

EFFECT OF GAS DIFFUSION IN GRAPHITIZED CARBON RODS ON THEIR GASIFICATION RATE WITH CARBON DIOXIDE^{1,2}

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At high temperatures, the experimental gasification rates of graphitized carbon rods are found to deviate progressively more from their intrinsic gasification rates, as temperature is increased. This is shown to be caused by the increasing control of the reaction by the rate of transport of carbon dioxide through the internal pores of the carbon rod. The diffusional-resistance concepts used to correct the apparent activity of catalysts to their true values are found to apply equally as well for the correction of the reactivity of carbon rods with carbon dioxide.

Introduction

Workers³⁻⁷ have shown that the physical structure of porous catalysts can be of importance in determining reaction rates. In general, the faster the reaction and the smaller the average pore size the smaller the fraction of the internal surface of the catalyst which participates in the catalytic reaction. This can result in the apparent activity of a catalyst deviating progressively more from the true activity as temperature is increased. Or, in es-

sence, if a reaction rate constant based on the experimental activity of a catalyst is used, the Arrhenius plot can show activation energies below the true value.

The above workers have shown that the physical properties of a catalyst, along with internal gaseous diffusion rates, can be used to quantitatively correct the apparent activity to the true activity of the catalyst. A similar approach has been employed in the present work to correct the apparent reactivity of graphitized carbon rods with carbon dioxide to the true value as the gasification temperature is varied from 970° to 1392°.

Experimental

The samples and reaction rate apparatus used were described in an accompanying paper.⁸ The apparatus and procedure used to experimentally determine the diffusion coefficient of hydrogen-nitrogen through the porous carbon rods, $D_{\text{eff}(\text{H}_2-\text{N}_2)}$, have been described previously.^{9,10} $D_{\text{eff}(\text{H}_2-\text{N}_2)}$ for pellets cut parallel and perpendicular to the direction of rod extrusion were 0.088 ± 0.005 cm.²/sec. (6 samples) and 0.053 ± 0.007 cm.²/sec. (8 samples), respectively, at S.T.P. conditions.

Results and Discussion

Instantaneous reaction rates at 11% burn-off are presented on an Arrhenius plot in Fig. 1. As previously reasoned,¹¹ in the simplest case the reaction rate can be expressed as $R = k(\text{CO}_2)(\text{C})$, where (CO_2) and (C) are the concentrations of carbon dioxide and carbon, respectively. In this particular case, the concentration of carbon is assumed proportional to weight of carbon, which is a constant at all temperatures for 11% burn-off. Furthermore, the concentration of carbon dioxide is taken as the average over the external sample length, it varying from 1.0 to 0.76 atm. for the temperature range investigated.

From Fig. 1, it is seen that the Arrhenius plot yields a straight line with an activation energy of 66 kcal./g. mole over the temperature range 970° to ca. 1130°. Above 1130°, the activation energy continually decreases, it having a value of 44 kcal./g. mole (a ratio of E_{true} to E_{exp} of 1.5) at 1392°.

A qualitative attempt at correcting for the increasing divergence of the experimental data from the straight-line Arrhenius plot can be made by dividing the above rates by the total surface area of the sample produced upon 11% burn-off. The

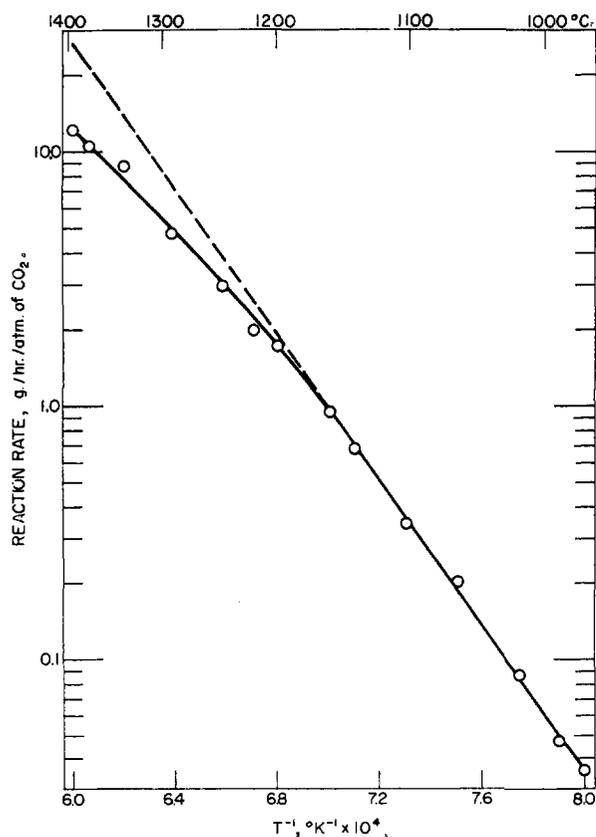


Fig. 1.—Arrhenius plot of instantaneous reaction rates at 11% burn-off.

(1) Based on a Ph.D. thesis submitted by Emile Raats to the Graduate School of The Pennsylvania State University, June, 1955.

(2) This paper presents the results of one phase of research carried out under Contract No. AT(30-1)-1710, sponsored by the Atomic Energy Commission.

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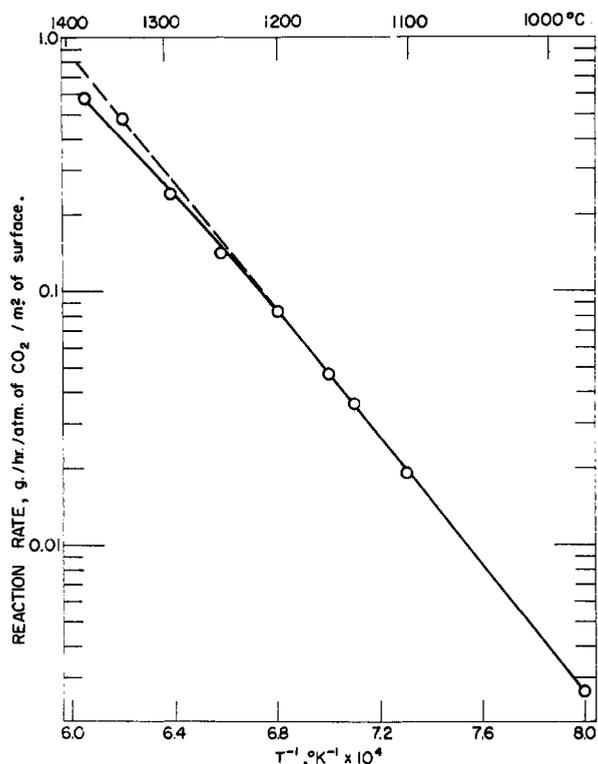


Fig. 2.—Arrhenius plot of instantaneous reaction rates per unit of total surface area at 11% burn-off.

concentration of carbon is now assumed proportional to its total surface area instead of its weight. Furthermore, as previously reasoned,⁸ the continual decrease in surface area with increasing gasification temperatures above 1224° is attributed to an increasing concentration of the reaction zone closer to the sample periphery. Therefore, this decreasing area is qualitatively related to the increasing control of the reaction by diffusion; and dividing through by the area should, to some extent, compensate for the influence of diffusional resistance. Figure 2 shows the Arrhenius plot, which yields a straight line over the temperature range 970° to ca. 1200°, with an activation energy of 58 kcal./g. mole. Above 1200° there is some decrease in activation energy to 51 kcal./g. mole. at 1372°, giving a ratio of E_{true} to E_{exp} of 1.1. However, the use of surface area to qualitatively correct for diffusional resistance is clearly demonstrated in this case.

A quantitative approach at correcting the experimental data for diffusional resistance can now be considered in line with the authors' introductory comments. The approach of Weisz and Prater⁵ is closely followed. Briefly, the experimental rate, dn/dt , divided by a diffusion factor, η , gives the corrected rate. For a spherical particle and a reaction with no volume change

$$\eta = \frac{3}{\varphi} \left(\frac{1}{\tanh \varphi} - \frac{1}{\varphi} \right) \text{ and } \gamma = R \sqrt{\frac{k_v}{D_{\text{eff}}}}$$

where R = particle radius, k_v = velocity constant per unit particle volume, and D_{eff} = the effective gas diffusion coefficient. Further, if a first-order reaction is assumed,¹² k_v can be eliminated giving a

(12) M. W. Thring and P. H. Price, *Iron and Coal Trades Rev.*, **169**, 347 (1954).

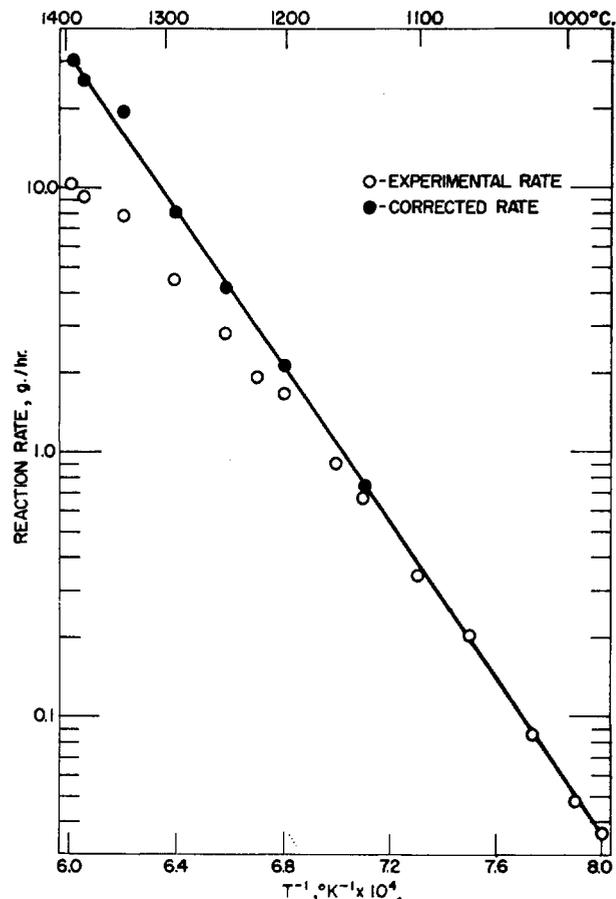


Fig. 3.—Arrhenius plot of instantaneous reaction rates at 11% burn-off with corrections for diffusional effects on first-order kinetics.

new modulus θ , which contains only observable variables.

$$\theta = \frac{R^2}{VD_{\text{eff}}} \frac{1}{(\text{CO}_2)} \frac{dn}{dt} = \varphi^2 \eta$$

where V = the external volume of the carbon sample and (CO_2) is again the average concentration of CO_2 along the external length of the sample.

Values of η are determined from a plot of η vs. $\varphi^2 \eta$ under the following conditions:

1. The same value of η is observed at 0.74φ for a first-order reaction with doubling of volume ($\text{C} + \text{CO}_2 = 2\text{CO}$), as is observed at φ for no volume change.¹³ This fact must be taken into account when the internal diffusion is occurring through pore diameters significantly greater than the mean free-path of the gas molecules. In the present case, internal diffusion through the carbon rods is visualized as primarily occurring between particle voids, which have their pore diameters concentrated above 10,000 Å.⁸ Since the mean free-path of molecules at 1 atm. pressure is ca. 1000 Å., the above correction is necessary.

2. Even though the above functions were specifically derived for a spherical particle, they are rather insensitive to particle geometry; and R may be considered the radius of the cylindrical carbon sample.¹⁴ This is a particularly good approxima-

(13) Ref. 5, p. 162.

(14) Private communication from P. B. Weisz, 1953.

tion in the present case, since reaction at the ends of the carbon sample is prevented by ceramic plates.

3. The effective diffusion coefficient, concerned with carbon dioxide diffusing through carbon monoxide, should be essentially identical to that for diffusion of carbon dioxide through nitrogen. The latter is calculated as a function of temperature for bulk diffusion (pore diameter $> 10,000 \text{ \AA}$. for atm. pressure reaction) from the experimental data by the relations $D \sim M^{-0.5}$ and $\bar{D} \sim T^{1.5}$. The experimental value of $D_{\text{eff}(\text{H}_2-\text{N}_2)}$ perpendicular to rod extrusion is used as a basis, since transport in this direction is obviously of primary importance in determining diffusional control.

4. The pressure differential from the exterior to the interior of the carbon rod caused by an increase in gas volume upon reaction and its effect in setting up forced flow of molecules from the sample is considered negligible.

Figure 3 shows the Arrhenius plot of the corrected rate data, it yielding a good straight line over the entire temperature range 970 to 1392° with an activation energy of 66 kcal./g. mole.

The effects of other assumptions on the diffusion factor, η , were investigated. If Knudsen diffusion is assumed to be affecting the reaction rates instead

of bulk diffusion, D is proportional to $T^{0.5}$ and condition 1 above can be ignored. However, this is seen to considerably over-correct the rate data; a rate of 37 g./hr. being calculated at 1292° as compared to a correct value of 8.0 g./hr., for example.

Golovina¹⁵ studied rates of diffusion of carbon dioxide through electrode-carbon membranes, prepared in essentially the same manner as the present rods, and found D to be proportional to $T^{1.3}$ over the temperature range 20 to 600°. If this relationship is used, the corrected rates are somewhat too high. However, this agreement can be improved by selecting a higher value for $D_{\text{eff}(\text{H}_2-\text{N}_2)}$ used in the calculations. Considering the fact that upon uniform gasification of a carbon rod at 900° some increase in $D_{\text{eff}(\text{H}_2-\text{N}_2)}$ was observed,¹⁶ an increase is perhaps not unreasonable. On the other hand, at high temperatures where diffusional effects become important, the D_{eff} for the interior portion of the rod, which is still unreacted, should primarily control the depth of reaction penetration.

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THE HYDROGEN ION COULOMETER

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A new type of coulometer is described based upon the removal of hydrogen ion and chloride ion from a standard solution of hydrochloric acid in potassium chloride solution. As little as one and as many as 360 coulombs have been successfully determined. The method is particularly suited for systems in which a predetermined quantity of electricity is to be passed through a solution. The end-point can then be selected with an ordinary pH meter at a pH equal to that of the distilled water used in preparing the standard solution.

Introduction

A number of coulometers for measuring small quantities of electricity have been described in the literature. With the exception of Meites' electro-mechanical coulometer^{1,2} and Wilson's mercury voltammeter^{3,4} these microcoulometers are adaptations of conventional coulometers to micro methods.⁵⁻⁷ The passage of 10 coulombs (approximately 1.04×10^{-4} equiv.) of electricity corresponds to the liberation of approximately 11.2 mg. of metallic silver in a silver coulometer or of 1.2 ml. of hydrogen in a gas coulometer. Determination of these small quantities by any customary method is susceptible to errors of at least several per cent. It is the purpose of this communication to describe a hitherto unreported system which can

readily detect and measure the passage of as little as one coulomb of electricity to a precision of a few parts per thousand.

The electrochemical reaction in this new coulometer is the removal of hydrogen and chloride ions from a standard solution of hydrochloric acid and potassium chloride in CO₂ free distilled water. One electrode, the anode, is of the silver-silver chloride type while the other is a platinum cathode. The end-point may be selected in the vicinity of pH 7.0 with an ordinary pH meter or the acid remaining may be titrated with standard base. Greater precision is obtainable if it is possible to bring the final pH to that of the distilled and CO₂-free water used in preparing the standard solution. An error of even 0.1 pH unit in estimating the end-point in the vicinity of pH 7.0 becomes a percentage error of only 0.025% when as little as 10⁻⁴ equivalent of hydrogen ion is determined.

Experimental

The essential features of the coulometer used in this investigation include a beaker of approximately 200-ml. capacity, a platinum electrode with a surface area of 4 sq. cm. and a silver foil electrode having a total surface area of 175 sq. cm. The solutions were prepared by weighing out

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