

## Concerning the Diffusion Kinetics of Combustion of Anthracite Coal\*

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### Abstract

A rate equation for the combustion of anthracite coal is derived, assuming that the diffusion entirely governs the kinetics of the process.

Coal powder are pressed in a form of equidimensional cylinder at constant pressure. The rate is measured by means of thermal balance. The effects of combustion temperature and molding pressure on the rate constant are investigated.

### Introduction

Although the diffusion kinetics of reaction in the solid state has been subjected to extensive study for many decades, our knowledge of the theory of such diffusion, particularly in porous solid, is extremely limited.

Jander<sup>1)</sup> derived in 1927, starting from a simplified treatment of the diffusion process, an equation, which expresses the dependence of the thickness of reacted bed on the duration of the reaction. He introduced also the degree of conversion of the material (instead of thickness of the reacted bed, which is difficult to determine) expressed by the ratio of the reacted volume to the total volume of the particles.

Ginstling-Brounshtein<sup>2)</sup> derived an equation for the kinetics of reactions in spherical particles from an approximate solution of the equation of the diffusion.

They assumed a model consisting of uniform radius spheres of one reactant B surrounded by the second reactant A. A diffuses into the surface of B through a layer of the product AB with immeasurably smaller than the velocity of the chemical reaction between A

and B, so that diffusion entirely governs the kinetics of the process.

These equations could not be applied to the isothermal combustion of the spherical substances, which are molded at constant pressure with the anthracite coal powder abundant in ash. During the reaction, the combustible materials in coal, such as carbon and volatile materials, change into the gases and the noncombustible ashes remain to form a layer, which gives a diffusional resistance.

The combustion velocity of the anthracite coal, which is molded from powder, depend on the velocity of chemical reaction in the solid, diffusion velocity of oxygen in the ash layer, and the external resistance of diffusion.

Namkoong's experimental work<sup>3)</sup> shows that the combustion rate of the anthracite coal below 600 degree C is dependent mainly on the chemical reaction at the reacting surface in the solid and on the diffusion velocity of oxygen in the ash layer between the temperatures 600 and 1,100 degree C.

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The purpose of this work is to find an equation, which expresses the thickness of the reacted bed of the anthracite coal, or the degree of conversion of the material versus time between 600 degree C and 1,000 degree C. In addition, the effect of the molding pressure of anthracite coal on the combustion rate is investigated.

### Theoretical

The concentration  $C(r)$  of oxygen in the layer of ash can be found from the solution of Fick's equation under limiting conditions for the case considered. (Fig. 1)

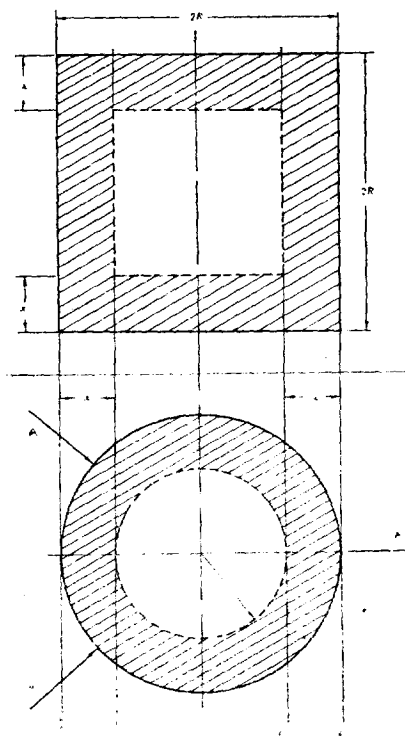


Fig. 1. Scheme of the Process

The following assumptions are made;

- 1) The ashes are distributed uniformly in the sample.
- 2) The concentration of oxygen at the outer surface of the sample is constant at  $C_o$ .
- 3) The same amount of reactant A diffuses through a given cross-section of the ash layer in unit time (steady diffusion).

Fick's equation in the case of spherical symmetry and in spherical coordinates has the form

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad \dots\dots\dots 1$$

Under the limiting conditions

$$r=R \quad C(r)=C_o \quad t>0 \quad \dots\dots\dots 2$$

$$r=R-x \quad C(r)=0 \quad t>0 \quad \dots\dots\dots 3$$

As the growth of the thickness of the ash layer is proportional to the quantity of oxygen diffusing through unit area of surface separating the ash layer from coal,

$$dx = \frac{1}{\varepsilon} dG = -\frac{D}{\varepsilon} \left( \frac{\partial C}{\partial r} \right)_{r=R-x} dt \quad \dots\dots\dots 4$$

Where  $\varepsilon$  is a proportionality coefficient, expressing the quantity of oxygen needed to react with unit volume of coal.

With the initial condition

$$t=0, \quad x=0 \quad \dots\dots\dots 5$$

As the solution of equation 1 under conditions 2 to 5 is not known, it is assumed for the first approximation (A), that the concentration gradient at the reacting plane is always constant.

$$\frac{dC}{dr} = b = \text{Constant} \quad \dots\dots\dots 6$$

Integrating the equation 6 under conditions 2

with condition  $r=0, \quad C=0$

$$b = \frac{C_o}{R} \quad \dots\dots\dots 7$$

Substituting this value in equation 4

$$\frac{dx}{dt} = \frac{D}{\varepsilon} \frac{C_o}{R} \quad \dots\dots\dots 8$$

Integrating equation 8

$$x = \frac{kt}{R} \quad \dots\dots\dots 9$$

$$\text{Where } k = \frac{DC_o}{\varepsilon}$$

As it is difficult to determine the thickness of the reacted bed, the degree of conversion of material  $\alpha$ , which is expressed by the ratio of the reacted volume to the total volume, is used.

$$\alpha = \frac{V_{\text{reacted}}}{V_{\text{total}}} = \frac{M_{\text{reacted}}}{M_{\text{total}}} \quad \dots\dots\dots 10$$

$$= \frac{\bar{M}_A + \bar{M}_C}{M_{\text{total}}} = \frac{(\bar{M}_A + \bar{M}_C) - \bar{M}_A}{M_{\text{total}} - M_{\text{ash}}} \quad \dots\dots\dots 11$$

$$= \frac{\bar{M}_C}{M_{\text{total}} - M_{\text{ash}}} \quad \dots\dots\dots 12$$

Where  $\bar{M}_A$ : The mass of ash in the reacted layer

$\bar{M}_C$ : The mass of combustible materials reacted

$M_{ash}$ : Total ash contained in the sample

$$\alpha = \frac{\frac{4}{3}\pi[R^3 - (R-x)^3]}{\frac{4}{3}\pi R^3} = 1 - \frac{(R-x)^3}{R^3} \quad \dots\dots\dots 13$$

Eliminating  $x$  from equation 13 and 9, it is obtained

$$1 - (1-\alpha)^{1/3} = \frac{kt}{R^2} = K_A t \quad \dots\dots\dots 14$$

Where  $K_A = \frac{k}{R^2}$

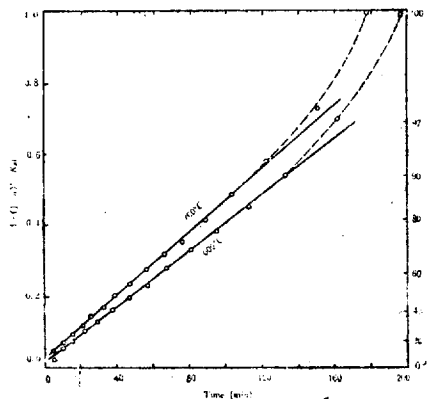


Fig. 2 Reaction Velocity Constant vs Time

Substituting  $\alpha$  from experimental data in equation 14,  $K_A t$  (product of isothermal reacting constant and time) versus  $t$  is plotted in Fig.2. The linearity of  $K_A$  is shown in the range from 20% to 90% of the degree of conversion  $\alpha$ . But it is clear that the reaction rate at the initial and final stage of reactions is higher than that of the assumption (A). It means, that the diffusion of oxygen through the ash layer governs the kinetics of the process.

Ginstling-Brounshtein derived the equation 16 for the kinetics of reactions in spherical particles from an approximate solution of the equation of diffusion, assuming that the concentration gradient at the reacting surface is always constant at any instant of time (steady diffusion).

$$\frac{\partial C}{\partial r} = \frac{C_s R}{r(R-r)} \quad \dots\dots\dots 15$$

Integrating equation 15 and substituting  $\alpha$ , eq. 16 is obtained,

$$1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3} = \frac{kt}{R^2} = K_B t \quad \dots\dots\dots 16$$

In Fig. 3 the concentration gradient distribution in the solid for this case is drawn.

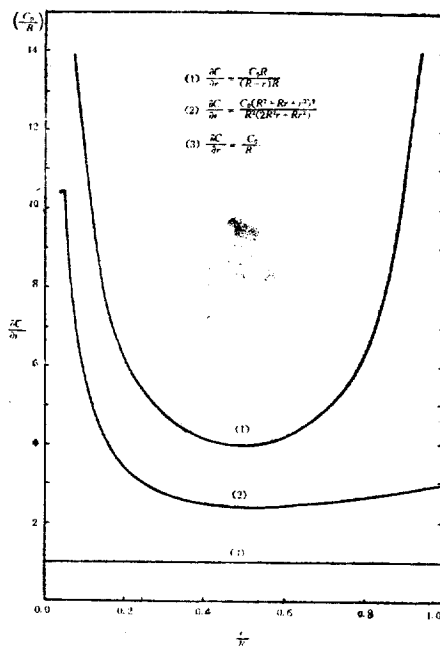


Fig. 3 Concentration Gradients at the Reacting Plane in Solid

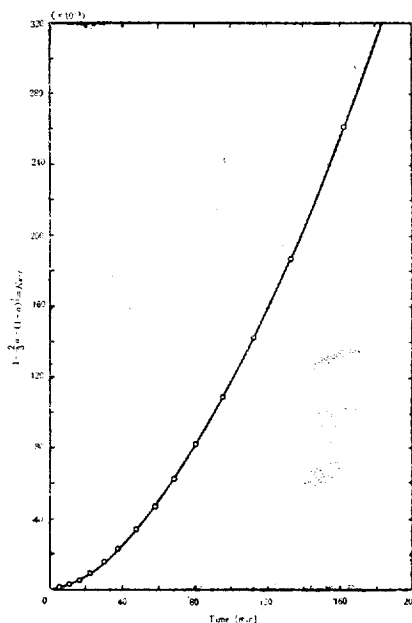


Fig. 4  $K_B.t$  vs Time According to Ginstling-Brounshtein Equation at 600°C

Substituting  $\alpha$  from experimental data in equation 16  $K_B t$  versus  $t$  is plotted in Fig. 4. The curve shows that, the reaction velocity constant of Ginstling-Brounshtein  $K_B^{(6)}$  is not constant. This means clearly that the isothermal combustion of coal can not be applied to the Ginstling-Brounshtein equation.

Using our experimental data, a plot  $K_B$  versus  $\alpha$  is drawn in Fig. 5 which shows  $K_B$  a linear function of  $\alpha$ . Therefore, the equation 16 is divided by  $\alpha$ , the following equation is obtained

$$\frac{1}{\alpha} \left\{ 1 - \frac{2}{3} \alpha - (1-\alpha)^2 \right\} = \frac{kt}{R^2} = K_c t \quad \dots\dots\dots 17$$

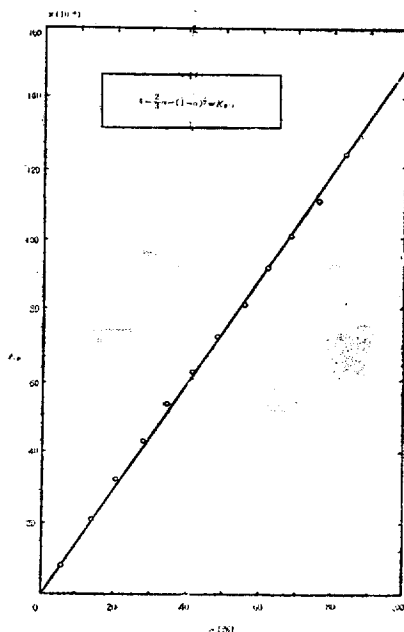


Fig. 5 Rate Constant  $K_B$  vs  $\alpha$  at 600°C

Substituting  $\alpha$  from experimental data in equation 17,  $K_c t$  versus  $t$  is plotted in Fig. 6, which shows a linear curve, the slope of which expresses the rate constant for this process.

In order to arrive at this equation the following concentration gradient in the reacting surface must be assumed.

$$\frac{\partial C}{\partial r} = \frac{C_0(R^2 + Rr + r^2)^2}{R^2(2R^2r + rR^2)} \quad \dots\dots\dots 18$$

In Fig. 3 the concentration gradient distributions are drawn as a function of  $\left(\frac{r}{R}\right)$

Substituting equation 18 in equation 4

$$\frac{dx}{dt} = \frac{DC_0}{\epsilon} \frac{[R^2 + R(R-x) + (R-x)^2]^2}{R^2(2R^2(R-x) + R(R-x)^2)} \quad \dots\dots\dots 19$$

Integrating equation 19 from  $x=0$  to  $x=R$  and rearranging

$$\frac{\left(2 - \frac{x}{R}\right)}{3 - 3\left(\frac{x}{R}\right) + \left(\frac{x}{R}\right)^2} \cdot \frac{2}{3} = \frac{kt}{R^2} = K_c t \quad \dots\dots\dots 20$$

Letting  $\alpha = 1 - \frac{(R-x)^3}{R^3}$  in equation 20, we obtain equation 17.

This equation most nearly satisfied the kinetics of diffusion process for combustion of the anthracite coal abundant in ash.

## Experimental

70 mesh underside powder of anthracite coal are pressed at constant pressures in cylindrical column of diameter 15 mm and of same height. The analysis of the sample is shown in Table 1.

Table 1

Fixed carbon	Volatile matter	Ash content	Water content
60.6%	2.4%	32.2%	4.8%

Before weighing the sample it is dried up at 350 degree C and put in the thermal balance, keeping the temperature of the furnace always constant. The

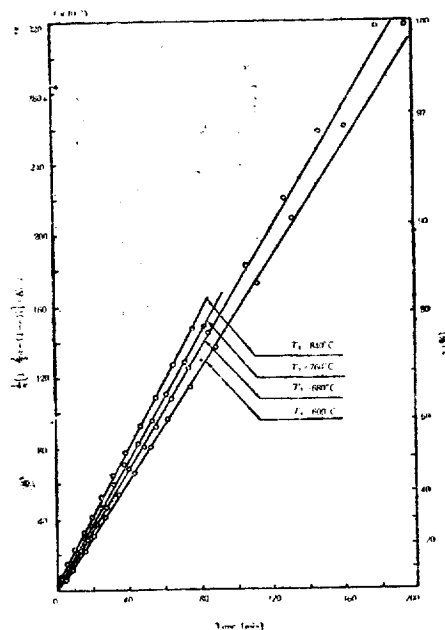


Fig. 6 Effect of Temperature on Reaction Time

decreasing weight of the sample is recorded during the combustion at temperature 600, 680, 760, and 840 degree C. According to the equation 17, it is calculated and the results are plotted in Fig. 6

The same procedure is repeated for the samples, which are pressed at constant pressure 100 kg/cm<sup>2</sup>, 600 kg/cm<sup>2</sup>, and 1,000 kg/cm<sup>2</sup>. The results are plotted in Fig. 7. The effect of the molding pressure of the

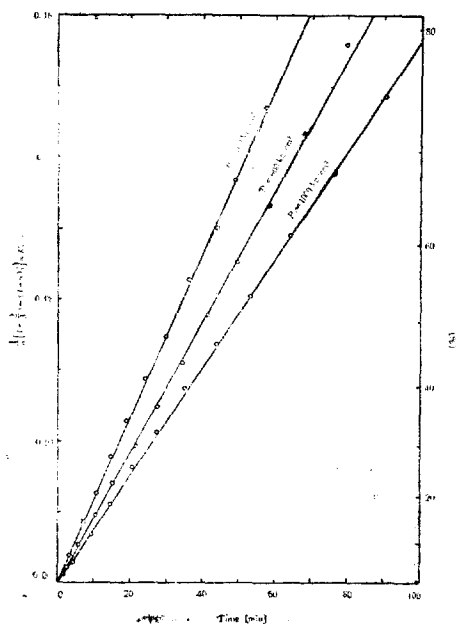


Fig. 7 Effect of Molding Pressure of Reaction Rate at 600°C

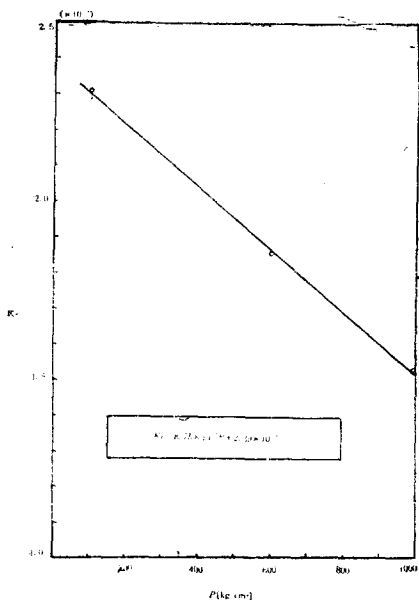


Fig. 8 Rate Constant vs Molding Pressure

coal from powder on the isothermal reaction velocity constant is shown in Fig. 8.

### Temperature Effect

The Arrhenius expression, which describes the temperature dependence of the reaction, is an equation of the form,

$$\frac{K}{K_0} = \exp(-E/kT) \quad \dots\dots\dots 21$$

Fig. 9 exhibits an Arrhenius plot of  $\log K$  versus reciprocal temperature  $1/T$  for equation 17. Finally, the isothermal rate constants for various temperatures are used to calculate an activation energy  $\bar{E}$  (1840 cal/mole) according to the Arrhenius equation.

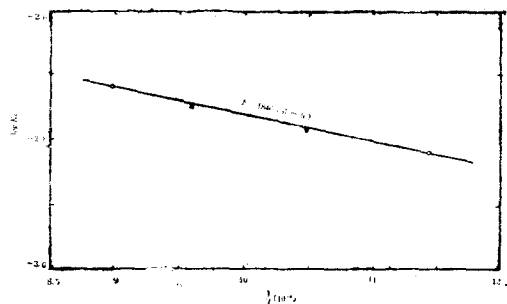


Fig. 9  $\log K$  vs Reciprocal Temperature

### Determination of Diffusion Coefficient

Serin and Ellickson<sup>4)</sup> have provided a simple means of determining  $K$  from experimental data for the equation of Dünwald and Wagner<sup>5)</sup>

$$1-\alpha = \left(\frac{6}{\pi^2}\right) \sum_n \left(\frac{1}{n^2} \exp(-n^2 \pi^2 D t / R^2)\right) \quad \dots\dots\dots 22$$

Which was derived assuming diffusion through the layer of reaction products on uniform spherical reactant particles to be rate governing.

$$\alpha = 1 - \left(\frac{6}{\pi^2}\right) \sum_n \left(\frac{1}{n^2}\right) \exp(-n^2 K t) \quad \dots\dots\dots 23$$

where  $K = \frac{\pi^2 D}{R^2}$

It is obvious that  $Kt$  determines a value of  $\alpha$  and vice versa. If we know the value of  $\alpha$  from experimental data, the corresponding value of  $Kt$  from equation 17 can be read from the curve of Fig. 7. Knowing the value of  $t$  to which this value of  $\alpha$  and therefore  $Kt$  corresponds, one can calculate  $K = \frac{\pi^2 D}{R^2}$  and therefore determines the diffusion coefficient of

the reaction at constant temperature.

The diffusion coefficients of oxygen in the samples at the given conditions are calculated and given in Table 2 and Table 3.

**Table 2**

$\alpha$	$D \times 10^4 (\text{cm}^2/\text{min}) \quad P=1,000 \text{ kg/cm}^2$			
	600°C	680°C	760°C	840°C
0.2	3.44	3.92	4.39	4.77
0.3	3.58	3.88	4.14	4.69
0.4	3.53	3.70	4.17	4.48
0.5	3.51	3.83	4.13	4.45
0.6	3.53	3.83	4.12	4.46
0.7	3.53	3.85	4.18	4.66
0.8	3.49	3.85	4.14	4.40
Dav	3.52	3.83	4.18	4.49

**Table 3**

$\alpha$	$D \times 10^4 (\text{cm}^2/\text{min}) \quad T=600^\circ\text{C}$		
	100 kg/cm <sup>2</sup>	600 kg/cm <sup>2</sup>	1,000 kg/cm <sup>2</sup>
0.2	5.33	4.29	3.44
0.3	5.32	4.08	3.58
0.4	5.34	4.18	3.53
0.5	5.32	4.24	3.51
0.6	5.25	4.25	3.53
0.7	5.33	4.24	3.53
0.8	5.29	4.26	3.49
Dav	5.31	4.21	3.52

### Nomenclature

b: a constant	[g-mole/cm <sup>4</sup> ]
C, C <sub>0</sub> : concentration of oxygen in a layer and at the boundary	[g-mole/cm <sup>3</sup> ]
D: diffusion coefficient	[cm <sup>2</sup> /min]
E: activation energy	[Ev/molecule]

G: The quantity of oxygen diffusing through unit area

	[g-mole/cm <sup>2</sup> ]
K <sub>A</sub> , K <sub>B</sub> , K <sub>C</sub> : rate constants	[min <sup>-1</sup> ]
k: a constant	[cm <sup>2</sup> /min]
k: Boltzmann constant	[E <sub>v</sub> /°K]
n: an integer series	[—]
P: molding pressure	[kg/cm <sup>2</sup> ]
T: temperature	[°K]
$\alpha$ : degree of conversion	[—]
$\epsilon$ : a proportionality coefficient	[g-mole/cm <sup>3</sup> ]

### Literature

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