A THEORETICAL AND EXPERIMENTAL STUDY OF CHROMATOTHERMOGRAPHY AT HIGH CONCENTRATIONS

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UDC 541.18.044

The concentration distribution produced by diffusion is examined; the differential equation has been solved numerically by computer to give working curves that define the physicochemical characteristics. An approximate analytical solution is also given.

A new chromatographic separation method has been described [1-4], which involves chromatothermography without a carrier gas; it differs from the same process operated at low concentrations [5] in that the moving temperature distribution causes the substance to reach high concentrations, and an additional flux appears, as in all chromatographic processes without carrier gases, and as a result the stationary concentration band is displaced ahead of the characteristic temperature. The theory of the equilibrium process in the absence of broadening by diffusion has been discussed [1, 3], and an attempt has been made also [2] to incorporate diffusion broadening. See [4] on the advantages of the new method and the scope for analytical use.

Here we examine in detail the effects of diffusion, and present possible ways of calculating those that enable one to examine the process over a wide range in the parameters and provide a rough choice of the separation conditions.

The broadening is described mathematically by a system of two differential equations in partial derivatives, which has been given previously [2]. The steady-state solution involves an ordinary Bernoulli differential equation of first order with nonlinear coefficients. An analytical solution has been derived for this [2] subject to rather crude assumptions about the coefficients, and this describes correctly only a small concentration range near the characteristic temperature. Here we present a more detailed description, and it is shown that a solution in quadratures can be obtained without assumptions about the coefficients. However, the expression is too cumbersome and requires a computer to derive the integrals. Exact solutions have been obtained by numerical integration of the initial differential equation by Euler's method. The necessary calculations are presented here for processing data for individual bands produced by carbon dioxide. The complete analytical solution has been simplified for use without resort to computer, subject to minimal assumptions. The final expression can be applied by a single numerical integration, which can be performed manually. Calculated curves are presented for a wide range of the parameters, and these are close to the exact computer curves.

The differential equation of [2] for the stationary concentration distribution takes the following form in dimensionless coordinates:

$$\frac{dN_1}{dx} = f_1(x)\,N_1 + f_2(x)\,N_1^2, \tag{1}$$

$$f_1(x) = K_2\left(1 - \frac{e^x}{1 - K_1x}\right);\quad f_2(x) = \frac{K_2e^x}{1 - K_1x}; \tag{2}$$

It follows from (1) and (2) that the process is controlled by the two dimensionless quantities K_1 and K_2.

Translated from Inzhenerno Fizicheskii Zhurnal, Vol. 27, No. 3, pp. 466-475, September, 1974. Original article submitted October 9, 1973.

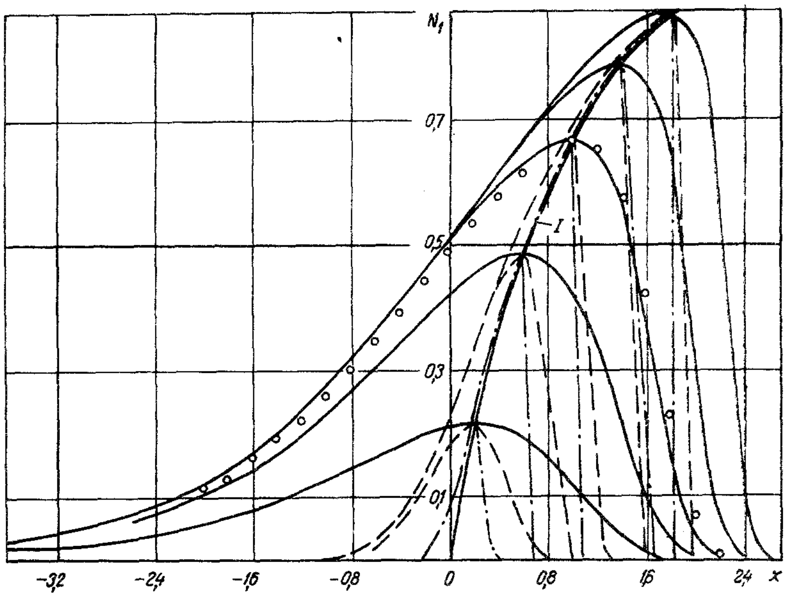

Fig. 1. $N_1(x)$ (concentration curves) for $K_1 = 0.1$; solid lines $K_2 = 1$, broken lines $K_2 = 10$, dot-dash lines $K_2 = 100$. The points have been calculated from (6) with $K_2 = 1$, $x_{max} = 1$; 1) equilibrium curve given by (3).

Equation (1) has been solved numerically with a Minsk-32 computer; the error in N_1 was 0.0005. The initial conditions were provided by using the point x_0 corresponding to the maximum on the curve. As in ordinary chromatography, there are deviations from equilibrium away from the peak. The peak itself corresponds to zero derivative, and (1) and (2) shows that it lies on the curve

$$N_1 = 1-(1-K_1x)e^{-x}, \tag{3}$$

corresponding to the equilibrium case examined in detail in [1, 3]. Integration of (1) gives $N_1(x)$, but the processing may be facilitated by using a computer program for constructing the curves, which can be printed out. In passing we determine the integral I, which is proportional to the amount of material injected into the column:

$$q = \frac{S\Gamma_{1x}}{\sigma}\int_{-\infty}^{\infty} N_1(x)\,e^{-x}dx = \frac{S\Gamma_{1x}}{\sigma} I. \tag{4}$$

We determine the values of K_1 and K_2 to be used from the following possible ranges for the physical parameters: α_0 = 1-10 cm/sec; γ = 1-20 deg/cm; T_x = 300-500°K; Q = 1-5 kcal/mole; D = 0.01-0.5 cm^2/sec; the calculations were performed for K_1 of 0.05, 0.1, 0.5, and K_2 of 1, 5, 10, 100, and 1000, these values covering virtually the whole possible range. Figures 1 and 2 show curves for various values of K_1, K_2, and x_0.

It is clear that increase in D (reduction in K_2) naturally distorts both branches of the output curve; if the concentration is less than 5%, one gets a symmetrical Gaussian peak near the characteristic point, which corresponds to ordinary low concentration chromatothermography [5]. If D is large, the curves become more symmetrical. If one reduces the amount q of substance injected, one gets symmetrical peaks for practically any values of the parameters, while the maxima themselves are not displaced from the characteristic temperature.

If D → 0 ($K_2 > 100$), the curves approximate to the equilibrium one, as (3) shows, with a common envelope and a steep leading edge; the origins of the curve approximates to the point with the characteristic temperature. Considerable deviations can occur from zero concentration at $x = 0$ if D is large, so the position of the characteristic temperature must be determined by experiment, in which one reduces the concentration until there is no shift in the peak position.

At high temperatures, there exists for each D an asymptotic curve for the various curves corresponding to different initial conditions. The curves corresponding to high concentrations run close together

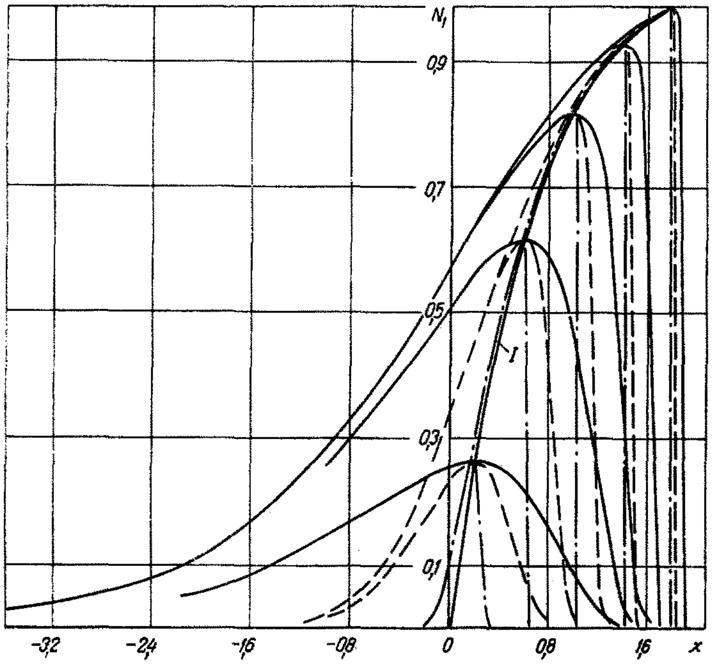

Fig. 2. $N_1(x)$ (concentration curves) for $K_1 = 0.5$; solid lines $K_2 = 1$, broken lines $K_2 = 5$, dot–dash lines $K_2 = 100$. 1) equilibrium curve given by (3).

near zero, but strictly speaking they never coincide by virtue of the uniqueness of the solution to (1). One could obtain the entire set of curves for Fig. 1 using the initial data for $x = 0$, but this would require the concentration at zero to be specified very accurately. Therefore, we specified the initial data at the peak. Then if there is considerable broadening by diffusion, it is incorrect to determine, as was done in [3], the value of σ and hence Q from the envelope; it is however correct to do this from the equilibrium curve of (3), which passes through the peaks.

The calculations show that variation of K_1 from 0.05 to 0.1 has little effect on the curve shape; increase in K_1 from 0.1 to 0.5 reduces the broadening of the leading edge appreciably. The sharpening factors (the temperature distribution and the additional flux) reduce the broadening at the high concentrations involved in overloaded chromatothermography, but they also produced skewness; the effects are less pronounced at low concentrations. The accumulated computer data provide an easy means of checking the calibration of q with respect to x^2 [4] for a wide range of conditions. Figure 3 shows curves as I, which is proportional to q; as D increases under fixed initial conditions [x_0, $N_1(x_0)$ and K_1]the material becomes distributed over a larger part of the sorbent, which occurs because the curves of the lower K_2 run at higher I. Figures 1-3 show that a linear calibration fits well to the high-concentration region actually used. The curve is not obliged to pass through zero at low concentrations, since in that case the Gaussian peak should not be displaced appreciably on increasing the amount input. Figures 1 and 2 show that the leading edge becomes very steep for $K_2 > 10$, so one can use a null detector for composition determination instead of an ordinary detector. Although the null detector only records the curve onset, and this is affected by diffusion, the calibration curves in fact remain closely linear [4].

These graphs allow one to decide approximately the optimal parameters as follows: oven length for given conditions (q, γ, α, w, D, etc.) and maximum input, provided that all the substance is in the oven. Then one can calculate the conditions that correspond to the production of specified concentrations ahead of the oven [1] and establish the maximum measurable concentration in the linear calibration curve. We consider as an example the calculation sequence required to find the maximum possible q.

Consider an oven with known temperature gradient γ and length l; preliminary tests with low concentrations indicate the origin corresponding to the characteristic temperature T_X. Given speeds α_0 and w for the flow and oven enable us to use the temperature correction [2] to calculate Γ_{1X}, while σ may be determined in several ways: calculated if Q is known for the system, or else from published values, or again from experiments under isothermal conditions, or else from chromatographic experiments using (3). The values for D for conditions close to those actually employed can often be found from the literature, so

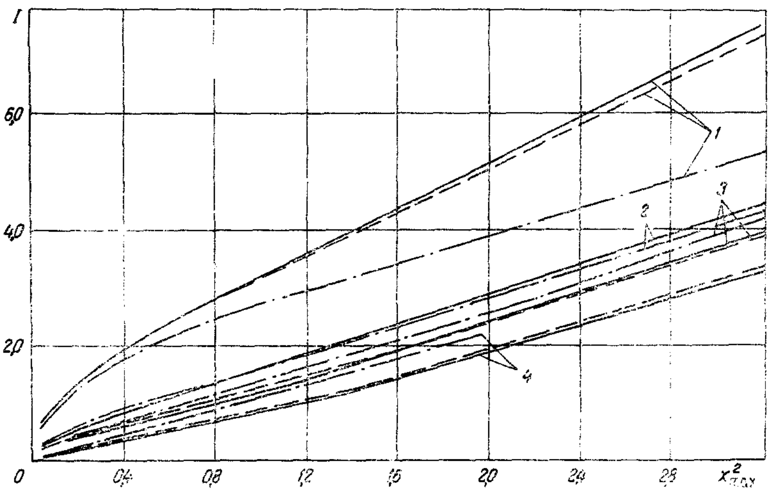

Fig. 3. Relation of I to x^2_{max}: 1) $K_2 = 1$; 2) 5; 3) 10; 4) 100. Solid lines $K_1 = 0.05$, broken lines $K_1 = 0.1$, dot–dash lines $K_1 = 0.5$.

one has available all the values needed to calculate K_1 and K_2. From Figures 1 and 2 one derives x_{max} by reference to the oven length l, which defines the end of the curve on the basis of the broadening, and then one uses Fig. 3 and (4) to calculate q.

We use Figs. 1-3 to consider the derivation of the effect of γ, w, α_0, and D on the output curve for particular numerical examples. We use the following numerical values for initial parameters: $q = 10$ cm³, $\gamma = 20$ deg/cm, $\alpha_0 = 1$ cm/sec; $w = 0.2$ cm/sec; $D = 0.2$ cm²/sec; $Q = 8000$ cal/mole, $T_x = 400$°K; $T_{room} = 300$°K, $S = 0.15$ cm², and the corresponding accessory quantities are then $\sigma = 0.5$ cm^{-1}; $K_1 = RT_x/Q = 0.1$; $K_2 = \alpha_0/D\sigma = 10$; $\Gamma_{1x} = \alpha T_x/wT_{room} = 6.7$; $I = q\sigma/\Gamma_{1x}S = 5$; Fig. 3 gives $x_{max} = 1.82$. The peak in the oven lies at $\psi_{max} = x_{max}/\sigma = 3.64$ cm from the characteristic temperature.

1. Effects of γ. We consider how the temperature gradient affects the result when q and the other parameters are constant. Let the new value of γ be 2 deg/cm, in which case $\sigma = 0.05$ and $K_2 = 100$, while Γ_{1x} is not dependent on γ and does not vary for a given system with a constant speed ratio between the flow and oven. As q is fixed, while the working conditions are varied, the new curve corresponding to the previous amount of material is displaced, and therefore the new value of I given by (4) will be 0.5; then the peak now lies at $x_{max} = 0.75$ and $\psi_{max} = 15$ cm, so the conditions approach isothermal as the gradient is reduced, and the curve stretches out along the oven, with the peak passing into a region of lower temperatures. The same conclusions could be drawn from a qualitative consideration. The calculations also show that there is not a large displacement in the peak even though γ and σ have been reduced by factors of 10, since factors that sharpen the band have more effect at low temperatures than high concentrations.

2. Effects of w. Let the new value be $w = 0.1$ cm/sec, while α_0 remains constant; this alters α_0/w and Γ_{1x}, and thus T_x should be altered, and also the origin. The new value T''_x may be found from the known previous value T'_x from the transcendental equation

$$\frac{\Gamma'_{1x}}{\Gamma''_{1x}} = \frac{\left(\frac{\alpha}{w}\right)' T'_x}{\left(\frac{\alpha}{w}\right)'' T''_x} \exp\left[\frac{Q}{RT'_x}\left(1 - \frac{T'_x}{T''_x}\right)\right].$$

This equation is solved numerically for the above values for the parameters to give $T''_x = 370°$ and $\Gamma''_{1x} = 12.3$; the accessory parameters become $\sigma = 0.585$ cm^{-1}, $K_1 = 0.093$, $K_2 = 8.5$, and $I = 3.18$, and Fig. 3 gives approximately $x_{max} = 1.63$ and $\psi_{max} = 2.8$ cm, so the distribution curve as a whole is advanced along the oven towards lower temperatures. The shift in the characteristic temperature can be found from

$$\Delta\psi = \frac{T'_x - T''_x}{\gamma} = 1.5 \text{ cm}.$$

The distance from the peak to T_x is reduced, and the curve in the layer becomes narrower, because the adsorption is increased, and the band for the given q takes up a smaller part of the oven.

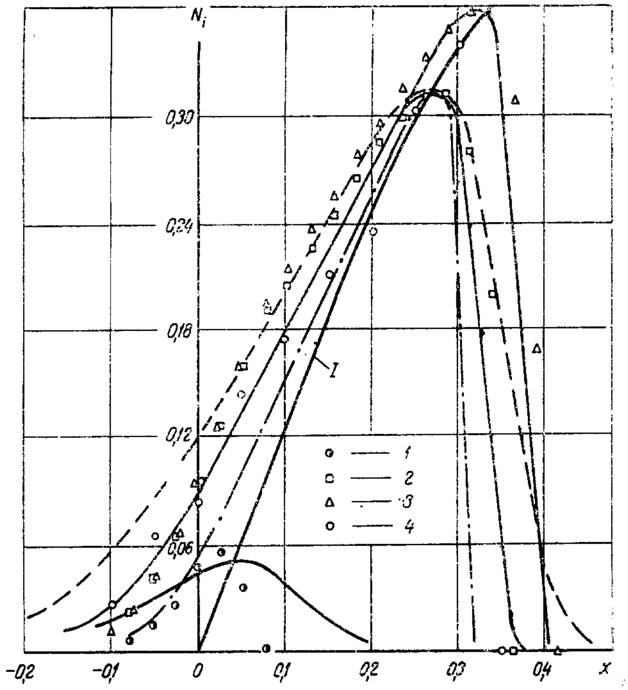

Fig. 4. Curves for CO_2 in air on MSM silica gel, $K_1 = 0.396$; $K_2 = 100$. Points from experiment: 1) $q = 0.5$ cm^3; 2) 10; 3) 14 cm^3; curves by calculation: solid lines $K_2 = 100$, $q = 10.1$; broken lines $K_2 = 50$, $q = 12.9$ cm^3; dot–dash lines $K_2 = 300$, $q = 7.65$ cm^3; I equilibrium curve given by (3); 4) curve calculated from (6) for $q = 10$.

However, although the curve has become narrower, the output curve recorded by the detector should become broader; in fact, as w has been halved, the distance from the characteristic curve to the peak is reduced by a factor 1.3 ($\psi'_{max}/\psi''_{max} = 3.64/2.8$), whereas the Henry factor is increased by a factor 1.84 ($\Gamma''_x/\Gamma'_x = 12.3/6.7$).

3. Effect of α_0 and D. We envisage the case of $\alpha_0/w = 5$ constant; as α_0 and D appear in the form α_0/D, it is best to consider the effects of changing this ratio. Let α_0/D change from 5 to 0.5, which affects only K_2, which becomes 1. Figure 3 shows that the new values for x_{max} and ψ_{max} for the previous q will be 1.42 and 2.84 cm respectively. Comparison of the initial and final curves in Fig. 1 shows that the peak position approaches the characteristic point as the effective diffusion coefficient increases or the flow speed is reduced, but the curve corresponding to $K_2 = 1$ takes up a much larger part of the oven, and the leading edge terminates at a large distance from T_x.

This model enables us to solve the inverse problem, namely to use experimental results to find the diffusion coefficient. Although D and α_0 appear as a ratio in (1), and therefore the effects of the thermal broadening to some extent are balanced out, we have to stress that the resulting value for D will be an effective one in view of the complexity of the actual thermal and hydrodynamic processes. The actual process may be affected by the sorbent heating rate, nonuniformity in the temperature distribution, and mixing in the flow, all of which appear inexplicitly in the defective diffusion coefficient, and which do not appear in our model.

We performed experiments on a column filled with MSM silica gel; the substance to be analyzed was CO_2, with the carrier gas air, and the flow rate $v_0 = 9.5$ cm^3/min, with a column diameter of 0.45 cm, oven speed $w = 4$ cm/min, $\gamma = 1.8$ deg/cm, and $T_x = 350$°C.

Figure 4 shows results from several runs for various q in terms of the dimensionless coordinate x; the distances on the chart have been converted to distances in the oven via $\psi = \psi_c\, w/v_c$; the value $\sigma = 0.013$ cm^{-1} was found from the graph in terms of $\ln(1-N_1)/(1-\gamma\psi/T_x)$ against ψ, where N_1 and ψ correspond to the peak on the curve. The value of Γ_{1x} was 8.4, with $K_1 = 0.396$. To find the K_1 from the curve corresponding to $q = 10$ cm^3 we chose the optimal K_2 to provide the best fit of the calculated curve to the experimental points. Figure 4 shows curves corresponding to several K_2; the best curve having $K_2 = 100$ is shown in solid line. The result for D, using a mixing factor of 0.75, was 1 cm^2/sec, which is 5-6 times the molecular diffusion coefficient given in handbooks. However, the difference arises because D includes additional broadening factors. The solid lines were calculated for $K_2 = 100$ for $q = 0.5$ and 14 cm^3. The deviations from experiment for small q indicate that our model is only an approximation to the actual process, although on the whole it correctly reflects in a qualitative fashion the basic trends in the process.

Numerical solution of (1) requires a computer, which is not always available; it is easier to use an analytical solution, and we have previously [2] derived such a solution, but with fairly crude assumptions: the exponential was expanded as a series taking only two terms, while the K_{1x} term was neglected in the denominator in (2). These assumptions enable us to describe correctly the output curve for range 0-0.4nx, i.e., low concentrations, where the distinctive features of chromatothermography have little effect. Here we present a revised analytical solution for a wider range in x.

We convert (1) via the substitution $N_1 = 1/z$ to a linear homogeneous equation, whose solution takes the following general form after reverse substitution:

$$N_1(x) = \frac{\exp\left[\int\limits_{x_0}^{x} f_1(x)\,dx\right]}{\bar{C} - \int\limits_{x_0}^{x} f_2(x)\exp\left[\int\limits_{x_0}^{x} f_1(x)\,dx\right]}. \tag{5}$$

We see from (5) with $x = x_0$ that $\bar{C} = 1/N_1(x_0)$, where $N_1(x_0)$ is the initial value of the concentration, which we took from the peak on the curve and which corresponds to (3). Equation (5) contains two integrals lacking explicit expressions, which are virtually impracticable to use without a computer. We can simplify this expression and operate with only one integral. The fraction $x/(1-x)$ can be replaced approximately by $1 + x + x^2$ with less than 5% error for $x < 0.4$; as the expression $f_1(x)$ in the denominator contains K_{1x}, and x does not exceed 0.5, we obtain satisfactory solution for x between 0 and 0.8, which corresponds to the actual working range in the technique. If K_1 is less than 0.5, one can use a wider range in x, and these simplifications then allow one to derive the integral of $f_1(x)$. The exponential will have to be expanded as a series to integrate the expression in the denominator of (5), which would involve considerable loss of accuracy. The final solution takes the form

$$N_1(x) = \frac{\exp\left[K_2\varphi_1(x,\ K_1)\Big|_{x_0}^{x}\right]}{\bar{C} - K_2\int\limits_{x_0}^{x}\varphi_2(x,\ K_1)\,dx}, \tag{6}$$

where

$$\varphi_1(x,\ K_1) = x - e^{x}\left[K_1^2x^2 + K_1(1 - 2K_1)x + (1 - K_1 + 2K_1^2)\right],$$

$$\varphi_2(x,\ K_1) = \frac{\exp\left[x + K_2\varphi_1(x,\ K_1)\Big|_{x_0}^{x}\right]}{1 - K_1x}.$$

Then to calculate the curve shape from (6) requires one to calculate only a single integral numerically using a comparatively simple integrand; these calculations can be performed manually by slide rule. If one uses a computer, the working time is very much reduced compared with numerical integration of (1). Figures 1 and 4 show examples of manual calculations, and it is clear that analytical solution via (6) (points on the curves) differs little from the exact computer solution of (1), which is shown in Figs. 1 and 4 by the solid lines.

NOTATION

N_1, volume concentration of test substance in gas phase, ml/ml of sorbent; ψ, coordinate inside oven reckoned from the point with the characteristic temperature, cm; ψ_c, coordinate of chart point, cm; v_c, chart speed, cm/sec; l, length of oven, cm; x, dimensionless coordinate; σ, parameter for temperature distribution and properties of test substance, 1/cm; γ, temperature gradient, deg/cm; T_x, temperature at characteristic point (corresponds to oven speed peak at low concentrations) °K; Q, heat of adsorption, cal/mole; R, universal gas constant, cal/deg·mole, α_0, linear flow speed at outlet, cm/sec; w, oven speed, cm/sec; D, effective diffusion coefficient referred to outlet; $f_1(x)$, $f_2(x)$, functions in (2); K_1, K_2, dimensionless quantities; q amount injected, cm³; S, column cross section, cm³; Γ_{1x}, Henry coefficient at characteristic temperature; I, integral in (4); C, constant of integration in (5).

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