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Gas Chromatography at High Eluent Pressures

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The influence of pressure on the efficiency of a chromatographic column and on the selectivity of the stationary phase has been investigated. The role of pressure gradients along the column has been demonstrated. It is shown that the efficiency can be drastically increased by turbulence in the carrier gas stream. A special study is made of the use of eluents under supercritical conditions, which permits involatile compounds with a molecular weight up to 4000000 to migrate along the column.
The use of chromatography in studies of non-ideality in the gas phase is discussed. In particular, we have considered the determination of the second mixed virial coefficients in the equation of state for the gas, and the non-ideality corrections needed to determine the activity coefficients of solutes. 115 references.

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I. INTRODUCTION

The most significant advances in analytical gas chromatography since 1958 are the use of capillary columns[1] and the development of highly sensitive detectors of the ionisation type[2,3]. These developments have transformed gas chromatography into a universal method of analysis of complex mixtures of organic and inorganic compounds, ranging from permanent gases to substances having vapour pressures of the order of thousandths of a mmHg at the temperature of the experiment[4]. The introduction of detectors sensitive to $10^{-7}-10^{-8}$ mg has allowed the size of the analytical sample to be made as small as $10^{-2}-10^{-4}$ mg.[5] The efficiency of capillary columns, measured in hundreds of thousands of theoretical plates, has now become commonplace[6,7]: conformational isomers[8] can often be separated, and isotope effects[9] can be studied. The time needed for a complete analysis has been shortened to the point that light hydrocarbon mixtures can now be separated in times of the order of a second[10,11].

Because these applications of gas chromatography fulfilled actual practical needs, their realisation was very rapid. It soon became apparent that analytical gas chromatography needed to be developed further before it could be applied to substances of high molecular weight and to relatively unstable compounds (without resorting to reaction chromatography).

Evidently, the scope of chromatographic separation can be extended towards high-molecular-weight compounds by decreasing the distribution coefficients of the sorbates. The major development in gas chromatography in recent years have been in this direction. The main stages in this development have been the introduction of gas–liquid chromatography, the use of carriers very lightly impregnated with the stationary phase, the adoption of capillary chromatography, the development of temperature programming, and the use of weak adsorbents. Actually, the partial Henry coefficient (the ratio of the capacities of the stationary and the mobile phase),

$$\Gamma^{\mathrm{I}} = \frac{t_R}{t_0} - 1 = \frac{c_s \varkappa_{\mathrm{I}}}{c_g \varkappa} \qquad (1)$$

is related to the retention time t_R of the sorbate. (t_0 is the retention time of the non-adsorbed material.) The Henry coefficient is determined by the concentration of the sorbate in the gas (c_g) and the sorption (c_s) phase, and by the ratio of the volumes κ and κ^{I} occupied by these phases in the column.

Thus, the use of gas–liquid chromatography, of weak adsorbents, and also of temperature programming leads to smaller values of c_s, whereas the use of columns with a small percentage of impregnant (capillary columns) decreases κ^{I} and increases κ.

The distribution coefficients can be further decreased (to the point where they are practically independent of the vapour pressure of the sorbate) by increasing the solubility of the sorbates in the mobile phase. To this end, the eluents are applied in the form of gases at high pressure, or liquids.

The earliest report of the successful application of gas chromatography at pressures above 100 atm was due to Klesper and coworkers[12], who were able to separate mixtures of porphyrins. Subsequent work by Giddings and coworkers[13–15], and also by Sie and coworkers[16–18], showed that polynuclear aromatics, polymers with molecular weights in excess of 400 000, and many other high-molecular-weight compounds can be separated by gas chromatography.

Giddings has pointed out[15] that gas chromatography at high pressures has three main advantages over liquid chromatography: 1) the distribution coefficient of the sorbates between the stationary and the mobile phase can be controlled over wide limits by changing the pressure; 2) the analysis is faster because the mobile phase is less viscous and the diffusion coefficients of the sorbates are higher; 3) detectors with much higher sensitivity can be used.

Increase in pressure within the column affects the analysis time, the selectivity of the column, and the efficiency of the process, and therefore pressure is one of the most important parameters of a fast column.

The "speed coefficient" is defined[19,20] as

$$\lambda = \frac{n_p \cdot K^2}{t} \sim k \left(\frac{\Gamma'}{\Gamma'+1}\right)^2 \cdot \frac{n}{t} \qquad (2)$$

where n_p is the number of peaks in the chromatogram, K is the degree of resolution of the least resolved pair, t is

the time of analysis, k_S is the selectivity coefficient for the sorbate, n is the number of theoretical plates, $\Gamma' = \Gamma\frac{K_I}{K}$ is the partial Henry coefficient (mean value for the components of the least resolved pair), Γ is the true Henry coefficient (ratio of concentrations of the sorbate, in g ml^{-1}, in the stationary and the mobile phase). Thus, since k_S is determined by the Henry coefficient for the components of the least resolved pair, and t is determined by the Henry coefficient of the most strongly held component of the mixture, all the quantities in the right-hand side of Eqn. (2) are a function of the nature of the eluent and of its pressure.

These relationships are discussed in the present review together with the possible practical applications of gas chromatography at high pressures.

In addition to its advantages in the field of analytical chromatography, the use of high pressures offers new scope in non-analytical applications of gas chromatography. These include methods of studying non-ideality in gases, the determination of the constants for phase equilibria in multicomponent systems, etc., which are also discussed in the following Sections.

II. INFLUENCE OF PRESSURE ON THE EFFICIENCY OF A CHROMATOGRAPHIC COLUMN

The effect of pressure on the efficiency of a chromatographic column has been discussed by many workers[21-34] in the absence of non-ideality effects, i.e. for pressures below 5 atm. Assuming pressure-independence of the dynamic viscosity of the carrier gas and of the permeability of the column, and also assuming laminar flow conditions, the square of the width of the band for a particular component,

$$\sigma_{st}^2 = \int_0^L H\left(\frac{P}{P_0}\right)^2 dx \qquad (3)$$

(where H is the height equivalent to a theoretical plate at the cross-section of the column where the pressure is P, and P_0 is the pressure at the column outlet) is given by

$$\sigma_{st}^2 = L\left(A + \frac{B}{\bar{P}\bar{\alpha}} + E\bar{P}\bar{\alpha} + C_2\bar{P}^{0.5}\bar{\alpha}^{0.5}\right)\frac{1}{\chi^2} + LC_1\bar{\alpha}\cdot\frac{1}{j^2} \qquad (4)$$

Here σ_{st} is the mean standard deviation (the half-width of the peak at a height $1/\sqrt{e}$ of the maximum height) on the layer of sorbent when elution occurs, L is the length of the column, A is the turbulent diffusion term in the equation for the height equivalent to a theoretical plate, B is the molecular diffusion term, E accounts for contributions from the wall effect, from outer diffusion of weakly sorbed materials, and from dynamic diffusion, C_2 is the mass transfer term for outer diffusion (as defined by Zhukhovitskii and Turkel'taub[35]), C_1 is the mass transfer term for inner diffusion, $\bar{P}$ is the mean pressure in the column, $\bar{\alpha}$ is the mean linear velocity of the carrier gas, the parameter χ is given by

$$\chi = \sqrt{\frac{2}{(P_1/P_0)^2 + 1}},\quad j = \frac{3}{2}\frac{(P_1/P_0)^2 - 1}{(P_1/P_0)^3 - 1},$$

P_1 is the pressure at the column inlet, and P_0 is the pressure at the column outlet.

At pressures of hundreds of atmospheres, when the deviations from ideality of the gas are large and neither the viscosity, nor the product $P\alpha$, nor the distribution coefficient of the sorbate are constant along the column, integration of Eqn. (3) leads to very complicated expressions[36].

The factors χ and j have very similar values, so that the ratio j^2/χ^2 does not exceed 9/8. Hence we may conclude[33] that the efficiency of the column is practically independent of the pressure drop and is determined only by the mean pressure in the column. Thus, if we assume that the spreading of the peak is limited by inner diffusion, the number of theoretical plates deduced from the experimental values of retention volume (V_R) and peak width (ω), both in ml, is

$$n = \frac{V_R^2}{\omega^2} = \frac{V_R^{02}}{j^2}\cdot\frac{j^2}{\omega^{02}} = n^0 \qquad (5)$$

Here $V_R^0 = V_R \cdot j$ is the corrected retention volume, $\omega^0 = \omega j$ is the corrected peak width, n^0 is the corrected number of theoretical plates corresponding to a mean pressure $\bar{P}$ in the absence of significant pressure gradients along the column.

If the term C_1 can be neglected, we may write[37]

$$n = \frac{V_R^{02}}{j^2}\cdot\frac{\chi^2}{\omega^{02}} = n^0\cdot\frac{\chi^2}{j^2} \qquad (6)$$

Thus, the decrease in the number of theoretical plates at high pressure gradients is not very large (and cannot exceed 11.1%†).

It follows that the height equivalent to a theoretical plate is

$$H = \frac{L}{n} = \frac{j^2}{\chi^2}\left(A + \frac{B}{\bar{P}\bar{\alpha}} + E\bar{P}\bar{\alpha} + C_2\bar{P}^{0.5}\bar{\alpha}^{0.5}\right) + C_1\bar{\alpha} \approx H^0 \qquad (7)$$

where H^0 corresponds to a mean pressure $\bar{P}$ and small pressure gradients.

Introducing the symbol $r = \bar{P}\bar{\alpha}$, the minimum value of H^0 is

$$H^0 = A + \frac{B}{r} + Er + C_2 r^{0.5} + C_1\frac{r}{\bar{P}} \qquad (8)$$

If, for simplicity, we ignore the term in C_2,

$$H^0_{min} = A + 2\sqrt{B\left(\frac{C_1}{\bar{P}} + E\right)}, \qquad (9)$$

and the corresponding value of r is

$$r_{opt} = \sqrt{\frac{B}{\frac{C_1}{\bar{P}} + E}} \qquad (10)$$

The effect of pressure on the analysis time can be characterised by the "speed coefficient". If, under the particular experimental conditions, the main contribution to the diffuseness of the bands comes from the terms E and C, it follows that[33]

$$\lambda \sim \frac{n}{t} \sim \frac{1}{E\bar{P} + C_1} \qquad (11)$$

The following conclusions may be made from the above considerations.

1. The efficiency of the column is degraded by operating at higher pressures if the optimum value of the carrier-gas velocity is used for the separation.

† It should be noted that these conclusions are independent of the chosen model for the spreading process. Identical results have been obtained using Giddings' "conjugated" theory[38].

2. The optimum carrier velocity decreases as the pressure in the column increases. Thus, as Fig. 1 shows, the left-hand branch of the hyperbola is shifted towards very low velocities when the pressure is increased.

3. The speed coefficient increases, tending asymptotically to a limit proportional to $1/C_1$, as the pressure decreases. Thus, it is desirable to use a moderate vacuum [33] when a short analysis time is required.

4. For a constant average velocity in the column, the relationship between H and the mean value of $\bar{P}$ is a hyperbola with a slanting, curved branch [28] [see Eqn. (7)].

5. The plot of H against α_0 (where α_0 is the linear velocity of the gas at the outlet of the column) is not a hyperbola. The right-hand side of the curve becomes steeper as the velocity increases [17,33] because of the decrease in the term $C_1 r/P$ [see Eqn. (8), with the assumption that $\bar{P}\bar{\alpha} = P_0\alpha_0$].

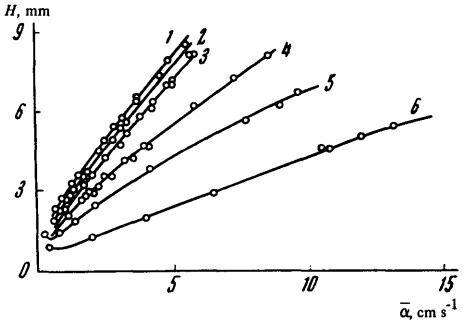


Figure 1. Effect of pressure on the dependence of the HETP on the mean velocity of the carrier gas. Sorbate: pentane; eluent: carbon dioxide. Temperature 40°. [17] Pressure: *1*) 50, *2*) 40, *3*) 30, *4*) 20, *5*) 10, *6*) 5 atm.

The effect of pressures of the order of tens or hundreds of atmospheres on the efficiency of the column is discussed by Giddings and coworkers [39-42]. Assuming that under these conditions the gas velocity is almost proportional to the inlet pressure P_1, Eqn. (7) takes the form

$$H \approx A + \frac{B}{P_1^2} + EP_1^2 + (C_1 + C_2)P_1 \qquad (12)$$

(where the symbols have the meaning already stated).

On the other hand, according to the "conjugated" theory of Giddings [39],

$$H \approx \frac{1}{\frac{1}{A} + \frac{1}{EP_1^2}} + \frac{B}{P_1^2} + C_1P_1 \qquad (13)$$

and, in our terminology, since $t = \frac{L}{\alpha}\Gamma_0$ where $\Gamma_0 = \Gamma\kappa_1 + \kappa$ and $n = L/H$,

$$\lambda \sim \frac{n}{t} \sim \frac{\alpha}{H\Gamma_0} \sim \frac{1}{\frac{H}{P_1}\Gamma_0} \qquad (14)$$

It follows from Eqns. (13) and (14) that the speed coefficient tends towards the limit $1/C_1\Gamma_0$ as the pressure increases (if we ignore the effect of pressure on the selectivity of the column).

Giddings has shown [43] that the minimum time to achieve an efficiency of n theoretical plates for an inlet pressure P_1 is

$$t = nC_1\Gamma_0 \cdot \frac{P_1^2}{P_1^2 - P_c^2}, \qquad (15)$$

where P_c is the "critical" pressure for the prescribed efficiency [44], whose numerical value is of the order of $4 \times 10^{-2}\sqrt{n}$ for conventional packed columns. If a separation criterion $K = 1$ is required, then

$$P_c \approx \frac{0.2}{K_c} \qquad (16)$$

For $P_1 \gg P_c$ and $t = nC_1\Gamma_0$, a very fast action becomes possible. Thus, Fig. 2 shows a chromatogram of petroleum gases obtained in under 1 min at $P_1 = 172.6$ atm.

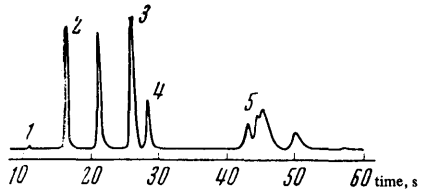


Figure 2. Separation of petroleum gas. Column length 1 m, internal diameter 0.47 mm. Sorbent: aluminium oxide. Pressure at column inlet 172.6 atm. Temperature 25°. *1*) air peak, *2*) propane, *3*) isobutane, *4*) n-butane, *5*) isobutene.

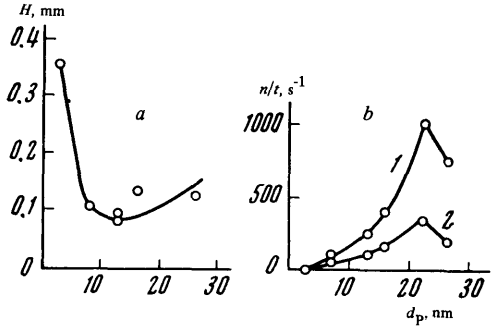


Figure 3. (*a*) Variation of HETP with average particle size of the filling (adsorbent: aluminium oxide) [40]. (*b*) Number of theoretical plates generated per second, *1*) for methane and *2*) for butane, against average particle size of the aluminium oxide [40].

In cases where the effect of non-equilibrium conditions can be almost completely eliminated, it becomes apparent that the efficiency is affected by the turbulent diffusion factor $A = 2\lambda_1 d_P$, where λ_1 is the tortuosity coefficient and d_P is the diameter of the sorbent particles. Fig. 3 shows plots of the height equivalent to a theoretical plate, and of the ratio n/t, against particle diameter for a column of 0.47 mm diameter.

Giddings finds that[43]

$$\frac{n^2}{t} = (10^6 \div 10^7)\Delta P, \qquad (17)$$

where ΔP is the pressure drop in the column.

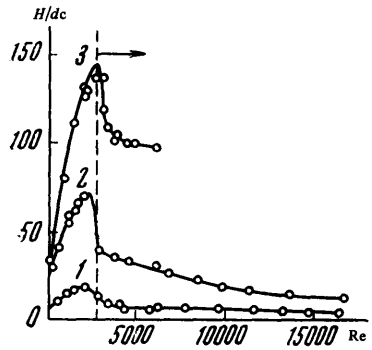


Figure 4. Reduced HETP against Reynolds number for: *1*) methane in nitrogen, *2*) pentane in nitrogen, and *3*) pentane in helium. Capillary column 21.3 m long. Temperature 0°.[45]

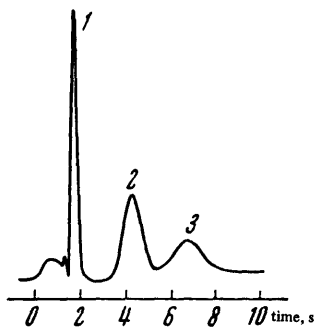


Figure 5. Chromatogram for the separation of light hydrocarbons in a stream of helium (turbulent regime, Re ≃ 7000). Temperature 74°. Pressure at column inlet 144 atm. *1*) propane, *2*) n-butane, *3*) n-pentane.[45]

All the considerations discussed above are based on the assumption of laminar gas flow, which is reasonable for normal gas velocities in a chromatographic column. Turbulent flow, which tends to equalise the velocities in a cross-section of the tube and to improve the mass transfer between the phases[45-52], produces a drop in the right-hand branch of the $H-\alpha$ curve at sufficiently high values of the Reynolds number ($\mathrm{Re} = \frac{d\alpha\rho}{\eta}$, where ρ and η are the density and the dynamic viscosity of the gas respectively, and d is the hydraulic diameter of the tube). Both the velocity and the density of the eluent increase with pressure: for example, for carbon dioxide the ratio ρ/η is 1000 s cm^{-2} at 80 atm (40°), as compared with 1 s cm^{-2} at 1 atm.[17]

Whereas the transition to the turbulent regime occurs at Re = 2130 in capillaries, in packed columns the turbulent regime is reached at Re values of the order of 1–100.[43]

Giddings and coworkers[45] achieved Reynolds number of the order of 16 000 at mean velocities in excess of 2000 cm s^{-1} and pressures up to 2000 atm, corresponding to almost sonic velocities at the column outlet. Fig. 4 shows plots of the efficiency (ratio of H to diameter) of a capillary column, coated with an adsorbent[53], against the Re number. It is evident that the efficiency increases sharply at the transition to the turbulent regime (the quantity H is smaller by a factor of 40 than the value expected from the conventional theory, which assumes laminar flow).

Giddings and coworkers have shown that at Re = 16 000 the speed coefficient is so high that the column generates 2500 theoretical plates per second for pentane (nitrogen carrier gas), and over 8000 theoretical plates for methane. Fig. 5 shows a chromatogram of light hydrocarbons, obtained at −74° and a column inlet pressure of 144 atm, corresponding to Re ≃ 7000.

Similar effects have been noted with packed columns[45].

III. INFLUENCE OF NON-IDEALITY IN THE GAS PHASE ON THE RETENTION OF SORBATES IN A CHROMATOGRAPHIC COLUMN

The influence of non-ideality of the carrier gas on the retention properties of sorbates was first recognised by Goldup and coworkers[54], who showed that the replacement of hydrogen by nitrogen as the carrier gas in long capillary columns operated with an inlet pressure of ~10 atm has a significant effect on the selectivity of the column towards hydrocarbon separation. The effect was ascribed[54,55] to the dependence of the coefficient Γ' upon the second virial coefficient in the equation of state of the gaseous mixture of sorbate and carrier gas. This dependence stems from the familiar expression[56]

$$\Gamma = \Gamma^0 e^{\beta P} \qquad (18)$$

where the coefficient Γ^0 corresponds to $P \to 0$, and β is a coefficient whose value depends on the non-ideality of the gas phase (see Section IV).

The present writers[57,58] have studied the chromatographic behaviour of hydrocarbons from wide petroleum fractions in capillary columns coated with octadec-1-ene and poly(ethylene glycol)-400 using inlet pressures up to 30 atm and helium, nitrogen, argon, and carbon dioxide as carrier gases.

Over that pressure range, an almost linear relationship was observed between the retention index of the sorbate and the mean column pressure, the slope $(\partial I/\partial P)_T$ being sensitive to the structure of the sorbate molecule and having different values for isoalkanes, alkenes, and aromatic hydrocarbons. This effect occasionally leads to an inversion of the elution order. In a poly(ethylene glycol) column, the retention index of alkylbenzenes changes by 30–40 units on raising the pressure to 30 atm, and this effect produces a large increase in selectivity for the separation of aromatic from aliphatic hydrocarbons.

Giddings' treatment[59] of the effect of non-ideality in the gas phase upon the retention characteristics is based on the expression

$$RT\left(\frac{\partial \ln \Gamma}{\partial P}\right)_T = -\delta V_1^0 \qquad (19)$$

where δV_1^0 is the change in partial molar volume of the sorbate on transfer from the liquid to the gas phase. Thus, whereas two sorbates may have practically identical retention characteristics ($\Gamma_1 = \Gamma_2$) at low pressures, it is possible to obtain a selectivity coefficient ($k_S = \frac{\Gamma_2 - \Gamma_1}{\Gamma_1}$) large enough for sharp separation by raising the pressure, provided that the δV_1^0 values for the two sorbates are sufficiently different. Integration of Eqn. (19) gives

$$k_s = -P\Delta(\delta V_1^0)/RT \qquad (20)$$

where $\Delta(\delta V_1^0)$ is the difference between the δV_1^0 values for the sorbates.

Thus, for example, if $k_S = 0.1$ is taken to give an acceptable separation of the sorbates, a pressure of the order of 500 atm is needed to achieve that value at $T = 300°K$ and for $\Delta(\delta V_1^0) = 5$ cm^3 mole^{-1}.

Of course, the latter expression must be used in conjunction with Eqn. (17), which describes the increase in separation with pressure for a constant selectivity coefficient.

Since increase of pressure is accompanied by an increase in the concentration of the sorbate in the gas phase, and therefore by a decrease in the distribution coefficient, the possibility arises of chromatographic analysis of substances whose volatility is insufficient for elution under normal conditions and also of compounds which are unstable at elevated temperatures.

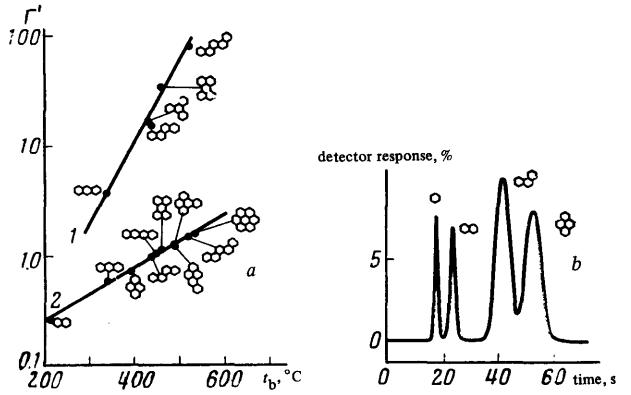


Figure 6. Separation of condensed polynuclear aromatic compounds by fluid chromatography. (*a*) Distribution coefficient against boiling point of the sorbates: *1*) High-temperature (460°) gas chromatography; adsorbent—aluminium oxide treated with NaOH; carrier gas—helium at 1.5 atm. *2*) Fluid-adsorption chromatography at 245°; adsorbent—unmodified aluminium oxide; fluid—isopropanol. (*b*) Fluid-adsorption chromatography; adsorbent—aluminium oxide; temperature 213°; pressure 50 atm.[18,60,61]

Thus, Klesper and coworkers[12] were able to elute from a chromatographic column a mixture of porphyrins, which were thermally unstable at temperatures above 150–170°, by using a mobile phase of Freons under supercritical conditions (150–170°, pressure up to 136 atm). Subsequently, Sie and Rijnders[18,60–62] made a detailed study of eluents (pentane, isopropanol, and diethyl ether) under supercritical conditions, and developed the method of "fluid" chromatography, by which they were able to analyse polynuclear aromatic hydrocarbons and other compounds with boiling points up to 600°. The volatility of the solvates increased by a factor of 10^3–10^4 under their conditions.

Fig. 6*a* shows plots of the coefficient Γ against the boiling point of the sorbate. It is evident that the increase in volatility on going to supercritical conditions is most marked for the heaviest sorbates. The elution of a mixture of benzene, naphthalene, phenanthrene, and pyrene on an aluminium oxide column at 213° and 50 atm (eluent: n-pentane) was completed in ~1 min (Fig. 6*b*).

Giddings and coworkers[13–15] used carbon dioxide and ammonia at supercritical temperatures and pressures up to 2000 atm as eluents. They observed the migration, along a column, of compounds with a molecular weight up to 400 000. The increase in the volatility of the sorbates in this case was of the order of 10^6.

The density of the mobile phase is one of the most important factors determining the solubility of sorbates in the mobile phase‡. Giddings and coworkers[15] considered the relationship between the density of the eluent and its solvent power. They used the Hildebrand solubility parameter[63] δ, whose magnitude can be defined as

$$\delta = 1.25 \cdot P_{cr}^{0.5} \cdot \rho/\rho_{liq}, \qquad (21)$$

where P_{cr} is the critical pressure, ρ is the density of the eluent, and ρ_{liq} is the density of the eluent in the liquid-like state. On reaching the density of the liquid (at pressures of the order of 1000 atm) the solubility parameter reaches its maximum value $\delta_{liq} = 1.25\, P_{cr}^{0.5}$. Assuming δ to be the same for a liquid and for a gas having the density of the liquid,

$$\delta = \delta_{liq} \cdot \rho/\rho_{liq} \qquad (22)$$

Thus, the nature of the eluent and its specific and non-specific interactions with the sorbate play a very important role in high-pressure chromatography, when the solubility of the sorbate in the mobile phase is comparable with its solubility in the stationary phase. For example, when helium is used as the eluent no appreciable change in the volatility of the sorbates is noted up to 2000 atm.[14,15] Migration of Ni-etioporphyrin II and etioporphyrin II has been observed[12] only in dichlorodifluoromethane at 68 atm and monochlorodifluoromethane at 95 atm. These compounds could not be made to migrate in other Freons. Dichlorodifluoromethane has been used also in the analysis of other metal complexes[64]. The use of ethylene as an eluent has been patented[67].

Since the density of the eluent in the supercritical state increases with pressure but decreases with temperature, it is desirable to work at temperatures only just above the critical temperature and at the highest possible pressures. Fig. 7 shows plots of the effect of temperature on the retention of sorbates[18]. Initially, because of the fast decrease in the density of the eluent with temperature, the solubility of the sorbate in the eluent decreases faster than its solubility in the stationary phase (or its adsorbability), and the distribution coefficient increases. At higher temperatures, however, when the density of the eluent has become low enough, the temperature dependence of the solubility of the sorbate in the stationary phase becomes

‡ For this reason, Giddings suggested the name "density chromatography" for this method[15].

predominant, leading to the decrease in retention with increase of temperature commonly observed in chromatography.

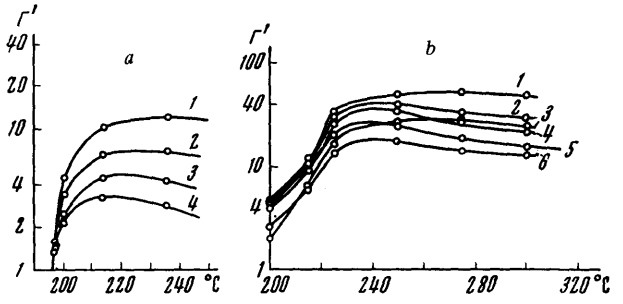


Figure 7. Effect of temperature on the retention of sorbates under fluid chromatography conditions. (*a*) Stationary phase poly(ethylene glycol)-6000 (~23 wt.% on Sil-O-Cel), fluid—n-pentane, pressure 35 atm: *1*) dioctyl phthalate, *2*) dihexyl phthalate, *3*) dibutyl phthalate, *4*) diethyl phthalate[18]. (*b*) Adsorbent—aluminium oxide, fluid—n-pentane, pressure 40 atm: *1*) 10-phenylanthracene, *2*) pyrene, *3*) 1,1-binaphthyl, *4*) 2-phenylnaphthalene, *5*) anthracene, *6*) phenanthrene[60].

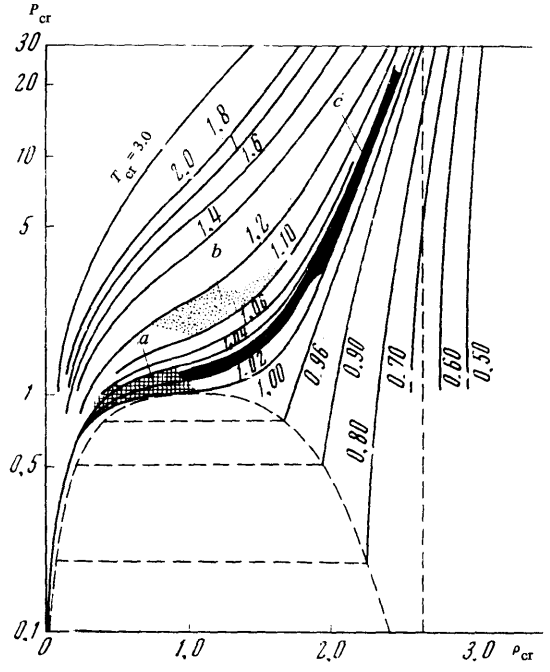


Figure 8. Phase diagram (P_{cr}–ρ_{cr}): *a*) working region of Sie and coworkers[18,60,61], *b*) working region of Klesper and coworkers[12,64], *c*) working region of Giddings and coworkers[13–15].

The diagram shown in Fig. 8 allows the chromatographic conditions used by different workers to be compared. Thus, Sie and coworkers[18,60,61] worked under conditions corresponding to a solubility parameter (δ) for the mobile phase in the range 0.9–2.8. Klesper and his coworkers[12,64] used values of δ between 2.4 and 4.5. On the other hand, Giddings and coworkers[13–15], who worked at pressures up to 2000 atm, obtained gas densities of carbon dioxide (at 40°) and ammonia (at 140°) close to the densities of the corresponding liquids and thus achieved δ values as high as 10. By using these dense eluents they induced migration along the column of compounds such as carotenoids, corticosteroids, nucleotides, carbohydrates, and various polymers. They showed that whereas ammonia (which tends to form hydrogen bonds) has the higher affinity for compounds with hydroxyl and amino groups, carbon dioxide is a better solvent for sorbates showing dispersion and donor–acceptor types of interaction, and can therefore be used to analyse terpenes, polyglycols, esters, alkanes, etc.[13–15] Figs. 9*a* and 9*b* are chromatograms of glycine derivatives and carotenes in dense ammonia and carbon dioxide respectively. The critical parameters of the substances used as eluents are listed in Table 1.

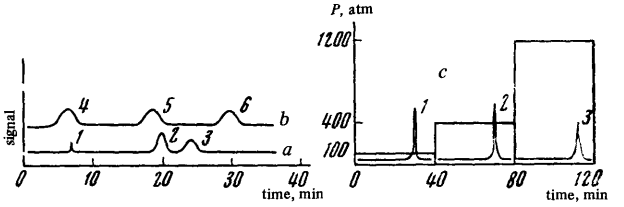


Figure 9. Migration of high-molecular-weight compounds in dense ammonia and carbon dioxide gas. (*a*) Separation in dense carbon dioxide at 500 atm. Column 1.5 m long, filled with 15% of poly(propylene glycol): *1*) air peak, *2*) β-carotene, *3*) α-carotene. (*b*) Separation in dense ammonia at 200 atm. Column 1.5 m long, filled with Porasil B: *4*) glycine, *5*) glycyl glycine, *6*) glycyl-lysyl-tyrosine. (*c*) Separation by a stepped pressure programme, using carbon dioxide at 40°: *1*) squalane, *2*) dinonyl phthalate, *3*) SE-30 silicone rubber (M = 400 000).[13–15]

Table 1. Critical parameters of fluids and working conditions of the columns.

Fluid	T_{cr}, °C	P_{cr}, atm	ρ_{cr}, g cm^{-3}	Working conditions		
				T, °C	P, atm	Refs.
Ammonia	132.3	111.5	0.235	140	< 200	13–15
Carbon dioxide	31.1	75.3	0.468	40	< 2000	13–15
Ethylene	9.90	50.3	0.211	20	100	67
Monochlorodifluoromethane	96	48.71	0.525	150–170	< 136	12
Dichlorodifluoromethane	111.5	40.61	0.558	130–160	< 210	12,64–66
Isopropanol	235.25	47.02	0.2727	245	45–50	18,60–62
Diethyl ether	193.61	36.27	0.2663	200	38–50	62
n-Pentane	196.62	33.31	0.238	213	35–50	18,60–62

By comparing the solvent powers of liquids and dense gases in the liquid-like state (Fig. 10)[14] we may conclude that dense carbon dioxide and ammonia are among the most powerful solvents. Thus, Giddings and coworkers[15] found that in the pentane–carbon dioxide system the solubility parameter δ of the dense eluent could be made greater than the corresponding parameter for the sorbate in the condensed state ($\Delta = \delta/\delta_0 = 1.37$). The same group

showed[15] that a threshold pressure exists at which the concentration of involatile compounds in the mobile phase becomes high enough for detection. Further increase in pressure accelerates the rate of migration of the sorbate.

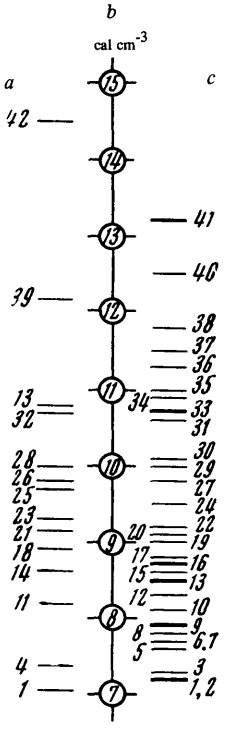


Figure 10. Schematic of (*c*) of the solvent power of gases compressed to a liquid-like state in comparison with (*a*) conventional solvents. (*a*) *1*) n-pentane, *4*) diethyl ether, *11*) cyclohexane, *14*) carbon tetrachloride, *18*) toluene, *21*) benzene, *23*) chloroform, *25*) ethyl acetate, *26*) acetone, *28*) dioxan, *32*) pyridine, *13*) isopropanol, *39*) ethanol, *42*) methanol. (*c*) Gases in the liquid-like state: *1*) n-pentane, *2*) nitrogen, *3*) carbon monoxide, *4*) sulphur hexafluoride.

Thus, in a stream of carbon dioxide the threshold pressure for $C_{18}-C_{36}$ n-alkanes is 87–105 atm, whereas for $C_{11}-C_{18}$ alcohols in a stream of ammonia it is 60–100 atm. Even the substances which are commonly used as stationary phases in gas chromatography can be eluted in a stream of dense carbon dioxide: squalane at 100 atm, dinonyl phthalate at 400 atm, poly(propylene glycol) at 700 atm, SE-30 silicone rubber with a molecular weight of 400 000 at 1200 atm, and Apiezon L at 1500 atm.

Data of this type, describing the migration of various compounds in dense ammonia at 140° and in dense carbon dioxide at 40°, are given in Table 2. At the threshold pressure, the following relationship was observed between the parameter Δ and the distribution coefficient Γ:

$$\Delta = 1 - \left(\frac{RT}{V_1^0\delta_0^2}\ln\Gamma\right)^{0.5} \qquad (23)$$

where V_1^0 is the molar volume of the liquid sorbate.

By analogy with temperature programming for the analysis of substances of widely differing volatilities, a stepwise pressure programme can be devised. Thus, Fig. 9*c* shows a chromatogram for the separation of squalane, dinonyl phthalate, and SE-30 silicone in carbon dioxide, carried out in pressure steps of 40 min duration[15].

Table 2. Migration of various substances in dense NH_3 and CO_2.

Substance	NH_3, 140°, 200 atm	CO_2	
		40°	Pressure, atm
Purines			
Adenine	—	+	1300
Guanine	—	—	1300
Caffeine	++		
Xanthine	—		
Nucleosides and nucleotides			
Adenosine, guanosine, uridine	++	+	1350
Adenylic acid	++		
Corticosteroids			
Cortisone, hydrocortisone	+	+	1300
Sterols			
Cholesterol, ergosterol, lanosterol	++	++	510
Sugars			
Ribose, arabinose, xylose	++	++	1350
Glucose, fructose, mannose, sorbose	++	++	1350
Galactose	+	—	1350
Maltose	++	++	1350
Lactose	++	—	1350
Terpenes			
α-Carotene, β-carotene, lycopene	dec	++	170
Squalene	++	++	510
Amino-acids			
Glycine	++	+	1350
Leucine, tryptophan, tyrosine, arginine, lysine	++	—	1350
Glycyl glycine, glycyl-*L*-leucyl-*L*-tyrosine	++		
Hyppuryl-*L*-arginine	—		
Proteins			
Trypsin, lysosin, apopheritin, γ-globulin	—		
Gelatin	—		
Cytochrome C	+		
Silicone oils and DS-200 rubbers	dec	++	700
OV-1	—		
OV-17	++		
SE-30	—	++	770*
Alkanes			
n-Octadecane, n-docosane, n-octacosane		++	136
Squalane	++	++	90*
Poly(ethylene glycols)			
P.e.g. 400		++	68*
P.e.g. 1000		++	115*
P.e.g. 4000		++	190*
P.e.g. 20000	++	+	
Other substances			
Quercetin	++		
Amygdalin	—		
Polysulphone	—		
Polyox	—		
Polystyrene 900	—		
Versamide 900	—		
Cellulose acetate	—		
L-glucose penta-acetate	++		
Poly(vinyl chloride)		+	1700
Polyethylene		—	1500
Dinonyl phthalate		++	165*
Apiezon *L*	—	++	820*

++Strong migration; + weak migration; —undetectable migration; *threshold pressure.

The choice of mobile and stationary phases for the separation of multicomponent mixtures has been discussed by Sie and Rijnders[18,60,61]. Thus, if the sorption capacity of the stationary phase is high, the elution of homologues is determined by the molecular weight (see *a*, *b*, and *c* in Fig. 11). But if the sorbate and the fluid are polar and the sorbent is non-polar, or vice-versa, the retention characteristics of the homologues become very similar (*d* and *e* in Fig. 11).

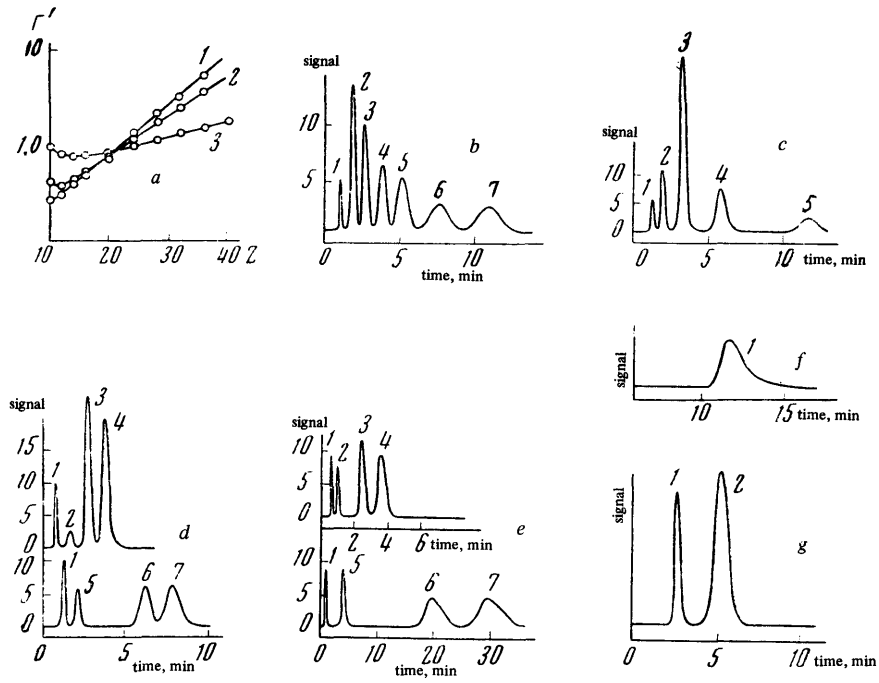


Figure 11. Separation of high-molecular-weight aromatic hydrocarbons in sorbate–fluid–stationary phase systems.

(*a*) Retention of dialkyl phthalates in: *1*) fluid—isopropanol, stationary phase—low-molecular-weight polyethylene; *2*) fluid—n-pentane, stationary phase—low-molecular-weight polyethylene; *3*) fluid—n-pentane, stationary phase—poly(ethylene glycol)-6000. n-Pentane at 213° and 42 atm, isopropanol at 245° and 49.5 atm. Polyethylene (~10 wt. %) and poly(ethylene glycol)-6000 (~23 wt. %) on Sil-O-Cel. *Z* is the number of carbon atoms in the phthalate molecule.

(*b*) Separation of phthalates according to molecular weight. Column length 2 m, inner diameter 6 mm, filled with polyethylene (~10 wt. %) on Sil-O-Cel. Fluid—isopropanol, temperature 245°, pressure 49.5 atm. *1*) Benzene, *2*) dihexyl phthalate, *3*) dioctyl phthalate, *4*) didecyl phthalate, *7*) dihexadecyl phthalate.

(*c*) Separation of some condensed aromatic hydrocarbons on an alumina-packed column. *1*) Benzene, *2*) naphthalene, *3*) phenanthrene, *4*) 1,2-benzanthracene, *5*) picene. Fluid—isopropanol at 245° and 45.2 atm; adsorbent—aluminium oxide.

(*d*) Separation of bi- and triaryl isomers. *1*) Benzene, *2*) biphenyl, *3*) *o*-terphenyl, *4*) *p*-terphenyl, *5*) naphthalene, *6*) 1,1′-binaphthyl, *7*) 2,2′-binaphthyl. Fluid—isopropanol at 245° and 45 atm; adsorbent—aluminium oxide.

(*e*) Separation of close-boiling polynuclear aromatic hydrocarbons. *1*) Benzene, *2*) naphthalene, *3*) phenanthrene (T_b = 336.8°), *4*) anthracene (T_b = 339.9°), *5*) pyrene, *6*) 3,4-benzpyrene (T_b = 495°), *7*) 1,2-benzpyrene (T_b = 493°). Fluid—n-pentane at 200° and 39.8 atm.

(*f*) Shape of the *m*-terphenyl peak (T_b = 364°) under conditions of high-temperature gas-adsorption chromatography. Carrier gas—helium; adsorbent—aluminium oxide treated with NaOH; temperature 350°; pressure 1.5 atm.

(*g*) Separation of *m*- and *p*-terphenyl (T_b = 576°) under conditions of fluid-adsorption chromatography. Fluid—isopropanol at 245° and 50 atm; adsorbent—aluminium oxide[18,60-61].

When considering the retention of sorbates at high pressures it is important to allow for eluent–sorbent interactions. Thus, solubility of the eluent in the stationary phase leads to the formation of a binary phase in gas–liquid chromatography[58]. In the gas-adsorption variant, if both the adsorbent and the eluent are polar the active centres on the surface of the adsorbent are deactivated by eluent molecules, which improves the symmetry of the chromatographic peaks and shortens the elution time. If a non-polar eluent is used, it is possible to add small amounts of a polar substance to the eluent.

In principle, one can define conditions such that the adsorbed eluent acts as a stationary phase and the retention is determined by the difference between the solubility parameters of the sorbate in one and the same compound in the liquid and the gaseous state respectively.

Chromatograms of polyphenyls are shown on Figs. 11*f* and 11*g*. They were obtained at high temperature (350°) on a column packed with alkali-modified alumina, and also by fluid-adsorption chromatography in a stream of isopropanol at 245° and 50 atm in a column packed with unmodified alumina. In the latter experiment, peaks from the heavier hydrocarbon were detected[61]. The influence of modification was observed also with adsorbents consisting of porous polymers[62].

Of course, the range of stationary phases which can be used at high pressures is limited, because of the increase in volatility at high pressure, and the choice of liquid stationary phase must taken account of the threshold pressure (see Table 2). A study of the stability of stationary phases in a stream of dichlorodifluoromethane[64] showed that poly(propylene glycol) and Apiezon M are lost from the column in a few minutes, and SE-52 silicone slowly volatilises. Nitrile silicone rubber was found to be stable up to 210 atm; Kel-F (polytrifluorochloroethylene) and some other phases were not eluted at all.

With pentane and isopropanol as eluents, polyglycols and low-molecular-weight polyethylene were used as stationary phases[18]; silicone rubbers, polysulphone, polystyrene, Apiezon, and some other stationary phases did not migrate in a stream of ammonia[13–15].

Detection can present some serious difficulties when chromatographic analysis is attempted in a stream of dense gas. Kobayashi and coworkers[68–70] used a katharometer and a radioactivity counter (because their sample was radioactive), both working at atmospheric pressure. However, at elevated pressure the use of a katharometer becomes unattractive because of the decreased sensitivity and the noise from density fluctuations and mechanical vibrations. The thermal conductivity of "fluids" is usually not very different from that of the sorbates. Klesper and coworkers[64] used a flow-through spectrophotometer cell working at pressures up to 100 atm.

Sie and coworkers[18,60–62] used a different method of detection. Their apparatus included a condensing system for the eluent, which was then led as a liquid to a quartz u.v. cell sensitive to aromatic compounds.

Lastly, the eluate from the column has been split into two streams[39,71–73], the main stream being discharged to the atmosphere and the remainder led to a flame-ionisation detector. In this method, of course, one must beware of condensation of high-boiling sorbates upstream from the detector. For this reason, Giddings[15] suggests pyrolysis of the eluate, followed by chromatographic or mass-spectrometric analysis of the resulting low-molecular products.

Data on the methods of detection, and also on the methods of introducing the eluent, used by various authors, are listed in Table 3.

IV. DETERMINATION OF PHYSICOCHEMICAL CONSTANTS OF COMPOUNDS BY GAS CHROMATOGRAPHY AT HIGH PRESSURES

Phase equilibria at high pressures and non-ideality of the gas phase can be studied by chromatographic methods only if strict correlations between the unknown parameters and the retention characteristics of the sorbate are available, with due allowance for the effect of pressure on the velocity distribution, on the viscosity of the eluent, and on the distribution coefficient of the sorbate, and also on the solubility of the carrier gas in the stationary phase[34,36,41,55,56,69,71,74–87].

Table 3. High-pressure chromatography conditions.

Expt. No.	Eluent, and maximum column pressure	Method of adding eluent	Method of sample injection	Detector, pressure	Refs.
1	Light gases, 25 atm	Gas cylinder, regulator, valve	Gas pipette, evacuated and filled with sample vapour. Sample injected in a stream of carrier gas	Flame-ionisation detector. Atmospheric pressure	71
2	Light hydrocarbon mixture 68 atm	Gas cylinder, regulator, valve	Piston injector	Katharometer, radio activity detector. Atmospheric pressure	68
3	Isopropanol, diethyl ether, n-pentane, 50 atm	Liquid, entrained by nitrogen, heated to T_{cr}	Pneumatic apparatus with a sample recess. Sample size: 15 μl of 0.1–1 wt.% soln.	Quartz u.v. cell. Eluate in liquid phase. Atmospheric pressure	18 60–62
4	Freons, 210 atm	Compressor	Solution of sample placed on glass piston. Solvent evaporated, piston inserted in sample injector, temperature and pressure raised, valve between injector and column opened	Flow-through spectrophotometer cell operating at column pressure	12 64–66
5	Gases in supercritical state, 2000 atm	High-pressure compressor	Bypass system with high-pressure valves	Flame-ionisation detector. Atmospheric pressure	13–15

For an ideal gas we have the law

$$\alpha = -\frac{K}{\eta} \cdot \frac{dP}{dl}, \tag{24}$$

where α is the linear velocity, η is the dynamic viscosity of the carrier gas, K is the permeability coefficient, dl is an element of length. It follows that the average pressure along the length of the column is

$$p = \frac{\int_0^L P\,dl}{\int_0^L dl} = \frac{\int_{P_0}^{P_1} -\frac{KP^2\,dP}{\eta P_0 \alpha_0}}{\int_{P_0}^{P_1} -\frac{KP\,dP}{\eta P_0 \alpha_0}} = \frac{\int_{P_0}^{P_1} P^2\,dP}{\int_{P_0}^{P_1} P\,dP} = \frac{2}{3} P_0 \frac{(P_1/P_0)^3 - 1}{(P_1/P_0)^2 - 1} = \frac{P_0}{j}, \tag{25}$$

where α_0 is the velocity of the gas at the outlet of the column of length L, j is the pressure gradient factor§ [see Eqn. (4)]. The effective retention volume (corrected for the dead volume of the column and reduced to the mean pressure), which is related to the distribution coefficient of the sorbate between the stationary and the mobile phase, is given by

$$\overline{\overline{V}}_N = (t_R - t_0) V_\alpha J_3^2, \tag{26}$$

where t_R is the retention time of the sorbate, t_0 is the retention time of the non-adsorbed gas, and V_α is the volumetric velocity of the gas at the column outlet. The distribution of pressure along the length of the column is

$$\frac{l}{L} = \frac{P_1^2 - P^2}{P_1^2 - P_0^2}, \tag{27}$$

where the pressure P corresponds to a cross-section at a distance l from the inlet of the column (see Fig. 12).

However, if the pressure is averaged over the dwell time of the sorbate in the column rather than along the length, and noting that $dt = \frac{\Gamma_0}{\alpha} dl$, where Γ_0 is the Henry coefficient[88], the following expression is obtained:

$$\overline{P} = \frac{\int_0^{t_R} P\,dt}{\int_0^{t_R} dt} = \frac{\int_{P_0}^{P_1} -\frac{KP\Gamma_0}{\eta\alpha^2}\,dP}{\int_{P_0}^{P_1} -\frac{K\Gamma_0}{\eta\alpha^2}\,dP} = \frac{\int_{P_0}^{P_1} \frac{P^3\,dP}{\alpha_0^2 P_0^2}}{\int_{P_0}^{P_1} \frac{P^2\,dP}{\alpha_0^2 P_0^2}} = \frac{3}{4} P_0 \frac{(P_1/P_0)^4 - 1}{(P_1/P_0)^3 - 1} = \frac{P_0}{j}, \tag{28}$$

where $j = J_4^3$, and the time-averaged effective retention volume is

$$\overline{V}_N = (t_R - t_0) V_\alpha \cdot J_4^3. \tag{29}$$

It can be shown that $J_3^2 J_4^3 = \chi^2$ [see Eqns. (4) and (25)], and $\overline{P}/\overline{\overline{P}} = J_3^2 J_3^4 = j^2/\chi^2$ [see Eqns. (4), (25), and (28)].

Eqns. (25) and (28) were deduced on the assumption that η and Γ_0 are constant and $P\alpha = P_0\alpha_0$ along the column.

Martire and Locke[75] determined the mean pressure of a non-ideal gas from the expression

$$P\alpha = (P\alpha)_{id}(1 + a_1 P) \tag{30}$$

Here the product $(P\alpha)_{id}$ corresponds to an ideal gas, $a_1 = \frac{B_{22}}{RT}$, and B_{22} is the second virial coefficient in the equation of state for the carrier gas.

In this case integration gives

$$\overline{\overline{P}} = \overline{\overline{P}}_{id} \frac{1 - a_1 P_0 J_3^4}{1 - a_1 P_0 J_2^3} \approx \overline{\overline{P}}_{id}[1 - a_1 P_0 (J_3^4 - J_2^3)] \tag{31}$$

§ In Everett's terminology[56], we assume

$$J_n^m = \frac{n}{m} \frac{(P_1/P_0)^m - 1}{(P_1/P_0)^n - 1}.$$

and

$$j \approx j_{id}[1 + a_1 P_0 (J_3^4 - J_2^3)]. \tag{32}$$

Giddings and coworkers[36] applied Eqn. (30) together with a relationship between viscosity and pressure:

$$\eta = \eta_{id}(1 + b_1 P) \tag{33}$$

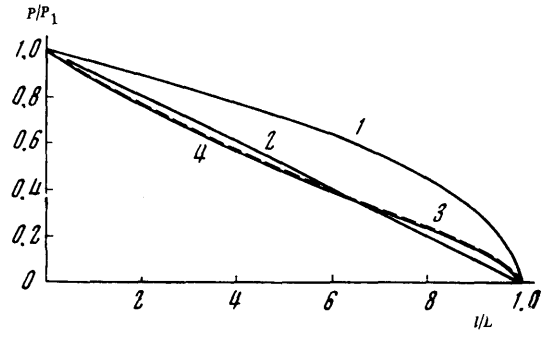


Figure 12. Pressure profile along column. Inlet pressure 1960 atm, outlet pressure 1 atm. *1*) Ideal gas, *2*) liquid, *3*) argon, *4*) nitrogen. Temperature 25°.[41]

The resulting expressions have the form

$$\overline{\overline{P}} \approx \overline{\overline{P}}_{id}[1 - (a_1 + b_1) P_0 (J_3^4 - J_2^3)] \tag{34}$$

and

$$j \approx j_{id}[1 + a_1 P_0 (2J_3^4 - J_2^3 - 1) + b_1 P_0 (J_3^4 - J_2^3)]. \tag{35}$$

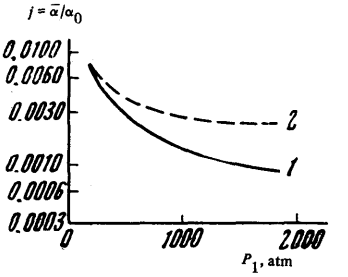


Figure 13. Correction $j = \bar{\alpha}/\alpha_0$ for: *1*) an ideal gas and *2*) nitrogen at pressures up to 2000 atm. Pressure at column outlet 1 atm, temperature 25°. (Constant Γ assumed.)[36]

The pressure profile in real gases is shown[41] in Fig. 12. The quantities j_{id} and j for nitrogen at 25° are compared[36] in Fig. 13. Lastly, Fig. 14 shows[36] the effect of pressure on the ratio $\overline{P}/\overline{\overline{P}}$, which is a correction to the term H in the equation, giving the contribution of diffusion in the gas phase to the height equivalent to a theoretical plate.

The change with pressure of the distribution coefficient Γ of the sorbate can be taken into account by using a linear [55,74]

$$\Gamma = \Gamma^0(1 + \beta P) \tag{36}$$

or a logarithmic [77]

$$\ln \Gamma = \ln \Gamma^0 + \beta P \tag{37}$$

correlation [see Eqn. (18)]. Here Γ^0 is the distribution coefficient extrapolated to zero pressure:

$$\ln \Gamma^0 = \ln \frac{RT}{\gamma_1^\infty V_3 P_1^0} - \frac{B_{11} - V_1^\infty}{RT} P^0, \tag{38}$$

$$\beta = \frac{2B_{12} - V_1^\infty}{RT}, \tag{39}$$

where γ_1^∞ is the activity coefficient of the sorbate at infinite dilution in the pure stationary phase, V_1^0 and V_1^∞ are the molar volume of the liquid sorbate and the partial molar volume of the sorbate at infinite dilution in the stationary phase respectively, V_3 is the molar volume of the pure stationary phase, P_1^0 is the saturated vapour pressure of the sorbate, B_{11} is the second virial coefficient of the sorbate vapour, B_{12} is the second mixed virial coefficient for the interaction between sorbate vapour and carrier gas.

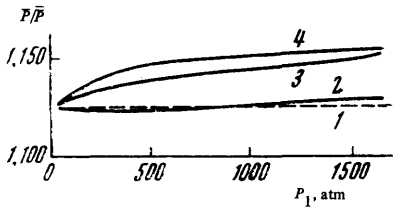


Figure 14. Plots of $\bar{P}/\bar{\bar{P}}$ against pressure at column inlet P_1 for: *1*) ideal gas, *2*) hydrogen, *3*) nitrogen, *4*) argon. Outlet pressure 1 atm, temperature 25°. [36]

Here, and elsewhere in this Review, the subscripts 1, 2, and 3 denote the sorbate, the carrier gas, and the stationary phase respectively.

Windsor and Young [79] obtained an expression for the effective retention volume in terms of the factor β:

$$V_N = \frac{\dfrac{\Gamma^0 V_3 J_3^2}{P_0}\left[\dfrac{e^{\beta P}}{\beta^3}(\beta^2 P^2 - 2\beta P + 2)\right]_{P_1}^{P_0}}{0.5\,[P^2]_{P_1}^{P_0}}, \tag{40}$$

and showed that this expression can be replaced, without significant loss of precision, by a much simpler expression of the type

$$\ln \bar{V}_N = \ln V_N^0 + \beta P_0 J_3^4 \tag{41}$$

(Desty and coworkers [55] used the factor J_3^2, and hence determined the quantity $\bar{\bar{V}}_N$.)

Cruickshank and coworkers [71,80], and also Giddings and coworkers [36], allowed for all three non-ideality factors (a_1, b_1, and β) simultaneously, but their final expressions were unwieldy.

Trestianu [89,91] systematised the published relationships between retention characteristics and column pressure. His results are summarised in Table 4.

Solubility of the carrier gas in the stationary phase is another possible source of variation in retention characteristics. Allowing for this factor, the expression for the effective retention volume at pressures where the third virial coefficient plays a significant role takes the form [80,81,92]

$$\ln V_N = \ln V_N^0 + \beta' P_0 J_3^4 + \zeta' (P_0 J_3^4)^2,$$

where

$$\beta' = \beta + \lambda\left[1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right]_0,$$

$$\zeta' = \frac{3C_{122} - 4B_{12}B_{22}}{2RT} + \varphi\left[1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right]_0 + \frac{\lambda^2}{2}\left[1 - \frac{\partial^2 \ln \gamma_1^\infty}{\partial x_2^2}\right]_0 + \frac{kV_1^\infty}{R\Gamma} \tag{42}$$

$\partial\gamma_1^\infty/\partial x_2$ is the change in the activity coefficient of the sorbate in the stationary phase with mole fraction x_2 of dissolved carrier gas, C_{122} is the third virial coefficient for the interaction between the sorbate and the carrier gas, k is a coefficient, λ and φ are constants in the series expansion of the mole fraction x_2 of the carrier gas dissolved in the stationary phase [81]: $x_2 = \lambda P + \varphi P^2 + \ldots$

Table 4. Expressions for j and V_N with allowance for non-ideality of the system [89].

Non-ideality $P\cdot\alpha$	Non-ideality η	Non-ideality Γ	j	V_N	Refs.
—	—	+	J_3^2	$\ln \bar{V}_N = \ln V_N^0 + \beta P_0 J_2^3$	55
—	—	+	J_3^2	$\bar{V}_N = V_N^0(1 + \beta P_0 J_3^4)$	56
+	—	—	$J_3^2[1 + a_1 P_0 (J_3^4 - J_2^3)]$	—	75
+	—	+	$J_3^2[1 + a_1 P_0 (2J_3^4 - J_2^3 - 1)]$	$\ln \bar{V}_N = \ln V_N^0 + \beta P_0 J_3^4$	77
+	+	+	$J_3^2[1 + a_1 P_0 (2J_3^4 - J_2^3 - 1) + b_1 P_0 (J_3^4 - J_2^3)]$	$\ln \bar{\bar{V}}_N = \ln V_N^0 + \beta P_0 J_2^3[1 - P_0 (a_1 + b_1)(J_3^4 - J_2^3)]$ $\ln \bar{V}_N = \ln V_N^0 + \beta P_0 J_3^4[1 - P_0 (2a_1 + b_1)(J_4^5 - J_3^4)]$	36

The general form of the gas solubility correction is

$$\exp\left[\left(\frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right)_0 (\lambda P + \varphi P^2 + \ldots) + \frac{1}{2}\left(\frac{\partial^2 \ln \gamma_1^\infty}{\partial x_2^2}\right)_0 \cdot (\lambda^2 P^2 + \ldots) + \ldots\right].$$

Eqns. (37)–(42) suggest the possibility of determining by a chromatographic method the activity coefficients of sorbates dissolved in the stationary liquid, corrected for the non-ideality of the gas phase (γ_1^∞). Since $V_N = \omega\Gamma$, where ω is the volume of the stationary liquid in the column, the quantity γ_1^∞ can be evaluated by extrapolation of the effective retention volume to zero mean pressure, followed by a correction for the non-ideality of the pure sorbate [second term on the right-hand side of Eqn. (38)]. The mean pressure is expressed as $P_0 J_3^4$.

Chromatographic determinations of activity coefficients from retention characteristics measured at pressures of 12–15 atm (where the influence of the third virial coefficient is not appreciable) have been reported [80,93–101]. Some workers have used several carrier gases in order to achieve greater precision.

The ordinate of the intersection of the linear plots for a single sorbate but different carrier gases (Fig. 15) defines the quantity V_N^0, which is independent of the nature of the chosen eluent. The precision of the chromatographic method of determining γ_1^∞ is evident from Table 5,

where the results are compared with data obtained by the static method.

Locke and Brandt[101] have calculated virial coefficients from the results of experiments at low pressures.

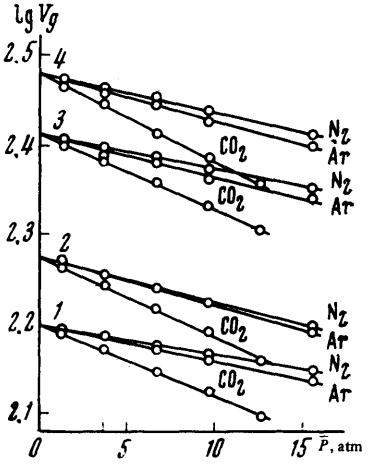


Figure 15. Logarithm of absolute specific retention volume against mean column pressure at 80° in nitrogen, argon, and carbon dioxide for: *1*) dioxan, *2*) n-octane, *3*) toluene, *4*) butyl acetate[73].

Pomazanov and Semkin[102] have determined the activity coefficients of sorbates of different types with a correction for non-ideality of the gas phase, calculated from experiments in columns with a different stationary phase. They were able to show the existence, in an experiment with a homologous series of n-alkanes and a stationary phase of squalane, of a real or hypothetical (i.e. with a non-integral number of carbon atoms) component such that the corrections for B_{11} and B_{12} are mutually compensating and $\gamma^{\infty} = \gamma$.

Table 5. Activity coefficients of hydrocarbons in dinonyl phthalate at 30°. Nitrogen carrier gas[74].

Sorbate	lg γ	lg γ∞	lg γ∞ (static results)
Benzene	—0.250	—0.253	—0.253
n-Pentane	0.022	0.034	0.035
n-Hexane	0.080	0.077	0.076
2,2-Dimethylbutane	0.098	0.103	0.095
Cyclohexane	—0.031	—0.032	—0.032
n-Heptane	0.123	0.117	0.114
n-Octane	0.161	0.153	0.153

Plots like those shown in Fig. 15 enable the second virial coefficients B_{12} for the interaction between sorbates and carrier gases to be determined, since the slope of the linear plot gives the parameter β in Eqns. (37) and (41). Data of this type are not freely available in the literature.

Expanding the compressibility coefficient of the gas mixture in a power series of $1/V$ (where V is the molar volume of the gas mixture)

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots, \tag{43}$$

B and C being the second and third virial coefficient, related to the interaction energy of two and three molecules respectively, we obtain the expression

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}, \tag{44}$$

where x_1 and x_2 are the mole fractions of components 1 and 2 in the mixture.

Desty and coworkers[55] used the expression

$$\ln V_N = \ln V_N^0 + \beta P_0 J_2^3, \tag{45}$$

to determine B_{12} for several hydrocarbons mixed with helium, hydrogen, nitrogen, or carbon dioxide in capillary columns with large pressure drops. However, Cruickshank and coworkers have shown[77] that these calculations are subject to large errors and can only be justified if the pressure drop is small. Hence, many other workers have used Eqn. (41) to determine second virial coefficients[72,73,93-96].

Their results (see Table 6) are in good agreement with values obtained by static measurements[103-105]. A number of conclusions regarding the validity of various methods of computing B_{12} have been made from these results. Thus, it has been shown[93,98] that in calculations using the principle of corresponding states the pseudo-critical temperature should be determined by Hudson and McCoubrey's method[107] rather than as the geometric mean of the critical temperatures of the components. It has been shown, also, that Lewis and Randall's rule[108]

$$B_{12} = 0.5(B_{11} + B_{22}) \tag{46}$$

is incorrect.

Semkin and Vigdergauz[73] have noted an approximately linear relationship between B_{12} and the number of carbon atoms in n-alkane molecules, which applies over a range of temperatures and for a number of carrier gases (Fig. 16).

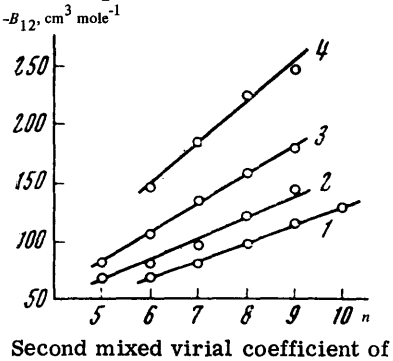


Figure 16. Second mixed virial coefficient of n-paraffins against number of carbon atoms in the molecule. Carrier gas: *1*) nitrogen, 80°, *2*) argon, 80°, *3*) argon, 50°, *4*) carbon dioxide, 80°.[73]

The largest error in the chromatographic determination of virial coefficients arises from the solubility of the carrier gas in the stationary phase. As shown by Everett

Table 6. Second mixed virial coefficients determined by chromatographic and by static methods

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
Acetone	Ar	80	58	72	
	CO_2	40	343	16	
		80	129	72	
Ethyl methyl ketone	N_2	80	36	73	
	Ar	50	86	72	
		80	65	72	
	CO_2	80	184	72	
1,1-Dichloroethane	CO_2	40	215	16	
Chloroform	N_2	80	12	73	
	Ar	50	60	72	
	CO_2	80	59	72	
		80	169	72	
Carbon tetrachloride	N_2	80	24	73	
	Ar	50	125	72	
		80	67	72	
	CO_2	80	154	72	
Nitromethane	N_2	80	41	73	
	Ar	50	91	72	
		80	62	72	
	CO_2	80	188	72	
Nitroethane	N_2	80	71	73	
	Ar	50	125	72	
		80	97	72	
	CO_2	80	247	72	
Dioxan	N_2	80	67	73	
	Ar	50	124	72	
		80	86	72	
	CO_2	80	136	72	
Butyl acetate	N_2	80	79	73	
	Ar	50	138	72	
		80	119	72	
	CO_2	80	260	72	
Methanol	CO_2	40	236	16	
Ethanol	N_2	80	10	73	
	Ar	50	118	72	
		80	46	72	
	CO_2	40	303	72	
		80	95	16	
Isopropanol	Ar	50	80	72	
		80	51	72	
	CO_2	80	127	72	
Propane	CO_2	40	99	16	
n-Butane	N_2	30	78	95	
		35	84	100	
		50	69	95	
		60	77	94.96	
	CO_2	40	153	16	
n-Pentane	H_2	25	−7	55	
			−3	55	
			−2	89	
	N_2	25	105	55	
			76	56	
			103	91	
		30	103	91	
		35	85	100	
		40	85	91	
		55	66	94.96	
		60	80	95	
			72	94.96	
		65	78	94.96	
		80	60	73	
	Ar	25	98	91	136±18
					125±23
		50	82	72	
		80	68	72	
	CO_2	25	173	55	
		40	198	16	
		80	76	72	
	O_2	25	152	55	
	CH_4	25	204	106	222±13
		50	138	106	190±12
	C_2H_6	25	414	106	448±16
n-Hexane	H_2	25	0	55	
			−6	91	
	N_2	25	128	55	
			112	91	
		30	108	95	
		35	113	100	
		40	107	95	
		50	79	91	
		55	90	94.96	
		60	93	95	
			98	94.96	
		65	104	94.96	
		80	69	73	
	Ar	25	124	91	149±65
					80±73
					180±50
		40	104	96	148±27
		50	106	72	108±32
			107	91	120±9
		65	100	91	
		80	81	72	

Table 6 (continued).

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
	CO_2	25	233	55	
		80	147	72	
	O_2	25	163	55	
	CH_4	25	292	106	261±60
		50	280	106	225±30
n-Heptane	H_2	25	36	55	
	N_2	35	132	100	
		40	111	91	
		60	101	94.96	
		75	87	94.96	
		80	81	73	
	Ar	50	136	72	
	CO_2	80	97	72	
		25	294	55	
		80	177	72	
	O_2	25	183	55	
n-Octane	H_2	40	−9	93	
		65.05	−22	93	
	N_2	100			−18±4
		35	143	100	
		60	119	94.96	
		75	92	94.96	
		80	98	73	
	Ar	50	160	72	
		80	122	72	
	CO	40	153	93	
		65.05	123	93	
		100			104±4
	CO_2	80	227	72	
n-Nonane	N_2	80	117	73	
	Ar	50	181	72	
		80	146	72	
	CO_2	80	249	72	
n-Decane	N_2	80	130	73	
Isopentane	H_2	25	−26	55	
	N_2	25	105	55	
		55	64	94.96	
		60	76	94.96	
		65	81	94.96	
	Ar	25	94	91	178±14
		35	78	100	
	CO_2	25	165	55	
	O_2	25	125	55	
	CH_4	25	199	101	
		80	123	101	
2,2-Dimethylbutane	H_2	25	−26	55	
			−9	91	
	N_2	25	105	55	
			88	56	
			94	91	
		35	60	100	
	Ar	25	108*	72	
			115	91	156±26
	CO_2	25	168	55	
	O_2	25	145	55	
	CH_4	25	216	106	
		50	154	106	
Cyclopentane	H_2	25	−5	55	
	N_2	25	91	55	
	Ar	25	108*	72	
	CO_2	25	197	55	
	O_2	25	152	55	
2,3-Dimethylbutane	H_2	25	−9	55	
	N_2	25	112	55	
		35	98	100	
	Ar	25	112*	72	
		35	98	100	
	CO_2	25	208	55	
	O_2	25	153	55	
2-Methylpentane	H_2	25	7	55	
	N_2	25	127	55	
		35	91	100	
	Ar	25	115*	72	147±49
		25	125	91	
	CO_2	25	206	55	
	O_2	25	155	55	
	CH_4	25	317	106	
		50	144	106	
3-Methylpentane	H_2	25	−3	55	
	N_2	25	117	55	
	Ar	25	116*	72	
		35	95	100	
	CO_2	25	211	55	
	O_2	25	163	55	
Methylcyclopentane	H_2	25	12	55	
	N_2	25	128	55	
	Ar	25	127*	72	
	CO_2	25	234	55	
2,2-Dimethylpentane	H_2	25	14	55	
	N_2	25	133	55	
	Ar	25	128*	72	
	CO_2	25	245	55	
2,4-Dimethylpentane	H_2	25	5	55	
	N_2	25	130	55	
		35	109	100	

Table 6 (continued).

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
	Ar	25	130*	72	
	CO_2	25	249	55	
	O_2	25	165	55	
2,2,3-Trimethylbutane	H_2	25	6	55	
	N_2	25	123	55	
	Ar	25	127*	72	
	CO_2	25	222	55	
	O_2	25	160	55	
3,3-Dimethylpentane	H_2	25	12	55	
	N_2	25	131	55	
	Ar	25	132*	72	
	CO_2	25	242	55	
	O_2	25	166	55	
Cyclohexane	H_2	25	18	55	
	N_2	25	120	55	
		35	122	100	
		60	80	94.96	
		80	63	73	
	Ar	25	130*	72	
		50	102	72	
		80	86	72	
	CO_2	25	236	55	
		80	163	72	
	O_2	25	163	55	
1,1-Dimethylcyclopentane	Ar	25	134*	72	
2-Methylhexane	H_2	25	35	55	
	N_2	25	135	55	
	Ar	25	137*	72	
	CO_2	25	272	55	
	O_2	25	175	55	
2,3-Dimethylpentane	H_2	25	6	55	
	N_2	25	133	55	
	Ar	25	135*	72	
	CO_2	25	264	55	
	O_2	25	167	55	
3-Methylhexane	H_2	25	32	55	
	N_2	25	136	55	
	Ar	25	138*	72	
	CO_2	25	276	55	
	O_2	25	180	55	
cis-1,3-Dimethylcyclopentane	Ar	25	136*	72	
trans-1,3-Dimethylcyclopentane	Ar	25	136*	72	
trans-1,2-Dimethylcyclopentane	Ar	25	136*	72	
3-Ethylpentane	H_2	25	36	55	
	N_2	25	144	55	
	CO_2	25	292	55	
	O_2	25	176	55	
2,2,4-Trimethylpentane	H_2	40	—4	93	
		65.05	—6	93	
		75	—		—18±4
	N_2	80	47	73	
	Ar	50	128	72	
		80	87	72	
	CO_2	80	147	72	
n-Pent-1-ene	H_2	35	19	100	
	N_2	35	64	100	
	Ar	35	84	100	
n-Hex-1-ene	H_2	35	13	100	
	N_2	35	110	100	
	Ar	35	110	100	
n-Hept-1-ene	H_2	35	2	100	
	N_2	35	142	100	
		60	95	94.96	
	Ar	35	139	100	
n-Oct-1-ene	Ar	35	136	100	
Buta-1,3-diene	CO_2	40	155	16	
Pyridine	N_2	80	42	73	
	Ar	50	115	72	
		80	95	72	
	CO_2	80	207	72	
Benzene	H_2	25	13	55	
		40	9	96	
		50	9	92	
			5	93	7.5±4
	He	50	—57	93	
			—49	93	
	N_2	20	120	96	
		25	117	55	
			109	94.96	
		30	107	94.96	
		32	103	99	
		35	104	94.96	
		40	96	99	
		40	108	91	
		50	94	96	
			90	99	
			87	93	
		55	86	96	
		60	98	94	
			93	96	
			89	96	
		65	92	96	
		75	79	96	

Table 6 (continued).

Sorbate	Carrier gas	°C	Experimental data: $-B_{12}$, cm^3 mole^{-1}	Experimental data: references	Static data Refs. 103-105: $-B_{12}$, cm^3 mole^{-1}
		80	74	73	
	Ar	35	135	100	
		40	126	96	
		50	117	72	
			90	96	
			79	93	
			88	91	
			85	93	
		65	100	91	
		80	105	72	
	CO	50	113	93	114±4
			122	93	
	CO_2	40	288	16	
		80	216	72	
	O_2	50	79	93	
	CH_4	50	155	93	
Toluene	N_2	80	94	73	
	Ar	50	135	72	
		80	120	72	
			123	58	
	CO_2	80	235	72	
Styrene	N_2	80	117	58	
	Ar	50	169	58	
		80	148	58	
	CO_2	80	300	58	
Fluorobenzene	N_2	32	117	99	
		40	93	99	
		50	96	99	
1,2-Difluorobenzene	N_2	50	95	99	
1,3-Difluorobenzene	N_2	50	97	99	
1,4-Difluorobenzene	N_2	50	94	99	
1,3,5-Trifluorobenzene	N_2	32	110	99	
		40	111	99	
		50	106	99	
1,2,3,4-Tetrafluorobenzene	N_2	50	110	99	
1,2,4,5-Tetrafluorobenzene	N_2	50	105	99	
Pentafluorobenzene	N_2	50	110	99	
Hexafluorobenzene	N_2	32	150	99	
		40	130	99	
		50	111	99	
		55	117	94	
		60	110	94	
		65	108	94	
		75	118	94	

*Obtained by interpolation from retention indices.

and coworkers[93], the solubility of carbon dioxide in octadecane produces an increase of β corresponding to an increase of B_{12} of 75 cm^3 mole^{-1}. When the solubility of the eluent is appreciable, the stationary phase should be treated as a binary system, and the retention characteristics should be determined with the help of expressions derived for multicomponent stationary phases[109,110].

By taking one of the experimental sorbates as standard, it is possible to calculate[58] relative values of $\partial \ln \gamma_1^\infty / \partial x^2$ [see Eqn. (42)]. Thus, ignoring the solubility of the carrier gas, the effective value of the second mixed virial coefficient can be obtained:

$$B_{\text{eff}} = B_{12} + 0.5\lambda\left(1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right) RT. \qquad (47)$$

Putting $\Delta B = B_{\text{eff}} - B_{12}$, we have

$$\Delta B_{\text{rel}} = \left(1 - \frac{\partial \ln \gamma_1^\infty}{\partial x_2}\right)_{\text{rel}}. \qquad (48)$$

The present writers have shown[57,58] that the retention indices of hydrocarbons[111] are almost linearly related to the mean pressure in the column over a range of pressures extending to at least 30 atm.

We have also proposed[72] an interpolation method of determining B_{12} from values of the retention index I:

$$\frac{\Delta I}{\Delta P} = \frac{(I_1 - 100Z)(\beta_{z+1} - \beta_z) - 100(\beta_x - \beta_z)}{b_2}, \qquad (49)$$

where $\Delta P = P_2 - P_1$, $\Delta I = I_2 - I_1$, I_1 and I_2 are the retention indices of the sorbate at column pressures P_1 and P_2 respectively,

$$\beta_i = \frac{2B_{12i} - V_{1i}^{\infty}}{2.303RT}, \quad i = x, z, z+1, \quad b_2 = \lg \frac{V_{gzP_2}}{V_{g(z+1)P_2}}$$

The latter quantity is the logarithm of the relative retention volume of n-alkanes differing by one carbon atom at pressure P_2, and i is the number of the sorbate.

Eqn. (49) allows the B_{12} coefficients to be determined with high precision if the B_{12} values for two normal alkanes are known. This method has been used to determine the second mixed virial coefficients for the interaction between the carrier gas and the components of a directly distilled light petroleum fraction (see Table 6).

In general, the best results are obtained by the interpolation method when the chosen standards are similar in structure to the experimental sorbates, because under these conditions the adverse influence of the solubility of the carrier gas in the stationary phase is minimised. Thus, benzene and styrene were chosen in a study[58] of aromatic hydrocarbons with carbon dioxide as carrier gas and poly(ethylene glycol)-400 as the stationary phase.

The calculation was made by means of the formula

$$\frac{\Delta G}{\Delta \bar{P}} = \frac{\beta^{(x)} - \beta^{(1)} - G_1(\beta^{(2)} - \beta^{(1)})}{(\lg V_N^{(2)} - \lg V_N^{(1)})_2}, \qquad (50)$$

where

$$\Delta G = G_2 - G_1, \quad \Delta \bar{P} = \bar{P}_2 - \bar{P}_1,$$

$$G = \frac{\lg V_N^{(x)} - \lg V_N^{(1)}}{\lg V_N^{(2)} - \lg V_N^{(1)}},$$

and the superscripts (x), (1), (2) correspond to the experimental sorbate and the two standard compounds. G_1 corresponds to pressure P_1, G_2 and $(\lg V_N^{(2)} - \lg V_N^{(1)})_2$ correspond to pressure P_2, and $\beta = \frac{2B_{12} - V_1^0}{2.303R}$.

The values of B_{12} obtained for alkylbenzenes are given in Table 7.

We have also proposed an interpolation method of calculating B_{12} from the linear retention index[115]

$$J = \frac{t_{Rx} - t_{Rz}}{t_{R(z+1)} - t_{RT}} + Z. \qquad (51)$$

An expression relating B_{12} to the change of linear retention index with pressure ($\Delta J/\Delta \bar{P}$) was obtained.

By analogy with the calculation based on logarithmic interpolation [Eqn. (50)], a relationship between $\Delta Q/\Delta \bar{P}$ and B_{12} was derived for compounds of similar structure on the basis of the function

$$Q = \frac{t_{Rx} - t_{R1}}{t_{R2} - t_{R1}} \qquad (52)$$

Here t_{R1} and t_{R2} are the retention times of the standards 1 and 2.

Very similar results were obtained by the two interpolation methods of calculating B_{12} (the linear and the logarithmic retention index method). This points to the desirability of using the simpler, linear functions J and Q.

Kobayashi and coworkers[68-70,82-84,112-114] studied gas–liquid equilibria in multicomponent systems including gaseous and liquid hydrocarbons. Their method consisted in introducing into a flowing mixture of sorbates a sample of an individual sorbate, either radioactive (using a radioactivity detector) or non-radioactive (using a katharometer detector). The distribution coefficient of the k-th component, equal to the ratio of its mole fractions in the gas and the liquid phase, was defined as

$$K_k = \frac{y_k}{x_k} = \frac{ZRTV_{liq}}{PV_N\left(1 - \sum \frac{y_i}{K_i}\right)}, \qquad (53)$$

where Z is the compressibility coefficient of the gas mixture, V_{liq} is the total number of moles of the liquid phase, and $\Sigma \frac{y_i}{K_i}$ is the sum of the ratios for all the components except the k-th.

Table 7. Second mixed virial coefficients (for 80°) obtained by interpolation using Eqn. (50).[58*]

Carrier gas	Ar	CO_2
Sorbate	$-B_{12}$, cm^3 mole^{-1}	$-B_{12}$, cm^3 mole^{-1}
Toluene	123	248
Ethylbenzene	138	271
p-Xylene	143	284
m-Xylene	141	282
Isopropylbenzene	148	286
o-Xylene	146	289
n-Propylbenzene	152	292
1-Methyl-3-ethylbenzene	154	309
Isobutylbenzene	159	–
1,3,5-Trimethylbenzene	160	325
s-Butylbenzene	160	312
1-Methyl-2-ethylbenzene	158	310
1,2,4-Trimethylbenzene	156	340
1-Methyl-3-propylbenzene	167	328
1-Methyl-2-isopropylbenzene	168	329
1-Methyl-4-propylbenzene	169	318
1,4-Diethylbenzene	168	342
n-Butylbenzene	168	345
1,3-Dimethyl-5-ethylbenzene	173	348
1-Methyl-2-propylbenzene	171	327
1,2,3-Trimethylbenzene	165	335
1,4-Dimethyl-2-ethylbenzene	174	348
1,3-Dimethyl-4-ethylbenzene	174	350
1,2-Dimethyl-4-ethylbenzene	177	354
1,3-Dimethyl-2-ethylbenzene	167	352
1,2-Dimethyl-3-ethylbenzene	168	349
1,2,4,5-Tetramethylbenzene	183	376
1,2,3,5-Tetramethylbenzene	183	380
1,2,3,4-Tetramethylbenzene	178	386

*Standard values of $-B_{12}$. With carbon dioxide carrier: benzene 216 cm^3 mole^{-1}, styrene 300 cm^3 mole^{-1}; with argon carrier: benzene 105 cm^3 mole^{-1}, styrene 148 cm^3 mole^{-1}.

The distribution coefficients of the light hydrocarbons have been determined in this way at pressures up to 136 atm.

Thus, gas chromatography at high pressures is potentially a very important technique both for analytical work and for the characterisation of physicochemical quantities such as the non-ideality parameters of the gas phase and the constants of phase equilibria.

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