Quantitative Gas Chromatography with Thermal Conductivity Detectors. A Fundamental Approach Based on Kinetic Theory[1]

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Abstract: The physics of the gas chromatographic thermal conductivity detector (TCD) involves heat transfer across a temperature gradient on the order of 300°/cm. In an ideal TCD, caloric energy is transferred solely by molecular collisions. Consideration of an applicable model of intermolecular potentials revealed that the thermal conductivity coefficient of a binary mixture of a carrier gas and a sample is governed by a linear mixing rule only when the components are matched with respect to molecular mass and collision diameters. Mixed carrier gases were "tailor made" accordingly and used to elute samples. These ternary systems (consisting of the two-component carrier plus sample) exhibited the expected additive thermal conductivity behavior of a quasi-binary gas. The predicted correlations have been verified experimentally with the aid of a "phantom-column chromatograph" which simulated the characteristic Gaussian shape of gas chromatographic elution patterns. A new calorie transport parameter, ΔQ, has been defined which has fundamental significance and can serve as a measure of eluted sample size. Reliance on ΔQ, in preference to peak heights or peak areas, converts quantitative gas chromatography from a tenuous empirical art into a genuine scientific methodology, suitable for quantitative analysis on the basis of judicious fundamental considerations.

Fourteen years have elapsed since James and Martin outlined the principles of gas chromatography in their classical papers.[2] A bibliography of several thousand analytical applications notwithstanding, a tenable quantitative theory of gas chromatographic elution "peaks" is still conspicuous by its absence, even for the commonly employed thermal conductivity detector (TCD). The relevant literature is replete with empirical calibration procedures. The interpretation of the TCD response has been the subject of much controversy. Some investigators have claimed that the peak heights represent a quantitative measure of the amount of sample eluted, while others preferred to utilize the "area" (integral) under the peaks as the meaningful quantity.[3,4] Conflicting views have been advanced concerning the relationship of TCD response to relative sample size in situations when a multicomponent mixture was resolved into discrete elution peaks. On the one hand, experimental evidence has been adduced suggesting that the peaks were proportional to the weight fractions of the corresponding components; on the other hand, results have also been reported which indicate that the various peaks represented measures of the respective mole fractions.[5]

The prevalence of such disagreements in the literature reflects the lack of adequate understanding of the basic significance of TCD signals. Yet, the physics of the TCD is remarkably simple. If convective effects are minimized by appropriate experimental design,[6] the TCD operates on the principle that caloric energy is transferred from a heated sensor (a thermistor in

modern practice) to a cold wall solely by molecular collisions in the ambient gas. Under conditions of invariant heat input, the temperature of the sensor (acting as a resistance thermometer in a Wheatstone bridge) is a function of the thermal conductivity coefficient, K, effective in the gaseous milieu. Hitherto quantitative gas chromatographic analysis with TCD's has implicitly relied on the assumption that thermal conductivities, of binary gas mixtures eluted in a peak, are governed by linear mixing rules of the type

$$K = X_1 K_1 + X_2 K_2 \qquad (1)$$

where X denotes mole fractions and the subscripts 1 and 2 identify the sample and the carrier gas, respectively. Compelling evidence is presented in this paper, indicating that approximation 1 holds only if and when carrier gases and samples are judiciously "matched" on the basis of theoretical considerations. Novel carrier gases are described, "tailor made" accordingly for quantitative gas chromatographic analysis. Equations are derived correlating experimental integrals with the number of moles of sample eluted in a given peak. Methods are discussed for calculating, from experimental chromatograms, the heats actually transported across the TCD. These caloric transport parameters have a much more fundamental significance than the raw data (*e.g.*, peak heights and peak areas) and are related to the actual thermal conductivities of the effluent gases involved.

Theory of the "Matched Carrier Gas"

From principles of kinetic theory, the rigorous matrix expression 2 has been derived in recent years[7] describing the thermal conductivity coefficient of a binary mixture of real gases

$$K = 4 \begin{vmatrix} L_{11} & L_{12} & X_1 \\ L_{21} & L_{22} & X_2 \\ X_1 & X_2 & 0 \end{vmatrix} : \begin{vmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{vmatrix} \qquad (2)$$

(1) Condensed from theses by B. B. Kebbekus, M. H. Barsky, and R. T. Rossi; supported by Public Health Service Grant No. HE-02342 from the National Heart Institute; presented in part before the Symposium on Gas Chromatography, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

(2) A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952); *Analyst*, **77**, 915 (1952).

(3) A. F. Williams, and W. J. Murray, *Talanta*, **10**, 937 (1963).

(4) M. Dimbat, P. E. Porter, and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956).

(5) L. C. Browning and J. O. Watts, *Anal. Chem.*, **29**, 24 (1957); A. E. Messner, D. M. Rosie, and P. A. Argabright, *ibid.*, **31**, 230 (1959).

(6) J. Bohemen and J. H. Purnell, *J. Appl. Chem.*, **8**, 433 (1958).

(7) E. A. Mason, *J. Chem. Phys.*, **28**, 1000 (1958); C. Muckenfuss and C. F. Curtiss, *ibid.*, **29**, 1273 (1958).

where

$$L_{11} = \frac{-4X_1{}^2}{K_1} - \frac{16T}{25p} \times$$

$$\frac{X_1X_2[(15M_1{}^2/2) + (5M_2{}^2/2) + 4M_1M_2A^*{}_{12}]\,2.39 \times 10^6}{(M_1 + M_2)^2 D_{12}}$$

(3)

$$L_{12} = \frac{16T}{25p}\frac{X_1X_2M_1M_2(10 - 4A^*{}_{12})2.39 \times 10^6}{(M_1 + M_2)^2 D_{12}}$$ (4)

K is expressed in cal/cm sec deg, and the subscripts are appropriately interchanged to obtain L_{22} and L_{21}. In eq 3 and 4, p is the total pressure expressed in dynes/cm², T is the temperature in °K, M denotes molecular weight, D's are mutual diffusion coefficients, and A^* is a dimensionless ratio of collision integrals. Assuming the prevalence of an applicable model of intermolecular potentials in which the small determinant elements L_{12} and L_{21} are neglected

$$A^*{}_{12} \longrightarrow A^*{}_{21} \longrightarrow {}^5/_2$$ (5)

and eq 2 reduces to

$$K = \frac{K_1}{1 + G_{12}X_2/X_1} + \frac{K_2}{1 + G_{21}X_1/X_2}$$ (6)

The dimensionless parameters G in eq 6 represent measures of the degree of dissimilarity between molecules 1 and 2 and can be assigned physical significance in the following context. At very low pressures (<1 mbar) there is no mutual hindrance of molecular motion. Consequently the rate of transport of heat through a gas is dependent only on the concentration (c) of available molecules. At more normal pressures, however, heat transfer is not only directly dependent on the number of molecules transporting but also inversely dependent on the number impeding transport. G_{12} is the ratio between the efficiency with which molecules 2 and molecules 1 impede transport of heat by molecules of type 1 and G_{21} has the converse significance.[8,9] Thus the relative contribution of K_1 in a mixture is proportional to the coefficient φ defined in eq 7.

$$\varphi_1 = c_1(c_1 + c_2G_{12})^{-1} = (1 + G_{12}X_2/X_1)^{-1}$$ (7)

The corresponding proportionality constant for the contribution of K_2 is

$$\varphi_2 = c_2(c_2 + G_{21}c_1)^{-1} = (1 + G_{21}X_1/X_2)^{-1}$$ (8)

Substitution of eq 7 and 8 in eq 6 yields

$$K = \varphi_1K_1 + \varphi_2K_2$$ (9)

It is evident that as molecules 1 and 2 become more similar in those properties which affect heat transport

$$G_{12} \longrightarrow G_{21} \longrightarrow 1 \left\{ \begin{array}{l} \varphi_1 = c_1(c_1 + c_2)^{-1} = X_1 \\ \varphi_2 = c_2(c_1 + c_2)^{-1} = X_2 \end{array} \right\}$$ (10)

and eq 6 reduces to the linear mixing rule 1.

Molecular properties which evidently affect the thermal conductivity behavior of gases include mass

Figure 1. Phantom-column chromatograph. TCD = thermal conductivity detector.

and "distance of closest approach." For the latter, the parameter σ in the standard equation for the Lennard-Jones (12, 6) potential provides a convenient measure.[10] Convincing experimental evidence is available in the literature[11] indicating that mixtures of polar and nonpolar gases may exhibit significant deviations from eq 1, under conditions when mixtures containing solely nonpolar components obeyed the linear mixing rule. Consequently, one would predict that the extent to which the thermal conductivity of a binary gas mixture, passing through the TCD, approximates a linear function of composition (in accordance with eq 1) may depend on the following variables: molecular weight, σ, polarity.

A substantiation of this prediction was undertaken in a series of experiments[12] in which selected gases were judiciously paired in order to discriminate between the effects of dissimilar molecular masses, σ parameters, and polarities. In each pair, one gas was used as carrier and the other as sample.

Further experiments were performed[12] in order to demonstrate the feasibility of preparing matched carriers ad hoc for analyzing specific samples. These carriers consisted of binary mixtures of gases so chosen as to achieve a balance between positive and negative deviations from additivity in thermal conductivity behavior.

Experimental Methodology

A split carrier gas stream apparatus was constructed of glass[12] and is diagrammed in Figure 1. In order to prevent spurious effects due to adsorption of gases on greased surfaces (which can be appreciable), the use of lubricants was avoided altogether with the aid of nylon connectors, Kovar-glass seals, and stainless steel valves.

The sample was eluted by diverting the carrier gas flow from the bypass through a filled sample loop of known volume. The sample was then distributed in the gas stream simulating a typical gas chromatography elution band by passing it through a "phantom column." This consisted of uncoated glass capillary tubing 3 m in length and 0.05 cm in internal diameter. The phantom column

(8) T. G. Cowling, P. Gray, and P. G. Wright, *Proc. Roy. Soc.* (London), **A263**, 161 (1961); **A276**, 69 (1963).

(9) For any specified gas pair G_{12} = constant, and G_{21} = constant'. Under these conditions eq 6 becomes identical in form with the widely used semiempirical "Wassiljewa equation" [*Phys. Z.*, **5**, 737 (1904)].
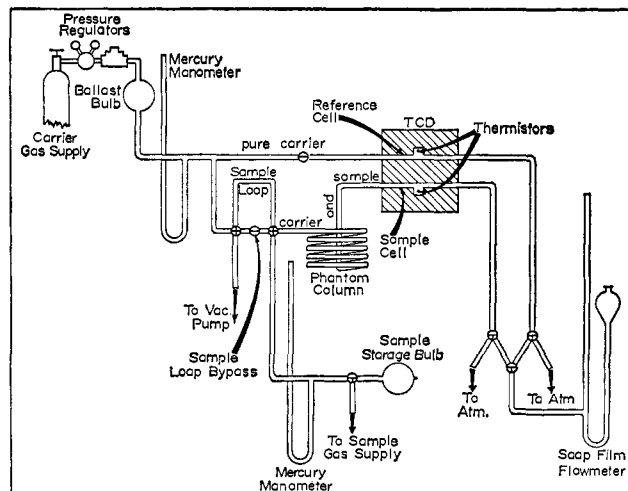
(10) See, *e.g.*, R. D. Present, "Kinetic Theory of Gases," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, p 248, eq 12-4.

(11) L. A. Bennett and R. G. Vines, *J. Chem. Phys.*, **23**, 1587 (1955).

(12) The dissertations (available through University Microfilms, Ann Arbor, Mich.) of junior authors M. H. Barsky and B. B. Kebbekus should be consulted for detailed information.
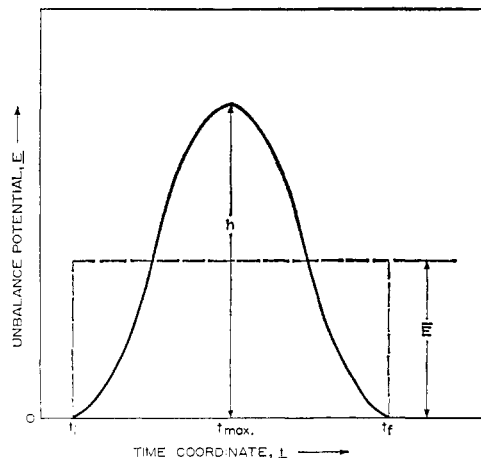
Figure 2. Typical gaussian elution pattern: h = peak height; $\bar{E}$ = mean response, defined in eq 12; $\int_{t_i}^{t_f} E dt = \bar{E}(t_f - t_i)$.

had no separatory properties but reproduced the spreading effect on the plug of sample, which would occur if it passed through a genuine gas chromatographic column. As a result of the random statistics which govern mutual diffusion of molecules in such a situation, this method yielded a Gaussian distribution of sample in the carrier, without the problems attendant on the use of packed columns, such as peak tailing, irreversible adsorption, andl ong retention times leading to excessive band broadening.

The geometry of the TCD was judiciously selected in order to minimize convective mixing. It was ascertained experimentally that 99 % (or better) of the caloric energy was transferred between the "hot" and "cold" sides of the TCD by a pure thermal conduction mechanism (molecular collisions). The TCD was constructed of a brass block, with two identical channels (thermal conductivity cells) drilled into it. The walls of these channels were isothermal with the block which was heated to a temperature of 50°. They served as the cold side of the thermal gradient (60-70° across a gap of 0.2 cm) maintained in each cell. The hot sides consisted of identical thermistors, heated at a constant rate by an appropriate electric current, and wired as arms of a differential DC Wheatstone bridge. The circuit was adjusted in such a manner that the unbalance potential, E, of the bridge provided a measure of the temperature difference between the thermistors in the two cells. Under the prevailing experimental conditions, $E = 0$ when pure carrier gas was passed through both cells at the same rate of flow. In contradistinction, $E \neq 0$ when pure carrier gas provided the heat-transfer medium in one cell (the reference cell) and an effluent of the phantom column, consisting of carrier plus sample, was fed through the second cell (the sample cell) at the same flow rate. As samples passed through the TCD, the unbalance potential of the Wheatstone bridge (conveniently traced on a strip chart recorder driven by a synchronous motor) yielded Gaussian patterns of $E(t)$ vs. time (t), as illustrated in Figure 2. These peaks were integrated with a polar planimeter, yielding elution areas corresponding to the integral

$$A = \int_{t_i}^{t_f} E dt \qquad (11)$$

where A is expressed in v sec, and the limits t_f and t_i are defined in Figure 2.

Significance of Elution Patterns

Peaks of the shape shown in Figure 2 represent the type of primary information which is accessible experimentally in elution chromatography with thermal conductivity detectors. The abscissa is simply a linear time coordinate. (An alternate plot can be obtained by multiplying with flow rate and using a corresponding volume abscissa.) The ordinate, however, is a transient unbalance potential which has a complex dependence on diverse factors. In an idealized first

approximation, the Gaussian shape is accounted for by the instantaneous abundance of the eluted sample in the carrier gas, which increases from the front of the peak (emergence time, t_i), attains a maximum at $t_{max} = (t_i + t_f)/2$, and decreases again until the emergence of the "tail" at $t = t_f$. The behavior of the "average sample molecule" is reflected by t_{max}, while the front and tail ends are caused by the random deviations in the statistical behavior of the total sample population. Regardless of the actual symmetry of the elution pattern, the integral A, defined in eq 11, is an evident measure of the totality of molecules of sample eluted in a peak. In contradistinction, peak height (h in Figure 2) could only serve as a comparable measure of sample size if the quantity ($t_f - t_i$) were constant, which is dependent on experimental conditions. Thus peak integrals are preferable to peak heights as quantitative measures, and molar normalization with respect to sample size is likewise preferable to weight normalization, on criteria of general applicability and directness of physical significance. It is convenient to define a mean TCD response, equivalent to specified value of A, viz.

$$\bar{E} = (t_f - t_i)^{-1}A \qquad (12)$$

The significance of $\bar{E}$ (expressed in volts) is apparent from Figure 2. It is the time-invariant TCD response obtained if a gas mixture containing a specified (time-invariant) mole fraction, $\bar{X}_1$, of sample were to flow through the relevant detector cell (everything else, including over-all flow rate, being equal). The value of $\bar{X}_1$ in this hypothetical "equivalent effluent" is selected so that the number of moles of sample passing through the cell in ($t_f - t_i$) sec will be equal to the actual amount of sample eluted in the corresponding Gaussian peak in the same time period.

The numerical value of $\bar{E}$ is still dependent upon several arbitrary experimental variables, including voltage used to power the thermistor bridge and resistivity coefficients of the thermistor elements with respect to temperature.

An enhanced level of significant generalization was attained by computing the calorie transport parameter, ΔQ, defined as

$$\Delta Q \equiv Q_{12} - Q_2 = a\bar{K}(T_s - T_w)(t_f - t_i) \qquad (13)$$

where Q_2 and Q_{12} denote heat (calories) transferred in the sample cell of the TCD from the hot sensor to the cold wall during time ($t_f - t_i$) by the carrier gas alone (in the absence of sample) and by the carrier plus sample, respectively; the subscripts s and w identify the sensor and the cold wall; a is an effective path length (cm) depending solely on the design of the TCD.

$$\bar{K} = \frac{1}{t_f - t_i}\int_{t_i}^{t_f} K dt \qquad (14)$$

is a mean thermal conductivity coefficient averaged over the actual Gaussian elution pattern. The basic significance of $\bar{K}$ is that it represents the thermal conductivity coefficient of the hypothetical equivalent effluent gas. The heat transferred when pure carrier passes through the TCD sample cell is given by an analog of eq 13, viz.

$$Q_2 = aK_2(T_s - T_w)(t_f - t_i) \qquad (15)$$

Interpretation of Experimental Data

In accordance with common experimental practice in gas chromatography, the following sequential procedure was used in quantitative work.

I. Pure carrier gas ($X_2 = 1$) was passed through the reference cell of the TCD in all experiments.

II. With pure carrier passing (at the flow rate F) through the sample cell of the TCD as well, the unbalance potential was adjusted to zero by use of variable resistors incorporated in the Wheatstone bridge circuit.

III. n_1 moles of a sample was eluted through the sample cell at the same total flow rate, viz.

$$F = n_1/\bar{X}_1(t_f - t_i) \tag{16}$$

Mean TCD response values ($\bar{E}$) were calculated for each peak from the corresponding elution area, using eq 12. From $\bar{E}$ and from the known values of the fixed resistor components of the Wheatstone bridge circuit, the average resistance, R, of the thermistor in the sample cell was computed. Subsequently, Q_{12} was calculated from the applicable heat balance equation

$$I^2R/J = Q_{12}(t_f - t_i) \tag{17}$$

where I is the current flowing through the thermistor and J denotes the Joule constant. Q_2 was evaluated in a similar manner from the value of R corresponding to $\bar{E} = 0$ (i.e., when pure carrier was flowing through both the reference and the sample cells of the TCD).

Peak areas, A, represent a valid proportional measure of the amount of eluted sample only if the variation of T_s [during the time period $(t_f - t_i)$] is small with respect to $(T_s - T_w)$. In contradistinction, reliance on ΔQ does not depend on this assumption. ΔQ is a parameter preferable to either A or $\bar{E}$ not only because of its obvious physical significance, but it also exhibits, in general, a better linear correlation with the eluted sample size, n_1. (The latter is the unknown determined in quantitative gas chromatographic analysis.) Indeed, a comparison of eq 1, 13, 15, and 16 yields

$$\Delta Q = (\text{constant})n_1 \tag{18}$$

whenever the linear mixing rule applies.

Results

Selection of Model Systems. Theoretical considerations presented earlier in this paper lead to the prediction that a linear correlation between eluted sample size and the calorie transport parameter, ΔQ, can be expected to prevail if the carrier and sample are both nonpolar and similar in terms of molecular weight and σ. Table I lists the gases used in this investigation for testing these predictions experimentally. Included in the table are numerical assignments of the relevant molecular properties on which the selection of the compounds was predicated.

The Matched Carrier Gas Concept. This was substantiated in a series of preliminary experiments where conditions were adjusted advisedly to meet the requirement

$$\frac{dT_s}{dt} \ll (T_s - T_w)/(t_f - t_i) \tag{19}$$

Table I. Molecular Parameters Affecting Additivity of Heat-Transfer Properties of Gases

Compound	Mol wt	σ^a	Dipole moment, D.
He	4.00	2.6	0
CO	28.01	3.6	0.1
N_2	28.02	3.7	0
C_2H_4	28.05	4.2	0
C_2H_6	30.07	4.4	0
A	39.94	3.4	0
CO_2	44.01	3.9	0
SO_2	64.07	4.3	1.60

^{a} "Distance of closests approach"—parameter in the Lennard-Jones equation: $u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. Assignments taken from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954, p 1110.

which warrants reliance on the peak area A (eq 11) as a satisfactory proportional measure of ΔQ. In order to minimize the number of measurements, the experiments were set up in accordance with a "factorial design," in which the numerical assignments of all three relevant variables ("factors") were "permuted" simultaneously, in concordance with statistical considerations.[13] Careful mathematical analysis of the data, utilizing applicable principles of error theory, permitted inferential conclusions at a confidence level of 95%, from work with five "model gas pairs." In each pair one gas served as the carrier for eluting six sample sizes of the other. Each experiment was carried out in triplicate. Thus, conclusions are based on the results of nearly a hundred discrete runs. The criterion for pairing was that each of the critical molecular properties listed in Table I be either (a) substantially similar for both carrier and sample, or (b) significantly different. Plots of experimentally obtained elution areas (as function of amount of sample size) were of three general shapes, viz.: shape I, linear over entire range; shape II, positive deviations from linearity; shape III, negative deviations from linearity. Typical examples are illustrated in Figure 3. A comprehensive summary of the paired gas experiments is presented in Table II.

Table II. Molecular Property Combination Experiments

Gas pairs		Molecular property combination code^a	Shape of plot obtained^b
Carrier	Eluted sample		
N_2	CO	ABC	I
N_2	C_2H_4	AbC	III
C_2H_6	SO_2	aBc	II
He	C_2H_6	abC	III
He	SO_2	abc	I

^{a} A, B, and C refer respectively to mass, σ, and polarity (dipole moment); upper case letters indicate the same level of the relevant parameter in carrier and sample; lower case letters indicate substantially different levels. ^{b} Shapes identified in Figure 3.

"Tailor-Made" Binary Carrier Gases. A new approach to quantitative analysis by gas chromatography was developed, with the following rationalization in

(13) R. A. Fisher, "The Design of Experiments," 5th ed, Oliver and Boyd, Ltd., Edinburgh and London, 1949.
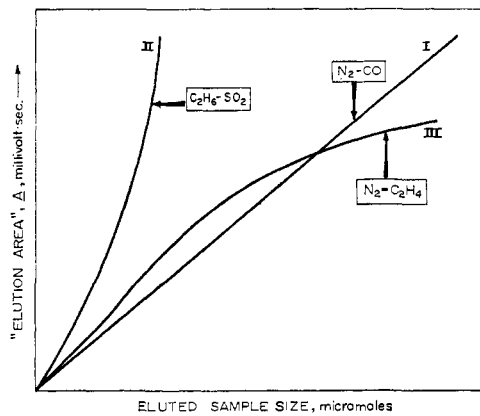
Figure 3. Representative plots of elution area $vs.$ sample size: shape I, linear; shape II, positive deviation from linearity; shape III, negative deviation. Carriers are listed first. A is defined in eq 11.
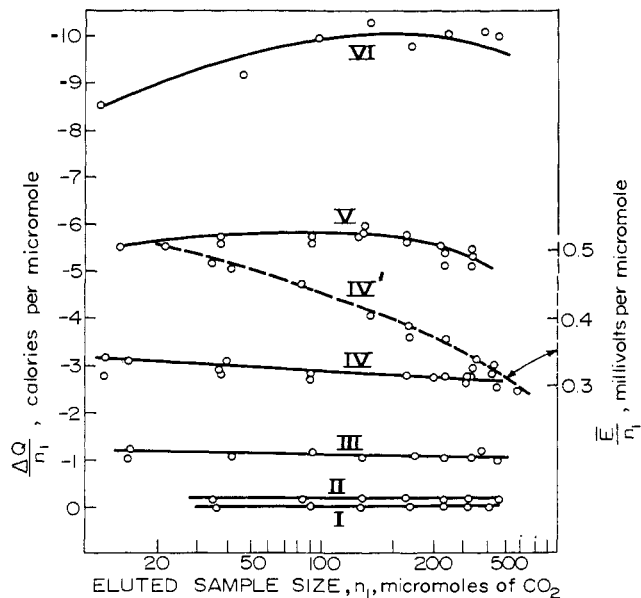

Figure 4. Results obtained in the elution of carbon dioxide with mixed carrier gases (argon plus helium): solid lines, $(\Delta Q/n_1)$ plotted $vs.\ n_1$; dotted line, $(\bar{E}/n_1)$ plotted $vs.\ n_1$; ΔQ, defined in eq 13; $\bar{E}$, same as in Figure 1. I, 100% A; II, 90 mole % A; III, 60% A; IV and IV', 30% A; V, 10% A; VI, 100% He.

mind. Current practice, relying on TCD elution patterns obtained with a universal carrier gas ($e.g.$, helium), is likely to be satisfactory only if, by fortuitous coincidence, its critical molecular properties happen to either be at comparable levels with those of the sample, or if the nonlinearizing effects compensate. In this context, carbon dioxide was selected as an illuminating example of an analytically significant sample: its gas chromatographic determination has been advocated for organic elemental analysis, supplanting laborious classical procedures.[14] Restricting (on considerations of preference for an inert eluent) the choice of carrier gases to the nonreactive aerogens, it is apparent from Table I that argon is preferable to helium as far as the linearization parameters are concerned. However, the sensitivity of any quantitative determination with the TCD is crucially dependent on an appreciable difference between the thermal conductivity coefficients of carrier and sample. This is qualitatively obvious from the physics of the TCD and mathematically evident from eq 1, 13, and 15. The relevant thermal conductivity coefficient assignments are: $K_{CO_2} = 3.32 \times 10^{-5}$; $K_{He} = 33.4 \times 10^{-5}$; $K_A = 3.88 \times 10^{-5}$ cal/cm sec deg. Thus argon is inferior to helium as far as sensitivity is concerned. A satisfactory compromise was achieved by using mixtures of argon plus helium as carrier gas for the elution of carbon dioxide. Experiments covered a range of sample sizes between 10 and 700 mmoles of carbon dioxide. Representative results[15] are shown in Figure 4, where the quantity $\Delta Q/n$ has been plotted $vs.$ the sample size, n_{CO_2}. In these plots ideal linearity would correspond to a line of zero slope; as can be seen in the figure this requirement was approximated within 1 and 3% in the presence of 60 and 30 mole% of argon, respectively. A selected plot of $\bar{E}/n_{CO_2}$ is presented (in dotted lines) for comparison. Everything else being equal, it documents the superiority of ΔQ over $\bar{E}$ in quantitative gas chromatography, especially when a wide range of sample sizes is involved.

(14) A. A. Duswalt and W. W. Brandt, $Anal.\ Chem.$, 32, 272 (1960); O. E. Sundberg and C. Maresh, $ibid.$, 32, 274 (1960); W. Walisch, $Trans.\ N.\ Y.\ Acad.\ Sci.$, [11] 25, 693 (1963).

(15) A similar pattern of results was obtained in a series of analogous experiments, where mixtures of helium and nitrogen were used as carrier gases: B. B. Kebbekus and J. Jordan, $Anal.\ Chem.$, 37, 1572 (1965).

Discussion

The plot shapes illustrated in Figure 3 and reported in Table II are accounted for as follows. The observed linear behavior of the N_2-CO pair is theoretically warranted because all the three critical molecular properties of the two components are matched. "Mismatching" yielded the following types of deviations from linearity.

α. $Differences\ in\ molecular\ weight$ produced $negative\ deviations$ ($i.e.$, a value of K smaller than predicted by eq 1), because mixing of molecules discrepant in mass decreases the fraction of kinetic entities which have higher than average velocity. Since kinetic energy is proportional to v^2, faster molecules are relatively more efficient in transporting energy. Consequently, a mismatched mass situation will tend to lower the thermal conductivity coefficient of gas mixtures.

β. $Discrepant\ \sigma's$ ($everything\ else\ being\ equal$) likewise yielded negative deviations, the mean free path being relatively smaller. This is reflected by a concomitant decrease of the effective thermal conductivity coefficient which is proportional to mean free path.

γ. $Discrepant\ polarities$, in contradistinction, yielded positive deviations from the additivity rule.

The observed negative deviation habitus (plot shape III) exhibited by the pair helium–ethane is due to a cooperative effect of $\alpha + \beta$. The similar behavior pattern of the nitrogen–ethylene pair is accounted for by effect β. The pair ethane–sulfur dioxide yielded plots of shape II (positive deviation from additivity) owing to the overwhelming prevalence of effect γ which overcompensated any contributions of effects α or β. The pair helium–sulfur dioxide, which also exhibited a linear plot (shape I), is an interesting illustration of the balancing of positive and negative deviations of α, β, and γ, in a situation when all the three relevant properties had discrepant levels.

In the two-component carrier gas experiments, the elution bands actually involved ternary mixtures of gases. However, eq 13 and 15 can be applied to these data also, by treating them as if they were quasi-binary mixtures of sample and carrier. In this case the quantity Q_2 refers to the heat transported by the "binary carrier." The results illustrated in Figure 4 indicate that the observed thermal conductivity behavior indeed corresponded to that of a pseudo-binary system. This is plausible, because in step I of the experimental procedure a thermal steady state was established by "zeroing" E, while the binary carrier passed through both TCD cells. The sample was then introduced (in step II) as a "perturbation."

The implication of the results of this investigation for quantitative analysis by gas chromatography is that a linear response can be elicited from a thermal conductivity detector by proper matching of molecular masses, distances of closest approach, and polarities between eluted sample and carrier gas. It is not required that the latter be homogeneous at the molecular level. Carriers can conveniently be prepared by mixing several gases; thus positive and negative deviations can be balanced. The mathematical formulation of an ideal carrier gas matching selection rule is

$$(10) \longrightarrow G_{12} = G_{21} = 1 \qquad (20)$$

Strict fulfillment of eq 20 would presumably make the linear mixing rule 1 prevail without restrictions for all values of $0 < X_1 < 1$. Certain other values of G_{12} and G_{21} can yield linear results over a restricted mole fraction range.

A comparison of curves I and VI in Figure 4 provides a striking illustration of the conflicting advantages of helium vs. argon (and vice versa) as preferred eluents for carbon dioxide. For optimizing the sensitivity of TCD response the sequence is He > A, because $(K_{He} - K_{CO_2}) \gg (K_A - K_{CO_2})$. In contradistinction,

A > He as far as linear behavior is concerned. This correspondence is not fortuitous. Indeed, kinetic theory requires that thermal conductivity coefficients of gases be ultimately dependent on the very same molecular parameters which govern the applicability of the linear mixing rule 1.

The results plotted in Figure 4 indicate that a workable compromise between the a priori conflicting linearity ($G_{12} = G_{21} = 1$) and sensitivity ($K_1 \ll K_2$ or vice versa) requirements can indeed be attained. For instance, carbon dioxide is analyzable with a precision and accuracy of 1%, utilizing as carrier gas a mixture of helium (20–30 mole %) and argon. On similar considerations other mixed carrier gases can be "tailor made" for the determination of various unknowns.

In general, the correlations elucidated in this investigation suggest the prospect of converting gas chromatography from a semiempirical art into a rigorous quantitative method. In this context, the calorie transport parameter, ΔQ, defined in eq 13, has genuine significance: it represents a proportional measure of the thermal conductivity coefficient of a hypothetical "averaged gas," whose properties have been integrated over the relevant Gaussian elution pattern and normalized with respect to the corresponding time interval. ΔQ is accessible directly from experimental data, relying solely on a simple (first law) equivalence expression between electric and caloric energy. Thus eq 13 and 15 in this paper are preferable to less general expressions available in the literature,[16] which correlate transient unbalance potentials with variables contingent on the experimental design of the TCD, or rely on tenuous empirical approximations for estimating thermal conductivity coefficients of gas mixtures.

(16) L. J. Schmauch and R. A. Dinerstein, *Anal. Chem.*, **32**, 343 (1960); B. D. Smith and W. W. Bowden, *ibid.*, **36**, 82 (1964).