the diffusivity at the mean film temperature $T$, $N_{CO_2}$ the rate of diffusion of carbon dioxide, $N_{CO}$ the rate of diffusion of carbon monoxide, $P$ the total pressure, $p$ the partial pressure of carbon dioxide and $x$ distance in direction of diffusion.

In this case, $N_{CO} = -2N_{CO_2}$. Equation (2) may be integrated between the limits $p = p_s$ at $x = 0$, and $p = p_g$ at $x = X$. We obtain the formula

$$N_{OC_2} = \frac{D}{RT} \frac{P}{X} ln \frac{1 + p_g/P}{1 + p_s/P}. \tag{3}$$

When the product is all carbon monoxide, the rate of reaction $K$ equals $N_{CO_2}$. Combining equation (3) and (2), we get the equation,

$$K = \frac{D}{RT} \frac{P}{X} ln \frac{1 + p_g/P}{1 + p_s/P}. \tag{4}$$

For simplifying the calculation we assume:

$$ln \frac{1 + p_g/P}{1 + p_s/P} = m \left( \frac{p_g}{P} - \frac{p_s}{P} \right)^q, \tag{5}$$

in which $m$ and $q$ are constants.

Combining equation (5), (4) and (1), the coefficint of reaction rate is given by the equation

$$k = \frac{K}{p_0 - P\left(\frac{RTX}{DPm}K\right)^{1/q}}. \qquad (6)$$

For convenience sake, if the value of $q$ can be assumed as in the order of 1.0, the partial pressure $p_s$ at the reaction surface is expressed as

$$p_s = \frac{p_0}{1 + \frac{RTX}{Dm} \cdot k}, \qquad (7)$$

although $m$ may be expected to change slightly according to the value of $p_s$ as described later.

Then, the specific rate of reaction $K$ is given by

$$K = \frac{p_0}{\frac{1}{k} + \frac{RT\overline{X}}{D \cdot m}}, \qquad (8)$$

The diffusivity $D$ is the function of the temperature and replaced by the equation $D_0(T/237)^n$, where $D_0$ is the diffusivity at standard temperature, $237^{\circ}K$, and $n$ is constant.

In this case, the film thickness $X$ is the sum of the bounded gas film thickness $F$ and that of the layer or ash. It is clear that diffusional resistance of the layer of ash will be larger than that of the gas film. Hence, the film thickness $X$ is given by

$$X = F + \alpha x, \qquad (9)$$

in which $\alpha$ is the factor for the coefficent of diffusional resistance for the ash layer ($\alpha > 1$) and $x$ the thickness of ash.

Substituting the expression (9) into equation (8), we obtain the final equation for the specific rate of reaction

$$K = \frac{p_p}{\frac{\sqrt{T_s}}{c}e^{+\frac{ER}{T_s}} + \frac{273R(F + \alpha x)}{D_0 m \cdot T^{n-1}}}. \qquad (10)$$

The denominator of equation (10) contains two additive terms, the first of which corresponds to a chemical resistance and the second to a diffusional resistance.

In order to test the validity of this type of mathematical analysis the experimental study of the reaction of coke with carbon dioxide under constant temperature and gas velocity was undertaken.

### 3. Experimental Procedure

The apparatus used is shown schematically in Fig. 2.

A piece of coke briquette fitting snugly into a crucible with cylindrical side was hung from one arm of a thermal balance into a vertical, cylindrical furnace through which a stream of carbon dioxide was passed with constant velocity. The weight decrease due to the reaction, $C + CO_2 = 2CO$, was determined by a continuous weighing device.

The analytical data of dry coke employed were as follows:



Fig. 2  Diagram of Experimental Apparatus.

E ; Furnace,  F ; Flow meter,
M ; Mirror,    T ; Telescope,
I ; Milivoltmeter, B ; Thermal
Balance,      A ; Gas Holder,
C ; $CO_2$-Bombe,    S ; Sample,
P ; Thermocouple.

|  | Fixed carbon | Volatile matter | Ash |
|---|---|---|---|
| Coke analysis, per cent | 67.5 | 10.2 | 22.3 |

The crucible used was of porcelain, 1.2 cm in internal diameter and 1.0 cm deep.

The coke was crushed and the powdered coke passing through a sieve of 60 meshes to an inch was employed for the experiment. Briquettes 1.2 cm in diameter and 1.0 cm high are stampted from the mixture of 90 per cent of the powdered coke and 10 per cent of the clay passing through a sieve of 60 meshes by a pressure of about 3000 Kg/cm².

The crucible, in which the briquette was fitted, was so suspended in the path of a carbon dioxide stream in a furnace that the mouth of the crucible was parallel to the gas stream, so that the coke is allowed to reaction with carbon dioxide in the sectional plane of the cylinder.

The temperature in the furnace was measured by a platinum, platinum-thermocuple placed near the specimen.

After the furnace temperature became constant the sample in crucible was placed into a certain position. Before all volatile matter escaped, sample was heated in this position about 10 minutes and then a stream of carbon dioxide
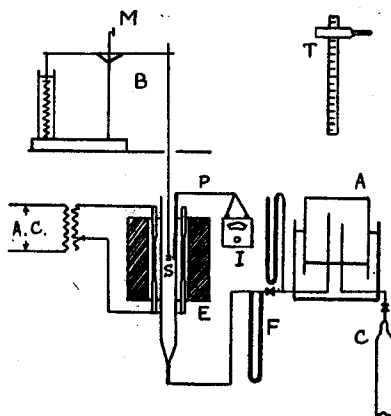
was admitted into the reaction space. It was found that, owing to the volatilisation of the much quantity of volatile matter the oxidation of carbon in the preparing heating can be neglected.

The normal carbon dioxide velocity employed was 5.2 cm per second at 0⁰C and 1 atmosphere pressure.

#### 4. Results obtained and Analysis of Results

The results of a typical set of runs are given in Fig. 3, in which the weight decreased is plotted versus the time exposure for various furnace temperature.

The specific rate of reaction $K$ can be obtained as the slop of the curves in Fig. 4 shows the specific rate of reaction $K$ plotted vs. the thickness of ash $x$. From the curves it is seen that the specific rate of reaction decreases with an increase of of the thickness.

This reaction is endothermic one, so that the mean temperature of the film overlying the fresh coke should be lower than the furnace temperature. It is desirable to know the reaction rate as a function of the mean temperature of the film rather than the furnace temperature. From the experimental results measured both temperatures it is obvious that the mean temperature is 30⁰C lower than the furnace temperature at 1200⁰C.

Hottel and co-workers [6] worked out the study of combustion of carbon in air, in which it was confirmed that, at high temperature the diffusion of gas to and from the carbon surface controlled the rate of combustion and the thickness of
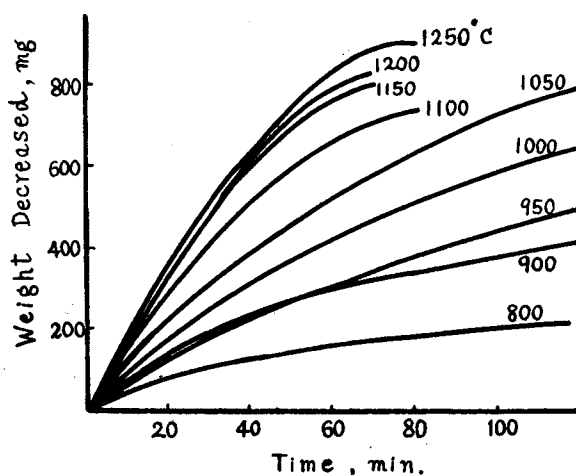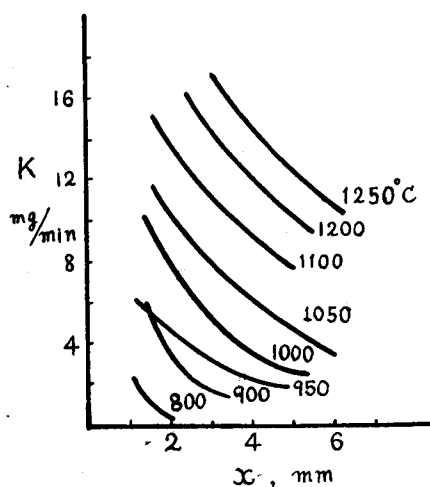


Fig. 3 Time-Weight Diagram



Fig. 4 The Relation between $K$ and $x$.

the film $F$ can be expressed by the following equation

$$F = \frac{d}{\delta} \left( \frac{T^{0.5}}{d u_0 \rho_0} \right)^{0.37}, \tag{11}$$

in which $d$ is the equivalent diameter of the specimen, $u_0$ the gas velocity at standard temperature, $\rho_0$ the density of gas at standard temperature, $T$ the mean film temperature and $\delta$ the constant.

In our case we use also the above equation for the calculation of thickness of the film. The value of $\delta$ is 1.16 for the carbon dioxide.

In regard to the coefficient $\alpha$ of diffusional resistance of ash, the following equation has been derived:

$$\alpha = \frac{1}{p'} = \frac{1}{1 - \frac{(1-f)\rho}{v}}, \tag{12}$$

where $p'$ is the porosity of ash, $f$ the fixed carbon content in the briquette, $\rho$ the bulk density of the briqutte and $v$ the apparent density of ash.

The heat of activation for this reaction is not constant, but changes with the type of carbon. For example, according to Clement,[2] the heat of activation for charcoal is 51,000 calories per gram mole, 47,000 cal. for coke and 32,000 cal. for anthrocite. Therefore, in our case, it is desirable to determine its value from the above experimental results.

Then, combining equation (6), (9) and (11) and substituting $P = p_0 = 1$, $a = 1.47$, $F = 0.22$ cm, $D_0 = 0.137$ cm²/sec, $m = 0.693$, $q = 1.18$ and $n = 1.75$, equation (6) becomes

$$k = \frac{K}{1 - \left\{ \frac{(0.22) + 1.47x)K}{0.631 \times 10^{-7} T^{0.75}} \right\}^{1/1.18}}. \tag{13}$$

Putting the experimental value of $K$ for the different mean film temperature and thickness of ash in equation (13), we can determine the value of $k$. The results obtained is shows in Fig. 6, on logarithmic scales of $k\sqrt{T}$ against $1/T$. From a slope and an intercept of the straight line in Fig. 5, $E$ and $c$ in equation (1) can be determined. The heat of activation $E$ and constant $c$ are obtained as 53.0 Kcal per mole and $8.9 \times 10^5$ respectively.

Using the obtained, rate of reaction $k$ we can calculate the partial pressure of carbon dioxide $p_s$ by equation (7) and then the specific rate $K$ by equation (10). In equation (7) and (8) the value of $m$ is not constant, but it changes from 0.500 to 0.693 according to the value of $p_s$, therefore we must use the

method of trial and error for the solution of (20). In this calculation it was assumed to be $T=T_s$.

In Fig. 6 the results of calculation by equation (10) are compared with the experimental data. The agreement between experiment and theory would seems to be satisfactory, des spite the influence of the reverse reaction has been neglect-
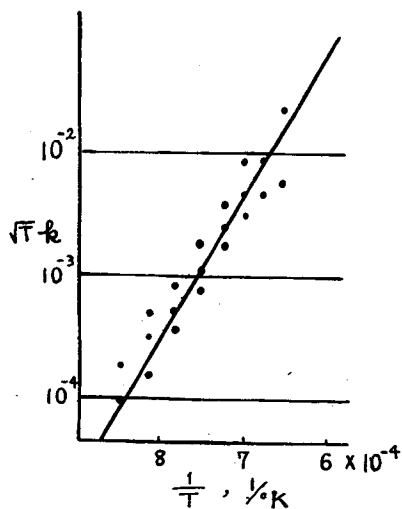


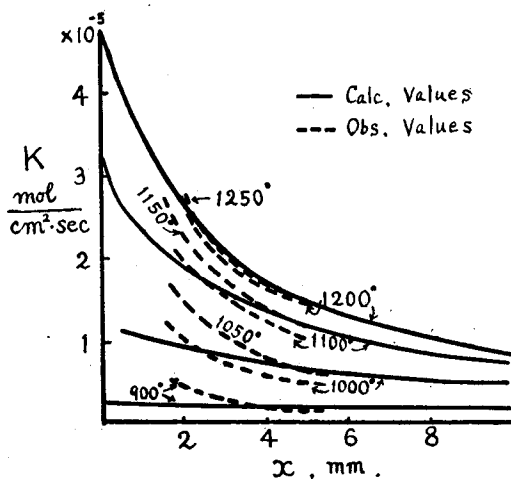Fig. 5  The Relation between the Rate of Reaction $k$ and the Temperature $T$.



Fig. 6  Comparison of Experimental Rates with Theoretical Prodiction of Rates.
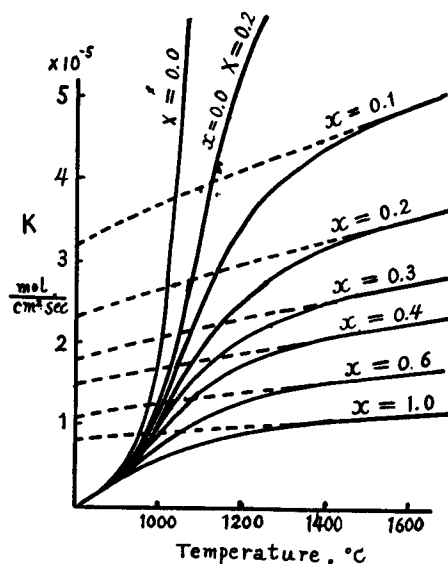


Fig. 7  Effect of Diffusion and Chemical Reaction on the Reaction $C+CO_2=2CO$.

ed and many other assumption have been introduced for our calculations.

The data in Fig. 6 are replotted in Fig. 7 with the mean film temperature $T$ as the abscissa. In this curves the dotted lines represent the results calculated the reaction rate $K$ in the case when only the diffusion is the controlling factor and the curve of $X=0.0$ that in the case when the chemical reaction is the controlling one.

From the curves in Fig. 7 it can be seen that the governing factor for the reaction below 900°C is the rate of chemical reaction. However, For the reaction above 1400°C the influence

of the diffusion phenomena predominates for the determination of the reaction rate.

## 5. Summary of Results

The results of this investigation may be summarized as follows:

(1) A quantitative formulation of the reaction rate of coke with carbon dioxide has been presented under the conditions, under which both diffusion and chemical reaction may be expected to control the reaction rate.

(2) In the temperature ranging from 900° to 1400°C, either diffusion or chemical reaction controls the reaction rate according to the reaction temperature.

(3) In regard to the diffusional resistance, the layer of ash overlying unreacted coke is highly important.

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