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GAS CHROMATOGRAPHY FROM THE STANDPOINT OF THE THEORY OF SETS

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SUMMARY

The relationship between chromatographic variables assuming a numbered set of rational values must be expressed in the form of Diophantic (undetermined) equations solved in rational numbers and having an infinite set of solutions (linear dependence, fractional linear dependence) as discussed in this paper. Chromatographic relationships satisfying this requirement are presented.

In recent years gas chromatography has developed at a remarkable rate. At present it is showing some tendency towards arranging the vast body of experimental and theoretical data available in some sort of system and verifying, in more detail the basic relationships and placing them on a firmer basis. When trying to prove the theory a particularly important role can be played by the methods of the theory of sets. Thus, it is desirable to use the theory of sets to establish and verify chromatographic relationships.

A set is a collection of elements possessing a certain common property. The sets can contain a finite number of members or an unlimited large infinite number of members. Two sets are considered equivalent if their elements can be placed in a mutually univocal correspondence. Numbered sets are equivalent to a set of numbers of a natural series or to a set of rational numbers, that is, all the members of a numbered set can be enumerated. Unnumbered sets are infinite sets of a higher power than the numbered ones.

Unnumbered sets are equivalent to a set of irrational numbers. The type of relationship between two physico-chemical (chromatographic) variables depends on the power of sets of values of variables. The power of sets of values of variables depends on the physico-chemical nature of the variable. Thus, *e.g.*, energy and related

values, because of the rule governing the quantification energy, must assume a numbered set of values. The values which are rational functions of energy values also assume a numbered set of values. A rational function is the ratio of polynomials with whole number coefficients. To find the power of a set of values of a variable, one should use the most general equations including this variable. In the thermodynamic equation $\Delta F = \Delta H - T\Delta S$, the energy values ΔF and ΔH assume the role of a numbered set of values, from which it follows that T and ΔS also must have a numbered set of values.

The partition coefficient depends on a change of free energy as shown by the following equation

$$\Delta F = RT \ln k$$

In this relation ΔF and T assume a numbered set of values, and $\ln k$ must also assume a numbered set of values.

The Kováts retention index is a fractional linear function of the logarithms of partition coefficients; the Kováts indices thus become a numbered set of values.

In the above examples the variables assuming a numbered set of values form particular types of rational functions (linear and fractional linear functions). As other examples of variables assuming a numbered set of values, time and space coordinates, and the number of carbon atoms in molecules of substances belonging to a homologous series may also be cited.

Concentration is an example of a variable assuming an unnumbered set of values. To demonstrate that concentration has an unnumbered set of values the equivalence of the sets of concentration values and of the real (irrational) numbers must be established.

Let us consider a flat square lattice, in the nodes of which the atoms or molecules of two kinds (A and B) are situated. By using the Cantor diagonal method all the nodes of the lattice can be enumerated. Let us now write the sequence of the numbers of the nodes: if there is an A atom in a node the number of the node in the sequence must be replaced by zero, while if there is an atom B in the node, the number is replaced by unity. In this way each pattern of atoms (or molecules) will be represented as a sequence of unities and zeros. A set consisting of a combination of zeros and unities corresponds to the whole set of concentration values. The collection of unities and zeros may be considered as a record of a real number in the dual system of calculus. The set of real numbers is unnumbered, hence the set of concentration values is unnumbered too.

It may be shown by the Diophantine analysis method¹ that, assuming a numbered set of values, the following relationships should exist between the variables:

Uni-univocal relations:

Non-uniform coordinates:

$$y = \frac{ax + b}{cx + d} \quad (1)$$

Uniform coordinates:

$$x_1 = ax_2 + b \quad (2)$$

Non-univocal relations:

$$y_1 = \frac{ax^2 + d}{bx^2 + c} \quad (3)$$

$$y_2 = \frac{fx + m}{bx^2 + c} \quad (4)$$

The relations are given with an accuracy to within projective transformations of variables.

The univocal relations between a numbered rational (x) and a real (y) variable are of the form: $y = e^x$ or $y = e^{Z(x)}$, where $Z(x)$ is a fractional linear function.

Eqns. 1-4 are Diophantine equations solved in rational numbers.

THE TEMPERATURE RELATIONSHIP

Since $\log V$, $\log k$, I , ΔI assume numbered sets of values, and the temperature dependence of these values is univariant, the temperature dependence of the logarithmic retention values (R) must appear as follows:

$$\log R = \frac{aT + b}{cT + d} \quad (\text{Antoine's equation})$$

This is confirmed in practice in chromatography.

RELATIONSHIPS IN HOMOLOGOUS SERIES

As the carbon number in molecules belonging to a homologous series of solutes assumes a numbered set of values, $\log V(n)$ must be of the form:

$$\log V = \frac{an + b}{cn + d}$$

With $c = 0$ this dependence acquires a more usual form: $\log V = An + B$.

In recent years, several workers have found deviations from the simple linear relationship in homologous series. From the standpoint of the theory of sets a more general relation of the first type (eqn. 1) should be valid.

One of the authors here (YU.N.B.)² has made a study of the dependence of the difference of retention indices on polar and nonpolar phases (ΔI) in homologous series of solutes on the carbon number and found that this dependence follows relation 1.

PIEROTTI³ and subsequently other workers have shown that the dependence of $\log k$ on the carbon number in homologous series of solvents or stationary phases is described by a fractional linear function of the number of carbon atoms in the solvent molecules.

The relationship between uniform quantities assuming a numbered set of values (e.g. logarithms of retention values of two solutes on several stationary phases, or logarithms of the retention values of a series of solutes on two stationary phases)

according to eqn. 2 must be a linear one. The methods of the theory of sets enable one to predict the type of relationship between the retention values and the physical properties, as well as between the heat and entropy of solution of substances in a sequence of solvents.

As an example of non-univocal relationships the equation describing the shape of a chromatographic peak may be considered. The vapour of the substance is passed through a tube filled with the sorbent. A system of coordinates moving along with the flow of the vapour of the substance is chosen. Let us assume that the continuous flow of the vapour of the substance, entering the column, consists of a set of narrow bands (zones) adjoining each other. The type of equation describing the shape of a narrow zone inside the column and the shape of the concentration front may be found. SCHAY⁴ examined the shape of this zone by using labelled substances. Carbon dioxide was passed through a column packed with silica gel. A sample of radioactive carbon dioxide was injected into the column and registered at the column outlet by a radioactivity counter. In a common frontal experiment no separate zones, constituting the flow of vapour, are discerned, and only the concentration front is observed. If it is assumed that both $\ln c$ and t (flow coordinate) form a numbered set of values, then the shape of the front may be described by the following equation:

$$\ln c = \frac{bt^2 + C}{at^2 + d} \quad (\text{S-shaped curve})$$

while the shape of a narrow zone of vapour of the substance may be described by

$$\ln c = \frac{bt^2 + C}{ft} \quad (\text{bell-shaped curve with a maximum})$$

In elution analysis only a single narrow zone of concentrations is injected into the column, and this zone, after having passed through the column, is registered by the detector. Therefore the shape of the peak in elution analysis must be described by the last equation. This equation describes asymmetrical peaks.

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