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RETENTION PARAMETERS IN GAS CHROMATOGRAPHY

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RETENTION PARAMETERS IN GAS CHROMATOGRAPHY

Abstract

The paper presents a revision of terms in Chapter 3.6 THE MOBILE PHASE and Chapter 3.7 RETENTION PARAMETERS IN COLUMN CHROMATOGRAPHY of the NOMENCLATURE FOR CHROMATOGRAPHY {*"Nomenclature for Chromatography (IUPAC recommendations 1993)"*, *Pure and Applied Chemistry*, **65** 819-872 (1993)}. with the aims of (i) emphasizing the physical meaning of the terms and (ii) specifying the temperatures and pressures for the terms for gas volumes and flow rates. A number of the original terms were found to be misleading or superfluous, including such terms as *corrected retention time*, *net retention time*, *total retention volume (time)*, *specific retention volume at 0 °C*, *relative pressure*, and their usage is strongly discouraged. Chapter 1.1 BASIC DEFINITIONS was supplemented with the terms *chromatographic system* and *chromatographic process*.

INTRODUCTION

This paper reexamines the terms for retention parameters in gas chromatography described previously in Chapter 3.6 and 3.7 of *The Nomenclature for Chromatography* [1] with the aims of (i) emphasizing the physical meaning of the terms and (ii) specifying the temperatures and pressures for the terms for gas volumes and flow rates.

When developing the theory of a process and defining the basic phenomena to be observed and the parameters to be measured during the process, one has to start by considering an idealized system. Thus, the ideal gas chromatographic system consists of an ideal gas mobile phase and an ideal liquid or solid stationary phase. This means that the mobile phase behaves and compresses like an ideal gas, thus meeting the requirements of the basic gas state equation

$$p \cdot V / T = nR = \text{constant} \quad (1),$$

whereas the stationary phase is totally incompressible. Moreover, the carrier gas is assumed to be insoluble in the stationary liquid phase and unretained by the solid adsorbent. It is further assumed that the molecules of the carrier gas do not interact with analyte molecules and do not compete with the interactions of the latter with the stationary phase. Needless to say, it is assumed that the chromatographic column has a constant diameter and the stationary phase is evenly packed in the column.

In this case, the retention of the solute (analyte) will depend only on its interaction with the stationary phase. Differences in the interactions of solutes with the stationary phase provide the basis for all types of chromatographic separations. In linear equilibrium chromatography it is further assumed that the equilibrium distribution of the solutes between the two phases of the chromatographic system is instantly established at every position in the moving chromatographic bands, so that only thermodynamic, and not kinetic phenomena have to be considered when describing the idealized chromatographic system.

The simplest way to quantitatively characterize the interaction of a solute with the stationary phase is by measuring the rate of migration of the solute along the

column and comparing this rate with the flow rate of the carrier gas (or, which is the same, with the migration rate of a hypothetical unretained test compound). Flow rates and migration rates are the volumes of the mobile phase which pass any column cross section in a specified period of time.

What we can measure in a typical gas chromatographic experiment, are the *inlet pressure* (p_i), *outlet pressure* (p_o), *ambient pressure* (p_a), *column temperature* (T_c), *ambient temperature* (T_a), and the *volume* (V) of mobile phase that leaves the column outlet in defined periods of *time* (t), and hence, the carrier gas *flow rate* (F).

Since the volume of a gas varies markedly with temperature and pressure, these two parameters have always to be precisely specified for any measured volume. If there is no restrictor installed at the column outlet and if the pressure drop within the detector is negligibly small, the column outlet pressure equals the ambient pressure, $p_o = p_a$. (In the case of linked gas chromatography-mass spectrometry, the outlet column pressure is often close to the vacuum in the mass spectrometer.) However, even in the case that the column temperature does not differ from the ambient temperature, the gas volume measured at the column outlet does not characterize the elution process inside the column, since the gas pressure in the column will differ from that outside. The pressure gradually drops from the value at the column inlet to that at the outlet. Consequently, the mobile phase gas expands as it moves along the column. Accordingly, gas volume flow rates, when measured at different cross sectional positions along the column, would show a gradual increase. These changes in the gas pressure, volume and flow rate are not linear within the column. The changes are slow at the beginning, but become more significant towards the column outlet. In order to characterize the chromatographic process in the column by using elution volumes, that were measured at ambient temperature and pressure at the column outlet, these values of the gas volume have to be corrected for the temperature and compressibility of the gas. In other words, the volumes have to be calculated for the column temperature and the appropriate gas pressure in the column, namely, *the average gas pressure over the column length* (\bar{p}).

In order to derive a formula for calculating the average gas pressure from the pressure at the column inlet and outlet, three important statements have to be accepted:

- (i) the averaged gas pressure value should meet the requirements of the basic ideal gas equation (1),
- (ii) *the volume of the mobile phase (carrier gas) that is contained in the column at any instant, irrespective of the nature of the gas, its viscosity, pressure, flow rate, pressure drop, or temperature, must be equal to the geometrical volume of space that is available for the mobile phase, that is the void volume (V_o) of the column.*
- (iii) *An unretained solute must elute from the column with the void volume of the mobile phase in the column.*

In gas chromatography, the volume of the mobile phase which is required for the elution of an unretained compound is measured experimentally *under ambient conditions* (V_M^a). It differs from the volume of the mobile phase in the column because the ambient pressure and temperature differ from the actual conditions within the column. (Extra-column volumes comprising the volumes of the sample injector, the detector, and connecting lines are assumed to be negligibly small and are not considered here). According to (i) - (iii), the following relationships must be valid:

$$\bar{p} \cdot V_o / T_c = p_o \cdot V_M^a / T_a \quad (2)$$

$$V_o = V_M^a \cdot (T_c / T_a) \cdot (p_o / \bar{p}) \quad (3),$$

which should allow the calculation of the actual gas volume involved in the elution of the unretained compound $V_o (\bar{p}, T_c)$ from the measured gas volume $V_M^a (p_o, T_a)$.

In equation (3), the temperature correction factor, (T_c/T_a) is usually larger than 1, since gas chromatography is normally conducted at elevated column temperatures. The term $p_o / \bar{p} = j$, called *the mobile phase compressibility correction factor*, is always smaller than 1 and shows to which extent the mobile phase was compressed while in the column, compared to the situation at the column outlet, where it was exposed to a lower pressure p_o . Symbol j was chosen for this correction factor (4), to commemorate James and Martin who first calculated and introduced this term as early as 1952 [2]:

$$j_3^2 = \frac{3}{2} \cdot \frac{(p_i / p_o)^2 - 1}{(p_i / p_o)^3 - 1} = p_o / \bar{p} \quad (4)$$

A detailed derivation of equation (4) for the compressibility correction factor, that provides the averaging of ideal carrier gas pressure over the column length, can be found in the literature [3, 4]. In the second reference [4], it was also shown that, alternatively, averaging of the varying pressure to which the analyte is exposed can be done over the time that the solute resides in the column. In this case, however, another j factor must be used, namely j_4^3 . Similarly, by using two different j factors, j_2^1 and j_3^2 , the flow rate F of the carrier gas can be averaged either over the column length or over the time of residence of a sample in the column. These various j values are presented in Table 1, according to the general expression by Everett [5] for different mobile phase compressibility correction factors:

$$j_n^m = \frac{n}{m} \cdot \frac{(p_i / p_o)^m - 1}{(p_i / p_o)^n - 1} \quad (5).$$

Table 1. Average values of mobile gas phase pressure and flow rates in a chromatographic column [4] (at $T_c = T_a$)

Averaging over the column length ($x=L$)		Averaging over the time ($t=t_M$) of residence of an unretained compound in the column	
Average pressure	Average flow rate	Average pressure	Average flow rate
$\bar{p}_x = p_o / j_3^2$	$\bar{F}_x = F_o \cdot j_2^1$	$\bar{p}_t = p_o / j_4^3$	$\bar{F}_t = F_o \cdot j_3^2$

From Equation (5), $m=1$, $n=2$ when the flow rate is averaged over the column length; $m=2$, $n=3$ when the pressure is averaged over the column length or the flow rate is averaged over time; $m=3$, $n=4$ when the pressure is averaged over the time that a solute resides in the column. For ideal as well as traditional gas chromatography, i.e., at moderate pressures and pressure drops, the “classical” James and Martin’s factor j_3^2 should be applied for calculating corrected retention parameters. Equations that incorporate j_4^3 and even j_5^4 have been suggested for chromatography with non-ideal carrier gases, especially at elevated pressure values and flow rates [6, 7].

The James and Martin compressibility correction factor j_3^2 can thus convert all volumes which were measured under ambient pressure conditions at the column outlet into the corresponding volumes *under the pressure averaged over the column length*:

$$\begin{aligned} \text{Corrected gas hold-up volume} & \quad V_M^o = V_M \cdot j_3^2 \\ \text{Corrected retention volume} & \quad V_R^o = V_R \cdot j_3^2 \\ \text{Net retention volume} & \quad V_N = (V_R - V_M) \cdot j_3^2 \end{aligned}$$

After being corrected for temperature and pressure* the hold-up volume becomes identical to the mobile phase volume in the column, i.e., the geometrical void volume of the column ($V_M^o = V_o$). Similarly, the corrected solute retention volume becomes expressed in the same volume units of the mobile phase under the actual conditions of chromatography. Therefore, the corrected retention and hold-up volumes can be simply related to the retention factor (k) as:

$$V_R^o = (1 + k) \cdot V_M^o \quad (6).$$

It is necessary to emphasize that the corrected (for temperature and pressure) retention volumes of analytes, as solute-characteristic retention parameters, are *independent of the pressure* of the carrier gas (both inside and outside the column). In full agreement with the initial model of ideal gas chromatography, they are entirely determined by the intensity of interaction of the solutes with the stationary phase not with the mobile phase and acquire therefore thermodynamic meaning. The thermodynamic significance is especially evident for the *specific retention volumes* (V_g , V_v , V_s) which are obtained by normalizing the *net retention volumes*, respectively, for the weight, volume of the stationary phase in the column or the surface area of the solid packing in the column. Specific retention volumes are proportional directly (or in the case of V_v equal) to the corresponding *distribution coefficients* K of the solutes between the stationary and mobile phases contained in the column at the column temperature [4].

While being independent of the pressure conditions during the chromatographic experiment, the corrected and specific retention volumes are still strongly dependent on the column temperature. If the free energy of transfer of the solute from the ideal gas phase into the liquid phase is ΔG , the temperature dependence of the distribution

* If the initial volume or flow rate was measured using a so-called soap bubble flow-meter, a third correction factor, $(1 - p_w/p_o)$, must be introduced, where p_w is the partial pressure of water vapor at ambient temperature, to take into account the dilution of the effluent gas with water vapor.

coefficients (and retention volumes) follows from the fundamental thermodynamic equation (7):

$$\Delta G = -RT_c \cdot \ln K = -RT_c \cdot \ln V_v \quad (7)$$

Accordingly, $\ln K$ and $\ln V_v$ should vary linearly with the inverse column temperature:

$$\ln V_v = -(\Delta G / R) \cdot 1 / T_c = -(\Delta H / RT_c + \Delta S / R) \quad (8)$$

which, indeed, was repeatedly shown to be the case (within temperature ranges where ΔH and ΔS remain constant). It is natural that corrected for column-averaged pressure and real column temperature values of retention volumes should be taken for plotting against inverted temperature according to (8). It must be mentioned in this connection that many text books, as well as the IUPAC document [1], misleadingly introduce a value called *specific retention volume at 0 °C*, which is obtained by multiplying the specific retention volumes by the ratio $(273.15/T_c)$. This term attempts to provide a base for comparing retention parameters at a standard temperature of 0 °C. As shown in the work of Davankov and Parcher [3, 8, 9], such a “recalculation to standard temperature” will significantly distort the actual relationship between retention volumes measured at different temperatures and it should never be applied. It is the volume, not the mass of the mobile phase that matters in the chromatographic elution process. Therefore, retention volumes can represent the process thermodynamics only under the condition that they relate to the actual situation in the column with respect to temperature and pressure.

Equally misleading are the recommended terms in ref [1], *corrected retention time* and *net retention time*, which incorporate the *mobile phase compressibility correction factor (j)*, as explained in [8]. Time has nothing to do with gas compressibility. This error is caused by the lack of a precise definition of the compressibility correction factor, which would clearly emphasize its simple and sole physical meaning, that is $p_o / \bar{p} = j$.

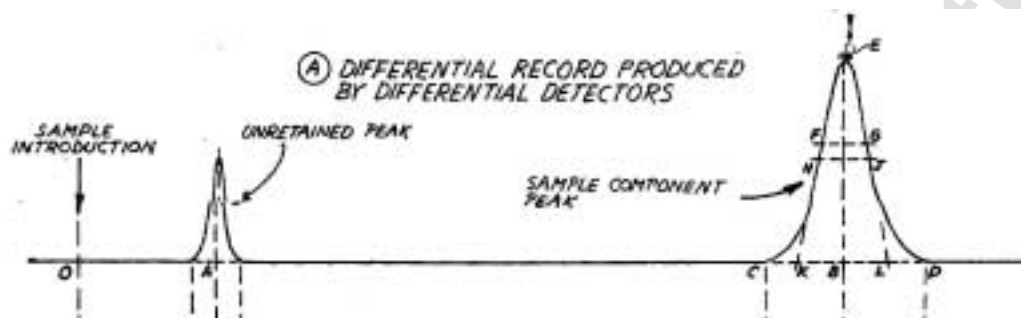
To take into account the physical sense of the j factors and paying attention to the averaging modes and actual pressures and temperatures of the carrier gas, the definitions of terms dealing with the mobile phase flow rate must also be provided with the relevant additional information, such as :

The mobile phase flow rate at the column cross section where the pressure is equal to the pressure averaged over the column length $F_{\bar{p}} = F_a \cdot j_3^2 \cdot (T_c / T_a)$.

The following section Terms and Definitions redefines only those terms (as compared to Chapter 3.6 and 3.7 in the original Nomenclature for Chromatography [1]) which require changes, as a consequence of the revised physical meaning of the measured or calculated chromatography conditions and solute retention parameters that are outlined above.

REVISED AND NEW TERMS AND DEFINITIONS

Changes from the recommendation given in [1]. References to Figures are to those in reference [1].



1.1 BASIC DEFINITIONS

1.1.01.1 Chromatographic system

A system formed by at least two immiscible phases in contact with each other, one of which is continuously moving relative to the other. Normally, one of the phases remains stationary, and is that part of the chromatographic system responsible for the retention of the analytes, whereas the moving part is responsible for their transportation.

1.1.01.2 Chromatographic process

The phase distribution that takes place when an analyte (or a mixture of analytes) is carried along the stationary phase by the movement of the mobile phase.

3.6 THE MOBILE PHASE

3.6.03 Mobile Phase Compressibility Correction Factor (j_3^2)

The ratio of the gas pressure at the column outlet (p_o) to the gas pressure in the column averaged over the column length (\bar{p}):

$$j_3^2 = p_o / \bar{p}$$

James and Martin presented the following equation for calculating the factor j_3^2 for an ideal carrier gas from its inlet pressure (p_i) and outlet pressure (p_o):

$$j_3^2 = \frac{3}{2} \cdot \frac{(p_i / p_o)^2 - 1}{(p_i / p_o)^3 - 1} = p_o / \bar{p}$$

Note: The factor j_3^2 is always smaller than 1. It shows the extent to which the mobile phase is compressed when residing in the column, as compared to the situation at the column outlet, where it is exposed to a smaller pressure, p_o , usually ambient pressure, p_a .

3.6.04 *Flow Rate*

The volume of mobile phase passing through the column in unit time. Since, in gas chromatography, the mobile phase is a compressible gas, the corresponding pressure and temperature conditions must be always specified.

3.6.04.1 *Carrier Gas Flow Rate at Ambient Temperature and Ambient Pressure (F_a)*

Carrier gas flow rate measured at the column outlet under ambient temperature and ambient pressure.

Note: Gas flow rate is often measured at the column outlet at ambient pressure (p_a) and ambient temperature (T_a in K) using a water-containing flow meter (the so-called soap bubble meter); this value is indicated with the symbol F . Since the carrier gas becomes diluted with water vapor in the soap bubble meter, the measured flow rate F must be corrected (reduced):

$$F_a = F \cdot (1 - p_w / p_a)$$

where p_w is the partial pressure of saturated water vapor at ambient temperature.

3.6.04.2 *Carrier Gas Flow Rate at Column Temperature and Ambient Pressure (F_c)*

Carrier gas flow rate at the column outlet corrected for column temperature and ambient pressure.

$$F_c = F_a \cdot (T_c / T_a) = F \cdot (1 - p_w / p_a) \cdot (T_c / T_a)$$

3.6.04.3 *Corrected Carrier Gas Flow Rate (Carrier Gas Flow Rate in the Column Cross Section with Pressure Equal to that Averaged over Column Length)*

$$(F_c^o = F_{\bar{p}})$$

Carrier gas flow rate corrected for column temperature and pressure averaged over column length.

$$F_c^o = F_{\bar{p}} = F_c \cdot j_3^2 = F_a \cdot (T_c / T_a) \cdot j_3^2 = F \cdot (1 - p_w / p_a) \cdot (T_c / T_a) \cdot j_3^2$$

3.6.04.4 *Carrier Gas Flow Rate Averaged over Column Length (\bar{F}_x)*

Carrier gas flow rate corrected for column temperature and averaged over column length.

$$\bar{F}_x = F_c \cdot j_2^1 = F_a \cdot (T_c / T_a) \cdot j_2^1 = F \cdot (1 - p_w / p_a) \cdot (T_c / T_a) \cdot j_2^1$$

$$\text{where } j_2^1 = 2 \cdot \frac{(p_i / p_o) - 1}{(p_i / p_o)^2 - 1}$$

3.7 RETENTION PARAMETERS IN COLUMN CHROMATOGRAPHY

3.7.03.1 *Hold-up Volume (at column temperature and ambient pressure) (V_M)*

The volume of the mobile phase required to elute the unretained compound from the chromatographic column and reported at column temperature and ambient pressure.

$$V_M = t_M \cdot F_c$$

Note: In gas chromatography and supercritical fluid chromatography, this value does not represent the mobile phase volume in the column.

3.7.03.3 *Hold-up Time (t_M)*

Time required for the mobile phase to pass through the chromatographic column. (Residence time of an unretained compound in the chromatographic column.)

Note: The *hold-up time* corresponds to the distance OA in Fig. 1, if the extra-column volumes have been eliminated. Sometimes it is also referred to as t_0 . This symbol, however, should be reserved to denote the retention time of an unretained compound in *exclusion chromatography*. Its use in *elution chromatography* is discouraged.

3.7.04 *Corrected Carrier Gas Hold-up Volume (at column temperature and pressure averaged over column length) (V_M^o)*

The volume of the mobile phase required to elute the unretained compound from the chromatographic column and reported at column temperature and pressure averaged over column length:

$$V_M^o = V_M \cdot j_3^2 = t_M \cdot F_c \cdot j_3^2 = t_M \cdot F_c^o$$

Note: The corrected gas hold-up volume equals the geometrical void volume of the column that is available to the mobile phase, $V_M^o = V_0$.

3.7.05.1 *Retention Volume (at column temperature and ambient pressure) (V_R)*

The volume of the mobile phase required to elute the compound of interest from the chromatographic column and reported at column temperature and ambient pressure.

$$V_R = t_R F_c$$

3.7.05.3 *Retention Time (t_R)*

Time required for the analyte to pass through the chromatographic column. (Residence time of the analyte in the chromatographic column.)

Note: The retention time corresponds to the distance OB in Fig.1A, if the extra column volumes have been eliminated.

3.7.07.1 *Adjusted Retention Volume (at column temperature and ambient pressure) (V_R')*

The retention volume minus the hold-up volume:

$$V_R' = V_R - V_M = (t_R - t_M) \cdot F_c$$

3.7.07.2 *Adjusted Retention Time (t_R')*

The retention time minus the hold-up time.

$$t_R' = t_R - t_M$$

Note: The adjusted retention time corresponds to the distance AB in Fig.1A.

3.7.08 *Corrected Retention Volume (at column temperature and pressure averaged over column length) (V_R^o)*

The volume of the mobile phase required to elute the compound of interest from the chromatographic column and reported at column temperature and pressure averaged over column length.

$$V_R^o = V_R \cdot j_3^2 = t_R \cdot F_c \cdot j_3^2$$

3.7.09 *Net Retention Volume (at column temperature and pressure averaged over column length) (V_N)*

The adjusted retention volume reported at column temperature and pressure averaged over column length:

$$V_N = V_R^o - V_M^o = V_R' \cdot j_3^2 = (t_R - t_M) \cdot F_c \cdot j_3^2 = t_R' \cdot F_c^o$$

3.7.11 *Specific Retention Volume (at column temperature and pressure averaged over column length) (V_g, V_v, V_s)*

The net retention volume per unit weight of stationary phase (V_g), unit volume of the stationary liquid phase (V_v), or unit surface area of the solid column packing (V_s).

TERMS TO BE DROPPED

These terms are regarded as obsolete and their use is strongly discouraged

3.6.02.4 *Relative Pressure (P)*

$$P = p_i / p_o$$

This term is superfluous. Moreover, P is dimensionless and should not be called “pressure”. Usage of the term is strongly discouraged.

3.7.05 *Total Retention Volume (Time)*

These terms are confusing in that they seem to include *the extra-column volume* (or the time required for the mobile phase to pass through *the extra-column volumes*), which they should not. Usage of the terms is strongly discouraged.

3.7.08 *Corrected Retention Time ($t_{R^{\circ}}$)*

The total retention time multiplied by the compressibility correction factor (j)

This term erroneously includes the *mobile phase compressibility correction factor* (j), as explained in [8]. Usage of the term is strongly discouraged.

3.7.09 *Net Retention Time (t_N)*

This term erroneously includes the *mobile phase compressibility correction factor* (j), as explained in [8]. Usage of the term is strongly discouraged.

3.7.11. 2 *Specific Retention Volume at 0 °C*

By multiplying the specific retention volume with the ratio ($273.15/T_c$), this term attempts to provide a base for comparing retention parameters at a standard temperature of 0 °C. As shown in [3, 8, 9], such a “recalculation to standard temperature” will significantly distort the actual relationship between the retention volumes measured at different temperatures and should not be applied. The use of this expression is strongly discouraged.

TABLES

Terms and symbols which have been defined or revised.

LIST OF TERMS

Adjusted retention time	3.7.07.2
Adjusted retention volume (at column temperature and ambient pressure)	3.7.07.1
Carrier gas flow rate	
at ambient temperature and ambient pressure	3.6.04.1
at column temperature and ambient pressure	3.6.04.2
averaged over column length	3.6.04.4
Chromatographic process	1.1.01.2
Chromatographic system	1.1.01.1
Corrected carrier gas flow rate	3.6.04.3
Corrected carrier gas hold-up volume (at column temperature and pressure averaged over column length)	3.7.04
Corrected retention volume (at column temperature and pressure averaged over column length)	3.7.08
Flow rate	3.6.04
Hold-up time	3.7.03.3
Hold-up volume (at column temperature and ambient pressure)	3.7.03.1
Mobile phase compressibility correction factor	3.6.03
Net retention volume (at column temperature and pressure averaged over column length)	3.7.09
Retention time	3.7.05.3
Retention volume (at column temperature and ambient pressure)	3.7.05.1
Specific retention volume (at column temperature and pressure averaged over column length)	3.7.11

LIST OF SYMBOLS

F_a	Carrier gas flow rate at ambient temperature and ambient pressure	3.6.04.1
F_c	Carrier gas flow rate at column temperature and ambient pressure averaged over column length	3.6.04.2 3.6.04.4
F_c^o	Corrected carrier gas flow rate	3.6.04.3
$F_{\bar{p}}$	Corrected carrier gas flow rate	3.6.04.3
\bar{F}_x	Corrected carrier gas hold-up volume (at column temperature and pressure averaged over column length)	3.7.04
j_3^2	Mobile phase compressibility correction factor	3.6.03
t_M	Hold-up time	3.7.03.3
t_R	Retention time	3.7.05.3

t_R'	Adjusted retention time	3.7.07.2
V_g	Specific retention volume per unit weight of stationary liquid phase (at column temperature and pressure averaged over column length)	3.7.11
V_N	Net retention volume (at column temperature and pressure averaged over column length)	3.7.09
V_M	Hold-up volume(at column temperature and ambient pressure)	3.7.03.1
V_M°	Corrected carrier gas hold-up volume (at column temperature and pressure averaged over column length)	3.7.04
V_R°	Corrected retention volume (at column temperature and pressure averaged over column length)	3.7.08
V_R	Retention volume (at column temperature and ambient pressure)	3.7.05.1
V_R'	Adjusted retention volume (at column temperature and ambient pressure)	3.7.07.1
V_s	Specific retention volume per unit surface area of stationary liquid phase (at column temperature and pressure averaged over column length)	3.7.11
V_v	Specific retention volume per unit volume of stationary liquid phase (at column temperature and pressure averaged over column length)	3.7.11

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