CRITICAL INLET PRESSURE FOR SEPARATION IN GAS CHROMATOGRAPHY

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The achievement of very difficult separations in gas chromatography requires the use of columns sufficiently long to generate the required number of theoretical plates. However, as length is increased the inlet pressure must also be increased in order to maintain flow. The question naturally arises as to whether manipulations in column length and flow velocity can be made in such a manner that the inlet pressure need not be increased indefinitely as the separation becomes more and more difficult. The answer to this question is important since there is a finite limit to the inlet pressure which can be used with any given system. Earlier theoretical results have indicated, however, that there is no simple escape from the pressure limitation imposed by difficult separations[1,2]. There appears to be a critical inlet pressure, p_c, for any specified separation. The separation cannot be achieved below this pressure. If, for example, one lowers the velocity of flow so as to reduce the flow resistance, the peak spreading is increased by molecular diffusion (due to the increase in residence time within the column). A longer column is thus needed to compensate for the added peak spreading and this, in turn, requires a further reduction in velocity. A theoretical limit is reached as column length approaches infinity and flow velocity approaches zero.

Two previous theoretical treatments have recognized the role of critical pressure in gas chromatography[1,2]. In the first case the concept arose as a rather incidental part of the study of minimum analysis time in gas chromatography. The derivation, directed toward other ends, was especially roundabout and difficult. In the second case the derivation was made on the basis of uniform columns, especially applicable to liquid chromatography. After the derivation was complete, averages were used to represent the highly non-uniform (due to compressibility) properties of the carrier gas. The results of this approximate treatment were close but not identical to those of the first treatment.

The object of this paper is to present a direct and exact treatment of the critical pressure in gas chromatography. This derivation, unlike the earlier ones, will demonstrate the role of gas compressibility and will relate the critical pressure directly to the partition coefficients of the component peaks.

LENGTH AND PRESSURE RELATIONSHIPS

Since high inlet pressures are necessary to maintain flow in long columns, the precise relationship between column length, pressure and flow velocity is needed.

We start out with a basic pressure-gradient equation[2]:

$$-dp/dz = 2\phi\eta v/d_p^2 \tag{1}$$

where $-dp/dz$ is the pressure gradient with the negative sign indicating the decrease of pressure toward the outlet. The term ϕ is a dimensionless structural parameter nearly constant for most packed columns at around 300 and equal to 16 for capillary columns. (For porous materials ϕ should be replaced by $\sim 300/\Phi$, where Φ is the fraction of gas in interparticle space.) The equation reflects the fact, observed in flow through granular materials, that the pressure gradient is proportional to the flow velocity, v, the viscosity, η, and inversely proportional to particle diameter, d_p, squared (the latter is in analogy to the Poiseuille equation).

Eqn. (1) can be easily integrated over the column length, L. First noting that the pressure–velocity product, pv, is constant in the column (as a result of Boyle's law), v may be written as $p_i v_i/p$, where p_i and v_i are inlet values. We then have:

$$\int_{p_i}^{p_0} p\,dp = -(2\phi\eta p_i v_i/d_p^2) \int_0^L dz \tag{2}$$

or:

$$p_i^2 - p_0^2 = 4\phi\eta p_i v_i L/d_p^2 \tag{3}$$

When P is used for the compression ratio, p_i/p_0, and Eqn. (3) rearranged, we get:

$$L = \frac{d_p^2 p_i}{4\phi\eta v_i}\left(\frac{P^2 - 1}{P}\right) \tag{4}$$

The very maximum use can be made of a given inlet pressure if the outlet is held near vacuum[3]. In this case P approaches infinity and the above equation reduces to:

$$L = d_p^2 p_i/4\phi\eta v_i \tag{5}$$

This is the desired relationship between length, inlet pressure and inlet velocity.

NUMBER OF THEORETICAL PLATES

A given separation, achieved at a fixed temperature, liquid load, etc., will require a certain minimum number of theoretical plates for its success. This can be shown to be:

$$N_{min} = 16 \, [Rs(V_m + KV_s)]^2/(V_s\Delta K)^2 \tag{6}$$

where Rs is the desired peak resolution, V_m and V_s the volume of mobile and stationary phases in the system, K the (mean) partition coefficient and ΔK the difference in K exhibited by the peaks in question. For difficult separations, where ΔK is small, the required number of plates, N_{min}, is obviously large.

In order to see if a sufficient number of plates are available in a column, it is necessary to write $N = L/H$, where H is the apparent (or measured) plate height. A simple but usually adequate equation for the latter is:

$$H = \tfrac{9}{8}(B'/p_i v_i + C_g' p_i v_i) + \tfrac{3}{2} C_l v_i \tag{7}$$

This equation is applicable only when $p_i \gg p_0$, as assumed here. The numerical factors, $9/8$ and $3/2$, originate as corrections for the pressure gradient[4]. The B' and C_g' terms represent longitudinal diffusion and non-equilibrium in the gas phase with the pressure dependence (originating in the diffusion coefficient) taken out. Thus these terms are equal to the usual B and C_g terms at unit pressure. Liquid non-equilibrium is represented by C_l.

With this expression for H, and with the column length, L, as found in Eqn. (4), the number of plates, L/H, becomes:

$$N = \frac{d_p{}^2 p_i}{4\,\phi\eta \left(9/8 \dfrac{B'}{p_i} + 9/8\,C_g' p_i v_i{}^2 + 3/2\,C_l v_i{}^2\right)} \tag{8}$$

The independent quantities of this equation are p_i and v_i; once these are chosen L is fixed by Eqn. (5). This equation shows that N decreases as the inlet velocity, v_i, becomes larger. With a given inlet pressure, particle size, etc., the very maximum in obtainable plates is approached as a limit when $v_i = 0$:

$$N_{\text{lim}} = 2\,d_p{}^2 p_i{}^2 / 9\,\phi\eta B' \tag{9}$$

or, if B' is written in terms of the gaseous diffusion coefficient at unit pressure, D_g', e.g., $B' = 2\,\gamma D_g'$, where γ is a structural parameter in the neighborhood of 0.6, this equation becomes:

$$N_{\text{lim}} = d_p{}^2 p_i{}^2 / 9\,\phi\gamma\eta D_g' \tag{10}$$

This number of plates must be equal to or greater than the number, N_{min}, required for the separation as shown in Eqn. (6). Thus for the separation of a given pair of components, the inlet pressure of the column must satisfy the following requirement:

$$p_i \geq (\phi\gamma\eta D_g')^{1/2}\,\frac{12\,Rs\,(V_m + KV_s)}{d_p V_s \Delta K} \tag{11}$$

THE CRITICAL PRESSURE

The right hand side of Eqn. (11) gives the lowest possible inlet pressure with which a resolution of Rs can be achieved for a pair of components having a difference ΔK in their individual partition coefficients. This pressure is termed the critical inlet pressure, i.e.:

$$p_c = 12\,(\phi\gamma\eta D_g')^{1/2}\,\frac{Rs\,(V_m + KV_s)}{d_p V_s \Delta K} \tag{12}$$

This can be conveniently expressed in terms of the R value:

$$R = V_m / (V_m + KV_s) \tag{13}$$

where R is the retention parameter indicating the velocity of the component peak divided by that of an inert (air) peak. After rearrangement:

$$p_c = 12\,(\phi\gamma\eta D_g')^{1/2}\,\frac{Rs}{d_p\,(\Delta K/K)\,(1 - R)} \tag{14}$$

where $\Delta K/K$ is the relative selectivity (this quantity also equals $\Delta t'/t'$, where t' is the retention time from the air peak).

An alternative to the above expressions for p_c can be obtained directly from Eqn. (10). Since $N_{\lim}$ is the largest number of plates obtainable with the inlet pressure p_i (assuming given values for d_p, η, etc.), we may solve for p_i and regard this as the critical (minimum) pressure for obtaining $N = N_{\lim}$ plates, *viz.*:

$$p_c = (9\phi\gamma\eta D_0'N)^{\frac{1}{2}} d_p \tag{15}$$

This is equivalent to the rigorous equation derived earlier[1].

It is useful to calculate a numerical p_c value to illustrate the critical-pressure concept. All quantities must be expressed in consistent units, *e.g.*, cgs. We may assume a typical case in which $\phi = 300, \gamma = 0.6, \eta = 10^{-4}$ poise, $D_0' = 5 \cdot 10^5$ g·cm· sec^{-3} ($D_0 = 0.5$ cm^2/sec at 1 atm), $d_p = 0.014$ cm ($\sim$ 100–120 mesh), $R = 0.5$ and $Rs = 1$. Upon substitution of these quantities into Eqn. (14) we get $p_c \cong 2 \cdot 10^5 \, K/\Delta K$, in cgs units. Since 1 atm is approximately 10^6 dyne·cm^{-2}, this becomes:

$$p_c = 0.2 \, K/\Delta K \text{ (in atmospheres)} \tag{16}$$

If, for example, it is necessary to separate two components with a relative selectivity, $\Delta K/K$, of $^1/_{50}$, the inlet pressure must exceed about 10 atm (this large value is not surprising when we consider that this separation would require 40,000 plates). This can be reduced to about 3 atm providing a coarse 30–40 mesh support is assumed.

While the treatment above is designed primarily for packed columns, it is equally valid for capillary columns. In the latter case the dimensionless constants are $\gamma = 1$ and $\phi = 16$. The column diameter, d_c, must replace the particle diameter, d_p, in the equations.

Strictly speaking, the equations for critical pressure are applicable only to columns existing as single segments. If several segments are linked together by pumps, these equations would apply only to the separation achieved in the individual segments.

The derivation given above is valid whether the column outlet is operated at reduced pressure or not. If the outlet is held at 1 atm, maximum use is not being made of the available inlet pressure. In any case the basic requirement for inlet pressure is $p_i \geq p_c$. If the outlet is held at 1 atm this simply increases the margin by which p_i must exceed p_c.

SUMMARY

The concept of the critical inlet pressure, p_c, the lowest possible pressure for achieving a given separation, is discussed. The theoretical approach to this parameter starts with the basic flow equation for an ideal gas in a packed column. The integrated

flow equation and an expression for the plate height are then used to formulate the number of plates in the column. The maximum value of this must be greater than the minimum needed to separate a given pair. This criterion is used to formulate an expression for the critical pressure. Several alternate equations are given and a numerical example is presented.

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