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A New Approach to Linear Temperature Programming Calculations

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Abstract

The theory of temperature programming has been reexamined. It is shown that a linear program leads to an explicit relation for the retention temperature in terms of the inverse exponential integral. Numerical examples are solved using a straight line plot of the exponential integral together with a plot based on the equivalent temperature concept. A simple explicit expression in terms of common functions for the retention temperature during linear temperature programming was deduced. This was made possible using the inverse log nonlinear program which can be made to approximate quite closely a linear program. This expression was used to explain the constancy of intervals and other phenomena encountered during the linear temperature programming of homologous series.

INTRODUCTION

A rigorous treatment of temperature programming is very difficult, and the equations derived are complicated even with a linear rate of temperature rise. The relations developed so far for linear temperature programming have been in terms of the not too common exponential integral (1–3). The difficulty in handling this integral has made it hard to explain and to give easy proofs for some of the phenomena encountered in the case of linear temperature programming.

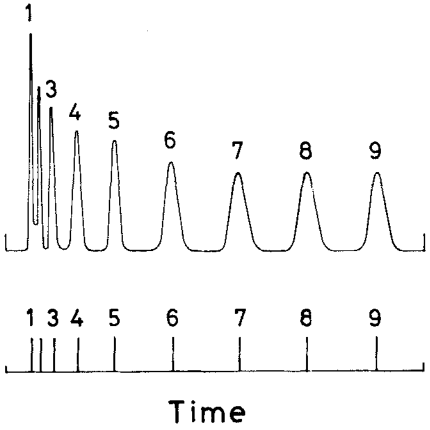

FIG. 1. Typical temperature programmed run.

regardless of the rate of temperature rise, the members of a homologous series emerge evenly spaced during linear temperature programming. It is also an experimental fact that with a high rate of temperature rise the spacings become even after the emergence of a small number of the first members, and the lower the rate of temperature rise, the greater the number of components which emerge unevenly spaced at the beginning of the chromatographic run. Figure 1 represents a typical temperature programmed run. The lower part of the figure is a symbolic representation of the positions of the peak maxima.

These and other phenomena are encountered experimentally, but it has been always difficult to give straightforward explanations or proofs. For example, if one starts with a linear rate of temperature rise equal to 0.1 °C/min or even 0.001 °C/min, will the spacings ever become even and, if so, at what carbon number and what is the magnitude of this constant spacing? So far, the answers to such questions have not been too easy mostly because no simple explicit relation for the retention temperature was deduced.

Several years ago it was pointed out by this author (*3*) that some nonlinear programs, such as the inverse linear and the inverse log programs, lead to analytic solutions in terms of simple and common functions. One of these programs (the inverse linear) was developed by this author in the same paper. It was also studied and developed further by Szepe (*4*), who found that easy expressions are obtained even if the column-free volume was taken into account.

There is, however, much more interest in linear temperature programming because it is easier to make instruments with linear programs. Furthermore, a nonlinear program can be approximated by a series of linear programs having different slopes.

Further investigations of the different nonlinear programs by this author showed that the inverse log program can be made to approximate quite closely a linear program over a large span of temperature rise. This made it possible to deduce easy and explicit relations for linear temperature programming, particularly for the retention temperature, and it was therefore easy to explain qualitatively as well as quantitatively many of the experimental findings.

ASSUMPTIONS MADE

It was necessary, however, to make some simplifying assumptions in order to avoid mathematical complications. The main assumptions made in the course of this treatment follow.

Assumption I

$$\frac{dt}{t_r} = \frac{dl}{L} \tag{1}$$

This is the fundamental differential equation. It means that at any point in the column shown in Fig. 2, the differential fractional length traversed is equal to the differential fractional time with respect to the isothermal retention time at the corresponding temperature. This equation is exact in the case of incompressible eluents. It also leads to correct answers in the case of compressible fluids whether it is a constant pressure or constant flow operation. This was shown to be true by this author and co-workers several years ago (*5*) as long as the integration is performed over the total column length, in which case the pressure effect cancels out.

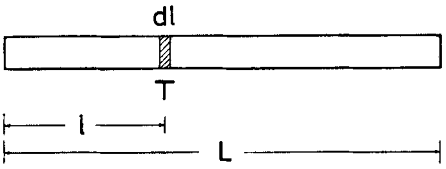

FIG. 2. Schematic of the column used for making assumptions.

Assumption II

$$t_r = ae^{b/T} \qquad (2)$$

Equation (2) means that the isothermal retention time t_r vs the temperature is a straight line on log-reciprocal chart paper as shown in Fig. 3A, where a and b are constants. This equation applies better to the net reten-

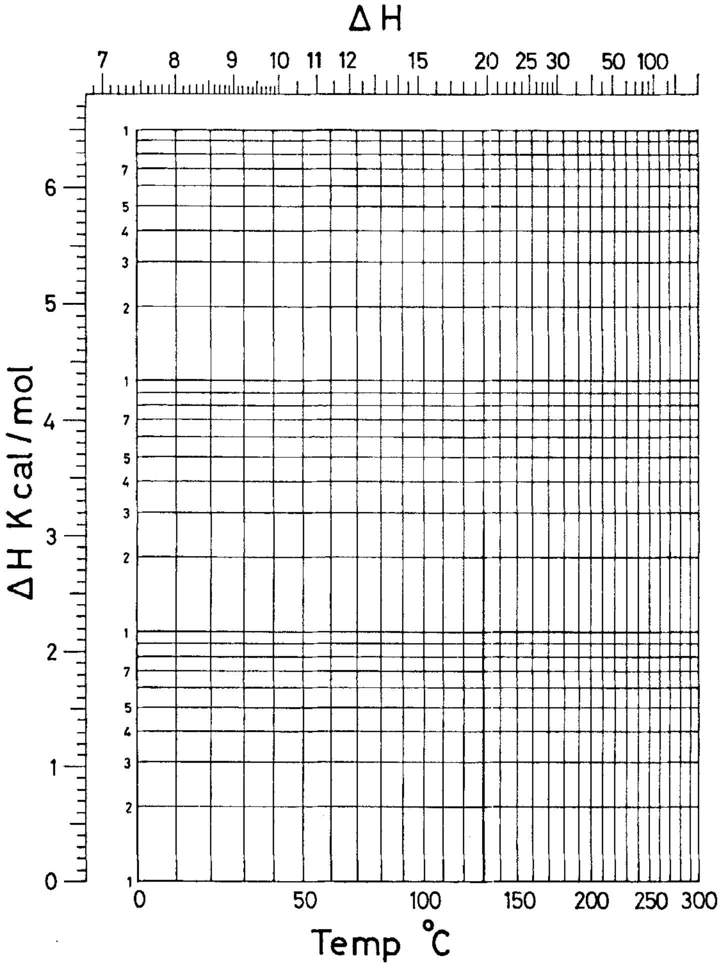

FIG. 3A. Log-reciprocal chart for Eq. (2).

tion time, but here we assume that it also applies to the uncorrected retention time and that the heat of solution ΔH is constant, $b = \Delta H/R$. The usefulness of the chart is increased by introducing an outside scale on which ΔH is read at the point where a parallel line from the origin meets the scale. This is accomplished easily with the help of a transparent sheet on which a large number of parallel lines are drawn at small distances from each other (Fig. 3B). For convenience, the abscissa in Fig. 3A is marked in °C.

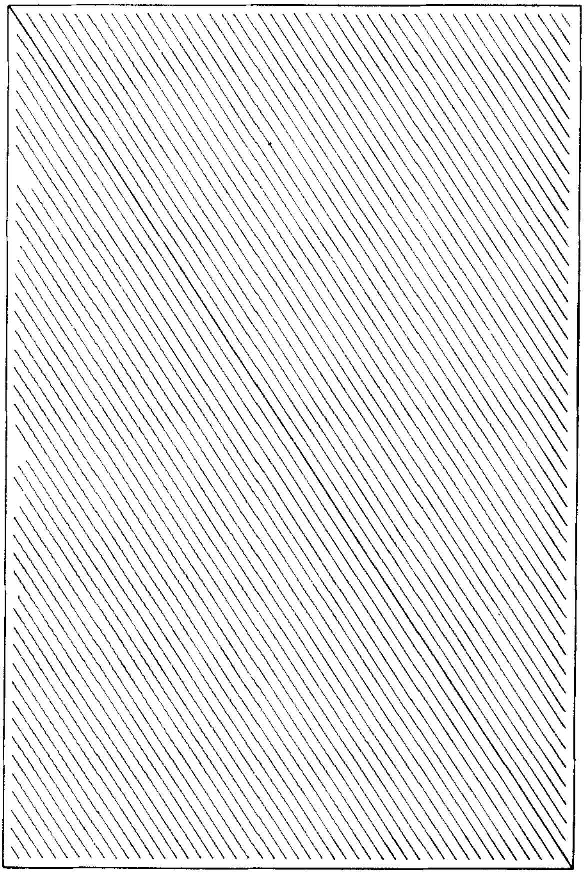

FIG. 3B. Overlay for Fig. 3A.

It is a well-known fact that except for the first few compounds and For homologous series the following two assumptions are also made:

$$\Delta H_n = \Delta H_{n-1} + \beta \tag{3}$$

and

$$t_{r,n} = t_{r,n-1}\alpha \tag{4}$$

For a homologous series, β is not a function of temperature or the carbon number n, while α is a function of temperature but not of n.

From the above equations one deduces the following relation for a

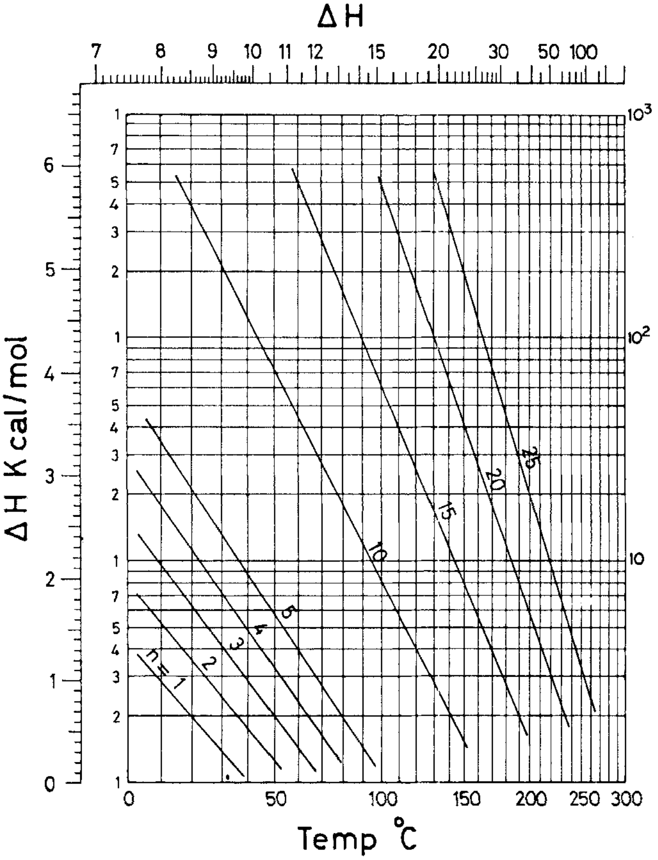

FIG. 4. Plot of Eq. (6).

homologous series:

$$t_{r_n} = t_{r_n,0} \exp\left(\frac{b_n}{T} - \frac{b_n}{T_0}\right) \tag{5}$$

or

$$t_{r_n} = t_{r_1,0}\alpha_0{}^{n-1} \exp\left[\frac{\Delta H_1 + (n-1)\beta}{RT} - \frac{\Delta H_1 + (n-1)\beta}{RT_0}\right] \tag{6}$$

Figure 4 is a plot of Eq. (6) on Fig. 3 where $t_{r_1,0} = 2$ min, $\alpha_0 = 1.8$ at 20°C, $\Delta H_1 = 6000$ cal/mole, and $\beta = 500$ cal/mole.

DEVELOPMENT OF THE FUNDAMENTAL RELATION FOR A LINEAR PROGRAM

For a linear program

$$T = T_0 + rt \tag{7}$$

where r is the linear rate of temperature rise and t is the time.

Substituting from Eqs. (2) and (7) into Eq. (1) and integrating over the whole column length between inlet temperature T_0 and outlet temperature T_f, one gets

$$\frac{ra}{b} = \Psi(h_f) - \Psi(h_0) \tag{8}$$

where

$$a = t_r e^{-b/T}$$

t_r is the retention time corresponding to temperature T, $b = \Delta H/R$, and

$$h = \frac{b}{T} = \frac{\Delta H}{RT}$$

$\Psi(h)$ is the exponential integral defined by the relation

$$\Psi(h) = \int_h^\infty (e^{-x}/x^2)\, dx \tag{9}$$

This integral is tabulated in many references and is plotted in Fig. 5 for values of h of chromatographic interest; namely, from $h = 6$ to $h = 17$. The ordinate is a multicycle log scale, and the scale of the abscissa is calculated according to a derived function in order to give a straight-line plot.

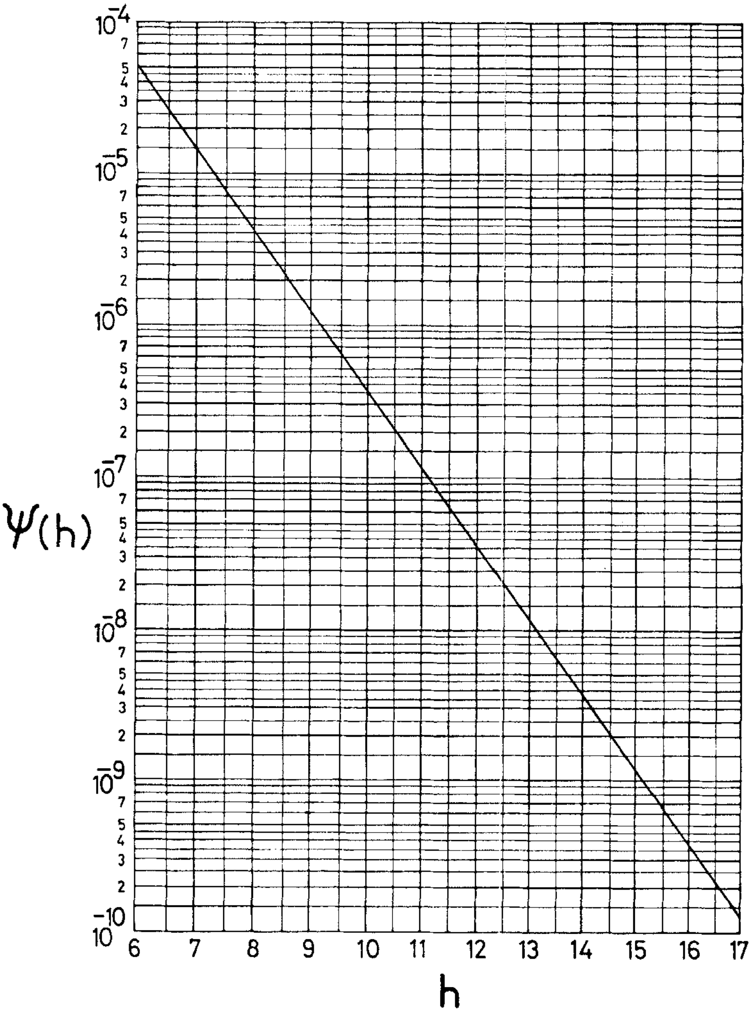

FIG. 5. Plot of Eq. (9) for values of h.

If in deriving Eq. (8) the integration was performed over a fraction x of the column between temperatures T_1 and T_2 instead of the total column length, one gets

$$xra/b = \Psi(h_2) - \Psi(h_1) \tag{10}$$

When h_2 and h_1 are fixed, Eq. (10) leads to

$$x_2/x_1 = r_1/r_2 \tag{11}$$

Which means that, between two fixed temperatures on the column length, the fraction of column covered by a component is inversely proportional to the rate of temperature rise.

This is an important relation. It is correct for incompressible eluents and should be used with some care in the case of compressible fluids because the pressure effect cancels out only over the total length of the column and not over a fraction of the column length.

AN EXPLICIT RELATION FOR THE RETENTION TEMPERATURE T_f

An explicit relation for T_f can be easily deduced from Eq. (8) which gives

$$\Psi(h_f) = \frac{ra}{b} + \Psi(h_0) \tag{12}$$

therefore

$$h_f = \Psi^{-1}\left[\frac{ra}{b} + \Psi(h_0)\right] \tag{13}$$

The symbol Ψ^{-1} represents the inverse of the exponential integral as much as the log function is the inverse of the exponential function. A table of the inverse exponential integral can be prepared from existing tables of the exponential integral. A graph of the inverse function may be prepared from that of the original function simply by making the ordinate an abscissa and vice versa. Since $h_f = b/T_f$, one gets a direct relation for T_f in terms of the inverse exponential function:

$$T_f = \frac{b}{\Psi^{-1}[(ar/b) + \Psi(h_0)]} \tag{14}$$

Although Eq. (14) is a direct or explicit relation of the retention temperature T_f, it is in terms of an uncommon function, namely, the inverse exponential integral function, and this restricts the use of Eq. (14). An explicit relation of T_f in terms of common and easy functions will be developed later in this paper.

THE EFFECT OF TEMPERATURE ON THE RELATIVE VOLATILITY

Assuming that

$$b_2 = b_1 + \beta$$

then

$$\alpha = \frac{t_{r_2}}{t_{r_1}} = \frac{t_{r_{2,0}} \exp\,[(b_2/T) - (b_2/T_0)]}{t_{r_{1,0}}\,[\exp\,(b_1/T) - (b_1/T_0)]}$$

so that

$$\alpha = \alpha_0 \exp\left(\frac{\beta}{T} - \frac{\beta}{T_0}\right) \tag{15}$$

THE EQUIVALENT TEMPERATURE CONCEPT

The equivalent temperature concept was first introduced by this author (*3*). The equivalent temperature T_e is defined as the temperature at which the isothermal retention time is equal to the programmed retention time t_p between inlet and outlet temperatures T_0 and T_f, respectively.

In temperature programming calculations, one is usually interested in one of the following:

(a) Given the final temperature T_f, what is r or t_p?
(b) Given r, what is T_f or t_p?
(c) Given t_p, what is r or T_f?

In all cases T_0 is also given. A plot of t_r vs T on log-reciprocal graph paper for the component under consideration should be available, or the data necessary to prepare the plot such as, for example, two isothermal retention times at two different temperatures.

Case (a) and Case (b) are solved directly using Eqs. (8) and (14), while Case (c) can be solved only by trial and error. It is possible to plot Eq. (8) in such a way that trial and error will not be needed for Case (c), but a much easier approach would be via the equivalent temperature concept.

In this case the constant a in Eq. (8) is given by

$$a = t_p \exp(-b/T_e)$$

and

$$r = \frac{T_f - T_0}{t_p} \tag{16}$$

Substituting in Eq. (8), one gets

$$\exp(-b/T_e) = \frac{\Psi(b/T_f) - \Psi(b/T_0)}{(T_f - T_0)/b} \tag{17}$$

A plot of Eq. (17) would be useful in calculating the linear rate needed to elute a component in a given time. One may plot b/T_e vs b/T_f with b/T_0 as the parameter. A more useful chart which can be conveniently used in solving Case (c) is prepared as follows.

Fixing Θ_0 in Eq. (17) at 20°C, Eq. (17) is solved and a table is prepared in which Θ_e is tabulated for different values of Θ_f with ΔH as the parameter (Table 1). Θ_0, Θ_f, and Θ_e are the inlet, outlet, and equivalent temperatures, respectively, in °C. Figure 6 is then drawn in which $\Theta_f - \Theta_e$ is plotted vs $\Theta_e - 20$ with ΔH as the parameter. One can show that Fig. 6 can be used to solve Case (c) regardless of the starting temperature. It is, in fact, a plot of $(\Theta_f - \Theta_e)'$ vs $(\Theta_e - \Theta_0)'$ with $\Delta H'$ as the parameter where

$$(\Theta_f - \Theta_e)' = (\Theta_f - \Theta_e)\frac{273 + 20}{273 + \Theta_0} = (\Theta_f - \Theta_e)f$$

Similarly,

$$(\Theta_e - \Theta_0)' = (\Theta_e - \Theta_0)\frac{273 + 20}{273 + \Theta_0} = (\Theta_e - \Theta_0)f$$

and

$$\Delta H' = \Delta H \frac{273 + 20}{273 + \theta_0} = \Delta H \times f$$

If, in preparing Table 1, the starting temperature was fixed at any Θ_r instead of 20°C, it should lead to the same result. In this case

$$f = \frac{273 + \Theta_r}{273 + \Theta_0}$$

TABLE 1

	Θ_e								
Θ_f	$\Delta H = 5$	6	7	8	9	10	11	12	15
30	25.1	25.1	25.1	25.2	25.2	25.2	25.2	25.3	25.3
40	30.3	30.4	30.5	30.6	30.7	30.8	30.9	31.0	31.2
50	35.7	35.9	36.1	36.3	36.5	36.7	36.9	37.1	37.6
60	41.3	41.6	41.9	42.3	42.6	42.9	43.2	43.5	44.3
70	46.9	47.4	47.9	48.4	48.8	49.3	49.7	50.1	51.3
80	52.6	53.3	54.0	54.6	55.2	55.8	56.4	57.0	58.5
90	58.4	59.3	60.2	61.0	61.8	62.5	63.2	63.9	63.9
100	64.3	65.4	66.4	67.4	68.4	69.3	70.2	71.0	73.3
110	70.2	71.5	72.8	74.0	75.1	76.2	77.2	78.2	80.8
120	76.2	77.7	79.2	80.6	81.9	83.1	84.3	85.4	88.4
130	82.2	83.9	85.6	87.2	88.7	90.1	91.4	92.7	95.9
140	88.2	90.2	92.1	93.9	95.6	97.1	98.6	100.0	103.6
150	94.2	96.5	98.6	100.6	102.5	104.2	105.8	107.3	111.2
160	100.3	102.8	105.2	107.3	109.4	111.2	113.0	114.6	118.8
170	106.4	109.1	111.7	114.1	116.3	118.3	120.2	121.9	126.4
180	112.4	115.5	118.3	120.8	123.2	125.4	127.4	129.3	134.1
190	118.5	121.8	124.8	127.6	130.1	132.5	134.6	136.6	141.7
200	124.6	128.1	131.4	134.3	137.0	139.5	141.8	143.9	149.3
210	130.7	134.5	137.9	141.1	143.9	146.6	149.0	151.2	156.9
220	136.8	140.8	144.5	147.8	150.8	153.6	156.2	158.5	164.5
230	142.8	147.1	150.0	154.5	157.7	160.7	163.3	165.8	172.1
240	148.9	153.4	157.5	161.2	164.6	167.7	170.5	173.1	179.6
250	154.9	159.7	164.0	167.9	171.5	174.7	177.6	180.3	187.2
260	170.0	166.0	170.5	174.6	178.3	181.7	184.8	187.6	194.7
270	167.0	172.3	177.0	181.3	185.2	188.7	191.9	194.8	202.2
280	173.0	178.6	183.5	188.0	192.0	195.7	199.0	202.0	209.7
290	179.0	184.8	190.0	194.6	198.8	202.6	206.0	209.2	217.2
300	185.0	191.0	196.4	201.3	205.6	209.5	213.1	216.4	224.6
310	191.0	197.3	202.9	207.9	212.4	216.5	220.1	223.5	232.1
320	197.0	203.5	209.3	214.5	219.1	223.4	227.2	230.7	239.5
330	202.9	209.7	215.7	221.0	225.9	230.2	234.2	237.8	246.9
340	208.9	215.9	222.1	227.6	232.6	237.1	241.2	244.9	254.3
350	214.8	222.0	228.4	234.2	239.3	243.9	248.1	252.0	261.6

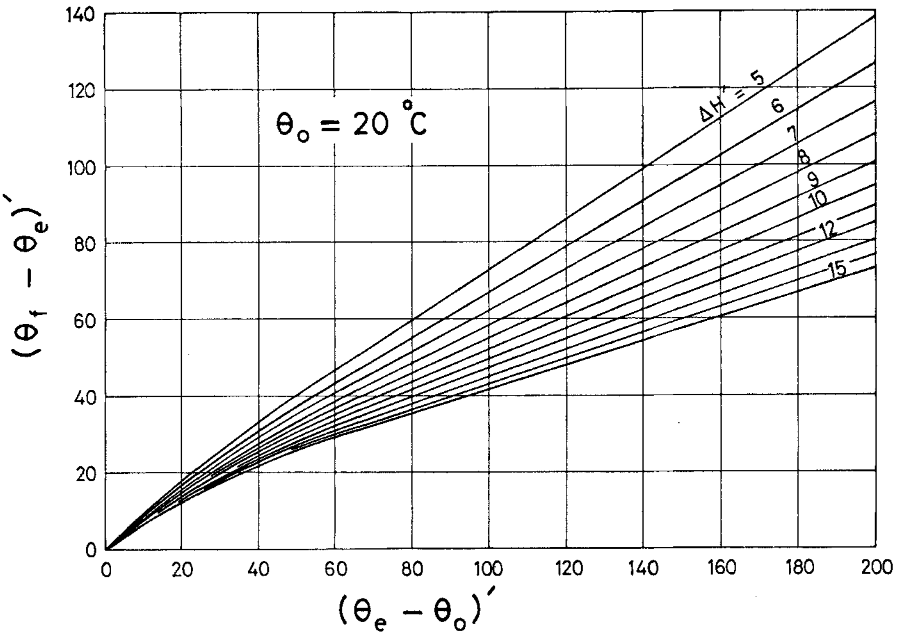

Fig. 6. Solution of Case (c).

Example 1

I. Starting from 40 °C at a rate of 20 °C/min, how long will it take to elute Component A in Fig. 7 and what is the outlet temperature?

II. What is the linear rate needed to elute Component A in 6 min starting from 50 °C?

Answer

I. From Fig. 7,

$$\Delta H = 8900 \text{ cal/mole}$$

$$t_r = 33 \text{ min at } 100\,^{\circ}\mathrm{C}$$

therefore

$$b = \Delta H/2 = 8900/2 = 4450$$

$$33 = ae^{4450/373}$$

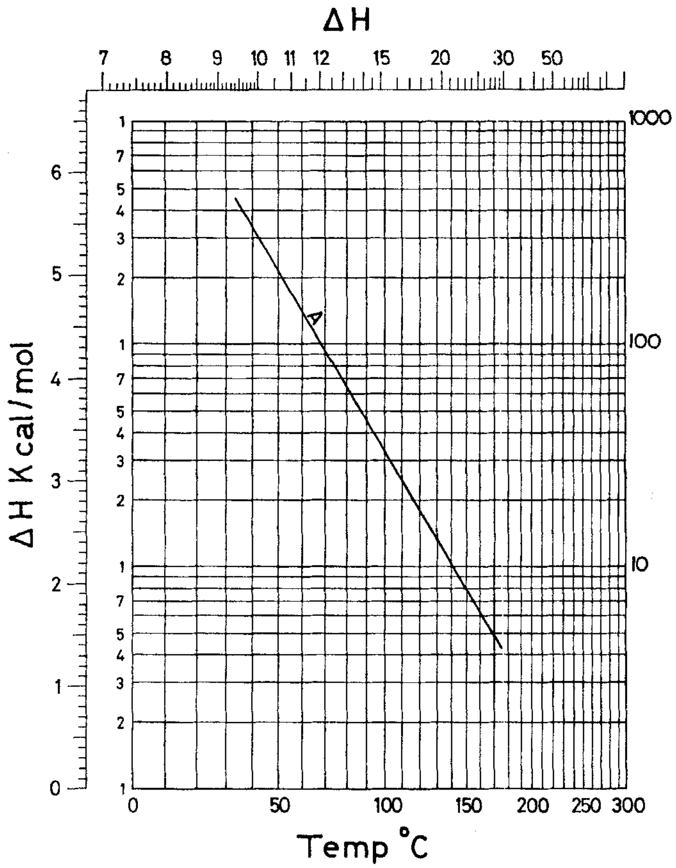

FIG. 7. Elution of Component A.

therefore

$$a = 2.17 \times 10^{-4}$$

$$h_0 = \frac{4450}{313} = 14.22$$

$$\Psi(h_0) = 2.7 \times 10^{-9} \qquad \text{(from Fig. 5)}$$

$$\Psi(h_f) = 2.7 \times 10^{-9} + \frac{20 \times 2.17 \times 10^{-4}}{4450} = 9.15$$

$$h_f = 9.15 \qquad \text{(from Fig. 5)}$$

therefore

$$T_f = 486\,^\circ\mathrm{K}$$

and

$$t_p = \frac{486 - 313}{20} = 8.65 \text{ min}$$

II. To avoid trial and error, Fig. 6 is used.

$$\Theta_e = 162\,^\circ\mathrm{C} \qquad \text{(from Fig. 7)}$$

$$\Theta_e - \Theta_0 = 162 - 50 = 112\,^\circ\mathrm{C}$$

$$(\Theta_e - \Theta_0)' = 112\frac{293}{323} = 101.6\,^\circ\mathrm{C}$$

$$\Delta H' = 8.9\frac{293}{323} = 8.07$$

From Fig. 6,

$$(\Theta_f - \Theta_e)' = 57\,^\circ\mathrm{C}$$

$$\Theta_f - \Theta_e = 57\frac{323}{293} = 62.8\,^\circ\mathrm{C}$$

$$\Theta_f - \Theta_0 = 112 + 62.8 = 174.8\,^\circ\mathrm{C}$$

$$r = 174.8/6$$

$$= 29.5\,^\circ\mathrm{C/min}$$

APPROXIMATING THE EXPONENTIAL INTEGRAL

The following approximation of the exponential integral for values of chromatographic interest was given by Giddings (*1*).

Approximation I

$$\Psi(h) = \frac{e^{-h}}{(h + 0.85)^2} \tag{18}$$

Following a systematic approach, a better approximation was deduced by this author (*6*) as follows.

Approximation II

$$\Psi(h) = \frac{4e^{-h}}{(2h - 1)(2h + 5)} \tag{19}$$

Another convenient approximation which is a little less accurate than Approximation II was also deduced by this author (*6*) as follows.

Approximation III

$$\Psi(h) = \frac{e^{-h}}{h(h + 1.8)} \tag{20}$$

This approximation is only slightly better than Approximation I, but it is sometimes more convenient to handle it analytically as will be seen later in deducing the average relative volatility during a temperature programmed run.

A comparison between the three approximations is given in Table 2.

MIDCOLUMN AND FRACTIONAL LENGTH TEMPERATURE

Even though the difference between inlet and outlet temperatures may be quite large, the temperature difference from the time the component reaches half the column and the time it reaches the column outlet is relatively small, being of the order of 20°C. If h_x is the value of h when

TABLE 2

	$\Psi(h)$			
h	Exact value	Approximation I	Approximation II	Approximation III
5	2.00×10^{-4}	1.97×10^{-4}	2.00×10^{-4}	1.98×10^{-4}
6	5.30×10^{-5}	5.28×10^{-5}	5.30×10^{-5}	5.30×10^{-5}
7	1.48×10^{-5}	1.48×10^{-5}	1.48×10^{-5}	1.48×10^{-5}
8	4.26×10^{-6}	4.28×10^{-6}	4.26×10^{-6}	4.28×10^{-6}
9	1.26×10^{-6}	1.27×10^{-6}	1.26×10^{-6}	1.27×10^{-6}
10	3.83×10^{-7}	3.86×10^{-7}	3.82×10^{-7}	3.85×10^{-7}
11	1.18×10^{-7}	1.19×10^{-7}	1.18×10^{-7}	1.19×10^{-7}
12	3.69×10^{-8}	3.72×10^{-8}	3.68×10^{-8}	3.71×10^{-8}
15	1.21×10^{-9}	1.22×10^{-9}	1.21×10^{-9}	1.21×10^{-9}
20	4.70×10^{-12}	4.74×10^{-12}	4.70×10^{-12}	4.73×10^{-12}
25	2.06×10^{-14}	2.08×10^{-14}	2.06×10^{-14}	2.07×10^{-14}

the component is at fraction x of the column length and if $\Psi(h_0)$ can be neglected in comparison with $\Psi(h_f)$ and $\Psi(h_x)$, which is generally the case when $T_f - T_0$ is more than 80 °C and x is bigger than 0.3, then from Eq. (8) one deduces that

$$x = \Psi(h_x)/\Psi(h_f) \tag{21}$$

From the tables of the exponential integral or from Fig. 5, it is possible to prepare a table which lists the values of $h_x - h_f$ corresponding to different values of x with h_f as the parameter.

The value of $h_x - h_f$ may be calculated analytically as follows: Starting with Eq. (20) (Approximation III) for the exponential integral, one gets

$$x = \frac{\Psi(h_x)}{\Psi(h_f)} = \exp\left[-(h_x - h_f)\right]\frac{h_f(h_f + 1.8)}{h_x(h_x + 1.8)}$$

let

$$(h_x - h_f) = y$$

Substituting in the above equation, we find

$$-\ln x = y + \ln\left(1 + \frac{y}{h_f}\right)\left(1 + \frac{y}{h_f + 1.8}\right) \tag{22}$$

Since y is small compared to h and since $\ln(1 + g) = g$ when g is a small fraction, Eq. (22) reduces to

$$-\ln X = y\left(1 + \frac{1}{h_f} + \frac{1}{h_f + 1.8}\right)$$

or

$$h_x - h_f = -\frac{\ln x}{1 + (1/h_f) + 1/(h_f + 1.8)} \tag{23}$$

$(h_x - h_f)$ was calculated for different values of x when h_f is equal to 6 and 12. The values obtained are tabulated in Table 3. $(h_x - h_f)_{\text{av}}$ in the table is the arithmetic average of the two values at 6 and 12.

AVERAGE RELATIVE VOLATILITY AND THE SIGNIFICANT TEMPERATURE

During temperature programming the relative volatility between two components changes continuously as the components move along the column. The relative volatility usually decreases as the temperature

TABLE 3

Fraction x	$h_x - h_f$		$(h_x - h_f)_{av}$
	$h_f = 6$	$h_f = 12$	
0.3	0.93	1.05	0.99
0.4	0.71	0.80	0.75
0.5	0.54	0.60	0.57
0.6	0.40	0.44	0.42
0.7	0.28	0.31	0.29
0.8	0.17	0.19	0.18
0.9	0.08	0.09	0.09

increases. In the case of isothermal chromatography and if we neglect the pressure effect when the eluent is compressible, the relative volatility will be given by the ratio of the two distances traveled by the two components along the column. It is also given by the ratio of the two retention times. During temperature programming, however, the ratio between the two distances traveled along the column up to any temperature T will have a value somewhere between the relative volatility at T and that at the initial temperature T_0. This ratio is called the average relative volatility and is equal to the isothermal relative volatility at a temperature T' which is called the significant temperature between T_0 and T. The significant temperature concept does not apply directly to the average relative volatility obtained from retention times in a temperature programmed run because in this case the two components have been subjected to different average temperatures. It applies only to the case of intrinsic resolution where the relative volatility is quite close to 1, in which case the two components have been subjected to the same temperature all the time.

In order to derive the equation from which α_{av} during a temperature programmed run can be calculated, we start by deducing the fundamental differential equation. We assume that during a temperature programmed run when the temperature of the column was equal to T, Components 1 and 2 were at distances l_1 and l_2, respectively, and that during a differential increment of time dt, Component 1 traveled a distance dl_1 while Component 2 traveled a distance dl_2, then $dl_1/dl_2 = \alpha$, where α is the isothermal relative volatility at temperature T.

By definition, α_{av} up to temperature T_L is equal to L_1/L_2, where T_L is the temperature when Component 1 has traveled a length of column equal to L_1 and Component 2 has traveled a length equal to L_2. Therefore

$$\alpha_{av} = \frac{L_1}{L_2} = \frac{\int_0^{L_1} dl_1}{\int_0^{L_2} dl_2} = \frac{L_1}{\int_0^{L_1} (dl_1/\alpha)} \tag{24}$$

or

$$\frac{1}{\alpha_{av}} = \frac{1}{L_1}\int_0^{L_1} \frac{dl_1}{\alpha} \tag{25}$$

Substituting from the fundamental relations

$$dl/L = dt/t_r \qquad \text{and} \qquad \alpha = t_{r_2}/t_{r_1}$$

one gets

$$\frac{1}{\alpha_{av}} = \int_0^{t_{p_1}} \frac{dt}{t_{r_2}} \tag{26}$$

where t_{p_1} is the programmed retention time for Component 1 but

$$t_{r_2} = a_2 \exp(b_2/T)$$

Therefore

$$\frac{1}{\alpha_{av}} = \frac{b_2}{ra_2}\left[\Psi\left(\frac{b_2}{T_{f_1}}\right) - \Psi\left(\frac{b_2}{T_0}\right)\right] \tag{27}$$

For Component 1, according to Eq. (8) we have

$$1 = \frac{b_1}{ra_1}\left[\Psi\left(\frac{b_1}{T_{f_1}}\right) - \Psi\left(\frac{b_1}{T_0}\right)\right] \tag{28}$$

where

$$b_2 = \Delta H_2/R$$

and

$$b_1 = \Delta H_1/R$$

from Eqs. (27) and (28), and neglecting $\Psi(h_0)$ in comparison with $\Psi(h_f)$, one gets

$$\alpha_{av} = \frac{b_1 a_2}{b_2 a_1}\frac{\Psi(b_1/T_{f_1})}{\Psi(b_2/T_{f_2})} \tag{29}$$

for simplicity we denote b_1/T_{f_1} by y_1, b_2/T_{f_2} by y_2, and

$$b_2 = b_1 + \beta$$

Substituting in Eq. (29) leads to

$$\alpha_{av} = \alpha_0 \frac{y_1}{y_2} \exp(-\beta/T_0) \frac{\Psi(y_1)}{\Psi(y_2)}$$

Applying Approximation III for the exponential integral where

$$\Psi(y) = \frac{e^{-y}}{y(y + 1.8)}$$

gives

$$\alpha_{av} = \alpha_0 \frac{e^{-y_1}}{e^{-y_2}} \left(\frac{y_2 + 1.8}{y_1 + 1.8} \right) \exp(-\beta / T_0) \tag{30}$$

Since $1 + x = e^x$ for a small value of x, then Eq. (30) leads to

$$\alpha_{av} = \alpha_0 \exp \left[\frac{\beta}{T_f} \left(1 + \frac{1}{(b_1 / RT_{f_1}) + 1.8} \right) - \frac{\beta}{T_0} \right] \tag{31}$$

Comparison with the equation which follows from the definition of the significant temperature, namely

$$\alpha_{av} = \alpha_0 \exp \left(\frac{\beta}{T'} - \frac{\beta}{T_0} \right) \tag{32}$$

leads to

$$T' = T_{f_1} \left(\frac{h_{f_1} + 1.8}{h_{f_1} + 2.8} \right) \tag{33}$$

This result may be compared with the Giddings' relation for the significant temperature:

$$T' = T_{f_1} \left(\frac{h_{f_1}}{h_{f_1} + 0.85} \right) \tag{34}$$

Both Eq. (33) and the Giddings' equation give results which are sufficiently close to each other. Equation (34) can be rearranged to give

$$h' = h_f + 0.85 \tag{35}$$

For comparison with the Giddings' formula, Eq. (33) is rearranged in the form

$$T' = T_f \left(\frac{h_f}{h_f + I} \right) \tag{36}$$

This equation leads to

$$h' = h_f + I$$

I is a function of h_f whereas in the case of Eq. (35) it is a constant equal

TABLE 4

h_f	6	7	8	9	10	11	12
I	0.77	0.80	0.82	0.84	0.85	0.86	0.87

to 0.85. By equating Eqs. (33) and (36), it can be shown that

$$I = \frac{h_f}{h_f + 1.8} \tag{37}$$

Table 4 lists the values of I corresponding to different values of h_f.

One can see from Table 4 that the average value of I for values of h_f from 6 to 12 is equal to 0.82, while the average is equal to the Giddings' value 0.85 for values of h from 8 to 12.

RELATION BETWEEN h' AND h_x

By comparing the values listed in Table 4 for the significant temperature with those listed in Table 3 for $h_x - h_f$, where h_x is the value of h at fractional length x, it is evident that the significant temperature is the temperature at a fraction equal to 0.37 of the column length. This conclusion is still subject to the condition that the difference between T_0 and T_f is large enough to make $\Psi(h_0)$ very small in comparision with $\Psi(h_f)$.

NONLINEAR PROGRAMS

As pointed out by this author (*3*), certain nonlinear programs lead to simple analytic expressions. Examples of such programs are:

1. The inverse linear program

$$T = \frac{T_0}{1 - c_1 t} \tag{38}$$

2. The inverse square root program

$$T = \frac{T_0}{1 - c_2\sqrt{t}} \tag{39}$$

3. The inverse log program

$$T = \frac{T_0}{1 - a_1' \log(1 + a_2 t)} \tag{40}$$

c_1, c_2, a_1', and a_2 are constants.

The inverse linear program gives a progressively increasing rate of temperature rise, and the inverse square root program gives a progressively decreasing rate of temperature rise, while the inverse log program gives a progressively increasing rate or a progressively decreasing rate depending on the values of the constants a_1' and a_2. The interest in this work is in the inverse log program because it can be made to replace a linear program for the purpose of easy computations.

THE INVERSE LOG PROGRAM

The inverse log program, as represented by Eq. (40), can be made to approximate quite closely a linear temperature program over a large span of temperature rise. In this case it can be demonstrated that the constant a_1' has a value close to 1 and, for simplicity, it is taken equal to 1 with little loss in accuracy, and Eq. (40) becomes

$$T = \frac{T_0}{1 - \log(1 + a_2 t)} = \frac{T_0}{1 - a_1 \ln(1 + a_2 t)} \tag{41}$$

where

$$a_1 = \ln_{10} e = 0.4343$$

a_2 is a function of the linear rate. The relation between a_2 and r is deduced by differentiating Eq. (41) with respect to t and equating $(dT/dt)_{t=0}$ to the constant rate r. This leads to the relation

$$a_2 = r/a_1 T_0 \tag{42}$$

Figure 8 is a plot of the three nonlinear programs (Eqs. 38–40) between $T_0 = 50\,°\mathrm{C}$ and $T_f = 200\,°\mathrm{C}$. The linear program is also shown for comparison. As can be seen from Fig. 8, the linear and inverse log programs are almost identical; the maximum deviation from one another being less than 1 °C as can be seen from Table 5

In plotting Fig. 8, the value of a_2 can be obtained by two different methods:

1. An exact method where T_0 and T_f are both known. Substituting in Eq. (41) gives the product $a_2 t_p$. If the linear rate is assumed to be 10°C/min, then t_p is equal to $(200 - 50)/10 = 15$ min. This gives a value of $a_2 = 0.0717$.
2. An approximate method using Eq. (42). This gives

$$a_2 = \frac{r}{a_1 T_0} = \frac{10}{0.4343 \times 323} = 0.0713$$

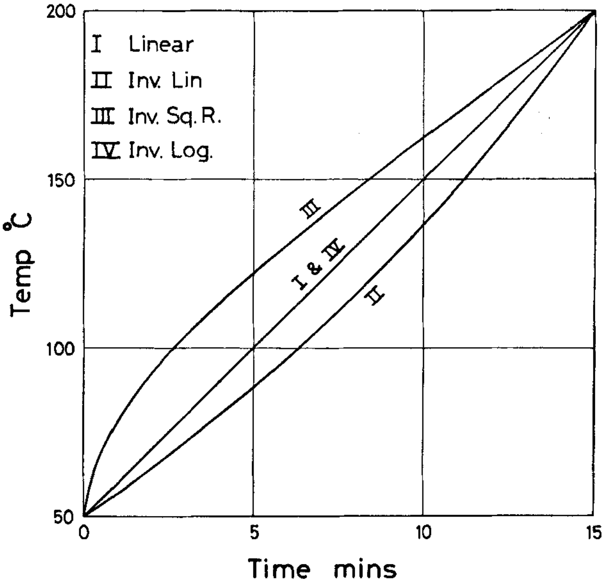

FIG. 8. Plot of three nonlinear programs.

TABLE 5

Time (min)	T_{linear} (°C)	$T_{\text{inv log}}$ (°C)	Deviation (°C)
0	50	50	0.0
1	60	60	0.0
2	70	70	0.0
3	80	79.9	−0.1
4	90	89.7	−0.3
5	100	99.6	−0.4
6	110	109.4	−0.6
7	120	119.3	−0.7
8	130	129.2	−0.8
9	140	139.1	−0.9
10	150	149.1	−0.9
11	160	159.1	−0.9
12	170	169.2	−0.8
13	180	179.4	−0.6
14	190	189.7	−0.3
15	200	200	0.0

As can be seen, the two values of a_2 are very close and this indicates that Eq. (42) is quite adequate.

DEVELOPMENT OF THE EXPLICIT RELATION FOR T_f IN TERMS OF COMMON FUNCTIONS

Substituting Eqs. (41) and (2) into Eq. (1) and integrating from $t = 0$ to $t = t_p$, one gets

$$\int_0^{t_p} \frac{dt}{a \exp\{(b/T_0)[1 - a_1 \ln(1 + a_2 t)]\}} = 1$$

Simplifying, one gets

$$\frac{1}{ae^{b/T_0}} \int_0^{t_p} (1 + a_2 t)^{a_1 b/T_0} \, dt = 1$$

which leads to

$$a_2 t_{r0}\left(\frac{a_1 b}{T_0} + 1\right) = (1 + a_2 t_p)^{(a_1 b/T_0)+1} - 1$$

Let

$$\frac{a_1 b}{T_0} + 1 = \gamma$$

then

$$t_p = \frac{1}{a_2}[(t_{r0} a_2 \gamma + 1)^{1/\gamma} - 1] \tag{43}$$

Since

$$t_p = \frac{T_f - T_0}{r}$$

and

$$a_2 = r/a_1 T_0$$

by substituting in Eq. (43), one gets

$$T_f = T_0 + a_1 T_0\left[\left(t_{r0}\frac{r\gamma}{a_1 T_0} + 1\right)^{1/\gamma} - 1\right] \tag{44}$$

or

$$T_f = (1 - a_1)T_0 + a_1 T_0\left(\frac{r t_{r0}}{a_1 T_0}\gamma + 1\right)^{1/\gamma} \tag{45}$$

Either Eq. (44) or Eq. (45) is an explicit relation for the retention temperature T_f in terms of simple common functions.

When the term (rt_{r_0}/a_1T_0) is large due to a large rate of temperature rise or a large isothermal retention time at T_0 or both, and because γ is a large number which may vary from 4 to 10 or more, then the Term 1 may be neglected relative to $(rt_{r_0}/a_1T_0)\gamma$ and we get

$$T_f = (1 - a_1)T_0 + a_1T_0\left(\frac{rt_{r_0}}{a_1T_0}\gamma\right)^{1/\gamma} \tag{46}$$

If T_{f_1} is the retention temperature corresponding to a rate r_1, and T_{f_2} is the retention temperature corresponding to a rate r_2, then

$$\frac{T_{f_1} - 0.5657T_0}{T_{f_2} - 0.5657T_0} = \left(\frac{r_1}{r_2}\right)^{1/\gamma} \tag{47}$$

Equation (47) gives the relation between the retention temperature and the linear rate of temperature rise when the inlet temperature T_0 is kept constant.

Example 2

Repeat Part I of Example 1, using equations developed in the last section and based on the inverse log-linear program.

Answer

Either Eq. (44) or Eq. (45) can be used.

Starting with Eq. (45) we have $r = 20\,°\mathrm{C/min}$, $T_0 = 313\,°\mathrm{K}$, $a_1 = 0.4343$, and t_{r_0} is read from Fig. 7 so that $t_{r_0} = 338$ min. ΔH is read on the outside scale and is equal to 8900 cal/mole.

$$b = \Delta H/2 = 4450$$

$$\gamma = a_1b/T_0 + 1 = 7.175$$

$$a_2 = \frac{r}{a_1T_0} = \frac{20}{0.4343 \times 313} = 0.147$$

Substituting these values in Eq. (45), one gets

$$T_f = 313 \times 0.5657 + 0.4343 \times 313[338 \times 0.147 \times 7.175 + 1]^{1/7.175}$$
$$= 486\,°\mathrm{K}$$

Which is the same value obtained in Example 1, and therefore

$$t_p = \frac{486 - 313}{20} = 8.65 \text{ min}$$

APPLICATION TO HOMOLOGOUS SERIES

Equation (45) can be used to develop useful relations for temperature programming of homologous series. Since for such series

$$t_{r_n,0} = t_{r_1,0}\alpha_0^{n-1}$$

on substituting in Eq. (45) one gets

$$T_{f_n} = (1 - a_1)T_0 + a_1 T_0\left(\frac{rt_{r_1,0}\alpha_0^{n-1}}{a_1 T_0}\cdot\gamma_n + 1\right)^{1/\gamma_n} \tag{48}$$

where

$$\gamma_n = (a_1 b_n/T_0) + 1 \tag{49}$$

and

$$b_n = \frac{\Delta H_n}{R} = \frac{\Delta H_1 + (n - 1)B}{R} \tag{50}$$

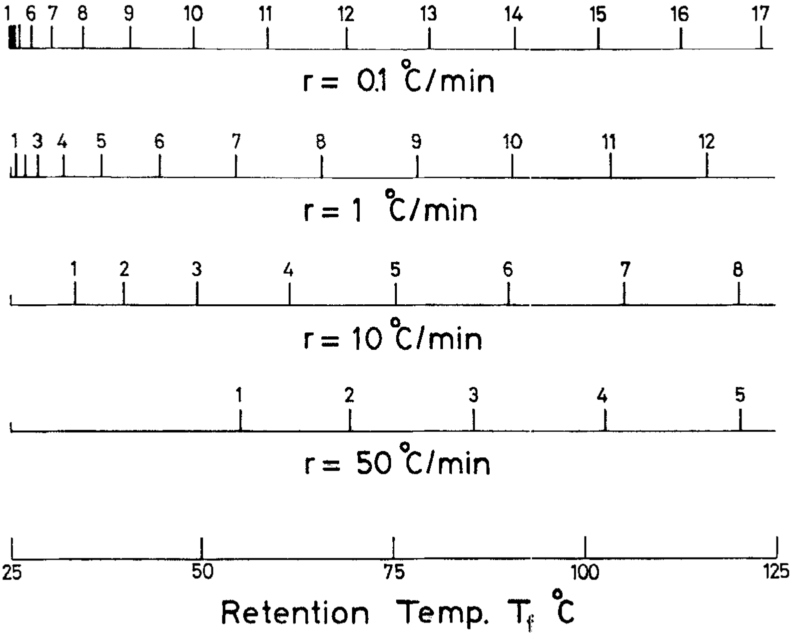

Fig. 9. Plot of n vs retention temperature T_f.

For simplicity, Eq. (48) may be written as

$$T_{f_n} = (1 - a_1)T_0 + a_1 T_0(K\gamma_n + 1)^{1/\gamma_n} \tag{51}$$

Equation (48) was solved for the following values.

$$\Delta H_1 = 6000 \text{ cal/mole}, \quad T_{r_1,0} = 1 \text{ min}$$

$$B = 500 \text{ cal/mole}, \qquad \alpha_0 = 1.8$$

and for values of r from 0.001 up to 50°C/min.

Figure 9 is a plot of n vs retention temperature T_f, and Fig. 10 is a plot of n vs retention time relative to Component 6. The plots were drawn for four different rates of temperature rise.

As can be seen from Fig. 9 and 10, the higher the linear rate r, the smaller the carbon number n at which the spacings become even. The spacings become even when the term $K\gamma_n$ in Eq. (51) becomes much larger than 1. At a high rate of temperature rise, this condition is reached with a small value of n, while at a small rate the value of n must increase to a certain value before the same condition is reached.

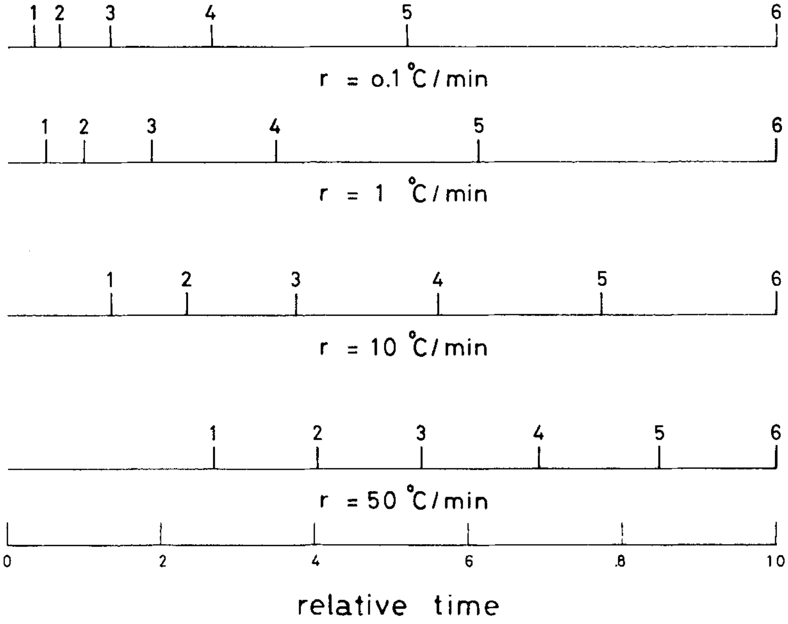

FIG. 10. Plot of n vs retention time for Component 6.

PROOF OF THE CONSTANCY OF ΔT_f DURING HOMOLOGOUS SERIES TEMPERATURE PROGRAMMING

It is possible to prove mathematically that when the value of $K\gamma_n$ is large enough, the components of a homologous series emerge evenly spaced. This can be accomplished with reference to Fig. 11.

Figure 11 gives the distribution of the components of a homologous series along the column. Figures 11(a), 11(b), and 11(c) give the distribution when components n, $n + 1$, and $n + 2$ are at the column outlet, respectively. If the relative volatility α was not a function of temperature, then Figs. 11(a), 11(b), and 11(c) would be identical except that each component r would be replaced by component $r + 1$ in the following figure. Since α is a function of temperature and usually decreases as the temperature increases, and also since the difference in temperature between consecutive figures is small (about 15°C), then the distances will be very slightly displaced (by about 2 to 3%) as we go from one figure to the next.

We let x_1 be the fraction covered by component $n + 1$ at temperature T_n when n is at the column outlet and x_2 be the fraction covered by component $n + 2$ when $n + 1$ is at the outlet. According to Eq. (11), a rate equal to $x_1 r$ would elute component $n + 1$ at temperature T_n.

Applying Eq. (47), one finds

$$\frac{T_n - 0.57T_0}{T_{n+1} - 0.57T_0} = \left(\frac{x_1 r}{r}\right)^{1/\gamma_{n+1}} \tag{52}$$

Similarly

$$\frac{T_{n+1} - 0.57T_0}{T_{n+2} - 0.57T_0} = \left(\frac{x_2 r}{r}\right)^{1/\gamma_{n+2}} \tag{53}$$

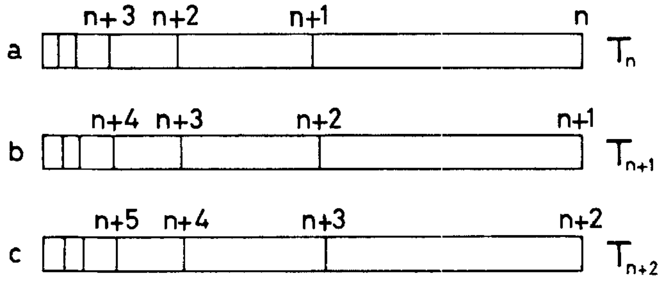

FIG. 11. Distribution of the components of a homologous series along the column.

Dividing Eq. (52) by Eq. (53) gives an equation which leads to the relation

$$T_{n+1} - T_n = T_{n+2} - T_{n+1} \tag{54}$$

This is because x_1/x_2 is a fraction close to 1 (about 0.97 or 0.98) and γ_{n+1} and γ_{n+2} are two large numbers, the ratio of which is also close to 1. Furthermore, the geometric average of two values whose ratio does not differ much from 1 is practically equal to their arithmetic average.

Equation (54) expresses the fact that, during temperature programming, the members of a homologous series (above a certain carbon number which is a function of the rate r) emerge from a chromatographic column evenly spaced. The details of the derivation of Eq. (54) are given later in Example 4.

A SIMPLE QUALITATIVE PROOF OF THE CONSTANCY OF ΔT_f

Since the retention temperatures in Figs. 11(a) and 11(b) differ by something like 15°C, it can be shown that the significant temperatures corresponding to these two figures will also differ by approximately 15°C. Applying Eq. (15), one can show that α decreases by about 2% in a 15°C span. The assumption, therefore, that Figs. 11(a) and 11(b) are identical is a reasonable assumption, so that

$$x_{n+1} = x_n \tag{55}$$

We know also that in the case of homologous series and for a fixed vapor pressure (fixed isothemal retention time t_r), the temperature difference between consecutive members is about the same. This may be expressed mathematically as

$$\left(\frac{\partial T}{\partial n}\right)_p = \text{constant} \tag{56a}$$

or

$$\left(\frac{\partial T}{\partial n}\right)_{t_r} = \text{constant} \tag{56b}$$

As an example, in the case of the paraffin hydrocarbon series, at a vapor pressure equal to 100 mm Hg, the corresponding temperatures are as shown in Table 6 (*7*).

TABLE 6

Carbon no. n	6		7		8		9		10
Temperature T (°C)	15.8		41.3		65.7		88.1		108.6
ΔT (°C)		25.5		24.4		22.4		20.5	

Assumptions (55) and (56b) are sufficient to prove that consecutive members should come out evenly spaced after a certain carbon number n_e. The reasoning goes as follows.

At the start of the chromatographic run the second component comes out too soon, having a vapor pressure less than that of Component 1 when it was at the outlet. Peak 2 will be broader than Peak 1. The same will also happen when Peak 3 comes out. Peak 3 will be wider than Peak 2 and the second spacing between Peaks 2 and 3 will be greater than that between Peaks 1 and 2. This will continue until the spacing is big enough to satisfy Eq. (56b). In this case Component $n + 1$ emerges at the same vapor pressure as component n and with the same width. Once this occurs the spacings will continue to be equal and consecutive members are eluted evenly spaced. If we assume that a spacing was greater than the one before it, this would mean that the same distance was covered in a longer time at a higher average velocity, which is impossible. Similarly, if we assume that a spacing is smaller than the one before it, this would mean that the same distance was covered in a shorter time at a smaller average velocity, which is also impossible. Therefore, all the spacings should be equal. Slight differences in the magnitudes of the spacings are due to slight inaccuracies in Assumptions (55) and (56).

MAGNITUDE OF THE TEMPERATURE DIFFERENCE ΔT_f FOR A HOMOLOGOUS SERIES

The retention temperature difference ΔT_{f_n} for a homologous series may be calculated from

$$\Delta T_{f_n} = T_{f_{n+1}} - T_{f_n} \tag{57}$$

and then, by substituting in Eq. (48), a relation is obtained for ΔT_{f_n}

An alternative derivation which leads to a simpler relation is to start with Eq. (56b) written in terms of the constant spacing, so that

$$\Delta T_f = \left(\frac{\partial T}{\partial n}\right)_{t_r} \tag{58}$$

For a homologous series. Eq. (6) gives the relation between t_r, n, and T. Since

$$\left(\frac{\partial T}{\partial n}\right)_{t_r} = -\left(\frac{\partial t_r}{\partial n}\right)_T \Bigg/ \left(\frac{\partial t_r}{\partial T}\right)_n \tag{59}$$

Then by partial differentiation of Eq. (6), once with respect to n and once with respect to T, one can show that

$$\Delta T_{f_n} = \frac{T^2[B\{(1/T) - (1/T_0)\} + R \ln \alpha_0]}{\Delta H_n} \tag{60}$$

RELATION BETWEEN n_e AND r

For a homologous series the carbon number n_e at which the spacings start to be equal during temperature programming is a function of the rate of linear temperature rise r; the higher the value of r, the lower the value of n_e and vice versa.

To deduce a mathematical relation between n_e and r, we make use of the fact that in Eq. (51), n approaches n_e as $(K\gamma_n + 1)^{1/\gamma_n}$ approaches $(K\gamma_n)^{1/\gamma_n}$. If Z is equal to the ratio $(K\gamma_n)^{1/\gamma_n}/(K\gamma_n + 1)^{1/\gamma_n}$, then we can assign to Z a value close to 1, say $Z = 0.98$, and n_e would be the value of n which satisfies the equation

$$\frac{(K\gamma_n)^{1/\gamma_n}}{(K\gamma_n + 1)^{1/\gamma_n}} = Z = 0.98 \tag{61}$$

This will lead to some mathematical difficulties. An alternative and much simpler approach may be followed at a little loss in accuracy by assuming a constant and reasonable value of K. For example, we may assume a value of $K = \ln 10 = 2.3 = 1/a_1$. This leads to

$$\frac{t_{r_{1,0}} {\alpha_0}^{n-1} r}{T_0} = 1 \tag{62}$$

This condition gives a value of n very close to n_e because the corresponding value of Z in Eq. (61) will vary from 0.98 to 0.995 as γ varies from 5 to 10, which shows that Eq. (62), in spite of its simplicity, is quite satisfactory.

Equation (62) leads to the relation

$$n_e = C_{\text{I}} + C_{\text{II}} \ln r \tag{63}$$

where

$$C_{\mathrm{I}} = 1 + \left(\ln \frac{T_0}{t_{r_1,0}}\right) \Big/ \ln \alpha_0$$

and

$$C_{\mathrm{II}} = -\frac{1}{\ln \alpha_0}$$

Example 3

For the homologous series in Fig. 4, and for a linear rate of temperature rise equal to (a) 3°C/min or (b) 0.01°C/min, calculate for $T_0 = 20°\mathrm{C}$:

1. n_e
2. The temperature and time from the start corresponding to n_e
3. The value of the temperature spacing between consecutive members at n_e

Answer

At 20°C, $t_{r_1,0} = 2$ min, and $\alpha_0 = 1.8$, with $r = 3°\mathrm{C/min}$:

1. The carbon number at the start of constant spacing is calculated from Eq. (63) so that

$$n_e = C_{\mathrm{I}} + C_{\mathrm{II}} \ln r$$
$$= 1 + \frac{\ln (293/2)}{\ln 1.8} - \frac{1}{\ln 1.8} \times \ln 3 = 7.61$$

2. The temperature corresponding to n_e is calculated from Eq. (48), where $a_1 = 0.4343$, $T_0 = 293$, $r = 3$, $t_{r_1,0} = 2$, $\alpha = 1.8$, $n - 1 = 7.61 - 1 = 6.61$,

$$\gamma_n = \frac{0.4343(6000 + 6.61 \times 500)}{1.987 \times 293} + 1 = 7.94$$

Substituting in Eq. (48), one gets

$$T_{f_n} = 0.5657 \times 293 + 0.4343 \times 293\left(\frac{3 \times 2 \times 1.8^{6.61} \times 7.94}{0.4343 \times 293} + 1\right)^{1/7.94}$$
$$= 350.4°\mathrm{K} = 77.4°\mathrm{C}$$

and the time from the start is (77.4 − 20)/3 = 18.1 min.

3. The value of the temperature increment at n_e can be calculated by two methods.

First method:

$$\Delta T_{f_{n_e}} = T_{f_{n_e+1}} - T_{f_{n_e}}$$

$$T_{f_{n_e}} = 350.4\,^\circ\mathrm{C}$$

$T_{f_{n_e+1}}$ is also calculated from Eq. (48). In this case $n - 1 = 6.61 + 1 = 7.61$

$$\gamma_{n+1} = \frac{0.4343(6000 + 7.61 \times 500)}{1.987 \times 293} + 1 = 8.31$$

Substituting in Eq. (48), one gets

$$T_{f_{n_e+1}} = 361.2 \qquad \text{and} \qquad \Delta T_{f_{n_e}} = 10.8\,^\circ\mathrm{C}$$

Second method: $\Delta T_{f_{n_e}}$ can also be calculated by substituting in Eq. (60). In this case

$$\Delta T_{f_{n_e}} = \frac{350.4^2[500\{(1/350.4) - (1/293)\} + 1.987 \ln 1.8]}{6000 + 6.61 \times 500}$$

$$= 11.7\,^\circ\mathrm{C}$$

At 20°C, $t_r = 2$ min, and $\alpha_0 = 1.8$, with $r = 0.01\,^\circ\mathrm{C/min}$.

1.

$$n_e = 1 + \frac{\ln(293/2)}{\ln 1.8} - \frac{1}{\ln 1.8} \times \ln(0.01) = 17.3$$

2. Substituting in Eq. (48) as in Part (a), except that in this case $n - 1 = 16.3$, and

$$\gamma_n = \frac{0.4343(6000 + 16.3 \times 500)}{1.987 \times 293} + 1 = 10.56$$

one gets

$$T_{f_{n_e}} = 338.4\,^\circ\mathrm{K} = 65.4\,^\circ\mathrm{C}$$

and the time from the start is $(65.4 - 20)/0.01 = 4540$ min.

3. To calculate $\Delta T_{f_{n_e}}$:

First method:

$$\Delta T_{f_{n_e}} = T_{f_{n_e+1}} - T_{f_{n_e}}$$

$T_{f_{n_e+1}}$ is also calculated from Eq. (48) where $n - 1 = 17.3$ and

$$\gamma_{n+1} = \frac{0.4343(6000 + 17.3 \times 500)}{1.987 \times 293} + 1 = 10.93$$

Substituting in Eq. (48), one gets

$$T_{f_{n_e+1}} = 346.3 \qquad \text{and} \qquad \Delta T_{f_{n_e}} = 346.3 - 338.4 = 7.9\,^\circ\text{C}$$

Second method: By substituting in Eq. (60) where $T = 338.4$ and $\Delta H_{n_e} = 6000 + 16.3 \times 500$, one gets $\Delta T_{f_{n_e}} = 7.61\,^\circ\text{C}$.

Example 4

Show that the statments upon which the derivation of Eq. (54) was based are correct.

Answer

Dividing Eq. (52)/Eq. (53), one gets

$$\frac{T_n - 0.57T_0}{T_{n+1} - 0.57T_0}\,\frac{T_{n+2} - 0.57T_0}{T_{n+1} - 0.57T_0} = \left(\frac{x_1^{1/\gamma_{n+1}}}{x_2^{1/\gamma_{n+2}}}\right) \tag{64}$$

Since x_1/x_2 is very close to 1, and since γ_{n+1} and γ_{n+2} are two large numbers whose ratio is also close to 1, it follows that the right-hand side is practically equal to 1. Substituting 1 for the right-hand side, $T_{n+1} - 0.57T_0$ becomes the geometric average between $T_{n+2} - 0.57T_0$ and $T_n - 0.57T_0$. The ratio of the last two values does not differ much from 1. In this case their geometric average is practically equal to their arithmetic average so that

$$T_{n+1} - 0.57T_0 = \tfrac{1}{2}[(T_{n+2} - 0.57T_0) + (T_n - 0.57T_0)]$$

which leads to

$$T_{n+1} = \tfrac{1}{2}(T_{n+2} + T_n)$$

or

$$T_{n+1} - T_n = T_{n+2} - T_{n+1} \tag{54}$$

A numerical verification of the above statements is as follows: According to the definition of γ given previously:

$$\gamma = \frac{a_1 b}{T_0} + 1$$

its value is very seldom less than 4, and the ratio $\gamma_{n+2}/\gamma_{n+1}$ is also very seldom more than 1.07. Furthermore, according to Eq. (32), the average relative volatility can decrease by no more than 3% in a 15°C span and also the fraction x is very seldom less than 0.5. Substituting these extreme values in the right-hand side of Eq. (64), one gets

$$\frac{x_1{}^{1/\gamma_{n+1}}}{x_2{}^{1/\gamma_{n+2}}} = \frac{0.5^{1/4}}{0.515^{1/4.3}} = 0.98$$

Substituting more realistic values, we find

$$(x_1)^{1/\gamma_{n+1}}/(x_2)^{1/\gamma_{n+2}} = 0.6^{1/7}/0.615^{1/7.4} = 0.993$$

Similarly, the ratio $(T_{n+2} - 0.57T_0)/(T_n - 0.57T_0)$ is very seldom greater than 1.2 and usually less than 1.14. This gives a geometric average equal to 1.068 compared to an arithmetic average equal to 1.070.

Furthermore, the right-hand side is almost always less than 1, and this makes the deviation from the arithmetic mean even less than the difference between the geometric and the arithmetic means. In other words, the two deviations tend to cancel one another, and Eq. (54) is sufficiently accurate.

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