Influence of Particle Boundary Area on the Dynamic Adsorption from Air-Vapor Mixtures

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Introduction

Gas flow through granular charcoals is visualized as following a tortuous path between particles and the stream lines frequently converged and diverged as the gas passed through the void space in residence times of 0.3 to 0.35 second. The number of gas collisions with the surface is extremely large ($\sim 10^{10}$ /sec) and the average time of adsorption on individual particles depends on the extent of the boundary area that is exposed to the gas flow. A quantity S_v has been defined as the aerodynamic boundary area of a unit volume of particles and a method for calculating this quantity indicated. 1 In the present work a charcoal was separated into four sieve fractions and each of these further separated into six particle-density fractions. A correlation with the particle boundary surface, Sy, will be discussed.

Bulk Densities of Particle Size and Particle Density Fractions

The charcoal was sieved into four fractions 14x16, 16x18, 18x20 and 20x30. The average particle size of each fraction was estimated from the arithmetic mean of the corresponding sieve openings (Table 1). Each of these fractions was then separated into six parts by passage over a "Whippet" Specific Gravity Table (Sutton, Steele and Steele, Inc., Dallas, TX). The bulk densities of the 24 fractions (determined by a 1-meter free fall into a graduated cylinder) are given in Table 1.

Sieve fractions Average opening (mm)	14x16 1.30	16x18 1.095	18x20 0.92	20x30 0.715
Density of Whole. Fraction	.620	.612	. 602	. 604
Fraction 1, low sp. gr.	.463	. 500	.460	. 507
Fraction 2	. 500	. 535	.539	. 560
Fraction 3	.534	. 577	.579	. 590
Fraction 4	. 580	.620	. 589	. 599
Fraction 5	.648	.684	.620	.619
Fraction 6, high sp. gr.	.723	.723	.676	.666

The bulk densities of the 24 fractions ranged from 0.46 to 0.72 g/cm³. The number of particles, n, per cm³ in each sieve fraction was determined by counting. Although the particle boundary area of each 20x30 particle is smaller than that of the 14x16 particle, S_v is greater for the 20x30 fraction because of the larger number of particles per unit volume.

Sieve Fractions	n
14x16	386/cm ³
16x18	550/cm ³
18x20	910/cm ³
20x30	$1560/cm^3$

Dependence of Pressure Drop on Flow Rate

The pressure-drop determinations were made in a glass tube 2.21 cm i.d. and 75 cm long. A differential water manometer was used for these measurements and a perforated stainless steel disc supported the sample. In the empty tube there was no measurable pressure gradient across the sample support. The gas flows were measured with a dry gas meter (DTM-115 Singer, American Meter Company, 10 L per revolution). Dry nitrogen or argon was used directly from the supply tanks. The sample was introduced through a long-stem funnel which extended to the sample support. The funnel was slowly raised and the sample was thus introduced with minimum packing. The height of the charcoal above the support was determined with a cathetometer and the bulk density was calculated from the weight of the carbon divided by its measured volume. The pressures drops were measured at ten different flow rates. The column was then gently vibrated until a smaller height was realized and the pressure drop again measured at different flow rates. Typical results (Figure 1) are for the sieve fraction 18x20 and show the pressure drop for ten



Fig. 1. Pressure Drop with Nitrogen Flows through Packings of the 18x20 Fraction at Five Different Bulk Densities

different nitrogen flows for each of five packing densities. The least-square slopes and intercepts were calculated and the values of $S_{\rm V}$ were then determined.

Calculation of Particle Boundary Area

 S_v was determined from the above pressure-drop measurements by the method suggested in 1938¹ which followed the earlier Kozeny assumption²that a column may be modeled by a group of parallel and equal size cylindrical channels. The total internal surface area is identified with the total particle surface area and the free internal volume is identified with the void volume. Ergun and Orning³ found that the ratio of pressure gradient to the superficial velocity of the gas was a linear function of the mass flow rate;

$$\frac{\Delta P}{L U_{m}} = a + b G. \qquad (1)$$

where a =
$$2\alpha\mu S_v^2 (1-\epsilon)^2/\epsilon^3$$
 (2)

and
$$b = (\beta/8) S_v (1-\epsilon)/\epsilon^3$$
 (3)

 ΔP = pressure drop, dynes/cm²

- L = height of bed, cm
- U_m = av. linear gas velocity using the cross section of empty tube, cm/sec
- G = mass flow rate, g/(sec)(cm²) (i.e. mass flow per unit cross section)
- µ = viscosity, poise
- $S_v = specific surface of particle, cm^2/cm^3 of particles$
- ε = fractional voids between particles
- α, β = constants

The mass flow rate (G) is defined as the mass of fluid per second per unit cross section of the tube and to convert the volume flow rate (cm^3/sec) (Figure 1) to mass flow rate at the experimental conditions of 24°C and 1 atmosphere, it is necessary to multiply the volume flow by .000300 for nitrogen and .000427 for argon.

The calculated values of S_v (Table 2) were of reasonable magnitude. Using the average of the sieve openings, which define each sieve fraction, the surface of the circumscribed sphere was calculated. These areas agreed rather well with S_v determined from the argon measurements.

Table 2. Comparison of Boundary Areas Determined from Sieve Analysis and from Pressure-Drop Flow Measurements

Sieve Fraction	Circumscribed Sphere (sieve analysis)	Boundary area, S N2 Argon		S _v (av.) Ratio
14x16	19.6	25.5	17.8	1.4
16x18	20.2	26.6	18.6	1.4
18x20	24.2	29.4	21.9	1.3
20x20	25.1	43.9	26.8	1.6

However, the S_v values determined from nitrogen measurements were larger, the ratio ranging from 1.3 to 1.6 times those for argon. Apparently, the nitrogen molecules in a dynamic gas flow system, interact with more of the boundary surface than do the argon atoms. The polarizability of nitrogen (1.76×10^{-24}) is somewhat greater than argon (1.63×10^{-24}) which is in the correct ratio, and the kinetic diameters are in the same order - N₂, 3.15 Å and Å, 2.95 Å.

The results (Figure 2) are for the four sieve fractions as a function of the particle boundary areas, determined with both argon and nitrogen. The breakthrough times to 0.2% increase with increase in S_v . The latter quantity was the largest for the 20x30 fraction because of the larger number of particles per unit volume. With the exception of one point, nitrogen through the 20x30 fraction, the breakthrough times have parallel behavior. The two lines are displaced about 8 cm² with the nitrogen having the greater value. In general, the correlations with the argon measurements are more consistent than those with nitrogen.



 $S_v(cm^4)$ per unit volume Fig. 2. Correlation of 0.2% Breakthrough Time with Particle Boundary Area

In the first stage of an adsorption process, the movement across the boundary area of the particles may be expressed as follows:

$$A = k_{f} \frac{S_{v}\varepsilon}{\rho_{B}} (p - p_{i})$$
(4)

where N_A = rate of transfer

N

- K_f = mass transfer coefficient
- $S_v =$ boundary surface of unit volume of particles
- ε = fractional void between particles
- $\rho_{\rm B}$ = bulk density of packing
- p = partial pressure in the gas flow
- p1 = partial pressure at the surface
 boundary

The second stage of adsorption is the penetration into the porous structure and the third stage is the actual adsorption of the molecule on a surface site. ,Since the application is concerned with very small penetration of a particular gas component, the first stage of adsorption appears to be the rate determining factor.

References

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