Regeneration of Powdered Activated Carbon

Part I. Thermal Decomposition Kinetics

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Kinetics of thermal regeneration of powdered activated carbon containing adsorbed sucrose was studied from 298 to 1033 K. Most of the data were obtained (by measuring mass vs. time of spent carbon samples) in a thermal gravimetric apparatus. The regeneration process was interpreted in terms of a two-step process: 1) low-temperature decomposition to an adsorbed intermediate and gaseous products; and 2) a higher temperature decomposition of adsorbed intermediate into adsorbed residual carbon and gaseous products.

Surface area measurements indicated that most of the original carbon surface, but not all, could be recovered by thermal (with inert gas) regeneration up to 773 K. If permanent loss in surface is to be avoided during continued, cyclical use of the carbon, reaction with an oxidizing gas would be required after thermal regeneration.

SCOPE

The use of activated carbon for water purification has become a widely used process. Cost considerations require re-use of the carbon and this necessitates regeneration equipment. The most widely used regeneration procedure is a thermal one followed by high-temperature gasification of residual deposited carbon with an oxidizing gas such as steam or carbon dioxide.

The design of equipment for optimum regeneration is hindered by the lack of fundamental information, especially kinetics data. The overall process, as practiced commercially, normally consists of three steps: drying of the wet, spent carbon at about 378 K, heating to 1073 K, and finally gasification of residual carbon. The second step is thought to be a complicated process involving decomposition of the original adsorbates and desorption of low molecular weight products, leaving adsorbed carbon. A major fraction of the original mass of adsorbate is removed in this thermal decomposition. However, cycling operation of adsorption and regeneration equipment requires removal of the adsorbed carbon. Otherwise, buildup of this residual carbon would ultimately render the adsorbent inactive. The objective of the third step is to remove this residual carbon by a gas-solid, oxidation reaction.

The research reported here was undertaken to clarify the behavior of adsorbed material during the drying and thermal decomposition steps and to determine kinetics of regeneration for all three steps, using a model adsorbate. Sucrose was chosen as a representative of relatively easily removed and typical contaminants in water. For example, polysaccharides are commonly found in the effluent from secondary (activated sludge) treatment plants and would be in the feed to tertiary (activated carbon) processes. The studies were carried out primarily in a thermal-gravimetric-analysis (TGA) apparatus that could be operated either isothermally or with a pre-set rate of temperature increase.

The drying and decomposition steps are analyzed in Part I and data for the oxidation of residual carbon are reported in Part II.

CONCLUSIONS AND SIGNIFICANCE

Sucrose loaded on activated carbon (Pittsburgh Activated Carbon, Type BPL) was found to decompose into gaseous products and intermediate, adsorbed products during drying at temperatures of 393 or 398 K. Kinetic studies in a TGA apparatus at 407 to 428 K confirmed this low-temperature process and gave about 1.5×10^5 J/mol as the activation energy.

TGA data for decomposition of the adsorbed intermediates could be interpreted by a first-order process resulting in adsorbed, residual carbon and gaseous products. The process was essentially complete at 773 K and about 9% of the mass of the original, adsorbed sucrose remained as residual carbon. The activation energy for this slower decomposition of intermediate is about 3.8×10^4 J/mol.

By using such a two-stage decomposition model, it was possible to predict reasonably well the complete curve of amount desorbed vs. temperature from 303 to 1033 K. It was found that the residual carbon could not be removed solely by heating from 773 to 1033 K.

Surface area measurements by nitrogen adsorption (at liquid nitrogen temperature) indicated that 93% of the surface of the virgin carbon could be regained by thermal regeneration up to 773 K. Further heating to 1033 K did not result in additional surface. Chemical reaction to remove the residual carbon would be required to regenerate to the original area of the virgin carbon.

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TABLE 1. PROPERTIES OF ACTIVATED CARBON

Origin:	Bituminous Coal (Pittsburgh Activated Carbon, type BPL)
Particle Size:	48 to 65 mesh; $(R_p)_{Ave} = 1.25 \times 10^{-4}$m
Particle Density:	800 kg/m^3
Nitrogen Surface Area:	720×10^5 m^2/kg
Pore Volume:	0.8×10^{-3} m^3/kg
Macropore Volume:	0.35×10 m^{-3}/kg (pore radius > 5 nm)
Micropore Volume:	0.45×10 m^{-3}/kg (pore radius < 5 nm)
Most Probable Micropore Radius:	0.8 nm

Powdered activated carbon has a cost advantage over granular material for water purification. Thermal regeneration of the spent carbon is a commercial process for the granular material but, as yet, has not been extensively used for regenerating powdered carbon. For either type of material the design of commercial units suffers from the lack of rate data for the regeneration reactions. Many studies (Berg et al., 1970; Hutchins, 1973; Loven, 1973; and Reed, 1970) are available on the overall technology of the process, but there is little information on the kinetics of the decomposition, desorption and reaction (for example, with steam) steps. Available data for the decomposition and desorption processes are reviewed here while the reaction literature is discussed at the beginning of Part II.

Suzuki et al. (1978) measured the weight change when spent, granular carbon samples were heated in an inert atmosphere. The base carbon was loaded with different, single organic adsorbates, and the resultant weight change vs. temperature curves were divided into three groups according to the ease of decomposition. Single desorption and cracking steps were then used to represent the numerous and complex processes that occurred. With these models and the experimental data, quantitative rate equations were obtained. Hernandez and Harriott (1976), in kinetic studies of combined decomposition and reaction, followed directly the efficiency of regeneration by measuring the adsorption capacity of powdered carbon at various times during the regeneration process. Kawazoe and Osawa (1977, 1978) measured changes in micro-pore volume during cycles of adsorption and regeneration of carbon loaded with phenol or polyethyleneglycol. In this indirect way they were able to evaluate the effect of successive regenerations.

In the investigation reported in Part I we measured the weight change with time and temperature when two types of samples of powdered carbon, loaded with sucrose, were placed in an inert atmosphere in a TGA apparatus. The data were analyzed in terms of a kinetics model for the decomposition and desorption processes that occurred.

EXPERIMENTAL

The experimental work consisted of three parts: preparation of spent carbon samples and determination of adsorption isotherms, TGA experiments, and measurement of surface areas.

Sample Preparation and Equilibrium Measurements

Virgin activated carbon, whose properties are given in Table 1, was first screened to obtain a 48 to 65 mesh fraction. This fraction was boiled in water to remove fines and dried in an oven at 393 K. Sucrose crystals (analytical grade, Mallinckrodt Chemical Company) were dissolved in distilled water and the carbon particles added to the flasks containing the solution. The flasks were then shaken automatically for three days at 303 or 308 K in a constant-temperature bath. Samples of solution were analyzed at intervals with a Beckman Total Organic Carbon Analyzer to ensure that equilibrium was attained. This required less than 24 hours.

After equilibrium adsorption, the carbon particles were recovered by filtration and dried by one of two methods:

A. vacuum drying at 298 K for 3.5 to 5.5 hours;

B. drying in an oven in the presence of air at 393 to 403 K for three days.

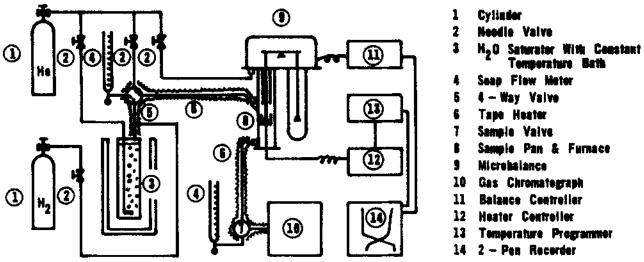

Figure 1 (a). TGA apparatus for kinetics experiments.

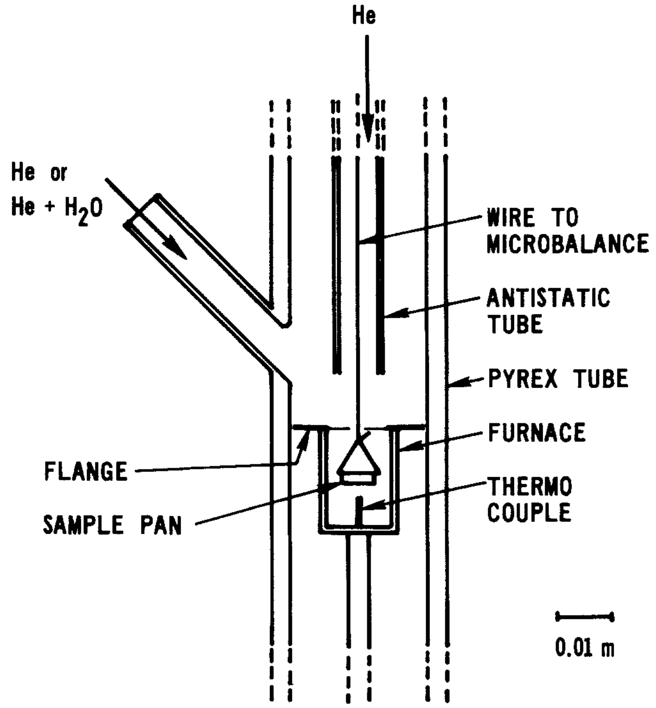

Figure 1 (b). Details of furnace and sample-pan assembly.

The amount adsorbed was determined either from the change in concentration of the sucrose solutions, or by weighing the carbon before adsorption and after drying. The isotherms so obtained covered a range of solution concentrations from 50 to 10,000 ppm and adsorbed concentrations up to about 0.25 kg/kg of virgin carbon. Carbon samples with the highest adsorbed concentrations were used for TGA studies in order to improve the accuracy of the data. The weight loss on drying by method B was significantly greater than by method A, indicating that some sucrose was decomposed and fractions desorbed in the temperature range 298 to 393 K.

TGA Experiments

Figure 1a shows a schematic diagram of the TGA apparatus (Perkin-Elmer Model TGS-2 with System 4 microprocessor controller) and accessories. The equipment provides for flowing a gas across a heated sample of carbon particles. There is instrumentation to control and record continuously the temperature and the mass of the sample. Preliminary experiments showed that the original arrangement of the apparatus in the region of the furnace, where the sample was located, needed to be modified to achieve good gas mixing. This is necessary for the reaction studies when steam-helium gas mixtures were used (Part II).

The modified arrangement is shown in Figure 1b and consisted primarily of a stainless steel doughnut shaped flange (outer diameter = 0.023 m, inner diameter = 0.01 m) resting on the furnace. This arrangement increased the resistance to flow sufficiently that the two feed gas streams (Figure 1b) were well mixed before reaching the pan holding the particles. The flow rate of helium in each entrance stream in Part I was 6.7×10^{-7} m^3/s (at 298 K and 1 atm). Also, it was found that the observed rate of weight change decreased slightly with the number of layers of particles placed in the pan, when steam was fed with helium (Part II). Presumably, this was due to incomplete mixing in the gaseous

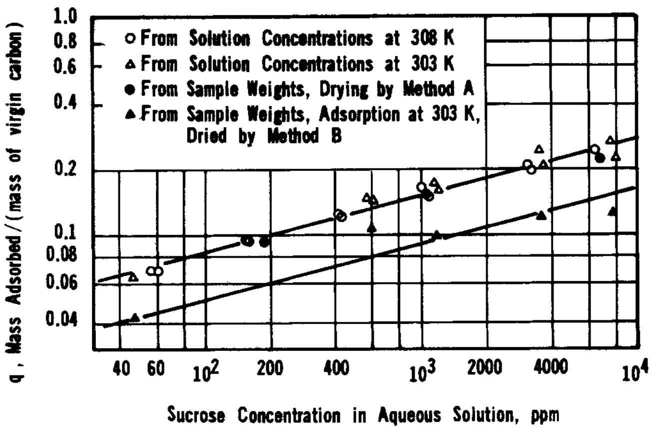

Figure 2. Adsorption equilibrium isotherms for samples A and B.

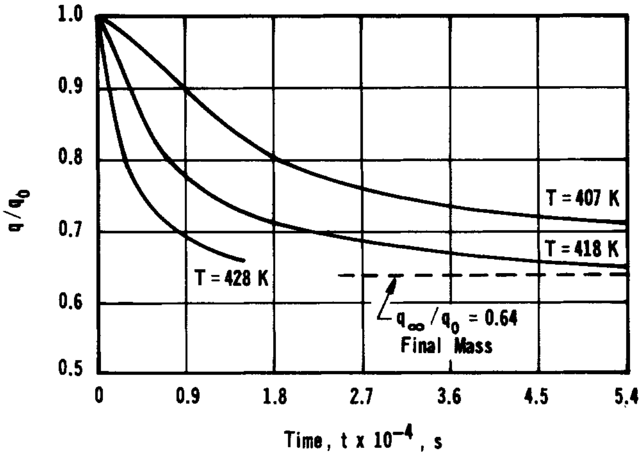

Figure 3. Low temperature kinetics data.

region around the particles when many layers were employed. Accordingly, most of the data were taken with but one layer.

A carbon sample of the order of 2×10^{-6}kg was placed in the platinum pan (diameter 5.8×10^{-3}m, depth 1.5×10^{-3}m) attached to the microbalance. The pan was positioned inside a small ceramic furnace (diameter 1×10^{-2}m, length 2.0×10^{-2}m) and the whole assembly located in the 2.48×10^{-2}m Pyrex tube.

Both samples A and B were studied in the TGA apparatus with a linear (with time) increase in temperature from 303 or 373 K to 1033 K. Three constant rates of temperature increase, 0.1, 0.2, and 0.3 K/s, were employed. The decomposition and desorption of sample A was also studied with a two-step temperature change: a rapid rise to 407, 418 or 428 K followed by a constant temperature period.

In decomposition-TGA experiments, it is important to maintain a very low oxygen concentration in the carrier gas. A high purity (99.995%) helium was used and care taken to eliminate leaks. The success of reducing oxygen was evaluated by measuring the weight change of virgin carbon when the temperature was increased, linearly (0.1K/s) to 1123 K, several times for the same sample. There was no observable change in weight ($< 10^{-9}$kg) below 1073 K after the second temperature increase. In the first temperature sequence there was a small loss in weight. This is discussed later.

Surface Area

Surface areas were measured by nitrogen adsorption in a Sorptometer for samples of virgin carbon, loaded samples A and B, and for samples A and B after treatment in the TGA apparatus with a linear temperature rise. The surface areas were calculated by the one-point method (based on the BET equation) of Kantro et al. (1967) using the amount adsorbed at a relative saturation pressure of $p/p^{sat} = 0.18$, at liquid nitrogen temperature.

ADSORPTION ISOTHERMS

Amounts adsorbed at 308 K, determined by measuring the concentration of sugar solutions, are shown by the upper curve in Figure 2. These results were compared with results obtained by weighing the carbon samples before and after drying by method A. The two sets of data agree, indicating that there is no decomposition or desorption where samples are dried in vacuum (method A). An isotherm for adsorption at 303 K is also shown in Figure 2. The former data agree well with the lower temperature results indicating that there is little difference in amount adsorbed between 303 and 308 K.

Results for samples dried by method B are shown by the lower curve in Figure 2. The amount adsorbed is now 64% (±15%) of that for samples dried by method A. This difference indicates that drying in air at 393-403 K decomposes and desorbs some of the sucrose adsorbed on the carbon. Since sucrose itself is non-volatile, the material desorbed must be volatile products of decomposition. The adsorbed structures retained on the carbon after the higher temperature drying of method B must be different from the original, adsorbed sucrose.

In commercial regeneration processes, the wet, spent carbon is first dried at atmospheric pressure in air at temperatures of about 373-378 K. Then the material is heated. Hence, the decomposition and desorption step using samples dried by method B represent more closely commercial drying processes.

LOW TEMPERATURE KINETICS: STUDIES WITH "A" SAMPLES

The rate of weight decrease for samples dried in vacuum at 298 K are illustrated in Figure 3 for three temperature levels. These runs were carried out at temperatures a little higher than the temperature used in method B. The data were obtained to confirm the low-temperature decomposition and desorption processes deduced from the isotherm results, and also to establish the kinetics of these processes. The amount of adsorbed material is expressed as q/q_o, where q is the ratio of the mass adsorbed per unit mass of virgin carbon and q_o is the initial value of q. For samples prepared by method A, q_o is the mass of sucrose adsorbed per unit mass of virgin carbon. The decomposition occurs more rapidly at the higher temperatures, and an equilibrium value of q/q_o in the region of 0.64 appears reasonable, in agreement with the results obtained in the isotherm studies (Figure 2).

The data in Figure 3 suggest that adsorbed sucrose decomposes in the range 407 to 428 K to intermediate adsorbed products. Further, some decomposition fragments are desorbed into the gas phase. The number and structure of the adsorbed products are not known. If we group the products into non-volatile and volatile fragments, the processes may be represented in a general way by the two steps:

$$\bar{S} \xrightarrow{k_1} g\bar{G} + i\bar{I} \tag{1}$$

$$\bar{G} \xrightarrow{k_g} G(g) \tag{2}$$

where adsorbed sucrose $\bar{S}$, first decomposes into a nonvolatile, adsorbed fragment $\bar{I}$, and a volatile fragment $\bar{G}$ which is subsequently desorbed into the gas stream. Suppose that the decomposition step is first order in moles adsorbed $\bar{N}_s$ per unit mass of virgin carbon. Then:

$$\frac{d\bar{N}_s}{dt} = -k_1\bar{N}_s \tag{3}$$

$$\frac{d\bar{N}_I}{dt} = ik_1\bar{N}_s \tag{4}$$

with initial condition

$$\bar{N}_s = \bar{N}_o,\ \bar{N}_I = 0 \text{ at } t = 0 \tag{5}$$

If, further, the desorption process is rapid with respect to decomposition ($k_g >> k_1$), the total amount q adsorbed at any time is:

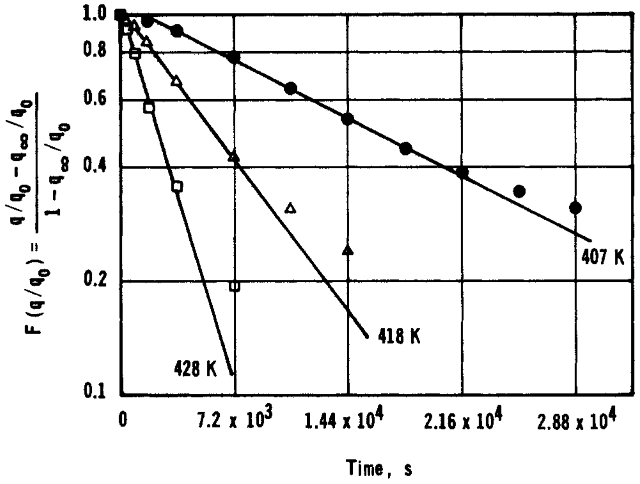

Figure 4. Low temperature kinetics data—fractional retention plot.

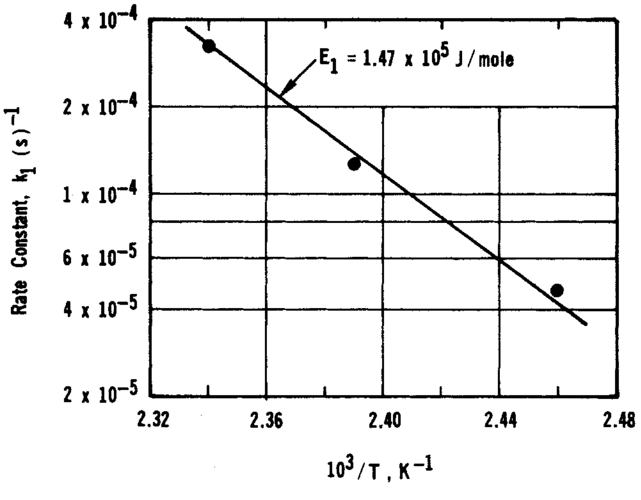

Figure 5. Temperature dependency of rate constant k_1 for low temperature decomposition of adsorbed sucrose.

$$q = M_s\bar{N}_s + M_I\bar{N}_I \tag{6}$$

Eqs. 3 and 4 can be integrated using Eqs. 6 and 5 to give:

$$F(q/q_o) = \frac{q/q_o - q_\infty/q_o}{1 - q_\infty/q_o} = \exp(-k_1 t) \tag{7}$$

where

$$\begin{aligned} q_o &= M_s\bar{N}_o \\ q_\infty &= iM_I\bar{N}_o \end{aligned} \tag{8}$$

Note that q_∞ is the mass adsorbed at $t = \infty$ for this low-temperature process. The ratio $q_\infty/q_o = iM_I/M_s$ is the final yield of intermediate; $1 - q_\infty/q_o$ represents the yield of gaseous products G.

For Eq. 7 to fit the data in Figure 3, a plot on semilog paper of $F(q/q_o)$ vs. t should yield a straight line. If q_∞/q_o is taken as 0.64, straight lines are obtained for each temperature as shown in Figure 4. The plot is for low time values since at large t the difference, $q/q_o - q_\infty/q_o$, is not accurate. The k_1 values calculated from the slopes of those lines are shown in Figure 5 on an Arrhenius plot. The line through the points in Figure 5 yields an activation energy of 1.47×10^5 J/mol according to the equation:

$$k_1 = (k_1)_o \exp - \left(\frac{E_1}{RT}\right)$$
$$= 1.7 \times 10^{14} \exp(-1.47 \times 10^5/RT) \tag{9}$$

The extent of decomposition of adsorbed sucrose in the B drying method can be roughly estimated from Eq. 9. Using T = 398 K to obtain k_1, and then calculating $F(q/q_o)$ from Eq. 7, yields the fraction of the sucrose remaining on the carbon. For t corresponding to three days, this fraction is 0.08, indicating that 92% of the adsorbed sucrose has decomposed during the B drying method. This approximate result suggests that essentially all of adsorbed material on the B samples are nonvolatile decomposition fragments ($\bar{I}$) of the original sucrose.

HIGH-TEMPERATURE KINETICS: STUDIES WITH "A" AND "B" SAMPLES

Typical mass vs. temperature curves for virgin carbon, sample B, and sample A are shown in Figure 6 for a rate of temperature rise of 0.1 K/s. The results are plotted as total mass per unit mass of initial virgin carbon, or $q + 1$. Approximately, the difference in initial values between samples A and B, $q_o - q_{oh} = 0.225 - 0.1275 = 0.0975$ kg/kg, represents the change in mass during drying process B. According to the postulates of the previous section, this can be interpreted approximately as the change in mass corresponding to the low-temperature decomposition of sucrose and desorption of volatile products. Similarly, the q_{oh} value of 0.1275 for sample B represents the mass (per unit of initial virgin carbon) of nonvolatile product $\bar{I}$ of the low-temperature decomposition process. The value for q_{oh} is slightly smaller than q_∞, probably due to experimental uncertainties.

The data in Figure 6 indicate that initial decomposition starts at about 420 K, which is below the melting point of sucrose (457 K). Qualitatively, we interpret the rapid decrease in mass, in the range 420-500 K for sample A, to the low-temperature decomposition-desorption process. The subsequent mass decrease for both samples A and B is due mainly to decomposition and desorption of the adsorbed intermediate ($\bar{I}$). The curves for samples A and B become almost coincident to each other above 773 K, and parallel to the curve for virgin carbon above 773 K. This behavior suggests that the ultimate decomposition product for adsorbed sucrose is carbon, and that the formation of this deposited carbon is complete at about 773 K. The small decrease

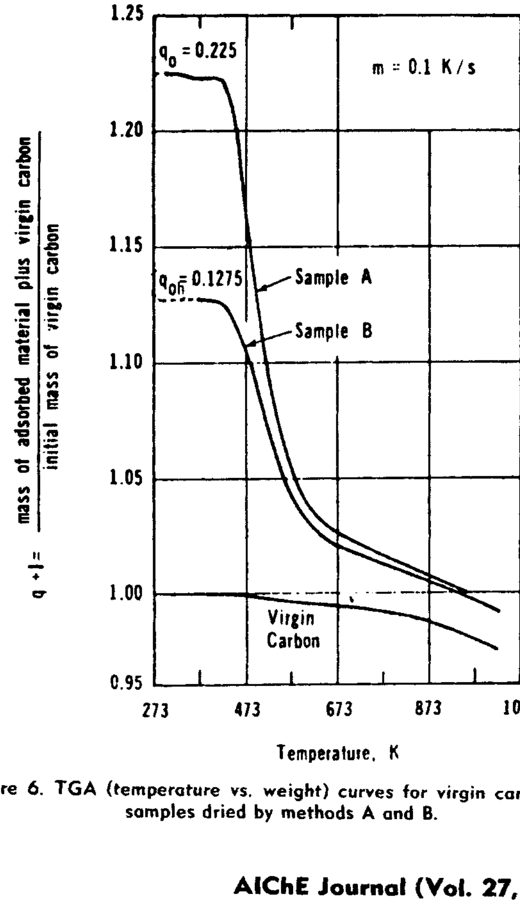

Figure 6. TGA (temperature vs. weight) curves for virgin carbon, and samples dried by methods A and B.

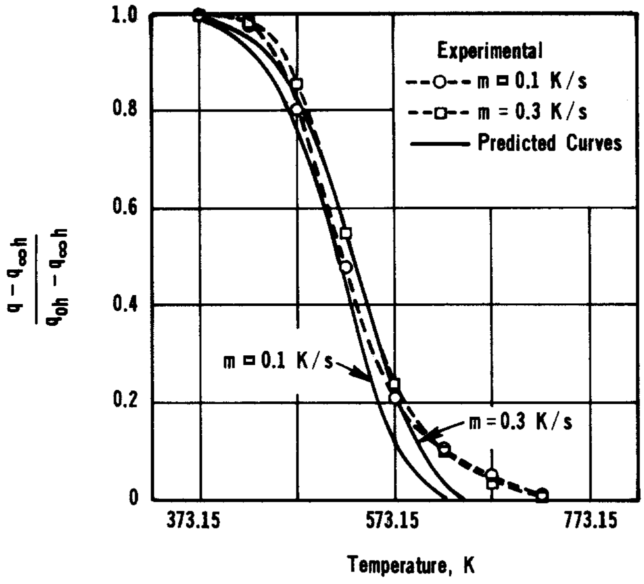

Figure 7. Experimental and predicted TGA curves for samples dried by method B.

(~2%) in mass of virgin carbon at high temperatures (up to 1073 K) is presumably due to vaporization or desorption of residual material in the carbon. This decrease would occur for any of the samples and explains why the curves are parallel at high temperatures. The near coincidence of the curves for samples A and B at high temperatures shows that the ultimate yield of activated carbon in a regeneration process is approximately the same, regardless of the drying method.

Suzuki et al. (1978) noted that plots of q/q_o vs. T were helpful to characterize TGA curves for different adsorbed species. Data for our sucrose samples (dried by method B) are illustrated in Figure 7 on a similar type of plot. It is noted that the difference between the curves for different rates of temperature change were small over the range 0.1 to 0.3 K/s. The curves in Figure 7 have been corrected for the change in mass of virgin carbon shown in Figure 6. Up to 773 K this correction was no more than 1%. The data illustrated in Figure 7 for B samples can be analyzed for the kinetics of the decomposition of intermediate product. The useful range of data is up to 773 K. Since some adsorbed carbon still exists at this temperature ($q > 0$ in Figure 6), it is necessary to plot the data as $(q - q_{\infty h}/(q_{oh} - q_{\infty h})$ rather than q/q_{oh}. Here $q_{\infty h}$ is the value of q at $T = 773$ K, and is different from q_∞ in Eq. 7.

Suzuki et al. (1978) suggested a thermal cracking model for the decomposition of adsorbed organics. We propose to use for the decomposition of intermediate $\bar{I}$ a modification of that idea. It is supposed that $\bar{I}$ is decomposed into easily desorbed light fragments, $\bar{G}'$, and adsorbed carbon $\bar{C}$. The two-step process may be written:

$$i\bar{I} \xrightarrow{k_2} g'\bar{G}' + c\bar{C} \tag{10}$$

$$\bar{G}' \xrightarrow{k_g'} G'(g) \tag{11}$$

where $k_g' >> k_2$.

TABLE 2. KINETIC PARAMETERS FOR HIGH-TEMPERATURE DECOMPOSITION (BASED ON DATA FOR B SAMPLES)

Heating Rate, K/s	$q_{\infty h}/q_{oh}$	$T_{\frac{1}{2}}$,K	1/s,K	$E_2 \times 10^{-4}$ J/mol	$(k_2)_o$,s^{-1}
0.1	0.170	521	139	3.90	11.7
0.2	0.104	524	143	3.79	16.8
0.3	0.124	530	144	3.84	25.0
0.1 (checkrun)	0.145	520	132	4.07	18.3

If the decomposition step is first order, the rates of change for moles of adsorbed I and C are:

$$\frac{d\bar{N}_I}{dt} = - k_2\bar{N}_I \tag{12}$$

$$\frac{d\bar{N}_C}{dt} = \frac{c}{i} k_2\bar{N}_I \tag{13}$$

It is supposed that k_2 follows the Arrhenius equation:

$$k_2 = (k_2)_o \exp{(- E_2/RT)} \tag{14}$$

The linear rate of temperature increase may be expressed as:

$$m = dT/dt \tag{15}$$

where m is a constant. The initial condition is:

$$\left.\begin{array}{l} \bar{N}_I = (\bar{N}_I)_o \\ \bar{N}_C = 0 \end{array}\right\} \text{at } t = 0 \tag{16}$$

Suzuki et al. (1978) has integrated Eq. 12 by using Eq. 15 to express $\bar{N}_I$ as a function of T. The result is:

$$\frac{\bar{N}_I}{(\bar{N}_I)_o} = \exp\left[\frac{(k_2)_o}{m}\frac{E_2}{R}\left\{\phi_2 - \frac{RT}{E_2}\exp\left(-\frac{E_2}{RT}\right)\right\}\right] \tag{17}$$

where ϕ_2 is the following function of E_2/RT:

$$\phi_2 = \int_{x_2}^{\infty}\left[\exp(-x_2)/x_2\right]dx_2 \tag{18}$$

and $x_2 = E_2/RT$. This result can be written in terms of $(q - q_{\infty h}/(q_{oh} - q_{\infty h})$ by noting that:

$$q = M_I\,\bar{N}_I + M_C\,\bar{N}_C \tag{19}$$

The relationship between $\bar{N}_I$ and $\bar{N}_C$ is given by eliminating $\bar{N}_I$ from Eqs. 12 and 13 and integrating the resultant differential equation. We obtain:

$$\bar{N}_C = - \frac{c}{i}\left[\bar{N}_I - (\bar{N}_I)_o\right] \tag{20}$$

Substituting Eq. 20 in Eq. 19 relates q *to* $\bar{N}_I$. This leads to:

$$\frac{q - q_{\infty h}}{q_{oh} - q_{\infty h}} = \frac{\bar{N}_I}{(\bar{N}_I)_o} \tag{21}$$

Eqs. 17 and 21 provide a relationship between $(q - q_{\infty h})/(q_{oh} - q_{\infty h})$, and temperature in terms of the two kinetic parameters E_2 and $(k_2)_o$. Experimental data for this relationship, as illustrated in Figure 7, (dotted curves), can then be used with Eqs. 17 and 21 to evaluate $(k_2)_o$ and E_2. An approximate graphical method of solution (Suzuki et al., 1978) is to use the temperature $T_{1/2}$ and slope S of the experimental curve at $q/q_o = 0.5$. A more accurate procedure would be an optimization technique to minimize the errors between the predicted and experimental curves illustrated in Figure 7. The first procedure should yield values of $(k_2)_o$ and E_2 which give a predicted curve in good agreement with experimental results near $(q - q_{\infty h})/(q_{oh} - q_{\infty h})$ of 0.5, while the second method could give better agreement over the whole range of fractional weight loss. The simpler graphical procedure is used here. From Eq. 17 and its derivative with respect to T, the following relations can be derived:

$$\frac{-(1/S)}{T_{\frac{1}{2}}} = \frac{2}{\ln(2)}\left[1 - \frac{E_2}{RT_{\frac{1}{2}}}\,\phi_{T_{\frac{1}{2}}}\exp\frac{E_2}{RT_{\frac{1}{2}}}\right] \tag{22}$$

$$(k_2)_o = \frac{2m}{-(1/S)\exp(-E_2/RT_{\frac{1}{2}})} \tag{23}$$

The integration to obtain $\phi_{T_{\frac{1}{2}}}$ can be carried out numerically to determine a unique relationship between $\phi_{T_{\frac{1}{2}}}$ and $E_2/RT_{\frac{1}{2}}$.

The values of E_2 and $(k_2)_o$ obtained from data for samples B with the three different rates of temperature rise are given in

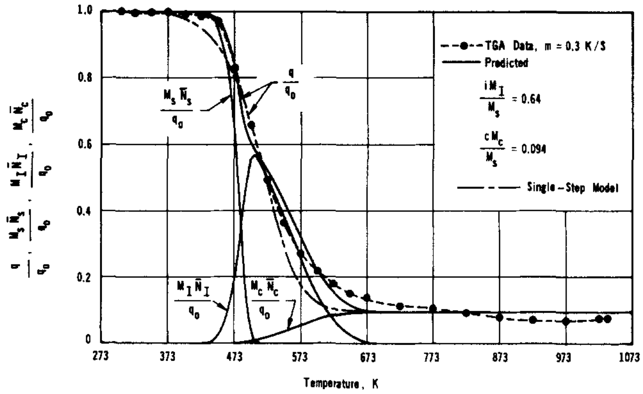

Figure 8. Experimental and predicted curves for samples dried by method A.

Table 2. A check run was made with three layers of particles in the pan and with the flange (Figure 1b) removed. The agreement of this check run with the results for the other three runs indicates that with our operating conditions mass transfer resistance between gas and particles was not important. For all runs in this study of decomposition, only helium was present in the two feed streams (Figure 1b). When one stream contained steam (Part II reaction experiments) the flange was found to be necessary in order to achieve a well-mixed feed. The agreement of the activation energy values in Table 2 for the three heating rates is good. The values of $(k_2)_0$ scatter more, but this is expected for this sensitive parameter. Predicted curves of fractional weight loss versus temperature were computed using Eqs. 17 and 21 and the $(k_2)_0$ and E_2 values in Table 2. These results, shown as solid curves in Figure 7, agree with the experimental curves in the central region. As expected, agreement is not as good at extreme values of the weight loss.

PREDICTED REGENERATION CURVES

In the prior sections, the kinetic parameters for low and high temperature regeneration have been evaluated separately in terms of a simple, decomposition-desorption model. Actually, the decomposition of adsorbed sucrose is a complex phenomena probably consisting of several competitive and consecutive reaction steps. Our purpose is to be able to predict, with as simple a theory as possible, regeneration curves over the whole temperature range, 273-773 K, as exemplified by the weight-loss curves for samples dried by method A. Predicted and experimental are illustrated in Figure 8 for $m = 0.3$ K/s, plotted as q/q_o versus temperature. Similar curves are obtained for other heating rates.

To determine predicted results we can employ Eq. 3 for the decomposition rate of adsorbed sucrose, the sum of Eqs. 4 and 12 for the net production rate of $\bar{I}$, and Eq. 13 for the production rate of adsorbed carbon. Using Eq. 15 to eliminate time, the resultant expressions for $\bar{N}_s$, $\bar{N}_I$ and $\bar{N}_C$ are:

$$m\frac{d\bar{N}_s}{dT} = -k_1\bar{N}_s \tag{24}$$

$$m\frac{d\bar{N}_I}{dT} = i\,k_1\bar{N}_s - k_2\bar{N}_I \tag{25}$$

$$m\frac{d\bar{N}_C}{dT} = -\frac{c}{i}k_2\bar{N}_I \tag{26}$$

The initial condition is:

$$\bar{N}_s = \bar{N}_o,\ \bar{N}_I = 0,\ \bar{N}_C = 0 \text{ at } t = 0 \tag{27}$$

The quantity q is equal to the retained mass of adsorbed sucrose, intermediate $\bar{I}$ and carbon $\bar{C}$:

$$q = M_s\bar{N}_s + M_I\bar{N}_I + M_C\bar{N}_C \tag{28}$$

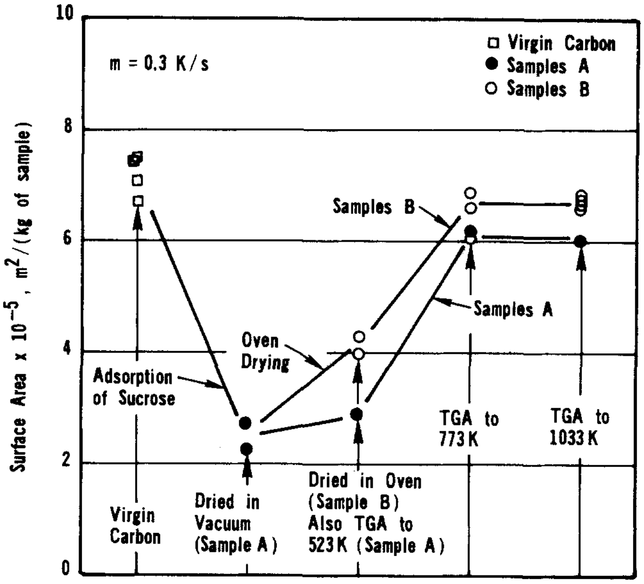

Figure 9. Surface area change during regeneration.

Eqs. 24-28 are solved numerically, starting at $t = 0$. In addition to the kinetic constants, it is necessary to know iM_I/M_s, which is the yield of intermediate product I. This was found to be 0.64 from the low-temperature studies. The final yield of adsorbed carbon cM_C/M_s is also necessary. It is known from the final (at $T = 773$ K) weight of the regenerated sample. The experimental data for all m values correspond to an average q/q_o of about 0.1, although it is somewhat different for different rates of temperature increase. The required values of $(k_2)_0$ and E_2 are given in Table 2 and $(k_1)_0$ and E_1 are stated in Eq. 9.

The predicted results are the upper solid curves in Figure 8. The agreement of experimental and predicted curves is reasonably good, particularly since independent, experimental kinetics data were employed. The deviation at high temperatures is because an average value (0.094) of the final yield for all three m values is used instead of the yield for $m = 0.3$ K/s. Interpretation of the whole experimental curve in Figure 8 as

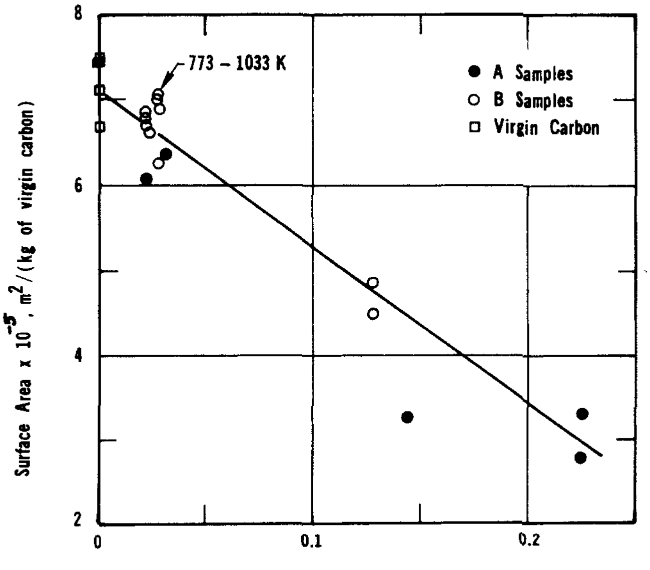

Figure 10. Surface area vs. mass adsorbed for thermal decomposition process.

single-step thermal cracking reaction gives $E = 4.32 \times 10^4$ J/mol and $k_o = 118\ s^{-1}$. These values are different from the values in Table 2 for the two-step model. Further, the theoretical curve corresponding to single-step model, which is also shown in Figure 8, deviates significantly from the experimental curve except at the mid point of reaction. It appears that a two-stage process is a reasonable way to describe the regeneration of activated carbon containing adsorbed sucrose. The lower solid curves in Figure 8 show the amount of sucrose, intermediate, and carbon remaining on the virgin carbon at any time. These curves demonstrate that sucrose decomposes rapidly to intermediate, while the decomposition of intermediate to carbon is a slower process.

Intraparticle diffusion is not likely to affect the overall kinetics of the regeneration. This conclusion follows from comparison of diffusion and reaction times. For our particles the diffusion time, R_p^2/D_e, can be estimated as follows. Molecular diffusivities of gaseous products such as CO, CO_2, CH_4 at an average temperature of 500 K are of the order of 2×10^{-4} m²/s. The effective D_e would be about one order of magnitude less, based upon a porosity of about 0.5 and tortuosity factor of 5. Then, with an average particle radius of 1.25×10^{-4}m (48 to 65 mesh size range), the diffusion time is about 8×10^{-4}s. At the same temperature, $1/k_1$ and $1/k_2$ are 2.6 and 54 s, both much larger than the diffusion time.

SURFACE AREA CHANGES DURING REGENERATION

Data for the change in mass adsorbed vs. time and temperature are helpful in formulating kinetics models for regeneration. However, surface area (determined by nitrogen adsorption, one-point method) is probably a more direct measurement of the restoration of adsorption capacity for adsorbates. Surface areas were obtained at various stages in the complete regeneration process (decomposition and reaction) and are presented in Part II. Here, we discuss the changes in area during the drying and decomposition steps, as shown in Figures 9 and 10.

Figure 9 displays the history of surface area per unit total mass of particles, starting with four reproducibility measurements for virgin carbon. The area is reduced by more than 60% in the preparation of A samples (vacuum drying of adsorbed sucrose), as noted by the two solid-circle points. Samples B, dried in an oven at 398 K, had areas but 40% less than the area of virgin carbon. Heating the vacuum-dried samples to 523 K in the TGA apparatus at a rapid rate increased the surface area, but to a value still less than that of the oven-dried sample. More surface appears to be regained by heating at a low temperature for a long time than rapid heating to a higher temperature. When the samples are heated in the TGA apparatus to 773 K most of the original surface of the virgin carbon is regained, 93% for B samples and 85% for A samples. Above 773 K there is no increase in area. This is consistent with the prior conclusion that nearly all of the intermediate had been converted to adsorbed carbon when the temperature reaches 773 K.

Figure 10 shows the same data as in Figure 9, but plotted as surface area vs. amount adsorbed, both per unit mass of virgin carbon. The relationship is approximately linear. However, it is noted that thermal regeneration alone is not sufficient to reduce q to zero, even at 1073 K. This is also apparent from the finite difference that exists between curves for virgin carbon and samples A or B in Figure 6. Thus, further regeneration, for example, by reaction with steam, is necessary in commercial processes if buildup of deposited carbon, by continued cycles of adsorption and regeneration, is to be prevented. Such regeneration by reaction is examined in Part II.

ACKNOWLEDGMENT

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NOTATION

c = stoichiometric coefficient for carbon
D_e = effective intraparticle diffusivity, m²/s
E_1 = activation energy of decomposition of sucrose to intermediate, J/mol
E_2 = activation energy of decomposition of intermediate to adsorbed carbon, J/mol
G, G' = gaseous products of decomposition reactions
g, g' = stoichiometric coefficients for gaseous products
$\bar{I}$ = intermediate product retained on the carbon
i = stoichiometric coefficient for intermediate product
k_1 = first-order rate constant for decomposition of sucrose to intermediate, L/s
$(k_1)_o$ = pre-exponential factor of Arrhenius equation for k_1, L/s
k_2 = first-order rate constant for decomposition of intermediate to adsorbed carbon, L/s
$(k_2)_o$ = pre-exponential factor of Arrhenius equation for k_2, L/s
k_g, k_g' = desorption rate constant for gaseous products, L/s
$\bar{N}$ = moles adsorbed, mol/(kg of virgin carbon)
M = average molecular weight, kg/mol
m = constant heating rate, K/s
q = mass adsorbed per unit mass of initial virgin carbon
q_∞ = mass adsorbed at infinite time (per unit mass of initial virgin carbon) for low-temperature decomposition; $q_{\infty h}$ = mass adsorbed at 773 K for high-temperature decomposition
q_o = mass adsorbed initially (time = 0) per unit mass of initial virgin carbon; q_{oh} = mass adsorbed at beginning of high-temperature decomposition
R = gas constant
R_b = average radius of carbon particle, m
$\bar{S}$ = adsorbed sucrose
S = slope of curve in Figure 7 at $(q - q_{\infty h})/(q_{oh} - q_{\infty h}) = 0.5$
T = temperature, K
$T_{\frac{1}{2}}$ = value of T at $(q - q_{\infty h})/(q_{oh} - q_{\infty h}) = 0.5$
t = time, s
x = E/RT
ϕ = exponential integral defined by Eq. 18

Subscripts

s = sucrose
I = intermediate product
C = adsorbed residual carbon
o = initial value
— = overbar designates an adsorbed quantity
1 = low-temperature decomposition
2 = high-temperature decomposition

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Part II: Steam-Carbon Reaction Kinetics

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The kinetics of the reaction between steam and spent activated carbon (from sucrose deposition) was studied at 1003 to 1123 K and 1 atm pressure. At these conditions some virgin carbon, upon which the sucrose was originally adsorbed, was also gasified. Rates of oxidation were essentially the same for spent and virgin activated carbon.

The kinetics data fit a Langmuir-Hinshelwood equation, originally proposed for gasification of other types of carbon, with an activation energy of 2.3×10^5 J/mol.

Surface area and pore volume measurements indicated that the adsorption capacity of the original carbon could be completely restored by thermal regeneration followed by reaction with steam. However, some activated carbon is lost implying that there would be an optimum extent of steam gasification in a cyclical adsorption-regeneration process.

SCOPE

Kinetics studies are reported in Part II for the reaction between steam and carbon remaining after spent activated carbon has been thermally regenerated. The samples used were those dried by method B (drying at 393-403 K for three days, see Part I) and then thermally regenerated with helium in the TGA equipment at a rate of temperature increase of 0.3 K/s. When the temperature obtained a desired level (between 1003 and 1123 K) the rate of the steam carbon reaction was evaluated by maintaining the samples in the TGA apparatus and measuring their weight change at constant temperature. During this reaction period a gas mixture of constant composition, consisting of helium, steam and hydrogen (for some runs) was passed over the sample. Rates of reaction were determined for steam concentrations from 0.04 to 6.0 mol% and hydrogen concentrations from 0 to 0.5 mol%. As indicated in Figure 6 of Part I, there was essentially no thermal decomposition between 773 and 1123 K. Hence, the runs made for the steam-carbon reaction over this temperature range were carried out with carbon samples of the same characteristics, even though they had been subjected to different temperatures of thermal decomposition.

The kinetics of the noncatalytic, steam-carbon reaction have been studied with many types of carbon (activated carbon from coconut shell charcoal—Gadsby et al., 1946 and Long and Sykes, 1948, 1950; coke from coal—Hunt et al., 1953; graphite from electrodes—Binford and Eyring, 1956). Interest in coal gasification has been the impetus for numerous investigations of both the H_2O-C and CO_2-C reactions; for example, Gadsby et al. (1948), Lewis et al. (1949), Goring et al. (1952), Johnstone et al. (1952), Pilcher et al. (1955), and Ergun (1956). The need to retard gas-carbon reactions in atomic reactors has stimulated numerous other kinetics works including those of Overholser and Blakely (1965), Blakely and Overholser (1965), Malinauskas (1970), and Strange and Walker (1976). Finally, the recent interest in regeneration of activated carbon used for water purification is leading to kinetics studies of the reaction between steam and thermally regenerated activated carbon (for example, Klei et al., 1975). As noted in Part I, thermal regeneration to 773 K reduces the adsorbed organic compounds to residual carbon. Hence, in the subsequent reaction with steam both residual carbon and base carbon can react. It is of interest to compare the rates of reaction for these two kinds of carbon.

Rate data for the reaction of carbon, from many sources, with steam follows the equation

$$R = \frac{k_1 p_{H_2O}}{1 + k_2 p_{H_2} + k_3 p_{H_2O}} \tag{1}$$

which has been proposed by Walker et al. (1959) and by Ergun (1962, 1965). However, there are large variations in the magnitude of the rates, the activation energy for k_1 and the effect of temperature on k_2 and k_3. Also, there is disagreement on the mechanism of the elementary processes leading to Eq. 1. It is generally accepted that carbon monoxide is produced at the carbon surface, but part of this CO may be converted to carbon dioxide by the water gas-shift reaction.

CONCLUSIONS AND SIGNIFICANCE

Our rate data for the regeneration of *activated* carbon with steam could be correlated with a Langmuir-Hinshelwood equation previously proposed for the steam-carbon reaction. The *measured* rate was the same for virgin activated carbon (coal-based BPL carbon from Calgon Corporation) and for thermally regenerated particles containing residual carbon from sucrose adsorption. Over the mass range of two to three times the amount of residual carbon, the mass decreases linearly with time.

The rate changed from first order to zero order with respect to steam as the water vapor concentration was increased from 0.04 to 6.0%. Hydrogen retarded the rate. Both effects are predicted by the Langmuir-Hinshelwood equation. The temperature dependency of the parameters in this rate equation indicated an activation energy of 2.3×10^5 J/mol.

By following thermal regeneration with reaction with steam, surface areas greater than that of the original virgin carbon

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K. Chihara and I. Matsui are on leave from the University of Tokyo.

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