

A QUANTITATIVE THEORY OF THE INTERRELATIONSHIP BETWEEN SOLUTE RETENTION VOLUMES IN GAS-SOLID AND LIQUID-SOLID CHROMATOGRAPHY. STUDIES ON WATER DEACTIVATED ALUMINA

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INTRODUCTION

In contrast to gas-liquid chromatography (GLC), which has been used in the analysis of an extremely large and varied number of sample types, gas-solid chromatography (GSC) has found only limited application as an analytical separation procedure, and its use has been confined largely to the determination of mixtures of the fixed gases and lower hydrocarbons. A number of reasons for the relative unpopularity of GSC separation are apparent. First, adsorption isotherms in GSC systems are frequently non-linear, even at low column loadings, and occasionally irreversible; this leads to several severely detrimental effects: component retention volumes which vary with sample size, band tailing, and incomplete recovery of sample from the column. Second, retention volumes in GSC are generally excessively large, particularly for large polar molecules, leading to impossibly long separation times for all but the simplest organic mixtures. Third, adsorbents are in general more difficult to standardize and reproduce than comparable liquid phases used in GLC; not only do adsorbent properties change markedly with subtle differences in the preparation of the solid phase, but the presence of small amounts of adsorbed material (particularly water) has a critical effect on adsorbent performance. Fourth, active adsorbents at elevated temperatures frequently induce catalytic alteration of the sample. Finally, the number of different, commercially available adsorbents which appear useful in GSC is relatively small, compared with the large number of different liquids available for GLC, and this has created the impression of greater flexibility or versatility for GLC *versus* GSC analysis.

GIDDINGS¹, in a recent communication, has pointed out that despite the above limitations on GSC, this technique may actually possess a greater future analytical potential than does GLC. The column efficiencies theoretically attainable in GSC appear to be several orders of magnitude higher than are possible in GLC, and GIDDINGS has also called attention to the unique selectivity provided by adsorption separation in some cases. Furthermore, many of the foregoing limitations on GSC are today more apparent than real. The highly sensitive detectors that have been developed for GLC permit GSC separations with extremely small sample sizes, which in turn means linear adsorption isotherms and constant sample retention volumes¹. Similarly, it has long been known in the case of liquid-solid chromatography that addition to the adsorbent of small quantities (less than a monolayer) of

strongly adsorbed substances suppresses the more active adsorption sites, hence reducing band tailing and increasing the sample sizes that can be used in linear isotherm operation. This same technique has been successfully applied to GSC by a number of different workers: EGGERTSEN *et al.*² who used squalane to deactivate carbon, SCOTT³ who used silicone oil to deactivate alumina, and PETITJEAN AND LEFTAULT⁴ who used various other heavy oils as well as pyrolysis products (coke?), to deactivate the oxide surface of aluminum capillaries. Adsorbent deactivation in this fashion can also reduce the excessive retention volumes characteristic of GSC to more convenient levels, as shown by SCOTT's work^{3,5} with water and NaOH deactivated alumina. With 40% NaOH on alumina SCOTT was able to separate *n*-alkanes boiling to C₃₆. Chemical modification of the surface can similarly be used in GSC to reduce retention volume⁶ and improve isotherm linearity⁷; thus, after reacting a silica surface with trimethylchlorosilane, VASIL'eva *et al.*⁶ found much lower retention volumes for benzene and *n*-hexane in GSC separations with this adsorbent than in comparable GLC systems. Variation of the geometrical structure of the adsorbent, particularly the elimination of small pores, can also improve isotherm linearity as discussed by KISELEV *et al.*⁷ for silica and HALÁSZ AND HORVÁTH⁸ for carbon. The use of an adsorbing carrier gas or vapor has been shown by GREENE AND ROY⁹ to give much the same advantages in GSC as adsorbent deactivation: improved band shape (and presumably greater isotherm linearity) and shorter retention volumes. Another expedient for reducing the retention volumes of sample components in GSC is by effectively reducing the amount of adsorbent in the column. HALÁSZ AND HORVÁTH⁸ accomplished this by using glass beads coated with carbon; they were able to separate the *n*-alkanes through C₁₃ in a short time. Similarly, KISELEV *et al.*⁷ used low surface area silica gels to accomplish the separation of the *n*-alkanes through C₂₀ in a reasonable time. The reduction of adsorbent surface area is precisely equivalent in this respect to dilution of the adsorbent by glass beads or other means. SCHWARTZ *et al.*¹⁰ have also described the use of adsorbent coated capillaries (similar to those of PETITJEAN AND LEFTAULT⁴, which appear to have much the same advantages in this respect as large pore adsorbents and coated glass beads. SCHWARTZ *et al.*¹⁰ also emphasize the advantage of these solid coated capillaries over liquid coated capillaries in their freedom from column bleeding.

Suppression of adsorbent activity by deactivation or by the use of an adsorbing carrier gas might also be expected to reduce the catalytic activity of the adsorbent, and hence minimize the likelihood of sample reaction in GSC separation. Adsorbent standardization has come to be less of a practical problem as more is learned about the variables which influence adsorbent behavior (*e.g.* see discussion in refs. 7, 11 and 12). Similarly, for maintaining the water content (and hence activity) of the adsorbent in GSC constant, SCOTT³ used water saturation of the incoming carrier gas. Finally, the limited number of adsorbents that have been used in previous GSC and LSC separations (principally alumina, carbon, silica, and molecular sieves) does not really imply a significant limitation in the separation possibilities of GSC, relative to GLC with its vast number of potential stationary phases. The separations provided by adsorbents are in many cases fundamentally different than those achievable with any liquid phase, while many structurally dissimilar liquids possess little uniqueness in their separation capabilities as GLC substrates. In addition, recent years have seen the creation of specific adsorbents¹³ for given separations, as well as the

synthesis of many new, unique adsorbents (for example molecular sieves of varying geometry).

The foregoing paragraphs suggest a potentially promising future for the GSC technique, and there are currently a number of groups actively working on the realization of this potential. It is therefore important to clarify the basic principles of GSC separation as quickly as possible. The usefulness of any elution chromatographic procedure can be evaluated in terms of two essentially independent considerations: column efficiency or band width, and separation factors or relative retention volumes. The theoretical treatment of GIDDINGS¹, which is concerned almost solely with column efficiency in GSC, seems to provide an adequate initial basis for guiding present experimental work aimed at optimizing column efficiency in GSC. A satisfactory overall theoretical framework requires a corresponding treatment of the variation of GSC retention volumes with solute molecular structure and experimental conditions. Previous theoretical and experimental investigations in this area are essentially non-existent. For the related technique of liquid-solid chromatography (LSC), a vast amount of experimental data have been acquired, and reasonably satisfactory theories of the dependence of solute retention volumes on molecular structure and experimental conditions have been set forth (*e.g.* see ref. 12). In general, some parallelism is expected between the relative separation of different compounds in GSC and LSC when the same adsorbent is used. Thus, for LSC separations on carbon, it has long been known that adsorption of the solute increases with molecular size or number of carbon atoms¹⁴, and is relatively unaffected by the presence of polar solute groups or double bonds, or even decreases with their addition to the solute¹⁵. Similarly, several GSC studies on carbon^{2,8,16-18} have confirmed a separation order according to carbon number or molecular weight, with little effect of solute double bonds or ring closures. GRIFFITHS *et al.*¹⁹ studied the displacement of a number of polar and hydrocarbon solutes from carbon, and HALÁSZ AND HORVÁTH⁸ carried out similar elution GSC studies on carbon; both groups again confirmed the preferential adsorption of the heavier hydrocarbons, particularly with respect to polar molecules of similar boiling points.

By contrast with adsorption on carbon, LSC separation on alumina or other metal oxides shows little dependence of solute adsorption on solute size or number of aliphatic carbon atoms, but a pronounced increase in adsorption with addition of polar groups or double bonds to the solute molecule. Similarly, in GSC separations over alumina, SCOTT³ has shown the preferential adsorption of ethylene relative to the larger propane on sufficiently active columns; PETITJEAN AND LEFTAULT⁴ have reported similar data for GSC separation over alumina. KLEMM *et al.*^{20,21} have studied both the LSC and GSC separation of several of the substituted hydrocarbons and pyridines on alumina, and found the GSC data²¹ "...consistent with data on adsorbabilities obtained earlier from (LSC)".

These past qualitative comparisons of separation in GSC and LSC systems have been useful in summarizing the differences in GSC between such adsorbents as carbon and the metal oxides. However, a more detailed theoretical analysis is required in order to take full advantage of our considerable knowledge and understanding of separation in LSC systems for application to corresponding GSC systems. Previous investigations carried out in this laboratory^{12,22-24} have resulted in a detailed, quantitative treatment for correlating and predicting retention volume data in

LSC separation over alumina and, to a lesser extent, other adsorbents. Certain theoretical considerations have been advanced¹² which suggest that this treatment might easily be generalized to include the similar treatment of retention volume in GSC systems. If so, this would permit the prediction of separation in GSC systems on the basis of comparable LSC data, and provide considerable insight into the factors controlling retention volume in various GSC systems. Finally, some measurements most conveniently carried out in GSC systems might shed additional light on the theory of separation in LSC, assuming the existence of a satisfactory unified theory of LSC and GSC separation.

With the foregoing considerations in mind, GSC separations were performed with a variety of organic solutes, using an alumina comparable to previously studied (*e.g.* ref. 12) samples. The interpretation, correlation, and generalization of these data was then carried out in terms of previous theories of LSC separation^{12, 22-24}.

EXPERIMENTAL

All of the experimental GSC data presently reported were obtained in conventional gas chromatography units equipped either with thermal conductivity or flame ionization detectors. Inlet He carrier gas could be water saturated at ambient temperature (21°) if desired by passing the gas through two large galvanized steel bubblers. The lines between the bubblers and the gas chromatography unit were preheated to approximately 83° by means of heating tape. The column was thermostated at 83° ± 1°, and exit flow rates were measured with a soap bubble flow meter. For the runs with water saturated He, the water content of the equilibrated adsorbent was chromatographically checked¹² following the GSC runs.

In one set of experiments the water content of the adsorbent was intentionally reduced to 1.5% H₂O-Al₂O₃ by bypassing the bubbler and passing dry He through the column for 24 h prior to running GSC separations (for a subsequent 4 h). The resulting water content of the adsorbent (1.5% H₂O) in this case was measured by the breakthrough time for water equilibrated He in a subsequent re-equilibration of the column with water (to 2.7% H₂O-Al₂O₃). All experiments were carried out with the precalcined (400°, 16 h) water deactivated Alcoa F-20 alumina used previously^{12, 22-24}.

Retention volumes in nominal ml as measured by the exit He flow rate and elution times were converted to specific corrected retention volumes U_g' : the actual volume of He (at column conditions of pressure and temperature) per gram of adsorbent required to elute a peak maximum, corrected for the dead volume of the column. U_g' is similar to the specific retention volume U_g defined by JANAK²⁵, and is defined in the present way for theoretical reasons (so as to be equivalent to retention volume in LSC systems). Actually, since the pressure and temperature corrections involved operate in opposition, there is little difference between values of U_g , U_g' , and the uncorrected (measured under ambient conditions) retention volume per gram of adsorbent. Duplicate determinations of U_g' for a single solute in different adsorbent columns showed good repeatability, averaging ± 3%.

All U_g' values reported are for linear isotherm column loadings. Linear column capacities (the amount of sample per unit weight of adsorbent sufficient to reduce the linear isotherm value of U_g' by 10%¹²) were measured for several solutes, and

all values were found to vary between $2 \cdot 10^{-4}$ to $5 \cdot 10^{-4}$ g/g for 2.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$. These linear column capacities are similar to those involved in comparable LSC systems²⁶. All U_{θ}' values for 2.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ were measured within the linear isotherm region, or extrapolated from values obtained at loadings below $2 \cdot 10^{-4}$ g/g. Column linear capacities for 1.5 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ were observed to be considerably lower, as expected²⁶.

Band shape and column efficiencies were not of major interest in the present studies. It was observed that most bands were symmetrical for elution from 2.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$, while slight tailing was observed for the bands eluted from 1.5 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$. All studies were carried out in the region of minimum HETP, and HETP was observed to be approximately constant for most solutes: 0.5 mm for the $1/8$ in. columns, and 2.0 mm for the $1/4$ in. columns.

For a number of solutes having retention volumes U_{θ}' greater than 300 ml/g on 2.7 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$, it was established by dual measurement with flame and thermal conductivity detection that two elution peaks are obtained; one at 320 to 350 ml/g, and a second one at some larger retention volume. The first peak was found to be a water peak (U_{θ}' for water approximately 370 ml/g), which appears to be the result of displacement of adsorbed water by initial adsorption of the solute. This phenomenon (double peaking) is even more common when the carrier gas is saturated with materials more weakly adsorbing than water, as will be discussed in a following paper.

A UNIFIED THEORY OF SOLUTE RETENTION VOLUME IN GSC AND LSC SEPARATION, AND ITS EXPERIMENTAL VERIFICATION

Development of the theory

In linear isotherm LSC or linear elution adsorption chromatography (LEAC), the equivalent retention volume of a solute \underline{R}° (ml/g) can be related¹² to adsorbent activity α and surface volume V_a , eluent strength ε° , the area A_s required by the solute for adsorption on the adsorbent surface, and the dimensionless free energy of adsorption of the solute from pentane onto calcined adsorbent S° :

$$\log \underline{R}^{\circ} = \log V_a + \alpha(S^{\circ} - A_s \varepsilon^{\circ}). \quad (1)$$

Values of the parameters V_a and α have been tabulated¹² for the adsorbents alumina, silica, Florisil, and "X" sieve; ε° values have been listed for a number of eluents^{12,22} and can be estimated for other eluents²² when certain solute parameters are available. Solute A_s values can be calculated in a straightforward fashion¹², and the solute adsorption energies S° can be quantitatively related^{12,23} to solute group adsorption energies, solute intramolecular steric and electronic interactions, and the orientation of solute groups with strong adsorbents sites. Presumably, these solute S° values (which vary with both solute and adsorbent type) determine the unique separation characteristics of both LSC and GSC systems.

Equation (1) has been derived on the assumption that a competition exists between a solute molecule and some number m eluent molecules for a given place on the adsorbent surface; it is further assumed that the net solute adsorption energy is given as the inherent solute adsorption energy minus m times the eluent adsorption energy. All solution energy terms are hence ignored in the derivation of equation (1),

and the empirical success of equation (1) in a variety of different eluent systems makes this omission appear justifiable. There are additional reasons for believing this latter approximation is valid in LSC systems. Thus, such exceptions to eqn. (1) as have been noted²² in the case of "anomalous" eluents have been shown to arise from peculiar interactions of the solute or eluent with the adsorbent, rather than corresponding solution interactions. Similarly, the eluent strength ε° of binary mixtures can be accurately predicted from the eluent properties of the constituent pure solvents¹² by assuming that only the adsorption energy terms are important. Finally, that this should be so (adsorption energy terms much more important than solution energy terms) is not really too surprising, considering that the solution energy terms appear to be generally much smaller than corresponding adsorption energy terms¹², and that only a fraction of the solution bonds are normally broken when a molecule adsorbs.

If the solution energy terms in LSC separation are in fact negligible, there is then little difference in the theoretical treatment of retention volume in LSC and GSC systems. In LSC systems, eluent strength values ε° are calculated relative to the standard weak eluent pentane ($\varepsilon^\circ = 0.00$). In GSC, when negligible adsorption of the carrier gas (or eluent) occurs, the effective ε° value of the carrier gas ε°_g will necessarily be negative. This is equivalent to a positive adsorption energy (per unit of area or A_s) for pentane, equal $-\varepsilon^\circ_g$. This value would be expected to vary between adsorbents in the same manner that the adsorption energy of pentane varies. An effect in GSC which is necessarily overlooked by any relationship (such as equation (1)) for retention volume dependence in LSC separation is the large increase in translational freedom which accompanies the transfer of a molecule from a fixed (adsorbed) phase to the gas phase. If we assume negligible translational freedom in the adsorbed or solution phases, this effect cancels out in LSC (as evidenced by the absence of any term reflecting this effect in eqn. (1)), while for GSC the net decrease in translational energy upon adsorption of a molecule will be equal to $1.5 R T$ (R is the gas constant, T the absolute temperature), which is equivalent to an added, constant term (-0.65) in eqn. (1). Finally, U_g' as defined in the EXPERIMENTAL section is thermodynamically equivalent to the quantity \bar{R}° in LSC. Thus, our final, revised equation for solute retention volume in linear isotherm GSC (corresponding to eqn. (1) in LSC) is simply:

$$\log U_g' = \log V_a - 0.65 + \alpha(S^\circ - A_s \varepsilon^\circ_g). \quad (2)$$

The experimental U_g' values acquired in the present study can be used to evaluate the validity of eqn. (2) for GSC separation. Before attempting this, however, it should be noted that $-\varepsilon^\circ_g$ will be large, and it is therefore of great importance that the A_s values selected for the various solutes studied be as accurate as possible. In previous LSC studies, using eqn. (1) to correlate retention volume data between different eluents, the range in eluent strength values for a given solute has generally been fairly small, and small errors in A_s have not been critical. Furthermore, most of the solutes studied in these previous LSC investigations have been relatively large, planar aromatics, where the calculation of A_s is simpler than for most of the solutes that could be conveniently studied in the present investigation. For these reasons, we will first turn to the re-examination of the calculation of solute A_s values, before attempting the experimental verification of eqn. (2) for GSC separation.

Calculation of solute A_s values

A_s values (molecular areas) for a number of organic molecules have been measured directly by the BET method, although these values are not always constant between different adsorbents²⁷, and even show marked variation for the same adsorbent type as pore diameter²⁸ or water content²⁹ is varied. A number of such data^{27, 30, 31} have been summarized in Table I. If we seek to generalize these data by comparison with calculated values (using covalent bond and Van der Waals radii as summarized by PAULING³²), the calculated values are invariably small because of inefficient packing on the adsorbent surface. Following a suggestion by PIERCE³²,

TABLE I
CORRELATION OF EXPERIMENTAL MOLECULAR AREAS A_s FROM BET DATA

Adsorbate	A_s (Å^2)			Calc. ^b
	Exptl.			
	Ref. 26 ^a	Ref. 29	Ref. 30	
Hydrogen		8.7		11.1
Methane		16.8	18	19.7
Acetylene		22.2		22.8
Ethane		23.7		27.3
Propane			40	34.9
1-Butene		42.7		41.5
<i>n</i> -Butane		46.9	47	42.3
Isobutane			33	42.9
Neopentane			38	42.9
<i>n</i> -Hexane	57.7			57.3
<i>n</i> -Heptane		62.5		64.8
Benzene	48.3	32.3		51.1
Ammonia		15.4		18.7
Oxygen		15.4		16.2
Nitrogen	(16.2) ^c	(16.2) ^c		17.0
Carbon monoxide		17.1		17.7
Carbon dioxide		20.5		21.5
Carbon disulfide		39.9		32.3
Fluorodichloromethane		40.2		36.1
Ethyl chloride	32.6	26.1		33.8

^a Data for carbon only.

^b From covalent and Van der Waals radii, assuming the latter is 0.5 Å greater for adsorbed molecules.

^c Standard.

we have attempted the calculation of these solute molecular areas assuming a Van der Waals radius larger than those of PAULING by 0.4–0.7 Å. The use of Van der Waals radii increased by 0.5 Å give the best fit to the data of Table I, and molecular areas calculated by this procedure are also included in Table I. The resulting agreement between calculated and experimental molecular areas is reasonably satisfactory ($\pm 4.3 \text{ Å}^2$ standard deviation, omitting the questionable value of LIVINGSTON for benzene). Presumably, the same method of calculating molecular areas can be used for the solutes presently studied to obtain A_s values with a similar precision.

Verification of equation (2) for GSC separation

Table II presents experimental U_0' values for 38 solutes in the system 2.7 %

TABLE II

SOLUTE RETENTION VOLUMES FOR GSC SEPARATION OVER 2.7% H₂O-Al₂O₃ AT 83°^a

Solute	Log U ₀ ' (exptl.)		(A _s) ^d	(S°) ^e	Log U ₀ '	
	Column 1 ^b	Column 2 ^c			Best exptl.	Calc. ^f
<i>Hydrocarbons</i>						
Propane		0.48	4.1	—0.04	0.48	0.14
n-Butane		0.85	5.0	—0.02	0.85	0.70
n-Pentane	1.23	1.23	5.9	0.00	1.23	1.21
n-Hexane	1.65	1.66	6.8	0.02	1.65	1.74
n-Heptane	2.09	2.10	7.6	0.04	2.10	2.22
n-Octane	2.51	2.55	8.5	0.06	2.53	2.75
n-Nonane		3.00	9.4	0.08	3.00	3.29
n-Decane		3.48	10.3	0.10	3.48	3.82
1-Hexene	1.82		6.7	0.64	1.82	2.03
Cyclopentane		1.14	5.2	0.08	1.14	0.85
Cyclopentene		1.31	5.1	0.70	1.31	1.14
1,4-Pentadiene		1.50	5.7	0.62	1.50	1.44
Benzene	2.06	2.07	6.0	1.86	2.06	2.33
Toluene	(2.51) ^g	2.70	6.8	1.92	2.70	2.82
o-Xylene		3.15	7.5	2.07	3.15	3.32
m-Xylene		3.08	7.6	1.98	3.08	3.33
p-Xylene		3.08	7.6	1.98	3.08	3.33
<i>Non-hydrocarbons</i>						
Dimethyl sulfide	1.85		4.2	2.65	1.85	1.73
Thiacyclobutane		2.30	4.7	2.65	2.30	2.02
Thiacyclopentane		2.88	5.0	2.92	2.88	2.35
Dimethyl ether	1.82		3.7	3.5	1.82	1.93
Ethyl bromide	1.55		3.9	2.0	1.55	1.19
Methyl iodide	1.29		3.7	2.0	1.29	1.07
1-Chlorobutane		2.21	5.8	2.0	2.21	2.29
Chlorobenzene	(2.55) ^g	2.73	6.8	2.06	2.73	2.90
Fluorobenzene	2.17		6.3	1.97	2.17	2.56
Acetone	(2.52) ^g	3.05	4.2	5.0	3.05	3.07
Acetonitrile	(2.55) ^g	2.72	3.1	5.0	2.72	2.43
Methanol	(2.54) ^g	3.54	2.9	6.5	3.54	3.16
Methyl acetate	(2.50) ^g	3.55	4.8	5.0	3.55	3.42
Nitromethane	(2.51) ^g	3.01	3.8	5.4	3.01	3.07
Water	2.57					
<i>Solutes for which U₀' could not be calculated</i>						
Cyclohexane	1.57		?	0.10		
Cyclohexene	1.82		?	0.72		
Carbon tetrachloride	1.69		5.0	?		
Dichloromethane	1.63		4.1	?		
Dibromomethane	2.18		4.6	?		
Chloroform	2.02		5.0	?		

^a Carrier gas: He saturated with H₂O at 21°.^b Thermal conductivity detection, 5.5 g adsorbent in 11 in. × 1/4 in. column, 60 ml/min carrier gas flow rate.^c Flame ionization detection, 1.25 g adsorbent in 11 in. × 1/8 in. column, 14 ml/min carrier gas flow rate.^d In units of 1/6 the area of a benzene molecule¹².^e Directly measured experimental values where possible^{21,34}, otherwise calculated according to ref. 12.^f From eqn. (2), assuming ε₀ equal —1.02, and using values of log V_a (—1.57) and α (0.57) from ref. 12.^g Value for water displacement peak.

$\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ at 83° . For 32 of these solutes it is possible to calculate A_s and S° values from previous LSC data. By rearrangement of eqn. (2) to express ε°_θ as a function of the remaining variables, a best average value of ε°_θ can be calculated from these data, equal -1.02 . Use of this value and the known values of α and $\log V_a$ from previous LSC studies¹² then permits the calculation of U_θ' values for each of these same 32 solutes. The resulting calculated values are compared in Table II with experimental values; the correlation is also shown graphically in Fig. 1. The overall agreement between experimental and calculated U_θ' values is impressive. The standard deviation between calculated and experimental values is ± 0.25 log units.

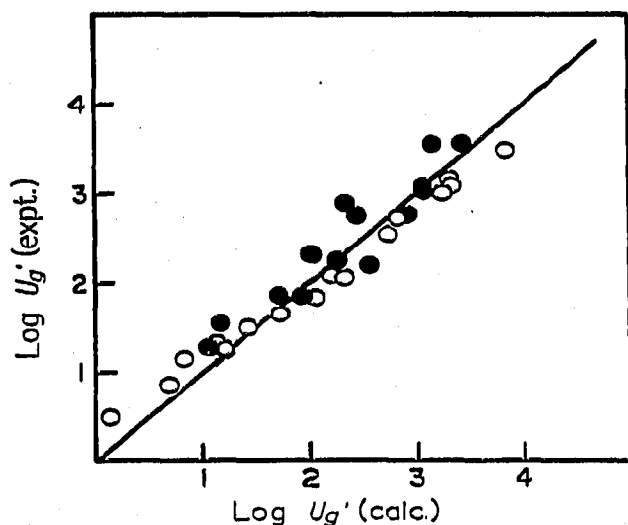


Fig. 1. Comparison of experimental U_θ' values with values calculated from eqn. (2): 2.7% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ at 83° . \circ = hydrocarbon values; \bullet = non-hydrocarbon values.

If we assume the 4.3 \AA^2 uncertainty in the A_s values of Table II which the correlation of Table I implies, this is equivalent to an uncertainty in the calculated values of U_θ' from Table II of ± 0.32 log units (4.3 \AA^2 is equal to $0.51 A_s$ units, and the uncertainty in U_θ' due to our assumed A_s values is then $\pm 0.51 \alpha \varepsilon^\circ_\theta$). Similarly, several of the S° values of Table II have been determined indirectly, and must be uncertain to the extent of at least $\pm 0.1-0.3$ log units, while the temperature extrapolation from room temperature¹² introduces an uncertainty of ± 0.1 log units in comparable LSC studies. Finally, similar correlations of eqn. (1) in LSC systems for data involving different eluents are never more precise than ± 0.1 log units, and the standard deviation tends to rise as the difference in eluent strengths increases; in the system of Table II we are essentially comparing two eluents of greatly differing strengths, pentane and He. On balance we can conclude that the correlation of Table II is certainly as good as could have been expected, and adequately verifies eqn. (2) as a sound relationship for correlating GSC and LSC data.

Additional data on a dryer adsorbent (1.5% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$) are shown in Table III and Fig. 2. Here, the ε°_θ value calculated from the data of Table II was used, so that these values of U_θ' could be calculated directly. For the five solutes with the exception of methyl iodide, the standard deviation between experimental and calculated U_θ' values is ± 0.26 log units, providing additional proof of the general validity of eqn. (2). The methyl iodide never cleared the column of 1.5% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$.

TABLE III

SOLUTE RETENTION VOLUMES FOR GSC SEPARATION OVER 1.5% H₂O-Al₂O₃ AT 83°^a

Solute	log U _g '		(A _g) ^b	(S°) ^b
	Exptl.	Calc. ^c		
n-Butane	1.15	1.20	5.0	0.02
n-Pentane	1.67	1.80	5.9	0.00
n-Hexane	2.19	2.40	6.8	0.02
1-Hexene	2.41	2.73	6.7	0.64
Carbon tetrachloride	2.24	2.55	5.0	2.09 ^d
Methyl iodide	> 3.0	1.64	3.7	2.0

^a Thermal conductivity detection, dry He carrier gas, 5.5 g adsorbent in 11 in. × 1/4 in. column, 60 ml/min carrier gas flow rate.

^b Same values as in Table II.

^c From eqn. (2); α equal 0.64, log V_a equal -1.40 (ref. 12); ϵ_g equal -1.02.

^d Calculated from U_g' value of Table I.

and is believed to have been catalytically decomposed by this more active alumina (probably by reaction with adsorbed water to give strongly held HI and methanol).

If solution interactions were significant in determining retention volume in LSC systems, these effects would be expected to be largest for the polar non-hydrocarbons of Table II. This in turn would result in apparently larger values of $-\epsilon_g^\circ$ for these solutes, since preferential solution interactions of pentane with the polar solutes would yield an effectively larger eluent strength for pentane. Similarly, the non-hydrocarbon data (solid circles of Fig. 1) would tend to lie above the average (solid line), while the hydrocarbon data (open circles) should lie below. If the two sets of compounds, hydrocarbons and non-hydrocarbons, of Table II are handled separately in determining ϵ_g° , values of ϵ_g° are obtained equal -1.00 and -1.06, respectively. While the value of $-\epsilon_g^\circ$ for non-hydrocarbons is thus slightly higher, the actual difference appears well within the experimental variability of the data. This is better illustrated by the extensive overlap of both open and closed circles in Fig. 1 about the solid line.

Some additional GSC retention volume data for separation on alumina have been reported in the literature, but in no case have sufficient data on the adsorbent

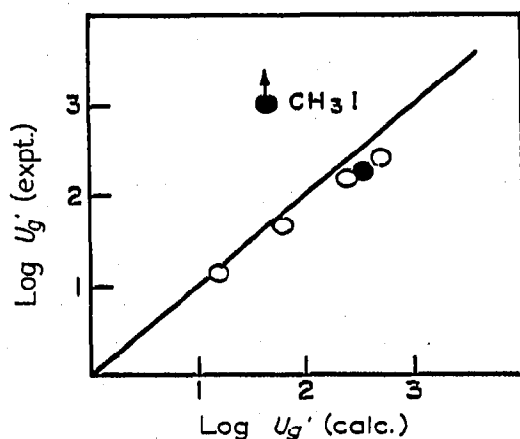


Fig. 2. Comparison of experimental U_g' values with values calculated from eqn. (2): 1.5% H₂O-Al₂O₃ at 83°. O = hydrocarbon values; ● = non-hydrocarbon values.

been reported to unambiguously determine the values of $\log V_a$ and α required by eqn. (2). If we assume that the "activity C" alumina reported by SCOTT³ is equivalent to fully deactivated Alcoa F-20 alumina (both adsorbents contain a monolayer of adsorbed water), the hydrocarbon retention volume data for this adsorbent (Appendix 2, ref. 3), can be correlated with eqn. (2) as shown in Fig. 3. The calculated values of U_g' appear to be uniformly low, implying that the surface volume V_a for SCOTT's adsorbent is higher than for Alcoa F-20 of similar deactivation; this seems not unreasonable. If $\log V_a$ is assumed 0.4 log units greater for SCOTT's alumina, a reasonable correlation of his data with eqn. (2) results (dashed line of Fig. 3). In any event,

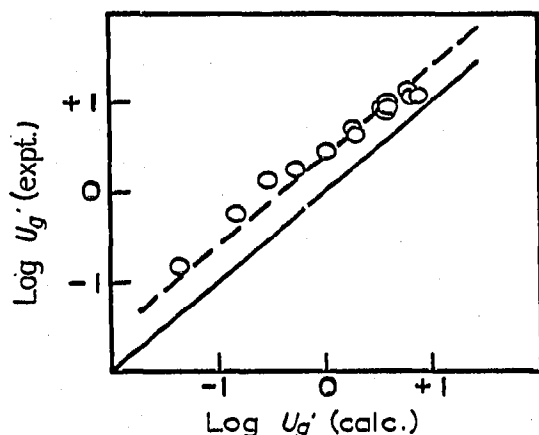


Fig. 3. Comparison of experimental U_g' values with values calculated from eqn. (2): Data of SCOTT³ (Appendix 2) for elution from alumina plus a monolayer of water at 15°; $\log V_a$ assumed equal -2.00 , α equal 0.57 in calculation. --- = calculated curve for $\log V_a$ equal -1.60 .

eqn. (2) predicts the correct relative retention volumes in Fig. 3 regardless of the value of $\log V_a$ assumed. We conclude that eqn. (2) is generally valid for predicting retention volume data in most GSC systems.

The *n*-alkane data of Figs. 1-3 show a definite tendency to fit a line of slightly lower slope, the calculated values for the small alkanes (C_1 - C_3) being low, and the values for the large alkanes (C_6 - C_{10}) high. This can be rationalized in terms of a small but consistent error in the calculation of the A_s values, as discussed in a later section.

DISCUSSION

Assuming the general validity of eqn. (2), there are a number of direct implications possible with respect to the potential of GSC in the separation of complex organic mixtures, particularly with alumina as adsorbent. First, with respect to the separation of isomers, eqn. (2) predicts that as long as the A_s values are equal (which is generally at least approximately true in the case of isomers), separation factors will be identical in LSC and GSC separation, assuming the same adsorbent, identical adsorbent activity, and equal column temperatures. This means that in principle many of the separation possibilities recognized in LSC can be transferred to GSC as well. However, the apparent advantage of GSC separation with respect to corresponding GLC systems tends to be reduced by two other considerations: GSC separations must always be carried out at higher temperatures and/or lower adsorbent

activities, which tends to reduce the separation factors for isomers, and many GLC systems show separations of isomers similar to those afforded by LSC (although frequently in reduced degree). Thus, while GIDDINGS¹ has referred to the good separation of *meta*- from *para*-xylene in a modified GSC system as an example of the unusual separations potentially available by GSC, many GLC systems are known which provide some separation of these two isomers. Similarly, while a number of similar separations of "positional" isomers in LSC over alumina have recently been cataloged²⁴, it is noted that these LSC separations become much poorer at low adsorbent activities. In general, we should conclude that reported isomer separations in LSC can provide useful guides for similar separations by GSC, that corresponding isomer separations will generally be less sharp by GSC than by LSC, and that we should not lose sight of the possibility of similar separations by GLC.

Another application of GSC which might appear potentially attractive arises from the marked selectivity of the metal oxides for polar molecules, permitting their ready separation by LSC from mixtures with less polar substances. It is interesting in this connection to compare the relative compound type selectivity of GSC over alumina with GLC separation over several common substrates. Table IV summarizes a number of experimental GLC data in this respect, along with calculated values for GSC over alumina. Compound type selectivity is here measured by the effect on solute retention volume of various polar groups, in terms of the equivalent number of methylene groups required to produce the same retention volume. It is seen that the selective retardation of the aliphatic hydroxyl, acetyl, and acetate groups on alumina ranges from 9-10 equivalent methylene groups, while the less polar

TABLE IV

COMPARISON OF COMPOUND TYPE SELECTIVITY IN GLC SEPARATION OVER VARIOUS LIQUID STATIONARY PHASES WITH GSC SEPARATION OVER ALUMINA

Solute group	Equivalent number of methylene groups ^a								
	GSC ^b		GLC ^c						
	P ^d	K ^e	R ^f	A ^g	B ^h	C ⁱ	O ^j	Q ^k	
-OH ^m	9.2	8.5	7.6	4.6	3.7	1.9	2.5	3.3	3.0
-CO-CH ₃ ^m	9.0	8.5	7.2	4.8	4.7	4.1	3.7	4.0	4.0
-CO ₂ CH ₃ ^m	9.8	7.7	6.7	4.9	4.5	4.3	4.3	4.2	3.9
-O- ^m	5.2	3.2	2.4	1.4	1.0	1.1	1.0	1.1	0.9
C ₆ H ₆ / <i>m</i> -C ₆ H ₁₄ ⁿ	1.4	3.7	3.4	1.6	1.2	1.1	0.5	0.7	1.6

^a Number of methylene groups required to replace group at right and give same solute retention volume.

^b Separation over alumina, any temperature; calculated values, eqn. (2).

^c Separation over indicated stationary phases at 100°; data of ref. 35.

^d Polydiethylene glycol succinate.

^e Polyethylene glycol.

^f Polyethylene glycol.

^g Diisodecyl phthalate.

^h Di-2-ethylhexyl sebacate.

ⁱ Silicone oil.

^j Silicone grease.

^k Apiezon "L".

^m Substituents on an alkyl chain.

ⁿ Increase in retention volume between benzene and *n*-hexane.

ether linkage increases retention volume by an equivalent of about 5 methylene groups. These calculated values would appear accurate to about ± 1 methylene group, on the basis of the correlation of Table II. The most polar liquid stationary phase, polydiethylene glycol succinate (P), is seen to be about equivalent to GSC over alumina in this regard, while the selectivity of the remaining stationary phases steadily declines as these liquids become less "polar". Similarly, the selectivity of GSC over alumina for unsaturated hydrocarbons can be measured by the increased retention volume of benzene relative to *n*-hexane; in this respect the data of Table IV show much *higher* selectivity in the case of the more polar GLC substrates than for GSC over alumina. While the data of SCOTT³ suggest that highly active aluminas may show somewhat increased selectivity for unsaturated hydrocarbons than indicated by LSC studies on less active adsorbents (Tables II-IV), the possibility of using GSC in separating the unsaturated hydrocarbons over highly active aluminas is ruled out by the experience of PETITJEAN AND LEFTAULT⁴, who noticed extensive reaction and loss of olefins under such conditions. Furthermore, separating even moderately complex (*i.e.* high molecular weight) samples by GSC appears to require highly deactivated adsorbents for convenient retention times, as well as for suppressing adsorbent catalyzed sample reactions. On balance, it appears that GSC over alumina offers little advantage over GLC with polar substrates in the selective separation of polar from non-polar sample components. Because of the similarity of the various metal oxide adsorbents in this respect (*e.g.* see comparison of alumina, silica, and Florisil³⁶), the same generalization can doubtless be applied to other metal oxide adsorbents as well.

A most important problem in GSC separation is the extension of the technique to as high boiling samples as possible, and some workers (*e.g.* ref. 5) have regarded the upper sample boiling point limitation in GSC to be higher than for GLC, because of the volatility and decomposition of liquid substrates at sufficiently high temperatures. The preceding study of alumina, in conjunction with the development of eqn. (2), permits us to examine the question of sample boiling point limitation in GSC in some detail. A major necessity for high temperature GSC operation with metal oxide adsorbents is heavy deactivation of the adsorbent, since a combination of high temperature and active adsorbent invariably results in reaction of some sample components during separation; furthermore, it has been noted in our laboratory³⁷ that GSC separations over undeactivated alumina at the highest temperatures practically lead to a much lower sample boiling point limit than in conventional GLC separation, because of the very strong adsorption of most molecules on such an adsorbent. This observation can be confirmed by simple calculation from eqn. (2): at 400° it is estimated that the U_0' value of *n*-C₃₀H₆₂ is about $5 \cdot 10^6$ (ml/g) on undeactivated alumina; under the same flow rates and column loadings of Table II, an elution time of about one year would be required!

Adsorbent deactivation by water as in the present studies is obviously restricted to lower temperature operation, since maintaining a deactivated adsorbent at high temperatures involves prohibitive water partial pressures in the carrier gas. For the present alumina, for example, it was found that the equilibrium water vapor pressure over 2.7% H₂O-Al₂O₃ is 1.4 mm at 24° (static measurement) and 18 mm at 83° (data of Table II). If a constant heat of water adsorption is assured, this means that use of 2.7% H₂O-Al₂O₃ at 150 and 250° would require water partial pressures

in the carrier gas of 140 and 1100 mm, respectively. Since it is unlikely that a more active alumina than this would be desirable in most GSC separations of heavy samples, the upper column temperature limit with water deactivation would seem to be about 250°. Under these conditions it can be calculated that $n\text{-C}_{20}\text{H}_{42}$ would have a U_g' value of about 10^4 ml/g, and would require about 16 h to elute, for a column size and eluent flow rate similar to that used in Table II.

A number of procedures other than elution with water vapor have been suggested for adsorbent deactivation in GSC, which seem suited for higher temperature GSC operation. Addition of up to a monolayer of nonvolatile liquid (or solid) to the adsorbent would seem to accomplish the same function as water addition, and would not require addition of excessive amounts of vapor to the carrier gas in order to maintain the deactivation of the adsorbent. PETITJEAN AND LEFTAULT⁴ used Apiezon L and polyester succinate to deactivate alumina coated capillaries, and claimed no change in the selectivity of the adsorbent for olefins and paraffins. SCOTT³, however, found that addition of silicone oil to alumina gave a complex combination of adsorption and partition effects. Experiments to be described in a following paper on GSC with an adsorbing carrier gas also show considerable adsorption of solutes on the surface of adsorbed vapor, and it is likely that similar adsorption on the deactivating liquid would occur in GSC with adsorbents deactivated by heavy liquids. Possibly the proper application of a deactivating non-volatile liquid to the adsorbent, so as to cover 50–90% of the surface in a monolayer and remove all active sites, would show a minimum of partition and adsorption on the deactivating liquid, but this remains to be investigated experimentally. PETITJEAN AND LEFTAULT⁴ have also suggested deactivating the surface of metal oxides with a layer of decomposition products (presumably carbon) formed by the *in situ* pyrolysis of an organic compound. This technique may eventually show some promise, although the latter workers were unsuccessful in applying it to their GSC system. A major problem in such a deactivation procedure is the production of large amounts of finely divided carbon on which adsorption can occur, leading effectively to GSC on carbon rather than the original metal oxide adsorbent. Finally, SCOTT⁵ has used NaOH to deactivate alumina to the point where $n\text{-C}_{30}\text{H}_{74}$ was eluted below 400°. The data of SCOTT⁵ can be used to calculate a surface volume and activity function for his adsorbent at 250°, 40% NaOH– Al_2O_3 : $\log V_a$, –1.8; α , 0.22, compared with values calculated for fully deactivated (monolayer adsorbed water) Alcoa F-20 at 250° of $\log V_a$, –2.0; α , 0.27. The major question with respect to SCOTT's adsorbent is what relationship it has to alumina, since sufficient NaOH has been added to produce several monolayers of adsorbed NaOH. The above adsorbent parameters suggest that 40% NaOH– Al_2O_3 is not greatly different from alumina deactivated with just less than a monolayer of adsorbed water, but this comparison may not be a critical one.

Other techniques for deactivating the adsorbent during GSC separation include elimination of small pores, which are believed to correspond to active adsorption sites⁶, and the use of adsorbing vapors in the carrier gas⁹ (other than water for surface deactivation). The former technique may well prove one of the most promising in this regard, while the latter technique can be further broken down into use of adsorbing carrier gas components plus water, and higher boiling substances instead of water. Both of these latter techniques are examined in a following paper.

The present studies contain certain implications for the theory of LSC as well as

GSC separation. Beyond verifying the assumption of negligible net solution interaction energies contained in our previous theory of LSC separation, the general validity of this LSC theory has been further confirmed by the extreme extrapolation involved in going from LSC to GSC systems. The present investigation has also been responsible for a further improvement in the calculation of solute A_s values for LSC as well as GSC systems (Table I). In this connection it should be pointed out that the calculation procedure of Table I gives the A_s values of the n -alkanes as $1.4 + 0.9n$, where n is the number of carbon atoms in the alkane. The data of Tables II to IV and Figs. 1 to 3, however, strongly suggest that a more accurate value is $A_s = 2.1 + 0.75n$. This change provides a small improvement in the fit of the latter data to eqn. (2), but makes quite a considerable change in calculation of U_0' for the larger n -alkanes as presented earlier in this section. The latter relationship for A_s was assumed in these calculations.

Another addition to the theory of LSC provided by the present study has been the measurement of S° values on alumina for the compounds CCl_4 , CHCl_3 , and CH_2Cl_2 (2.1, 2.7, 2.9, respectively), which in turn permits the calculation of eluent strength values ε° for these solvents as in a previous treatment²¹ (see Table V).

TABLE V
ELUENT STRENGTH VALUES FOR DIFFERENT SOLVENTS

Eluent	ε°	
	Exptl.	Calc.
CCl_4	0.18	0.33
CHCl_3	0.40	0.37
CH_2Cl_2	0.42	0.43

Agreement between calculated and experimental ε° values is satisfactory for the last two eluents, but the calculated value is considerably too high for CCl_4 . This suggests some peculiarity in the elution behavior of CCl_4 which deserves further study.

Finally, if we recognize that the adsorption energy of the He carrier gas used in the present study is actually zero, or close to it, then we can set up an absolute scale of ε° values (adsorption energies per unit area) to replace the previous relative scale based on pentane as reference eluent (for alumina as adsorbent). The revised absolute ε° values then range from 0.00 for He, to 1.02 for n -pentane, and 1.97 for methanol. The range 1.02 to 1.97 corresponds to normal LSC separation (no known liquid eluents are significantly weaker than pentane), and absolute values of ε° close to 0.00 correspond to normal GSC. It is interesting to speculate on what sort of separations would involve absolute ε° values intermediate between 0.00 and 1.00. The use of a strongly adsorbing carrier gas (other than the water required to maintain adsorbent activity) is a possibility examined in a following paper. Another possibility is use of eluents maintained at the critical state by means of high temperatures and pressures, where the eluent properties of the solvent should be intermediate between those of the liquid and gas phase; related separations have been described by KLESFER AND CORWIN³⁸. Separations carried out in this area intermediate between LSC and GSC are virtually unknown, and it seems worthwhile to investigate their potential.

SUMMARY

A simple theory is proposed which relates solute retention volume in gas-solid and liquid-solid chromatography, and a quantitative equation has been derived which permits retention volume in gas-solid chromatography to be predicted upon the basis of previously measured liquid-solid chromatographic data. A number of experimental retention volume data have been measured for the gas-solid chromatographic separation of several solutes on alumina of varying water content; these data are accurately correlated by the above equation, verifying the theory. The future potential of gas-solid chromatography for the separation of complex organic mixture has been briefly examined in terms of the theory, and some of the problems of gas-solid chromatography are discussed.

REFERENCES

- 1 J. C. GIDDINGS, *Anal. Chem.*, 36 (1964) 1171.
- 2 F. T. EGGERSTEN, H. S. KNIGHT AND S. GROENINGS, *Anal. Chem.*, 28 (1956) 303.
- 3 C. G. SCOTT, *J. Inst. Pet.*, 45 (1959) 118.
- 4 D. L. PETITJEAN AND C. J. LEFTAULT, *J. Gas Chromatog.*, 1, No. 3 (1963) 18.
- 5 C. G. SCOTT AND D. A. ROWELL, *Nature*, 187 (1960) 143.
- 6 V. S. VASIL'eva, I. V. DROGALEVA, A. V. KISELEV, A. YA. KORABLEV AND K. D. SHCHERBAKOVA, *Doklady Akad. Nauk SSSR*, 136 (1961) 852.
- 7 A. V. KISELEV, YU. S. NIKITIN, R. S. PETROVA, K. D. SHCHERBAKOVA AND YA. I. YASHIN, *Anal. Chem.*, 36 (1964) 1526.
- 8 I. HALÁSZ AND C. HORVÁTH, *Anal. Chem.*, 36 (1964) 1178.
- 9 S. A. GREENE AND H. E. ROY, *Anal. Chem.*, 29 (1957) 569.
- 10 R. D. SCHWARTZ, D. J. BRASSEUX AND G. R. SHOEMAKE, *Anal. Chem.*, 35 (1963) 496.
- 11 L. R. SNYDER, *J. Chromatog.*, 11 (1963) 195.
- 12 L. R. SNYDER, *Adv. Anal. Chem. Instr.*, 3 (1964) 251.
- 13 F. H. DICKEY, *Proc. Natl. Acad. Sci. U.S.*, 35 (1949) 227; *J. Phys. Chem.*, 59 (1955) 695.
- 14 R. J. P. WILLIAMS, C. HAGDAHL AND A. TISELIUS, *Arkiv Kemi*, 7 (1954) 1.
- 15 B. J. MAIR, in I. M. KOHLTOFF AND P. J. ELVING (Editors), *Treatise on Analytical Chemistry*, Part I, Vol. 3, Interscience, New York, 1961, p. 1498.
- 16 LU PEI-CHANG AND K'ANG T'AN, *Jan Liao Hsüeh Pao*, 1 (1960) 47; *C. A.*, 54 (1960) 25704.
- 17 M. C. SIMMONS AND L. R. SNYDER, *Anal. Chem.*, 30 (1958) 32.
- 18 W. SCHNEIDER, H. BRUDERRECK AND I. HALÁSZ, *Anal. Chem.*, 36 (1964) 1533.
- 19 J. H. GRIFFITHS, D. H. JAMES AND C. S. PHILLIPS, *Analyst*, 77 (1952) 897.
- 20 L. H. KLEMM, E. P. ANTONIADES, G. CAPP, E. CHIANG AND E. Y. K. MAK, *J. Chromatog.*, 6 (1961) 420.
- 21 L. H. KLEMM AND S. K. AIREE, *J. Chromatog.*, 13 (1964) 40.
- 22 L. R. SNYDER, *J. Chromatog.*, 16 (1964) 55.
- 23 L. R. SNYDER, *J. Chromatog.*, 17 (1965) 73.
- 24 L. R. SNYDER, *J. Chromatog.*, to be submitted.
- 25 J. JANÁK, *Collection Czech. Chem. Commun.*, 18 (1953) 798.
- 26 L. R. SNYDER, *J. Chromatog.*, 5 (1961) 430; 8 (1962) 178.
- 27 C. PIERCE AND B. EWING, *J. Phys. Chem.*, 68 (1964) 2562.
- 28 A. V. KISELEV, in D. H. EVERETT AND F. S. STONE (Editors), *Structure and Properties of Porous Materials*, Academic Press, New York, 1958, p. 201.
- 29 M. P. MAKSIMOVA, E. E. VASSERBERG AND A. A. BALANDIN, *Izv. Akad. Nauk SSSR, Old. Khim. Nauk*, (1963) 17.
- 30 H. K. LIVINGSTON, *J. Colloid Sci.*, 4 (1949) 447.
- 31 W. F. K. WYNNE-JONES, in D. H. EVERETT AND F. S. STONE (Editors), *Structure and Properties of Porous Materials*, Academic Press, New York, 1958, p. 38.
- 32 L. PAULING, *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, N.Y., 1940, Chapt. V.
- 33 C. PIERCE, personal communication.
- 34 L. R. SNYDER, *J. Chromatog.*, 6 (1961) 22; 8 (1962) 319; *Anal. Chem.*, 33 (1961) 1538.
- 35 P. R. SCHOLLY AND N. BRENNER, *Inst. Soc. Am. Proc.*, 2 (1959) 111.
- 36 L. R. SNYDER, *J. Chromatog.*, 12 (1963) 488.
- 37 E. C. SCHULTER, personal communication.
- 38 E. KLESPPER AND A. H. CORWIN, *J. Org. Chem.*, 27 (1962) 700.