

"THE REACTION OF COKE WITH CARBON DIOXIDE"

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Earlier studies of the kinetics of the CO_2 -C reaction have generally been deficient for one or both of two reasons: either the data were based on imprecise methods of determining the extent of reaction (e.g., product gas analysis, reactant weight decrease, pressure variation) or the data did not yield information concerning local- or point-reaction rates, which are the kind of data required for formulating kinetic mechanisms. Most commonly the data were on reaction in a tube of finite length, packed with carbon.

The present studies were of mono-layers of carbon particles resting on a screen up through which the reactant gas mixtures were passed, the system being maintained isothermal. Details of the apparatus and experimental techniques are given by Wu (1). The reactant gases were CO_2 , CO_2 - N_2 mixtures, and CO_2 - CO mixtures. Before each run the system was evacuated, following which reactant gas was passed through for 10 to 15 minutes. Because of the high reactivities of H_2O and O_2 relative to CO_2 the gas mixture was dried by passage through a bed of Drierite and then stripped of trace oxygen by contact with reduced copper turnings at 415°C . After the furnace had reached the desired temperature level the screen with the carbon particles was introduced by a magnetically operated slide mechanism the smooth operation of which prevented disturbance of the carbon bed. After a specified time the carbon bed was quickly removed, cooled and weighed. The decrease in weight of the carbon and the time of reaction were used to determine the specific reaction rate for each run.

The solid reactant used was from the same lot used by Gilliland et al (2) and by Graham (3) in fluidized beds. The effect of particle size from 80-100 mesh to 10 mm diameter was determined in the present studies. The coke contained 9.5 weight per cent ash and a small percentage of V.C.M. Reaction rates, R , mg c/g.c. min., are expressed on an ash-free basis and corrected for loss of V.C.M. as a function of reaction time, temperature and particle size on the basis of experiments made in pure N. The maximum weight loss correction for V.C.M. amounted to 1.5% of the initial weight of the particles.

The various reaction rate terms used are defined as follows:

(1) The instantaneous specific reaction rate R_i is defined as the rate of decrease in weight of carbon based on unit weight W of carbon at the fractional residual carbon $W/W_0 = F$:

$$R_i = \frac{-dW}{W d\theta} = \frac{-d \ln W}{d\theta} = \frac{-d \ln (1-F)}{d\theta} \quad (1)$$

(2) The initial specific reaction rate R_0 is defined as the rate of decrease in weight of carbon based on unit weight of carbon at $F=0$:

$$R_0 \equiv - \left(\frac{dW}{W d\theta} \right)_{F=0} \equiv - \left(\frac{d \ln (1-F)}{d\theta} \right)_{F=0} \equiv \left(\frac{dF}{d\theta} \right)_{F=0} \quad (2)$$

(3) The average specific reaction rate R_{av} is defined as the time mean of the instantaneous specific reaction rate R_i from $F=0$ to $F=F$:

$$R_{av} \equiv \frac{\int_0^{\theta} R_i d\theta}{\theta} \equiv \frac{\int_0^{\theta} \frac{-dW}{W} d\theta}{\theta} \equiv \frac{W_0 - \frac{dW}{W} - \ln (1-F)}{\theta} \quad (3)$$

The experimental results, all obtained at a total pressure of 780 mmHg, can be classified into the following two groups:

1. Experiments using New England coke particles of 50-60 mesh.

The gas flow rate, except in the velocity runs, was maintained constant.

(a) N_2 blank runs: Typical results are listed in Table 1, as fractional decrease in weight of the sample, F_{N_2} , calculated from the data on an ash-free basis at different temperatures.

(b) CO_2-N_2 runs: Five temperatures (1500, 1600, 1700, 1800 and 1900°F) were investigated. The time of reaction was adjusted for each run to give approximately 10% reaction. In Figure 1 the values of the average specific reaction rate R_{av} are plotted vs the partial pressure of CO_2 on semi-logarithmic coordinates. For each pair of curves the upper one shows R_{av} calculated on an ash-free basis, and the lower one shows that calculated on an ash-free basis, after being corrected for V.C.M. based on the N_2 blank runs.

(c) CO_2-CO runs: These data are shown in Figure 2.

(d) Velocity runs: The temperatures investigated were the same as in the CO_2-N_2 runs. Since the gas flows were in the laminar region a linear plot of R versus the reciprocal of the gas flow rate gave straight lines which could be extrapolated on a straight line through the data points to the origin, corresponding to the reaction rate in pure CO_2 , uncontaminated by the CO produced.

TABLE 1

Evolution of VCM as a function of time and temp. in N_2 50-60 mesh particles.

TEMP. °F	1500		1600		1700		1800		1900		
$F_{N_2} \times 10^3$	8.8	7.9	10.3	8.1	15	11.6	19	14.5	11	9	6.7
θ , min	610	463	240	100	120	60	90	60	30	15	10

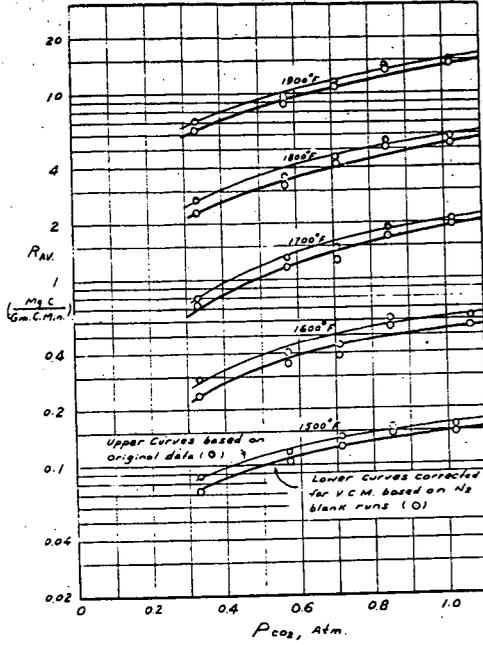


Figure 1. Effect of Partial Pressure of CO_2 and Temperature on Reaction Rate of 50-60 Mesh Coke Particles. Total Pressure 1.026 atm; H_2 as Diluent.

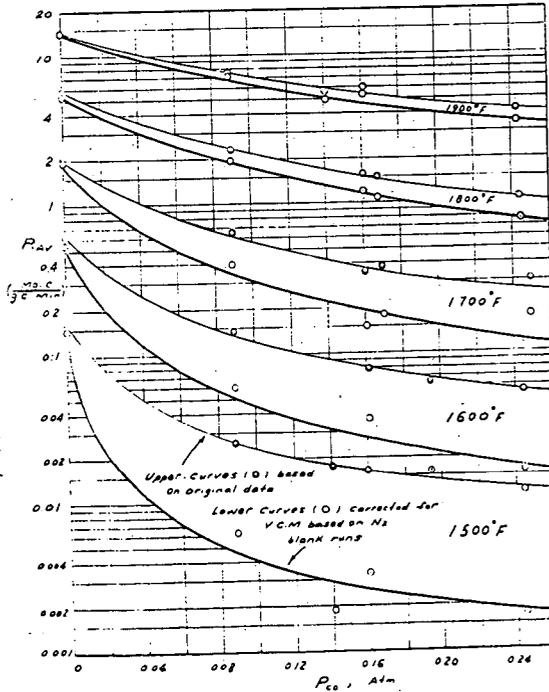


Figure 2. R_{AV} vs. P_{CO} For CO_2-CO Runs (New England Coke, 50-60 Mesh)

2. Experiments using New England coke particles of different sizes, reacting with pure carbon dioxide at 1800°F.

(a) N₂ blank runs: The fractional gasification in N₂ for the 8-12 mesh particles at any given time was about 60 per cent of that for the 50-60 mesh data shown in Table 1 and that for the 80-100 mesh particles was about 50 per cent greater. The effect of further increase in particle size up to nearly 10 mm diameter was a very small, less than 10 per cent decrease in gasification below that for the 8-10 mesh particles.

(b) Time runs: Reaction runs were made with samples of particle sizes between 8-100 mesh. Six different particle sizes were used, namely, 8-12, 16-20, 30-40, 50-60, 70-80, and 80-100 mesh. Each sample weighed about 0.1 gram. The values of R_{av} calculated from the corrected data are plotted vs θ in Figure 3 together with lines of constant F.

Effect of Particle Size

DISCUSSION OF RESULTS

From slopes of the curves of R_{av} vs θ in Figure 3 values of R_i were calculated and extrapolation of these to $F=0$ gave R_0 . Values of R_0 and the maxima of R_i are shown as a function of initial particle diameter in Figure 4.

From Figure 3 it is clear that the reaction rate is influenced not only by the fractional decrease in weight of carbon, F, but also by the diameter of the coke particle, D.

For all sizes investigated, R_i initially increased, reached a maximum, and then declined with further reaction. There was a pronounced trend for the maximum to occur at larger F values when smaller particles were used.

The shift of $R_{i(max)}$ to larger values of F with decrease in particle size can be explained as being due to the presence in the coke of ash, which amounts to 9.5%. In the case of the large particles, only a relatively small fraction of the weight of the particle has to be reacted to form a substantial layer of ash on the surface. The ash coating then makes the carbon less accessible to the reacting gas, and the reaction rate falls off. However, in the case of the small particles, a large fraction of the weight of the particle must be burned away to produce the substantial ash layer that retards further reaction.

The effect of initial particle size on the specific reaction rate as shown in Figure 3 may be explained as follows: (1) In the larger size range, 2-10 mm, the reaction occurs in a thin porous coke layer dependent in thickness on the ratio of the rate of diffusion of CO₂ into the particle to the rate of reaction on the surfaces of the pores but independent of particle diameters, thus the rate is proportional to the superficial surface area of the particles - a slope of minus unity in Figure 3. (2) As the particle size is further reduced, 1.5 to 0.5 mm, the thickness of the

diffusion-reaction zone becomes comparable with the particle radius and all of the particle volume becomes active, specific reaction rate becomes nearly independent of particle size. (3) With further decrease in particle size it is possible that the average depth of the pores in which reaction occurs is also reduced thus accounting for the increase in specific reaction rate as the particle size is reduced from 0.5 to 0.17 mm. It should also be noted that the initial apparent density of the coke particles (1.0 g/cc for massive particles) increased from 2.0 g/cc to 2.8 g/cc as the particle size was reduced in this size range, probably due to a loss of ash in the grinding and sieving process. This could also be advanced as an explanation for the increase in specific reaction rate as size decreases in this size range.

Effect of Fractional Reaction

In other experiments (1) with ash-free electrode carbon gasified in CO₂ it was found that, presumably because of an increase in surface area with progress of reaction, the instantaneous specific reaction rate was a linear function of the weight fraction gasified:

$$R_i = R_o \left(1 + \frac{m}{R_o} F\right), \text{ where } m/R_o \text{ was 14 for 50-60 mesh particles.}$$

In the present experiments the effect of the ash as shown in Figure 3 is apparently to accumulate to such an extent that the increase in surface area due to reaction is finally offset by the accumulation of ash.

The present data on coke can be correlated by the empirical expression

$$R_i = R_o \left(1 + \frac{m}{R_o} F\right) e^{-5.5DF^{1.85}}$$

in which the exponential represents the retarding effect of the ash and m is a function of initial particle diameter

$$m = \frac{10(2 + \log_{10} D)}{R_o}, \quad D \text{ in mm}$$

It is interesting to note that m for 50-60 mesh from this equation for coke is 13 vs the 14 reported for electrode carbon. The studies of Goring (4), Oshima and Fukuda (5) and of Duffy and Leinroth(17) show similar results on high-ash cokes.

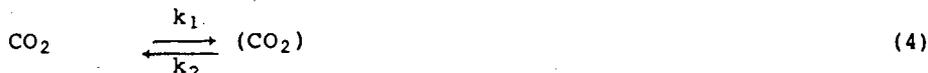
Kinetics

1. Langmuir-Hinshelwood derivation

Hinshelwood et al (16) presented the following derivation as representative of the simplest application of the early ideas of Langmuir (6) on the effect of surface adsorption on heterogeneous reactions. Note that Langmuir himself did not present the following derivation, and in fact stated in 1915 (7) that he did not believe

carbon dioxide was adsorbed in the reaction of carbon with carbon dioxide. He gave instead the first step of the mechanism of Semechkova and Frank-Kamenetzky.

Hinshelwood et al made the assumption that both the reactant, CO_2 , and the retarding product, CO , are adsorbed as such on the carbon surface, and that the rate of reaction is proportional to the fraction, s , of the surface covered by the reactant. The mechanism can then be expressed by the following equations:



in which equations, (...) represents gas in the adsorbed state.

The surface consists of equivalent and independent reaction sites, each of which can be occupied by one CO_2 or one CO molecule. When a steady state on the surface is attained, the rate of reaction per unit surface is then given by:

$$\text{Rate} = k_5 s_1 = \frac{k_5 k_1 P_{\text{CO}_2}}{1 + \frac{k_3}{k_4} P_{\text{CO}} + \frac{k_1}{k_2 + k_5} P_{\text{CO}_2}} \quad (7)$$

2. Derivation of Semechkova and Frank-Kamenetzky (8)

The assumptions made are that carbon dioxide is not adsorbed as such, but reacts with the carbon to give an atom of oxygen which remains on the surface, and a molecule of carbon monoxide which passes into the gas phase. The adsorbed oxygen atom, taking up an atom of carbon from the surface forms gaseous carbon monoxide at a steady rate. Carbon monoxide present in the gas phase is always in equilibrium with carbon monoxide in the adsorbed state on the surface (this is the sole part of the reaction scheme which is identical with the previous derivation). There is a distinction between the adsorbed oxygen and the adsorbed carbon monoxide. The following equations express the mechanism:



in which CO^* represents an O atom adsorbed on carbon, and (CO) represents CO in the adsorbed state.

When a steady state on the surface is attained, the rate is found to be:

$$\text{Rate} = k_7 s_3 = \frac{k_6 P_{\text{CO}_2}}{1 + \frac{k_3}{k_4} P_{\text{CO}} + \frac{k_6}{k_7} P_{\text{CO}_2}} \quad (11)$$

It is seen that also this expression is of the same form as equation (7).

3. Modified Semechkova and Frank-Kamenetzky Derivation (1)

In this derivation the assumption is also made that carbon dioxide is not adsorbed as such, but reacts with the carbon to form a gaseous carbon monoxide molecule, and an adsorbed oxygen atom, which is next transformed at a steady rate, not to gaseous CO, but to (CO) , the adsorbed CO, the concentration of which on the surface is in equilibrium with the CO in the gas phase.

The following equations represent this mechanism:



At steady surface state the following relations hold:

$$\text{Rate} = k_8 s_3 = \frac{k_6 P_{\text{CO}_2}}{1 + \frac{k_3}{k_4} P_{\text{CO}} + k_6 \left(\frac{1}{k_8} + \frac{1}{k_4} \right) P_{\text{CO}_2}} \quad (15)$$

which equation is seen to be of the same form as (7) and (11) and of the general type

$$R = \frac{K_1 P_{\text{CO}_2}}{1 + K_2 P_{\text{CO}} + K_3 P_{\text{CO}_2}} \quad (16)$$

The applicability of the Langmuir type equation can be tested, and the constants involved evaluated by application to the data obtained in both $\text{CO}_2\text{-N}_2$ and $\text{CO}_2\text{-CO}$ runs shown in Figs. 1 and 2. It is evident that where the surface is completely characterized by F, as shown before, the instantaneous specific reaction rate at any F could be used for this evaluation. However, R_0 was chosen as a reference value for testing the validity of the proposed Langmuir equation. The procedure used was as follows:

In the case of the CO₂-N₂ runs, the term K₂ P_{CO} is 0, if the effect of the CO generated during the reaction can be neglected. The equation can hence be reduced and rearranged to:

$$\frac{P_{CO_2}}{R_O} = \frac{K_3}{K_1} P_{CO_2} + \frac{1}{K_1} \quad (17)$$

If the proposed equation fits the data, then for a specific reaction temperature when P_{CO₂}/R_O is plotted vs P_{CO₂} on linear coordinates a straight line with slope K₃/K₁ and intercept 1/K₁ should result, from which values of K₁ and K₃ can be evaluated. The data for 1900°F are shown in Figure 5; the intercept gives K₁ = 28.6 and the slope gives K₂ = 0.56.

When the equation is applied to the CO₂ - CO runs, rearrangement of the equation to a more convenient form is possible by substituting P_{CO₂} + P_{CO} = π, where π is the total pressure on the reaction system. The rearranged equation then becomes

$$\frac{P_{CO_2}}{R_O} = \frac{K_2 - K_3}{K_1} P_{CO} + \frac{1 + K_3 \pi}{K_1} \quad (18)$$

For a specific reaction temperature when P_{CO₂}/R_O is plotted vs P_{CO} on linear coordinates, a straight line with slope K₂-K₃/K₁ and intercept 1+K₃π/K₁ should be obtained. With the aid of the values for K₁ and K₃ calculated from the results of the CO₂-N₂ runs at the same temperature, K₂ can then be evaluated from the slope of this line. Figure 6 shows the 1900°F data, the slope is 0.6 from which K₂ = 18.

The data for the other temperatures were similarly treated and over the range of variables investigated, R_O for 50-60 mesh particles could be represented by a Langmuir type equation of the following form:

$$R_O = \frac{K_1 P_{CO_2}}{1 + K_2 P_{CO} + K_3 P_{CO_2}}$$

The values of K₁, K₂ and K₃ are listed in Table 2 and shown on logarithmic-reciprocal temperature coordinates in Fig. 6.

TABLE 2
Langmuir Equation Constants

(50-60 mesh)

Constants	Reaction Temperature, °F				
	1500	1600	1700	1800	1900
K ₁ (mg.C./gm.C.min.atm)	0.23	0.9	3.18	10.2	28.5
K ₂ (atm ⁻¹)	423	178	78	36	18.
K ₃ (atm ⁻¹)	0.5	0.45	0.39	0.35	0.56

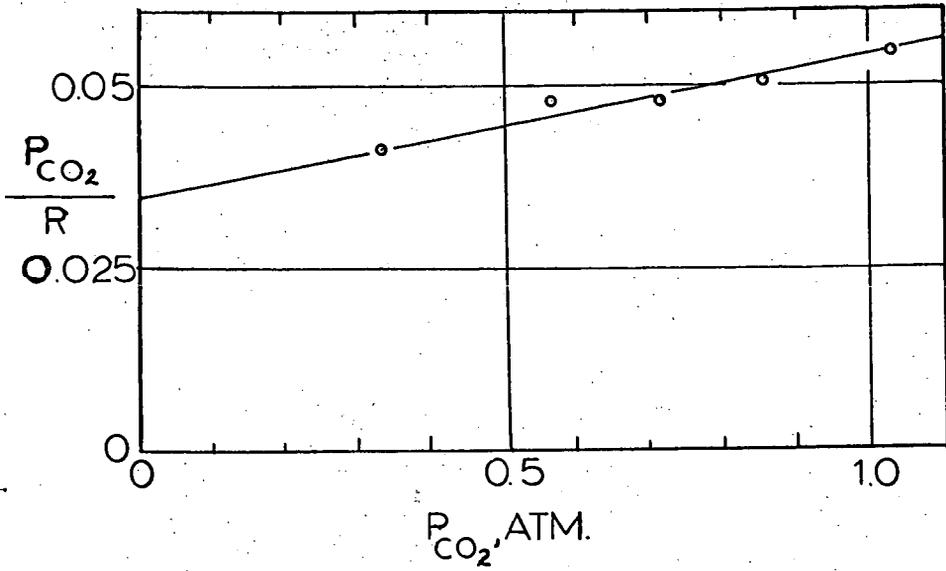


Figure 5. Test of Langmuir Isotherm
1900 F., 50-60 Mesh

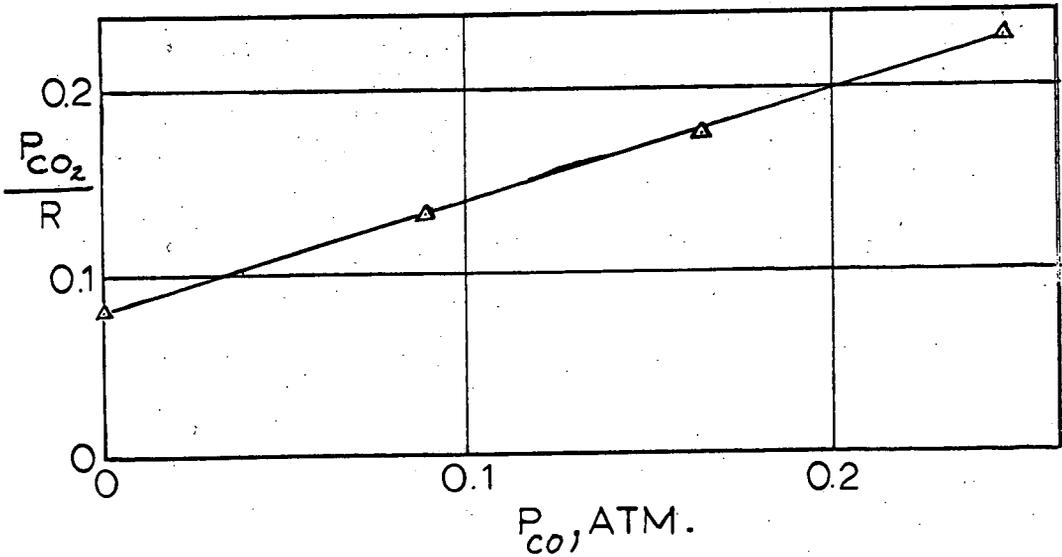


Figure 6. Test of Langmuir Isotherm
1900 F., 50-60 Mesh

From the straight line shown on Fig. 6 the values of K_0 and E were calculated for each constant and are listed in Table 3 :

TABLE 3

Values of E and K_0 in $K = K_0 e^{-E/RT}$

(50-60 mesh)

E_1 111,000 (Btu/lb mole)	K_{10} 5.2×10^{11} (mg C/gm C min atm)
E_2 72,500 "	K_{20} 3.6×10^{-6} (atm ⁻¹)
E_3 11,000 "	K_{30} 3×10^{-2} (atm ⁻¹)

It is to be noted that, if the equation describes a rate affected by surface adsorption of CO and CO₂, i.e., if the Langmuir-Hinshelwood derivation is substantially correct, then the signs of the three E's are as expected. E_2 and E_3 are associated with adsorption phenomena which should become less important as the temperature rises, whereas E_1 ($= E_2 + E_3$) is the primary measure of effect of temperature on reaction rate.

4. The Temkin adsorption isotherm

A major theoretical deficiency of the Langmuir adsorption isotherm is the implicit assumption of uniform heat of chemisorption and hence of surface activity. For most real surfaces the heat of adsorption changes with the degree of occupation of the surface (9), (10), (11) and (12). A linear decrease in heat of adsorption with fractional surface coverage leads to an isotherm for which the fractional surface coverage is proportional to the logarithm of the pressure of the adsorbing gas. This isotherm has been named after Temkin (13) although the concept appears in the works of earlier Russians (14), (15)

If the heat of adsorption, q , falls linearly with the fraction of surface occupation, S ,

$$q = q_0 (1 - \beta S)$$

the isotherm is given by

$$S = \frac{RT}{q_0 \beta} \ln A_0 P \quad (19)$$

where, β = a constant

q_0 = a constant

$A_0 = a_0 e^{q_0/RT}$

a_0 = constant

If it is assumed that chemisorption of CO₂ is fast compared with subsequent surface reactions and that the rate of surface reaction is directly proportional to the fraction of the surface covered then

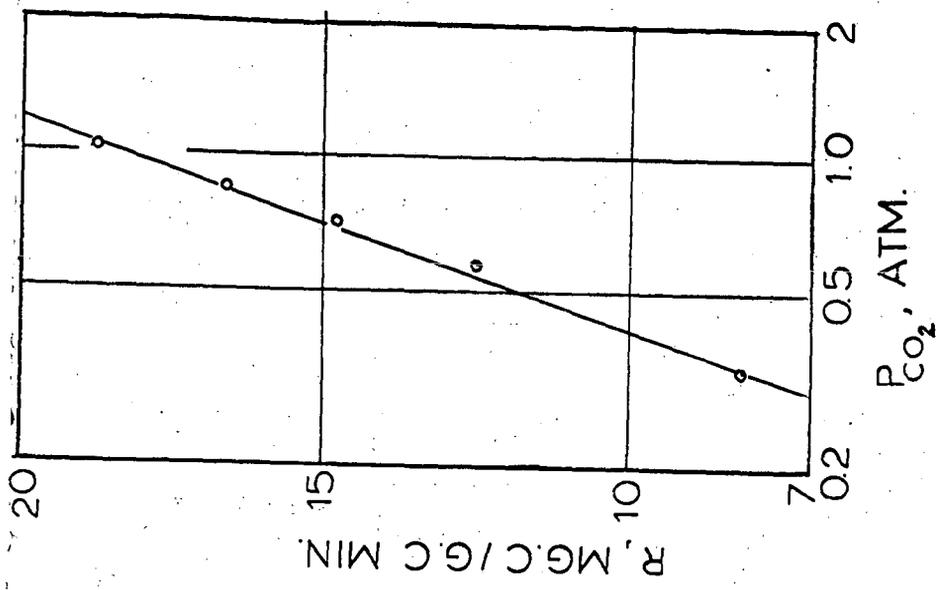


Figure 8. Test of Temkin Isotherm, 1900 F.

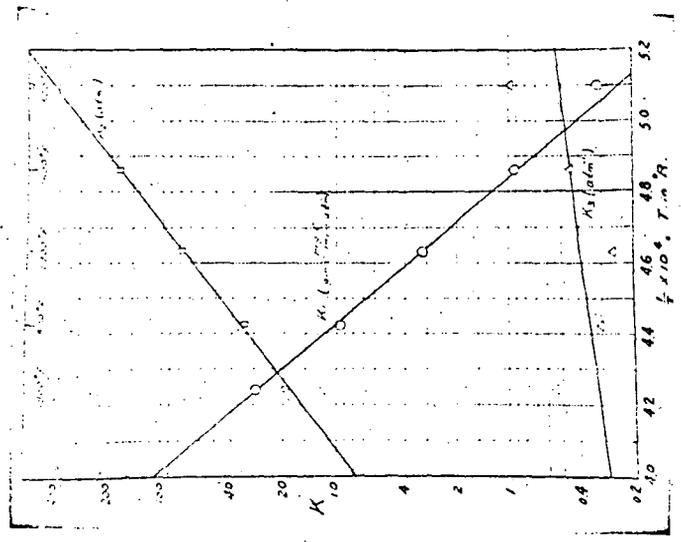


Figure 7. Arrhenius Plot of Reaction Rate Constants, 50-60 Mesh Coke.

$$R_o = \frac{k e^{-E/RT}}{\beta q_o} RT \ln A_o + \frac{k e^{-E/RT}}{\beta q_o} RT \ln P_{CO_2} \quad (20)$$

$$R_o = a(T) + b(T) \ln P_{CO_2} \quad (21)$$

Thus a plot of reaction rate versus logarithm of the pressure should be linear. Fig. 7 shows the data for 50-60 mesh particles in pure CO₂ at 1900°F. The data for other temperatures are correlated equally well.

From Eqs. 19, 20 and 21

$$\frac{a}{b} = \ln a_o + \frac{q_o}{RT} \quad (22)$$

Thus a plot of a/b versus $1/T$ should give a straight line with slope q_o/R . The present data give a value of heat of adsorption of CO₂ of 2400 Btu/lb mole and an intercept $\ln a_o = 1.4$ at $1/T = 0$.

Since q_o probably does not vary greatly with temperature b/T should be exponential in $1/T$. This was found to be so, giving a value $b/T = 81 \times e^{-45,600/RT}$.

No attempt has been made to treat the CO₂-CO mixture data using the logarithmic adsorption isotherm.

ACKNOWLEDGEMENT

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