Diffusion and Adsorption of Krypton and Xenon in Underground Materials

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Equilibrium and dynamic adsorption capacities and diffusion and adsorption co-efficients were determined for Kr and Xe in different soil and underground materials. The equilibrium adsorption capacity of the tested materials for Xe was found to be larger than that for Kr by a factor of 2 to 3. The diffusion coefficients of Xe and Kr in air are 0.096 and 0.135 cm²/sec. Their effective diffusion coefficients in packed columns were smaller than in air, owing to effect of tortuosity and adsorption.

$\mathbf{A}$ theoretical evaluation of the underground disposal of krypton-85 released from nuclear fuel reprocessing plants (11) has been made based on different assumptions concerning the diffusion and adsorption of the gas in underground material. Experimental data available for the diffusion and adsorption of noble gases in soil and underground materials are very scarce, and therefore it was felt necessary to check experimentally the validity of the assumptions made in the theoretical evaluation.

Experimental studies were performed for the determination of the diffusion and adsorption parameters of krypton and xenon in soil and underground materials. Xe was chosen in the present study in addition to Kr for the following two reasons:

Demonstration of an efficient adsorption capacity of soil and underground formations for Xe may indicate the feasibility of underground disposal of fission noble gases resulting from nuclear reactor accidents [e.g., Loft experiment (13)].

The diffusion coefficients of Xe and Kr differ only by about 40% (5), while their adsorption coefficients measured on different materials (such as charcoals and zeolites) differ by up to about an order of magnitude (8). Consequently, the difference obtained in the retention (peak) times of these two gases on the same material and same experimental conditions in a chromatographic column could be clearly interpreted whether they are governed by a pure diffusion or both diffusion and adsorption mechanism (retention time is the modal time required for a gas molecule to pass through a column).

Equilibrium and dynamic adsorption capacities and diffusion and tortuosity coefficients have been measured for Kr and Xe in different soil and underground materials and compared with those obtained in relatively high adsorbent materials (e.g., charcoal) and relatively low adsorbent materials (e.g., lucite).

EXPERIMENTAL

Materials. The diffusion and adsorption of Kr and Xe were studied in the following materials: Charcoal (cocoanut charcoal, Fisher Scientific Co.); lucite (Rohm and Haas); Idaho Falls regolith (samples obtained from the site of the Loft experiment at Idaho Falls); and magnesium vermiculite (Zonolite Co., Travelers Rest, NC).

Samples extracted from the core drilling performed at the Joy test well No. 1 at the ORNL hydrofracturing site (coordinates: N, 17-115.00: E, 28-317.00; elevation 760.96) were characterized as follows: depth 1598-1613 ft; limestone, granular and fine, composed of 80% quartz, 10% illite, and 5% chlorite. In the present work this material will be called limestone; depth 2697-2712 ft; shale and limestone interbedded, composed of 20% calcite, 15% quartz, 40% illite, 10% chlorite. In the present work this material will be called shale.

Table I shows the physical properties measured for the different materials used. The physical parameters listed in Table I were assumed to influence the adsorption properties of the materials for krypton and xenon.

The materials were ground, if necessary, and sieved to $-30 +$ 50 U. S. sieve mesh, except for lucite, the particle size of which was $-30 + 60$ U. S. sieve mesh.

The experiments were performed on the materials as received in the laboratory as well as on the materials after being heated at 400°C for 4 hr to drive off all adsorbed water and gases.

Stable krypton (Air Reduction Co.) and xenon (Airco Co.) labeled with ⁸⁵Kr and ¹³³Xe obtained from the ORNL Isotope

Table I. Physical Properties of Materials Used in Diffusion and Adsorption Experiments

Material	Specific surface area, m²/g	Moisture content, %	Porosity of unpacked material, cc/cc	Bulk density of unpacked material, g/cc	Porosity of column packed material, cc/cc	Bulk density of column packed material, g/cc
Charcoal (unheated)	786				0.70	0.54
Lucite (unheated)	0.018				0.36	0.72
Idaho Falls regolith (unheated)	27.5	0	0.59	0.76	0.49	1.2
Idaho Falls regolith (heated)	25		0.55	0.83	0.50	1.3
Vermiculite (unheated)	0.44	6	0.38	0.61	0.53	0.72
Vermiculite (heated)	0.96		0.64	0.59	0.52	0.78
Limestone (unheated)	3.43	4	0.58	1.0	0.51	1.2
Limestone (heated)	5.35		0.53	0.91	0.36	1.2
Shale (unheated)	2.63	0	0.54	0.92	0.50	1.2
Shale (heated)	4.74		0.55	0.90	0.39	1.1

Department were used in the experiments, at different partial pressures, ranging from 0.13-380 mm Hg.

Apparatus and Procedure. Equilibrium adsorption isotherms were measured for Kr and Xe at room temperature (23 ± 3°C). The apparatus consisted of closed glass containers of 100 and 300 ml volume, having two sampling ports closed by rubber septums.

In the same series of experiments, known amounts of solid materials (50-150 grams) were introduced in the containers, while one container was kept empty as a control experiment. After introduction of solid materials, given amounts of labeled Kr or Xe of measured activities were injected by a syringe into the containers, through the sampling ports, in volumes corresponding to the desired partial pressure of the gas. The partial pressure of the gas in these experiments varied between 0.13 to 18 mm Hg.

The containers were then rotated to achieve good mixing between the solid and gaseous phases. Adsorption of the gases on the solid was measured by determining the activity of samples of the gaseous phase extracted with a syringe from the containers, at specified intervals, until there was no change in activity in successive samples.

The activity of the gaseous samples was measured in a well-type NaI crystal scintillation detector connected to a single-channel gamma spectrometer. The resolution time of the circuit was 3×10^{-6} μsec.

The diffusion and dynamic adsorption experiments were performed in chromatographic columns of 122 and 15.2 cm length and 9.5 and 12.7 mm in diameter, respectively. The solid-packed columns were filled with the solid material by introducing small amounts of material and tapping the column after each partial packing.

The inlet of the column was provided with an injection port closed by a rubber septum, through which samples of krypton and xenon were injected into the column. The outlet of the columns was connected to a GM tube (1.4 mg/cm² window) located in a flow-through plastic housing and a lead-shielding container, to a 64-Scaler (Radioactive Products Inc., Detroit, Mich.) and a Honeywell Brown Elektronik Recorder. The resolution time of this circuit was of the order of 10^{-6} μsec.

The 122-cm long columns were used to study the diffusion and adsorption of Kr and Xe in presence of a carrier gas flow (1.7 to 6 ml/min flow rate), while in order to shorten the duration of the experiment, the 15.2-cm long columns were used to study the diffusion and adsorption of the gases in absence of any carrier gas. The latter columns were insulated with asbestos wire to keep constant temperatures throughout the experiments. In the experiments performed in presence of a carrier gas flow, the pressure in the column was measured in addition to the carrier gas flow rate. Kr and Xe labeled with ^{85}Kr and ^{133}Xe were injected by a syringe (1-50 μl) into the inlet injection port, at partial pressures varying from 15-380 mm Hg.

In designing the experimental systems for the diffusion and dynamic adsorption experiments, it was assumed that the major parameter and random processes which influence the downstream migration of a gas in a gas-solid chromatographic column are: tortuosity, molecular diffusion, eddy diffusion, and adsorption kinetics.

The flow rate, density, and viscosity of the carrier gas and size of column packing particles were chosen so that eddy diffusion would be negligible as compared to molecular diffusion (4). In addition, the following systems were chosen in the diffusion and dynamic adsorption experiments to make possible the separate study of the other parameters: empty columns, in which molecular diffusion was assumed to govern the transport of the gas, since due to lack of solid packing in the column, the tortuosity and adsorption coefficients are equal to zero; columns packed with Idaho Falls regolith, saturated with stable Kr, in which molecular diffusion and tortuosity were assumed to govern the transport of the gas, since due to satura-

tion of the column packing with Kr, additional adsorption of Kr, including isotopic exchange effect, is assumed to be negligible; columns packed with different adsorbent materials in which molecular diffusion, tortuosity, and adsorption were assumed to govern the transport of the gas.

Air was generally used as the carrier gas flow in these experiments. However, in some experiments in which the diffusion and adsorption of Kr were to be determined in a column packed with Idaho Falls regolith, saturated with stable Kr, the following modification was made: The column was saturated with stable Kr by passing through it for 10-22 hr a stream of stable Kr at an identical flow rate to that to be used in the experiment.

From the measured activity of the eluted Kr and Xe, the data required for the determination of the effective diffusion coefficient, tortuosity coefficient, and adsorption capacity were obtained.

Methods of Calculation of Diffusion and Adsorption Data. In the computation of the equilibrium adsorption data, consideration was given to the pore volume and bulk density of the adsorbents and to the depletion of Kr and Xe from the supply container. Due corrections were made in the calculations for the radioactive decay of ^{133}Xe and for the adsorption of the gases on the container wall or ports, as measured in the empty control experiment.

From the difference between the activity expected in the free volume of the containers holding the adsorbents and that found, the adsorption capacity of the different adsorbents for Kr and Xe was calculated, taking into consideration the standard deviation in the different stages of the computation.

Figure 1 shows a typical elution chromatogram (differential counts) obtained in the dynamic experiments performed in columns in presence of a carrier gas flow. Figure 2 shows a typical chromatogram (integrated counts) obtained in the experiments performed in columns, in absence of carrier gas. The integrated-count chromatograms were transformed into breakthrough percentage curves, as function of time. Figure 3 shows a typical breakthrough percentage curve obtained from the chromatogram data of Figure 2.

From the chromatograms and breakthrough percentage curves, the following data were computed:
Number of Theoretical Plates, N (2)

$$N = 8 \left(\frac{l}{w} \right)^2 \tag{1}$$

Height Equivalent of a Theoretical Plate, H (cm)

$$H = \frac{L}{N} \tag{2}$$

Effective Diffusion Coefficient, D_{eff} (cm²/sec) (2, 12)

$$D_{eff} = \frac{Hu}{2} \tag{3}$$

$$u = \frac{L}{t} \tag{4}$$

By use of Equation 3 it was considered that at Reynolds numbers below unity, molecular transport govern axial dispersion of the injected pulse (4). The Reynolds numbers, Re, were computed from the relationship (6):

$$Re = \frac{dv\rho}{\mu} \tag{5}$$

Tortuosity Coefficient, γ, in a column in which no adsorption takes place (e.g., in a Kr saturated column) (9),

$$\gamma = \frac{D_{eff}}{D_{g}} \tag{6}$$

Adsorption Capacity of Solid for Gases, k (gas, grams/solid, grams), obtained from the conservation equation in a chromatographic column, also used by Kaufman and Orlob (7) to express the average velocity of a flow of a contaminant dissolved in ground water:

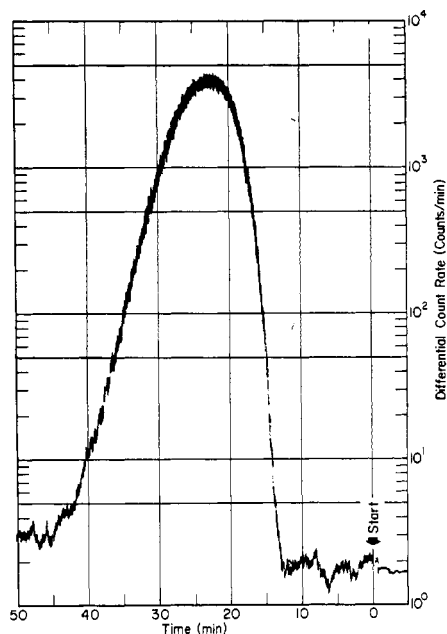$$\frac{u}{u'} = \frac{1}{1 + \dfrac{kS}{PC_0}} \qquad (7)$$

u', in the experiments in which a carrier gas flow was used, was determined from the relationship (9):

$$u' = \frac{F}{AP} \qquad (8)$$

In the experiments in which no carrier gas flow was used, u' was considered to be:

$$u' = \frac{u''}{P} \qquad (9)$$

Dynamic Adsorption Coefficient, as proposed by Browning et al. (3)

$$K = \frac{tF}{m} \qquad (10)$$

In all these computations, due corrections were made for the distortion of the data caused by the presence of a connecting tube between the outlet of the column and the GM tube and by the finite volume of the flow-through detector. These corrections were made by injecting a pulse of the gas directly into the connecting tube to the detector and substracting the data obtained in the direct injections from the data obtained in the different experiments.

RESULTS AND DISCUSSION

Equilibrium Adsorption. Figures 4 and 5 show the adsorption isotherms of Kr and Xe on different adsorbent

Figure 1. Typical elution chromatogram of ^{85}Kr (differential counts)
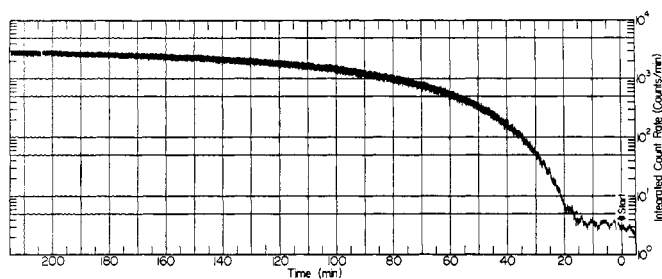
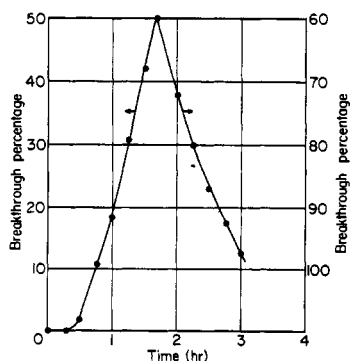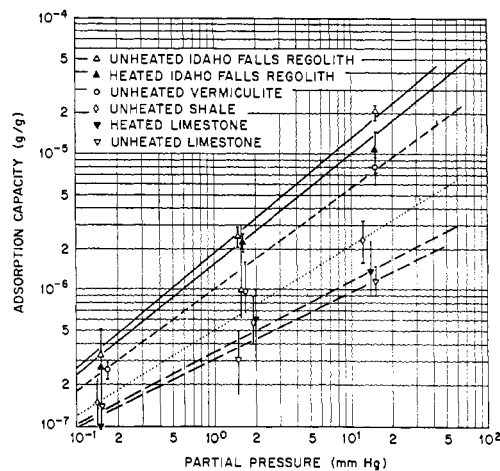**Figure 2.** Typical elution chromatogram of ^{85}Kr (integrated counts)

Figure 3. Typical breakthrough percentage curve obtained from an elution chromatogram (integrated counts—Figure 2)
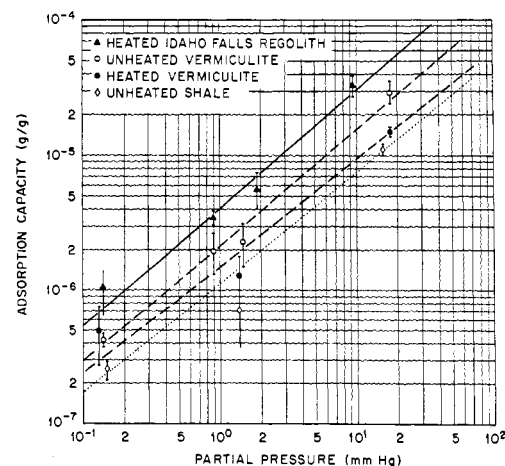

Figure 4. Adsorption isotherms of Kr (23 + 3°C)

Figure 5. Adsorption isotherms of Xe (23 + 3°C)

materials. It is seen that the adsorption capacity of the tested adsorbents for Xe is larger than that for Kr by a factor of 2 to 3.

It was expected that adsorbents with a higher specific surface area would have a higher adsorption capacity. However, comparison of the data shown in Figures 4 and 5 indicate that there is no clear relationship between the adsorption capacity of the materials and their specific surface area as shown in Table I. This might be explained by the differences in the pore size distribution in the different materials tested (see, e.g., Figures 6 and 7), the relationship between the pore size and
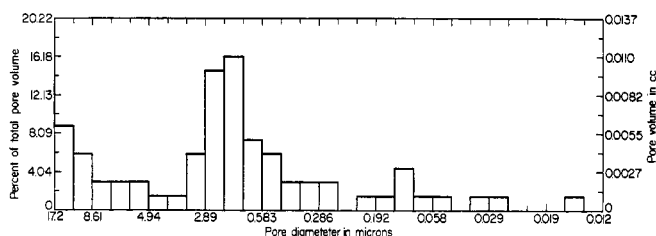

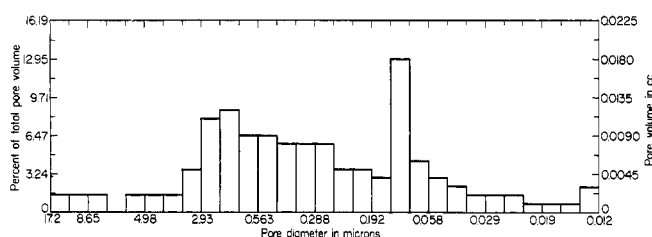**Figure 6. Pore size distribution in Idaho Falls regolith**

Figure 7. Pore size distribution in vermiculite

the atomic radii of Kr and Xe, and the technique of measurement of the specific surface area of the adsorbents. More work has to be done to clarify this relationship.

It is also interesting to note that there is no significant difference between the adsorption capacity of heated (at 400°C) and unheated absorbents for Kr and Xe. However, the moisture content of the unheated adsorbents (Table I) was relatively low, so that no significant difference in the adsorption capacities due to differences in moisture content, was to be expected. Also the specific surface area of the unheated Idaho Falls regolith was found to be larger than that of the heated regolith (Table I).

Diffusion and Dynamic Adsorption Experiments. Table II shows the effective diffusion coefficients and tortuosity coefficients of Kr and Xe in different systems and the dynamic adsorption capacity of different materials for these gases. Reproducibility of results was within less than ±1.6%. A minimum of two and up to five identical measurements were performed. The accuracy of the results is limited by a number of factors such as accuracy of the measurement of the breakthrough time, of the elution curve parameters u and w, flow of carrier gas, and porosity of packing.

It is estimated that the adsorption capacity is accurate to within 8%, while other data are accurate to within less than 6%. It should be stressed that the dynamic adsorption capacity, as determined in the present experiments, is proved only for a system in which molecular diffusion is the main mechanism which governs the dispersion of the gases. Indeed, the Reynolds numbers as calculated in the experiments in which a carrier gas flow was used, are of the order of magnitude of 10^{-3}–10^{-4} and therefore by far within the range in which molecular transport governs the axial dispersion of the injected pulse (4).

Also, the almost identical results obtained in both series of experiments performed in presence or absence of a carrier gas

Table II. Diffusion and Adsorption of Kr and Xe in Dynamic Systems

Gas	Partial pressure of gas, mm Hg	Adsorbent in column	Flow of carrier gas, ml/min	u, velocity of gas, cm/sec	D_{eff}, cm²/sec	u', theoretical velocity of gas, cm/sec	u/u'	k, adsorption capacity, Equation 7, g/g^a	K, dynamic adsorption coefficient, Equation 10, g/g^a	Tortuosity coefficient
					Column Length, 120 Cm					
Kr	15	Empty	4	4.55×10^{-2}	1.35×10^{-1}	9.38×10^{-2}	1.02	0		
Xe	15.5	Empty	4	9.75×10^{-2}	9.6×10^{-2}	9.38×10^{-2}	1.04	0		
Kr	15	Lucite	4	2.33×10^{-1}	9×10^{-2}	2.6×10^{-1}	0.90	8×10^{-9}	6.7×10^{-8}	
Xe	15.5	Lucite	4	2.14×10^{-1}	4.8×10^{-2}	2.6×10^{-1}	0.82	2.6×10^{-8}	1.15×10^{-7}	
Kr	15	Idaho regolith	4	1.22×10^{-1}	6.3×10^{-2}	1.86×10^{-1}	0.65	2.0×10^{-8}	8.9×10^{-8}	
Kr	380	Idaho regolith	4.1	1.18×10^{-1}	6.4×10^{-2}	1.92×10^{-1}	0.61	3.6×10^{-8}	8.7×10^{-8}	
Kr	380	Idaho regolith	6	1.43×10^{-1}	7.6×10^{-2}	2.83×10^{-1}	0.51	5.4×10^{-8}	1.1×10^{-7}	
Kr	380	Satd. Idaho regolith	1.7	8.55×10^{-2}	6.7×10^{-2}	8×10^{-2}	1.06	0	5×10^{-8}	0.50
Kr	380	Satd. Idaho regolith	4	1.97×10^{-1}	6.3×10^{-2}	1.86×10^{-1}	1.04	0	5.2×10^{-8}	0.47
Kr	380	Satd. Idaho regolith	6	3.2×10^{-1}	8.9×10^{-2}	2.83×10^{-1}	1.12	0	4.8×10^{-8}	0.66
Xe	15.5	Idaho regolith	4	9.15×10^{-2}	2.8×10^{-2}	1.86×10^{-1}	0.49	9.6×10^{-8}	1.7×10^{-7}	
Kr	15	Charcoal	4	4.26×10^{-3}	2.4×10^{-3}	1.33×10^{-1}	0.031	5.8×10^{-6}	4.4×10^{-6}	
Xe	15.5	Charcoal	3	5.1×10^{-4}	9.7×10^{-5}	1.34×10^{-1}	0.0038	8.3×10^{-5}	4.35×10^{-5}	
					Column Length, 15.2 Cm					
Kr	15	Empty	...	1.9×10^{-2}	1.3×10^{-1}					
Xe	15.5	Empty	...	1.92×10^{-2}	8.7×10^{-2}					
Kr	15	Lucite	...	4.17×10^{-2}	7.75×10^{-2}	5.27×10^{-2}	0.8	1.9×10^{-8}		
Xe	15.5	Lucite	...	4.8×10^{-2}	8.2×10^{-2}	5.4×10^{-2}	0.88	1.5×10^{-8}		
Kr	15	Idaho regolith	...	2.63×10^{-2}	5.6×10^{-2}	3.8×10^{-2}	0.69	2.5×10^{-8}		
Xe	15.5	Idaho regolith	...	2.04×10^{-2}	3.3×10^{-2}	3.84×10^{-2}	0.53	8×10^{-8}		
Kr	15	Vermiculite	...	3.22×10^{-2}	5.35×10^{-2}	3.67×10^{-2}	0.88	1.4×10^{-8}		

^{a} Computed for 3×10^{-2} mm Hg partial pressure.

flow, indicate that indeed the mechanism which governed the axial dispersion of the pulse in all these experiments is molecular diffusion.

Effective Diffusion Coefficients. The diffusion coefficients of Kr and Xe as determined in empty columns (0.135 and 0.096 cm²/sec, respectively) are in agreement with the values found by other workers (1, 5). It is also seen that for all the materials tested, the effective diffusion coefficients in packed columns are smaller than in the empty columns owing to the effect of tortuosity. A further decrease in the effective diffusion coefficient occurs as a function of the adsorption capacity of the column packing: the higher the adsorption capacity of the packing, the lower the effective diffusion coefficient of the gas.

Tortuosity Coefficients. Tortuosity coefficients were computed using Equation 6 for those systems in which no adsorption of the gases on the column packing was found. The tortuosity coefficients for Kr in columns packed with Kr-saturated Idaho Falls regolith was 0.47–0.66 at carrier gas flow rated ranging from 1.7–6 ml/min.

Dynamic Adsorption Capacity. The dynamic adsorption capacities of the materials tested, for Kr and Xe, in a system in which molecular diffusion governed the axial dispersion of the gases, are close to the equilibrium adsorption capacities measured in our experiments for Idaho Falls regolith and vermiculite and in those experiments performed by Lloyd and McNees (10) for charcoal. Also, the adsorption capacities as measured in both experimental systems, in presence and in absence of a carrier gas flow are almost identical.

The results in Table II, especially the comparison between the adsorption capacity of Kr-saturated Idaho Falls regolith with that of natural Idaho Falls regolith, indicate a definite adsorption retention of both Kr and Xe on the different materials tested. They also indicate the validity of Equation 7 in evaluating the velocity of underground movement of a gas, governed by molecular diffusion and adsorption, as proposed in the theoretical evaluation (11). While the adsorption capacity, as determined by Equation 7 was zero for Kr-saturated Idaho Falls regolith, a definite adsorption capacity was found for materials which were tested.

However, the use of Equation 10 as proposed by Browning et al. (3) in evaluating the dynamic adsorption capacity of an adsorbent does not appear to be adequate, since some of the results found in the present determination of the dynamic adsorption capacity are higher than the equilibrium adsorption values. It seems that the high values, found in this determination for the adsorption capacities, result from the fact that no consideration is given in Browning's equation to the tortuosity effect. This is apparently brought out by the fact that for highly adsorptive materials (e.g., charcoal) in which the tortuosity effect is negligible as compared to the adsorption effect, the values computed for the adsorption capacity by Equation 10 agree with the values for the equilibrium adsorption (10).

ACKNOWLEDGMENT

NOMENCLATURE

A = cross sectional area of the empty column, cm²
C_o = concentration of gas pulse, g/ml

d = diameter of packing particles, cm
D_{eff} = effective diffusion coefficient, cm²/sec
D_g = diffusion coefficient of the gas in air, as determined in an empty column, cm²/sec
F = volumetric flow rate of the carrier gas, ml/sec
H = height equivalent of a theoretical plate, cm
k = adsorption capacity of solid for gases, gas, g/solid, g
K = dynamic adsorption coefficient, cc (STP)/g adsorbent
l = distance on chromatogram, from the injection point to the point of 50% breakthrough, cm
L = length of column, cm
m = amount of adsorbent in column, grams
N = number of theoretical plates
P = porosity of packing in column, ml/ml
Re = Reynolds number
S = bulk density of column packing, g/ml
t = time elapsed from injection to 50% breakthrough of the pulse, sec
u = superficial velocity of movement of the gas pulse, cm/sec
u' = superficial velocity of movement of the gas pulse in a packed column, unaffected by sorption, or theoretical velocity of gas, cm/sec
u'' = superficial velocity of movement of the gas pulse, as determined in the empty column
v = superficial velocity of carrier gas, cm/sec
w = width of elution curve at $1/e$ of the height, cm

GREEK LETTERS

γ = tortuosity coefficient
μ = viscosity of carrier gas, cP
ρ = density of carrier gas, g/ml

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