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# Efficiency for unretained solutes in packed column supercritical fluid chromatography
# I. Theory for isothermal conditions and correction factors for carbon dioxide

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**Abstract**

A general theory for efficiency of nonuniform columns with compressible mobile phase fluids is applied to the elution of an unretained solute in packed-column supercritical fluid chromatography (pSFC). The theoretical apparent plate height under isothermal conditions is given by the Knox equation multiplied by a compressibility correction factor $f_1$, which is equal to the ratio of the temporal-to-spatial average densities of the mobile phase. If isothermal conditions are maintained, large pressure drops in pSFC should not result in excessive efficiency losses for elution of unretained solutes.

*Keywords:* Supercritical fluid chromatography; Efficiency; Pressure drop

## 1. Introduction

Numerous studies have examined the effects of pressure drop on efficiency in pSFC [1–15]. In early work Mourier et al. [11] demonstrated that significant efficiency losses can occur at low average column pressures and large pressure drops, and attributed the loss of efficiency to density gradients. Schoenmakers and Uunk [14] concluded that column performance is limited by a maximum allowable pressure drop and minimum outlet pressure, especially at low mobile phase densities. In a series of investigations on the effects of pressure drop on apparent efficiency in pSFC, Berger et al. [1–4] argued that under most conditions large pressure drops have little to do with efficiency loss, and that other factors such as limited solubility of the solute or the formation of a thick layer of adsorbed mobile phase may be contributing factors to efficiency loss at low temperatures and pressures. Li et al. [9] found no significant effects from pressure drop on the apparent efficiency of packed capillary columns.

In addition to the experimental studies cited above, several theoretical treatments have appeared [5,6,15–19]. Most are based on Giddings' general theory for the efficiency of nonuniform columns, which is based on the notion of solute velocity gradients [20]. Poe and Martire [16] developed general expressions for apparent plate height with compressible mobile phase fluids, applicable to GC, SFC and HPLC. Predicted efficiencies agreed with general trends, but no direct comparison to experimental data was provided. Janssen and coworkers developed numerical methods to predict retention times and apparent plate heights [6,15]. Predicted values agreed well with experimental data for open-tubular columns [6], and for packed columns except at low outlet pressures [10]. Blumberg and Berger [17,18] developed a general model for nonuniform chromatography and concluded that only very sharp changes in solute velocity, not normally encountered in practical SFC, would lead to significant changes in efficiency. The overall impression that one gets

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from these papers is that the theory does not predict the large losses of efficiency reported in some studies for pSFC.

Berger has indicated that efficiency losses associated with pressure drop can be avoided by operating above 100 °C or 150 bar [3]. At lower temperatures and pressures efficiency losses can be quite severe in pSFC, and it is under these conditions that existing theory does not predict the observed behavior. In an effort to better understand the factors that lead to efficiency loss under these conditions, the present study examines the effects of pressure drop on efficiency for elution of unretained solutes. Although of little interest in practical SFC, its study can offer insights into dispersion processes in the mobile phase without the complicating effects of variable retention in the stationary phase. In this paper explicit mathematical relationships for the apparent plate height of unretained solutes in pSFC are developed, based on the rigorous application of established theories, and data for the compressibility correction factor for carbon dioxide are generated. Application of the results to experimental studies is presented in a subsequent paper.

## 2. Theory

### 2.1. Local plate height for an unretained solute

For a uniform column, that is one in which the properties of the mobile and stationary phases do not vary with time or position in the column, the plate height observed at the outlet is the same as the local plate height at any point in the column. To represent the local plate height we have chosen to use the equation developed by Knox and Scott [21] for liquid chromatography using porous silica microspheres as the packing material.

$$h = \frac{B}{\nu} + A_o\nu_o^{1/3} + C_o\nu_o \tag{1}$$

where $h$ is reduced plate height, given by $H/d_p$ where $H$ is plate height and $d_p$ is the particle diameter; $\nu$ is reduced velocity, given by $ud_p/D_m$ where $u$ is the linear velocity of the mobile phase, and $D_m$ is the diffusion coefficient of the solute in the mobile phase; $\nu_o$ is the reduced velocity of the mobile zone, which includes only that mobile phase in the interparticle space which is moving; the subscript o in $A_o$ and $C_o$ indicates the coefficient is associated with $\nu_o$.

The $B$ and $C$ terms of the Knox equation depend on retention. The retention factor is defined by IUPAC [22] as

$$k = \frac{V_R - V_M}{V_M} \tag{2}$$

where $V_R$ and $V_M$ are elution volumes for the solute and mobile phase, respectively. For a uniform column, the retention factor is constant and is equal to the local retention factor

$$k' = \frac{\text{moles of solute in stationary phase}}{\text{moles of solute in mobile phase}} \tag{3}$$

which is also described here as the phase capacity factor. For a nonuniform column, in which the local retention factor varies, the observed retention factor is equal to the temporal average of the local retention factor [23]

$$k = \langle k' \rangle_t \tag{4}$$

When porous packings are used, that portion of the mobile phase which is in the intraparticle space (inside the particles) is essentially stagnant, giving rise to a stagnant zone and a mobile zone. This leads to the definition of the zone capacity factor [21]

$$k'' = \frac{\text{moles of solute in the stationary zone}}{\text{moles of solute in the mobile zone}} \tag{5}$$

We use the symbol $k'$ to represent the local retention factor in contravention to the IUPAC recommendation in order to clearly distinguish it from the observed retention factor $k$, and to be consistent with the terminology employed by Knox and Scott [21] for the phase and zone capacity factors.

The value of $A_o$ in Eq. (1) is believed to depend weakly on retention, but it is usually treated as an empirical constant.

The expression for $B$ is

$$B = 2\left(\gamma_m + \frac{k'\gamma_s D_s}{D_m}\right) \tag{6}$$

where $\gamma$ is an obstruction factor to diffusion, $D$ is the solute diffusion coefficient in the indicated phase, and the subscripts m and s refer to the mobile and stationary phases, respectively. For an unretained solute ($k' = 0$) the expression simplifies to

$$B = 2\gamma_m \tag{7}$$

The expression for $C_o$ is

$$C_o = \frac{1}{30}\frac{k''}{(1+k'')^2}\frac{D_m}{D_{sz}} \tag{8}$$

where $D_{sz}$ is the solute diffusion coefficient in the stationary zone [21]. The zone capacity factor is related to the phase capacity factor by the equation

$$k'' = \frac{k' + \phi}{1 - \phi} \tag{9}$$

where $\phi$ is the fraction of total eluent which is stagnant. Because an unretained solute spends time only in the mobile phase,

$$D_{sz} = \gamma_{sm} D_m \tag{10}$$

where $\gamma_{sm}$ is the obstruction factor in the stagnant mobile phase. Setting $k' = 0$ and combining Eqs. (8)–(10) yields

$$C_o = \frac{\phi(1-\phi)}{30\gamma_{sm}} \tag{11}$$

The reduced velocity of the mobile phase and of the mobile zone are related by the equation

$$\nu = \nu_o(1 - \phi) \tag{12}$$

Combining Eqs. (1), (11) and (12) yields a relationship for the reduced plate height for an unretained solute in terms of $\nu$ and column constants:

$$h = \frac{2\gamma_{\mathrm{m}}}{\nu} + A\nu^{1/3} + \frac{\phi}{30\gamma_{\mathrm{sm}}}\nu \tag{13a}$$

where $A = A_{\mathrm{o}}/(1-\phi)^{1/3}$. Rewriting in simple form,

$$h = \frac{B}{\nu} + A\nu^{1/3} + C\nu \tag{13b}$$

where the constants $B$ and $C$ do not depend on mobile phase conditions. The $C$ term in Eqs. (13a) and (13b) is equivalent to the expression given by Knox and Scott for an unretained solute, and requires no assumptions regarding steric exclusion of the solute within the stationary zone.

### 2.2. *Apparent plate height for an unretained solute under isothermal conditions*

When a compressible fluid is used as the mobile phase and a significant pressure drop exists across the column, we have a nonuniform column in which the density and velocity of the mobile phase vary along the length of the column. Other important chromatographic properties such as viscosity, diffusivity, and distribution coefficients may also vary with axial position in the column. In this treatment we assume isothermal conditions, ignoring the potential for generation of axial and radial temperature gradients, which are addressed in a subsequent paper [24]. The retention and efficiency parameters observed at the column outlet may differ from the local values at any point in the column. Terminology for the observed and local retention factors were discussed in the preceding section. The plate height observed at the column outlet is referred to as apparent plate height.

The general treatment for apparent plate height for nonuniform columns was developed by Giddings [20,25] who derived the general relation

$$\hat{H} = L\frac{\int (H/u_{\mathrm{s}}^2)\,\mathrm{d}z}{[\int (1/u_{\mathrm{s}})\,\mathrm{d}z]^2} \tag{14}$$

where $\hat{H}$ is the apparent plate height, $H$ is the local plate height, $L$ is the column length, $u_{\mathrm{s}}$ is the local velocity of the solute zone, and $z$ is the axial position on the column. Casting $H$ and $u$ in terms of mass flow rate and density, and introducing expressions for temporal and spatial average quantities, Poe and Martire [16] showed that the above relation can be written as

$$\hat{H} = \frac{\langle H(1+k')^2\rho\rangle_{\mathrm{t}}}{\langle 1+k'\rangle_{\mathrm{t}}^2\langle\rho\rangle_{\mathrm{z}}} \tag{15}$$

where $k'$ is the local retention factor, $\rho$ is the local mobile phase density, and the subscript $t$ or $z$ indicates that the temporal or spatial average of the quantity inside the brackets is taken. If the quantities $H$ and $k'$ can be written in terms of mobile phase density, and the mobile phase density at the inlet and outlet of the column are known, then the apparent plate height can be calculated [16,26]. Eq. (15) can also be written in terms of the reduced plate height, replacing $\hat{H}$ with $\hat{h}$ and $H$ with $h$.

For an unretained solute $k' = 0$, and Eq. (15) written in terms of reduced plate height becomes

$$\hat{h} = \frac{\langle h\rho\rangle_{\mathrm{t}}}{\langle\rho\rangle_{\mathrm{z}}} \tag{16a}$$

which when applied to Eqs. (13a) and (13b) and expanded yields

$$\hat{h} = \frac{1}{\langle\rho\rangle_{\mathrm{z}}}\left(B\left\langle\frac{\rho}{\nu}\right\rangle_{\mathrm{t}} + A\langle\rho\nu^{1/3}\rangle_{\mathrm{t}} + C\langle\rho\nu\rangle_{\mathrm{t}}\right) \tag{16b}$$

Noting that the linear velocity $u = \dot{m}_{\mathrm{o}}/\rho$, where $\dot{m}_{\mathrm{o}}$ is the mass flow rate per unit area, the reduced velocity can be written as

$$\nu = \frac{\dot{m}_{\mathrm{o}}d_{\mathrm{p}}}{\rho D_{\mathrm{m}}} \tag{17}$$

For dilute gases the product in the denominator $\rho D_{\mathrm{m}}$ is constant, and this is approximately true for supercritical fluids as well [27]. Therefore, at constant mass flow rate, as long as the density drop is not too large, the reduced velocity, and consequently the local reduced plate height, is nearly invariant along the column. Eqs. (16a) and (16b) can therefore be written as

$$\hat{h} \cong \frac{\langle\rho\rangle_{\mathrm{t}}}{\langle\rho\rangle_{\mathrm{z}}}\left(\frac{B}{\nu} + A\nu^{1/3} + C\nu\right) \tag{18a}$$

where the reduced velocity is computed at $\rho = \langle\rho\rangle_{\mathrm{t}}$. This equation can be rewritten as

$$\hat{h} \cong f_1 h \tag{18b}$$

where

$$f_1 = \frac{\langle\rho\rangle_{\mathrm{t}}}{\langle\rho\rangle_{\mathrm{z}}} \tag{19}$$

is the compressibility correction factor and $h$ is the local reduced plate height.

## 3. Discussion

### 3.1. *Correction factor for apparent plate height*

The expression for apparent reduced plate height given by Eq. (18b) is equivalent to the relation reported by Giddings et al. [28] for ideal gas chromatography when only the tubewise constant plate height terms are included. The compressibility corrrection factor $f_1$, however, is defined here in general terms for real gasses. For an ideal gas it can be shown [16] that the expression for $f_1$ in Eq. (19) reduces to

$$f_1 = \frac{9}{8}\frac{(P^4-1)(P^2-1)}{(P^3-1)^2} \tag{20}$$

where $P = p_i/p_o$ is the compression ratio in terms of the inlet and outlet pressures, in agreement with the expression reported by Giddings. For nonideal fluids such as carbon dioxide under SFC conditions, values of $f_1$ can be computed numerically using the approach described in Appendix A.

The correction factor $f_1$ is a measure of the predicted efficiency loss due to pressure drop for an unretained solute under isothermal conditions. While it is of little direct interest in practical SFC, a knowledge of its value is critical to our efforts to ascertain the causes of observed efficiency losses. Appendix B lists the numerical values of $f_1$ for carbon dioxide over a range of temperatures and pressures relevant to pSFC. The data show that under most practical SFC conditions, with outlet pressures exceeding 100 bar and pressure drops less than 30 bar, efficiency losses for unretained solutes should not exceed a few percent. Even under the most extreme conditions efficiency losses for an unretained solute due to pressure drop alone should never exceed about 20%.

Also included in Appendix B is the relative difference between values of $f_1$ for real and ideal gasses computed by Eqs. (19) and (20). With differences typically on the order of a few percent, the data indicate that Eq. (20) can provide a reasonable estimate of $f_1$ for carbon dioxide for most practical SFC conditions.

An alternative expression for $f_1$ developed by Janssen et al. [15] is

$$f_1 = \frac{4}{3}\frac{(1+\Gamma+\Gamma^2)}{(1+2\Gamma+\Gamma^2)} \tag{21}$$

where $\Gamma = \rho_i/\rho_o$ is the compression ratio in terms of inlet and outlet densities. Eq. (21) was derived based on the assumption that the density gradient along the column is linear, and provides an attractive alternative to Eq. (19) for the computation of $f_1$ because it does not require the use of numerical methods. Values for $f_1$ computed from Eq. (21) for the conditions in Appendix B agreed very well with those obtained from Eq. (19) using numerical integration, with differences of less that 1% for all pressure combinations at temperatures above 70 °C. When temperatures down to 40 °C were included, similar agreement was observed as long as the outlet pressure was at least 90 bar and the pressure drop did not exceed 60 bar. For most practical SFC conditions the agreement was better than 0.1%.

### 3.2. *Validity of the final equations for apparent plate height*

Eqs. (18a) and (18b) provide a basis to evaluate the mobile phase contributions to efficiency loss associated with pressure drop in SFC. For a given set of operating conditions the factor $f_1$ can be computed as described above. The local plate height term $h$ can be determined under near-uniform column conditions where $f_1 \cong 1$ using an incompressible mobile phase such as a liquid or supercritical fluid at high density. The experimental results under nonuniform conditions can then be compared directly to the predicted behavior based on Eqs. (18a) and (18b). This approach is used in a subsequent paper [24].

The validity of Eqs. (18a) and (18b) depends on the assumption that even at large pressure drops in SFC the reduced velocity is nearly constant along the column. This assumption was tested using the computerized model described in Appendix A to compute the efficiency for elution of methane with carbon dioxide mobile phase on a 150 mm × 2.0 mm I.D. column packed with 5 μm porous silica particles over a range of mass flow rates yielding large pressure drops at the temperatures and temporal average densities listed in Appendix B. The model employs reduced densities, $\rho_R = \rho/\rho_c$, where $\rho_c$ is the critical density and is equal to 0.468 g/cm$^3$ for carbon dioxide. For a given set of Knox coefficients, Eqs. (18a) and (18b) were used to compute the predicted estimates of $\hat{h}$ under highly nonuniform conditions at $\langle\rho_R\rangle_t = 1.0$, referred to here as $\hat{h}_{est}$, where the reduced velocity was computed at $\rho_R = 1.0$. These values were compared to the exact $\hat{h}$ values computed from Eqs. (16a) and (16b), in which the local reduced velocity is a function of the local density and the local diffusion coefficient, which depends on the local viscosity (see Appendix A), and does not assume that $\rho D_m$ is constant. The accuracy of the results from Eqs. (16a) and (16b) is probably limited by the model used for computing $D_m$, which is assumed to be a smooth function of viscosity. The agreement between Eqs. (16a), (16b), (18a) and (18b) was very good. The largest errors in $\hat{h}_{est}$ relative to $\hat{h}$ were 0.50% at 40 °C ($\Delta p = 43$ bar, $f_1 = 1.20$), and 0.36% at 50 °C ($\Delta p = 55$ bar, $f_1 = 1.12$), where $\Delta p$ is the column pressure drop. Eqs. (18a) and (18b) thus provide a satisfactory estimate of the apparent plate height for an unretained solute, and the compressibility factor $f_1$ is a valid measure of the theoretical loss of efficiency for elution of an unretained solute from a column operated under nonuniform, isothermal conditions. While the validity has been tested only for methane as a solute, there is no obvious reason why similar results should not be expected for other unretained solutes.

## 4. Conclusions

The results in this paper provide a basis for further studies on the effects of pressure drop on efficiency in SFC by providing explicit equations for predicting the efficiency for unretained solutes. We have focused on unretained solutes in order to eliminate the complicating effects of changes in retention on efficiency. Specifically, it has been shown that for elution of an unretained solute under isothermal conditions in SFC using porous microparticulate packings:

(1) the local reduced plate height $h$ can be described by a simplified form of the Knox equation in which the coefficients are independent of the mobile phase conditions;
(2) the apparent reduced plate height $\hat{h}$ is adequately described by the approximate relation $\hat{h} \cong f_1 h$, where the

factor $f_1$ is the ratio of temporal-to-spatial average densities of the mobile phase;

(3) the predicted efficiency losses under practical SFC conditions are insignificant, in agreement with earlier studies, and do not exceed 20% even under extreme conditions.

It should be emphasized that these conclusions apply specifically to pSFC performed under *isothermal* conditions. In a subsequent paper [24] evidence is presented to show that isothermal conditions may not be routinely achieved in pSFC, and that excessive efficiency losses associated with large pressure drops are due primarily to the generation of radial temperature gradients.

## 5. Nomenclature

| | |
|---|---|
| $A, B, C$ | Knox coefficients for terms using reduced velocity of mobile phase |
| $A_o$, $B_o$ | Knox coefficients for terms using reduced velocity of mobile zone |
| $d_p$ | particle diameter |
| $D_m, D_s, D_{sz}$ | solute diffusion coefficient: in the mobile phase; in the stationary phase; in the stationary zone |
| $f_1$ | compressibility correction factor |
| $h$, $\hat{h}$ | local reduced plate height, apparent reduced plate height |
| $H$, $\hat{H}$ | local plate height, apparent plate height |
| $k, k', k''$ | retention factor, phase capacity factor, zone capacity factor |
| $\dot{m}_o$ | mass flow rate per unit area |
| $p_i, p_o, \Delta p, P$ | column inlet pressure, outlet pressure, pressure drop, ratio of $p_i$ to $p_o$ |
| $u$, $u_s$ | linear velocity of the mobile phase and the solute |
| $V_R$, $V_M$ | elution volume for the solute and the mobile phase |
| $\langle\rangle_t$, $\langle\rangle_z$ | for enclosed quantity: temporal average and spatial average |

*Greek letters*

| | |
|---|---|
| $\phi$ | fraction of the total eluent that is stagnant |
| $\gamma_m$, $\gamma_{sm}$, $\gamma_s$ | obstruction factor to diffusion in the mobile phase, the stagnant mobile phase and the stationary phase |
| $\nu$, $\nu_o$ | reduced velocity of mobile phase and the mobile zone |
| $\rho$, $\rho_c$, $\rho_R$ | density of the mobile phase, critical density, reduced density |
| $\rho_i$, $\rho_o$ | inlet density, outlet density |
| $\Gamma$ | ratio of inlet density to outlet density |

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## Appendix A. Model for apparent plate height in SFC

### A.1. Overview

The retention and efficiency of unretained and retained solutes in SFC with $CO_2$ mobile phase on packed and open-tubular columns is modeled for isothermal, constant mass flow conditions. The model is based on the treatment for apparent plate height with compressible mobile phase fluids reported by Poe and Martire [16]. The retention factor, apparent plate height, and related temporal and spatial average quantities are calculated at user-specified temperature, mobile-phase density and mass flow rate. The model is implemented in a program written in Microsoft QuickBASIC 4.5. Data are generated for the construction of isopycnic (constant density) plate height curves for any combination of column length, diameter, and particle size or film thickness, using neat $CO_2$ based on user-provided input of solute and column properties, including appropriate relations for the dependence of solute retention on density and temperature and coefficients for the Knox equation. The two principle quantities of interest are the apparent reduced plate height

$$\hat{h} = \frac{\langle h(1+k')^2 \rho_R \rangle_t}{\langle 1+k' \rangle_t^2 \langle \rho_R \rangle_z} \tag{A1}$$

and the observed retention factor

$$k = \langle k' \rangle_t \tag{A2}$$

where $h$, $\rho_R$, and $k'$ are the local values of reduced plate height, reduced density and retention factor, respectively, and the subscripts t and z indicate the temporal and spatial average quantities of the enclosed terms.

### A.2. Equations for local and average mobile phase and solute properties

Calculation of local and average mobile phase and solute parameters is based on the treatment by Martire et al. [23,26]. The principle equations from those references are presented here.

#### A.2.1. Mobile phase properties

The Jacobsen–Stewart modification of the Benedict–Webb–Rubin (BWR) equation of state for carbon dioxide [29,30] is used to calculate density and the isotherm derivative $(\partial P_R/\partial \rho_R)_T$

$$P = \rho RT + \sum_{i=1}^{32} N_i X_i \tag{A3}$$

$$(\partial P/\partial \rho)_T = RT + \sum_{i=1}^{32} N_i X_i \tag{A4}$$

where $N_i$ are constants and $X_i$ are functions of $\rho$ and $T$. Viscosity is calculated from a fit to tabulated data [31] using the expression

$$\eta_R = \sum_{i=0}^{4} \sum_{j=0}^{4} c_{i,j} T_R^j \rho_R^i \tag{A5}$$

The values of $N_i$ and expressions for $X_i$ in Eqs. (A3) and (A4) and the coefficients $c_{i,j}$ in Eq. (A5) are tabulated in reference [26]. In general, reduced parameters are used: $P_R = P/P_c$, $\rho_R = \rho/\rho_c$, $T_R = T/T_c$, and $\eta_R = \eta/\eta_o$ where $P_c$, $\rho_c$ and $T_c$ are the critical pressure (73.84 bar), density (0.468 g/cm$^3$), and temperature (304.2 K), and $\eta_o$ is the viscosity of carbon dioxide at 1 bar for the specified temperature.

### A.2.2. *Spatial and temporal average quantities*

Spatial and temporal average densities are given by

$$\langle \rho_R \rangle_z = \frac{\int_{\rho_{R,out}}^{\rho_{R,in}} \rho_R D_z(\rho_R)\, d\rho_R}{\int_{\rho_{R,out}}^{\rho_{R,in}} D_z(\rho_R)\, d\rho_R} \tag{A6}$$

$$\langle \rho_R \rangle_t = \frac{\int_{\rho_{R,out}}^{\rho_{R,in}} \rho_R D_t(\rho_R)\, d\rho_R}{\int_{\rho_{R,out}}^{\rho_{R,in}} D_t(\rho_R)\, d\rho_R} \tag{A7}$$

where $\rho_{R,in}$ and $\rho_{R,out}$ are the inlet and outlet reduced densities. The spatial and temporal distribution functions are evaluated at constant temperature using reduced quantities:

$$D_z(\rho_R) = \eta_R^{-1} \rho_R \left( \frac{\partial P_R}{\partial \rho_R} \right)_T \tag{A8}$$

$$D_t(\rho_R) = \eta_R^{-1} \rho_R^2 \left( \frac{\partial P_R}{\partial \rho_R} \right)_T \tag{A9}$$

The details of calculation are given by Martire et al. [26], although in that paper the core of the distribution function $\eta_R^{-1}(\partial P_R/\partial \rho_R)_T$ is expressed as a polynomial fit to the data at a specified temperature, whereas in this program the viscosity and isotherm derivative are evaluated separately in the numerical integration process, wherein the isotherm derivative is evaluated numerically using Newton's method.

Other average quantities are calculated in a similar manner from the general expressions

$$\langle Q \rangle_z = \frac{\int_{\rho_{R,out}}^{\rho_{R,in}} Q D_z(\rho_R)\, d\rho_R}{\int_{\rho_{R,out}}^{\rho_{R,in}} D_z(\rho_R)\, d\rho_R} \tag{A10}$$

$$\langle Q \rangle_t = \frac{\int_{\rho_{R,out}}^{\rho_{R,in}} Q D_t(\rho_R)\, d\rho_R}{\int_{\rho_{R,out}}^{\rho_{R,in}} D_t(\rho_R)\, d\rho_R} \tag{A11}$$

where $Q$ is a function of density.

## A.3. *Calculation routines and equations*

The computational approach can be viewed as occurring in several major processes which are described below with the principal equations used in each. Modeling for a packed column is assumed in the following discussion.

### A.3.1. *Provide column and solute information*

Pertinent data on column geometry are provided by the user, including column length and diameter, and packing parameters including particle size $d_p$, interparticle porosity $\varepsilon_e$ and total porosity $\varepsilon_t$. Solute properties including the molar mass and molar volume at the boiling point for the purpose of estimating the diffusion coefficient, and expressions relating the capacity factor to temperature and reduced density are also provided by the user.

### A.3.2. *Specify mass flow rate, temperature and density*

A set of mass flow rates $m_o$ is defined at a specified combination of temperature and $\langle \rho_R \rangle_t$ for each plate height curve to be generated. For each temperature and density combination, the mass flow rate is incrementally increased to a preset maximum value or until the Reynolds number at the outlet exceeds 20 to avoid conditions with excessive turbulent flow.

### A.3.3. *Calculate flow-related quantities*

For each value of $m_o$ the corresponding inlet and outlet pressures, linear velocity and other flow-related quantities are determined. Isothermal conditions are assumed.

The linear velocity is

$$u = \frac{\dot{m}_o}{\rho} \tag{A12}$$

where $\dot{m}_o$ is the mass flow rate per unit area. The observed linear velocity is the temporal average [23], which is given by

$$\langle u \rangle_t = \frac{\dot{m}_o}{\langle \rho \rangle_t} \tag{A13}$$

Darcy's law relates linear velocity to pressure drop

$$u = \frac{B^o}{\varepsilon_e \eta} \frac{\Delta P}{L} \tag{A14}$$

where $B^o$ is the specific permeability, $\varepsilon_e$ the interparticle porosity, $\eta$ the viscosity of the mobile phase, $\Delta P$ the pressure drop, and $L$ the column length. The specific permeability is given by the Kozeny–Carman equation

$$B^o = \frac{d_p^2 \varepsilon_e^3}{180(1-\varepsilon_e)^2} \tag{A15}$$

where $d_p$ is the particle diameter and $B^o$ has units of cm$^2$.

Combining Eqs. (A13) and (A14) yields

$$\frac{\dot{m}_o}{\langle \rho \rangle_t} = \frac{B^o}{\varepsilon \langle \eta \rangle_t} \frac{\Delta P}{L} \tag{A16}$$

Eq. (A16) is solved at the specified values of $\dot{m}_\text{o}$ and $\langle\rho\rangle_\text{t}$ to yield the required values of inlet and outlet density and the corresponding pressure drop.

### A.3.4. Evaluate $\hat{h}$ and k

With inlet and outlet densities determined above, we proceed to compute the principle quantities of interest given by Eqs. (A1) and (A2). The terms in Eq. (A1) for the apparent reduced plate height are defined in the same manner as above and evaluated by numerical integration:

$$\langle h(1+k')^2\rho_\text{R}\rangle_\text{t} = \frac{\int_{\rho_\text{R,out}}^{\rho_\text{R,in}} h(1+k')^2\rho_\text{R} D_\text{t}(\rho_\text{R})\,\text{d}\rho_\text{R}}{\int_{\rho_\text{R,out}}^{\rho_\text{R,in}} D_\text{t}(\rho_\text{R})\,\text{d}\rho_\text{R}} \quad \text{(A17)}$$

$$\langle 1+k'\rangle_\text{t} = \frac{\int_{\rho_\text{R,out}}^{\rho_\text{R,in}} (1+k')D_\text{t}(\rho_\text{R})\,\text{d}\rho_\text{R}}{\int_{\rho_\text{R,out}}^{\rho_\text{R,in}} D_\text{t}(\rho_\text{R})\,\text{d}\rho_\text{R}} \quad \text{(A18)}$$

Expressions for local values of the quantities $h$, $k'$ and dependent terms are written in terms $\dot{m}_\text{o}$, $\rho$ and $T$.

The local plate height $h$ is given by the Knox equation [21] in terms of reduced velocity

$$h = \frac{B}{\nu} + A\nu^{1/3} + C(k')\nu \quad \text{(A19)}$$

where

$$\nu = \frac{ud_\text{p}}{D_\text{m}} = \frac{\dot{m}_0 d_\text{p}}{\rho D_\text{m}} \quad \text{(A20)}$$

where $D_\text{m}$ is the diffusion coefficient of the solute which is estimated by the equation of Sassiat et al. [32]

$$D_\text{m} = \frac{(8.6\times10^{-15})TM_\text{s}^{1/2}}{\eta V_\text{eb}^{0.6}} \quad \text{(A21)}$$

where $T$ is the temperature in Kelvin, $M_\text{s}$ is the molar mass of the solvent (44.0 g/mol), $\eta$ is the viscosity of the solvent in Pa s, $V_\text{eb}$ is the molar volume of the solute at its boiling point in cm$^3$/mol, and $D_\text{m}$ has units of m$^2$/s. The Knox $C$ term is given by

$$C(k') = \frac{1}{30\gamma_\text{sm}\phi}\left(\frac{\phi+k'}{1+k'}\right)^2 \quad \text{(A22)}$$

where $\phi$ is the fraction of total eluent that is stagnant and is given by

$$\phi = \frac{\varepsilon_\text{t}-\varepsilon_\text{e}}{\varepsilon_\text{t}} \quad \text{and} \quad \varepsilon_\text{i} = \frac{\varepsilon_\text{t}-\varepsilon_\text{e}}{1-\varepsilon_\text{e}} \quad \text{(A23)}$$

where $\varepsilon_\text{e}$, $\varepsilon_\text{i}$, and $\varepsilon_\text{t}$ are the interparticle, intraparticle, and total porosities. Default values of $\varepsilon_\text{e}$ and $\varepsilon_\text{t}$ are specified in the program as 0.4 and 0.7, respectively. $\gamma_\text{sm}$ is the obstructive factor to diffusion in the stationary zone, and is set equal to the intraparticle porosity. This corresponds to an implicit assumption that we have a fully permeating solute [21]. The local retention factor is given by

$$k' = k^0 + \exp(a\rho_\text{R} - b\rho_\text{R}^2) \quad \text{(A24)}$$

where $k^0$ is the retention factor for ideal gas chromatography and the parameters $a$ and $b$ depend on temperature [33]. At low densities the $b$ term is negligible, and $k^0$ is determined by extrapolation of a plot of $\ln k'$ versus $\rho_\text{R}$. Employing the preceding equations to evaluate the dependent terms, the apparent reduced plate height $\hat{h}$ is calculated using Eq. (A16).

The observed retention factor is

$$k = \langle k'\rangle_\text{t} = \frac{\int_{\rho_\text{R,out}}^{\rho_\text{R,in}} k' D_\text{t}(\rho_\text{R})\,\text{d}\rho_\text{R}}{\int_{\rho_\text{R,out}}^{\rho_\text{R,in}} D_\text{t}(\rho_\text{R})\,\text{d}\rho_\text{R}} \quad \text{(A25)}$$

which is evaluated by substituting the expression for the local retention factor given by Eq. (A24).

## Appendix B. Values of *f*1 for carbon dioxide

| Temperature (°C) | Outlet pressure (bar) | Pressure drop (bar) | | | | | | | | | | Percent difference from ideal gas | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | Average | Maximum |
| 40 | 60 | 1.007 | 1.031 | 1.117 | 1.197 | 1.197 | 1.182 | 1.166 | 1.151 | 1.140 | 1.130 | 9.9 | 17.4 |
| 40 | 70 | 1.010 | 1.071 | 1.129 | 1.129 | 1.118 | 1.108 | 1.099 | 1.092 | 1.086 | 1.080 | 6.6 | 11.8 |
| 40 | 80 | 1.027 | 1.058 | 1.058 | 1.054 | 1.050 | 1.047 | 1.044 | 1.042 | 1.040 | 1.038 | 2.4 | 5.3 |
| 40 | 90 | 1.005 | 1.008 | 1.009 | 1.010 | 1.010 | 1.011 | 1.011 | 1.011 | 1.011 | 1.011 | −0.8 | −2.5 |
| 40 | 100 | 1.001 | 1.001 | 1.002 | 1.003 | 1.003 | 1.004 | 1.004 | 1.005 | 1.005 | 1.005 | −1.2 | −2.7 |
| 40 | 110 | 1.000 | 1.001 | 1.001 | 1.001 | 1.002 | 1.002 | 1.002 | 1.003 | 1.003 | 1.003 | −1.2 | −2.6 |
| 40 | 120 | 1.000 | 1.000 | 1.001 | 1.001 | 1.001 | 1.001 | 1.002 | 1.002 | 1.002 | 1.002 | −1.1 | −2.4 |
| 40 | 130 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.001 | 1.001 | 1.001 | 1.002 | 1.002 | −1.0 | −2.2 |
| 40 | 140 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.001 | 1.001 | 1.001 | 1.001 | −0.9 | −2.0 |
| 40 | 150 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.001 | 1.001 | 1.001 | −0.8 | −1.8 |
| 50 | 60 | 1.005 | 1.019 | 1.043 | 1.084 | 1.136 | 1.168 | 1.178 | 1.176 | 1.170 | 1.163 | 8.2 | 13.3 |
| 50 | 70 | 1.005 | 1.021 | 1.053 | 1.096 | 1.124 | 1.134 | 1.134 | 1.130 | 1.125 | 1.120 | 6.8 | 10.3 |
| 50 | 80 | 1.006 | 1.027 | 1.059 | 1.081 | 1.090 | 1.091 | 1.090 | 1.087 | 1.084 | 1.081 | 4.8 | 7.1 |
| 50 | 90 | 1.008 | 1.027 | 1.043 | 1.050 | 1.052 | 1.052 | 1.052 | 1.050 | 1.049 | 1.048 | 2.5 | 3.9 |
| 50 | 100 | 1.006 | 1.014 | 1.019 | 1.022 | 1.023 | 1.024 | 1.024 | 1.024 | 1.024 | 1.024 | 0.5 | 1.3 |

| Temperature (°C) | Outlet pressure (bar) | Pressure drop (bar) | | | | | | | | | | Percent difference from ideal gas | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | Average | Maximum |
| 50 | 110 | 1.002 | 1.005 | 1.006 | 1.008 | 1.009 | 1.010 | 1.010 | 1.011 | 1.011 | 1.012 | −0.5 | −1.7 |
| 50 | 120 | 1.001 | 1.002 | 1.003 | 1.003 | 1.004 | 1.005 | 1.005 | 1.006 | 1.006 | 1.007 | −0.8 | −1.9 |
| 50 | 130 | 1.000 | 1.001 | 1.001 | 1.002 | 1.002 | 1.003 | 1.003 | 1.004 | 1.004 | 1.004 | −0.8 | −1.9 |
| 50 | 140 | 1.000 | 1.000 | 1.001 | 1.001 | 1.001 | 1.002 | 1.002 | 1.002 | 1.003 | 1.003 | −0.8 | −1.8 |
| 50 | 150 | 1.000 | 1.000 | 1.000 | 1.001 | 1.001 | 1.001 | 1.002 | 1.002 | 1.002 | 1.002 | −0.7 | −1.7 |
| 60 | 60 | 1.004 | 1.015 | 1.031 | 1.053 | 1.081 | 1.112 | 1.139 | 1.156 | 1.164 | 1.166 | 6.0 | 10.7 |
| 60 | 70 | 1.004 | 1.014 | 1.031 | 1.054 | 1.082 | 1.106 | 1.123 | 1.131 | 1.134 | 1.134 | 5.5 | 8.9 |
| 60 | 80 | 1.004 | 1.014 | 1.032 | 1.054 | 1.075 | 1.090 | 1.099 | 1.103 | 1.104 | 1.103 | 4.6 | 6.9 |
| 60 | 90 | 1.004 | 1.015 | 1.031 | 1.048 | 1.061 | 1.068 | 1.073 | 1.074 | 1.075 | 1.074 | 3.4 | 4.8 |
| 60 | 100 | 1.004 | 1.014 | 1.026 | 1.035 | 1.042 | 1.046 | 1.048 | 1.049 | 1.050 | 1.050 | 2.0 | 2.9 |
| 60 | 110 | 1.003 | 1.010 | 1.017 | 1.021 | 1.025 | 1.027 | 1.029 | 1.030 | 1.030 | 1.031 | 0.9 | 1.4 |
| 60 | 120 | 1.002 | 1.005 | 1.009 | 1.011 | 1.013 | 1.015 | 1.016 | 1.017 | 1.018 | 1.018 | 0.0 | −0.8 |
| 60 | 130 | 1.001 | 1.003 | 1.004 | 1.006 | 1.007 | 1.008 | 1.009 | 1.010 | 1.011 | 1.011 | −0.4 | −1.2 |
| 60 | 140 | 1.000 | 1.001 | 1.002 | 1.003 | 1.004 | 1.005 | 1.005 | 1.006 | 1.007 | 1.007 | −0.5 | −1.4 |
| 60 | 150 | 1.000 | 1.001 | 1.001 | 1.002 | 1.002 | 1.003 | 1.003 | 1.004 | 1.005 | 1.005 | −0.6 | −1.4 |
| 70 | 60 | 1.003 | 1.013 | 1.026 | 1.042 | 1.061 | 1.082 | 1.104 | 1.123 | 1.139 | 1.149 | 4.3 | 8.8 |
| 70 | 70 | 1.003 | 1.011 | 1.023 | 1.039 | 1.058 | 1.078 | 1.096 | 1.111 | 1.122 | 1.129 | 4.1 | 7.6 |
| 70 | 80 | 1.003 | 1.010 | 1.022 | 1.037 | 1.055 | 1.071 | 1.085 | 1.096 | 1.103 | 1.107 | 3.7 | 6.2 |
| 70 | 90 | 1.003 | 1.010 | 1.021 | 1.035 | 1.049 | 1.062 | 1.071 | 1.078 | 1.082 | 1.085 | 3.1 | 4.8 |
| 70 | 100 | 1.002 | 1.009 | 1.019 | 1.031 | 1.041 | 1.049 | 1.056 | 1.060 | 1.063 | 1.064 | 2.3 | 3.4 |
| 70 | 110 | 1.002 | 1.008 | 1.016 | 1.024 | 1.031 | 1.037 | 1.041 | 1.043 | 1.045 | 1.047 | 1.6 | 2.2 |
| 70 | 120 | 1.002 | 1.006 | 1.012 | 1.017 | 1.022 | 1.025 | 1.028 | 1.030 | 1.031 | 1.032 | 0.8 | 1.2 |
| 70 | 130 | 1.001 | 1.004 | 1.008 | 1.011 | 1.014 | 1.016 | 1.018 | 1.020 | 1.021 | 1.022 | 0.3 | 0.5 |
| 70 | 140 | 1.001 | 1.003 | 1.005 | 1.007 | 1.009 | 1.010 | 1.012 | 1.013 | 1.014 | 1.015 | −0.1 | −0.7 |
| 70 | 150 | 1.001 | 1.002 | 1.003 | 1.004 | 1.006 | 1.007 | 1.008 | 1.008 | 1.009 | 1.010 | −0.3 | −0.9 |
| 80 | 60 | 1.003 | 1.011 | 1.023 | 1.036 | 1.051 | 1.068 | 1.084 | 1.100 | 1.115 | 1.128 | 3.1 | 6.8 |
| 80 | 70 | 1.003 | 1.010 | 1.020 | 1.032 | 1.047 | 1.062 | 1.077 | 1.092 | 1.104 | 1.114 | 3.0 | 6.3 |
| 80 | 80 | 1.002 | 1.008 | 1.018 | 1.029 | 1.043 | 1.057 | 1.070 | 1.082 | 1.092 | 1.100 | 2.8 | 5.5 |
| 80 | 90 | 1.002 | 1.008 | 1.016 | 1.027 | 1.039 | 1.051 | 1.062 | 1.071 | 1.079 | 1.084 | 2.5 | 4.5 |
| 80 | 100 | 1.002 | 1.007 | 1.015 | 1.024 | 1.034 | 1.044 | 1.052 | 1.059 | 1.065 | 1.069 | 2.1 | 3.4 |
| 80 | 110 | 1.002 | 1.006 | 1.013 | 1.021 | 1.029 | 1.036 | 1.042 | 1.047 | 1.051 | 1.054 | 1.6 | 2.5 |
| 80 | 120 | 1.002 | 1.005 | 1.011 | 1.017 | 1.023 | 1.028 | 1.033 | 1.036 | 1.039 | 1.041 | 1.1 | 1.6 |
| 80 | 130 | 1.001 | 1.004 | 1.009 | 1.013 | 1.017 | 1.021 | 1.024 | 1.027 | 1.029 | 1.031 | 0.7 | 1.0 |
| 80 | 140 | 1.001 | 1.003 | 1.006 | 1.010 | 1.013 | 1.015 | 1.017 | 1.019 | 1.021 | 1.022 | 0.3 | 0.5 |
| 80 | 150 | 1.001 | 1.002 | 1.004 | 1.007 | 1.009 | 1.011 | 1.012 | 1.014 | 1.015 | 1.016 | 0.0 | −0.3 |
| 90 | 60 | 1.003 | 1.010 | 1.021 | 1.032 | 1.045 | 1.059 | 1.073 | 1.087 | 1.099 | 1.111 | 2.4 | 5.2 |
| 90 | 70 | 1.002 | 1.009 | 1.018 | 1.028 | 1.040 | 1.053 | 1.066 | 1.078 | 1.090 | 1.100 | 2.3 | 4.9 |
| 90 | 80 | 1.002 | 1.007 | 1.015 | 1.025 | 1.036 | 1.048 | 1.059 | 1.071 | 1.081 | 1.089 | 2.2 | 4.5 |
| 90 | 90 | 1.002 | 1.007 | 1.014 | 1.022 | 1.032 | 1.043 | 1.053 | 1.063 | 1.071 | 1.078 | 2.0 | 3.9 |
| 90 | 100 | 1.002 | 1.006 | 1.012 | 1.020 | 1.029 | 1.038 | 1.046 | 1.054 | 1.061 | 1.067 | 1.7 | 3.2 |
| 90 | 110 | 1.001 | 1.005 | 1.011 | 1.018 | 1.025 | 1.033 | 1.040 | 1.046 | 1.051 | 1.055 | 1.5 | 2.5 |
| 90 | 120 | 1.001 | 1.005 | 1.009 | 1.015 | 1.021 | 1.027 | 1.033 | 1.038 | 1.042 | 1.045 | 1.1 | 1.8 |
| 90 | 130 | 1.001 | 1.004 | 1.008 | 1.013 | 1.018 | 1.022 | 1.026 | 1.030 | 1.033 | 1.036 | 0.8 | 1.2 |
| 90 | 140 | 1.001 | 1.003 | 1.006 | 1.010 | 1.014 | 1.017 | 1.021 | 1.023 | 1.026 | 1.028 | 0.5 | 0.8 |
| 90 | 150 | 1.001 | 1.003 | 1.005 | 1.008 | 1.011 | 1.013 | 1.016 | 1.018 | 1.020 | 1.021 | 0.3 | 0.4 |
| 100 | 60 | 1.003 | 1.010 | 1.019 | 1.030 | 1.042 | 1.053 | 1.066 | 1.078 | 1.089 | 1.099 | 1.9 | 4.1 |
| 100 | 70 | 1.002 | 1.008 | 1.016 | 1.026 | 1.036 | 1.047 | 1.059 | 1.070 | 1.080 | 1.090 | 1.8 | 3.9 |
| 100 | 80 | 1.002 | 1.007 | 1.014 | 1.022 | 1.032 | 1.042 | 1.052 | 1.062 | 1.072 | 1.080 | 1.7 | 3.6 |
| 100 | 90 | 1.002 | 1.006 | 1.012 | 1.020 | 1.028 | 1.037 | 1.047 | 1.055 | 1.064 | 1.071 | 1.6 | 3.3 |
| 100 | 100 | 1.001 | 1.005 | 1.011 | 1.017 | 1.025 | 1.033 | 1.041 | 1.049 | 1.056 | 1.062 | 1.4 | 2.8 |
| 100 | 110 | 1.001 | 1.004 | 1.009 | 1.015 | 1.022 | 1.029 | 1.036 | 1.042 | 1.048 | 1.053 | 1.2 | 2.3 |
| 100 | 120 | 1.001 | 1.004 | 1.008 | 1.013 | 1.019 | 1.025 | 1.031 | 1.036 | 1.041 | 1.045 | 1.0 | 1.8 |
| 100 | 130 | 1.001 | 1.003 | 1.007 | 1.012 | 1.016 | 1.021 | 1.026 | 1.030 | 1.034 | 1.038 | 0.8 | 1.3 |
| 100 | 140 | 1.001 | 1.003 | 1.006 | 1.010 | 1.014 | 1.018 | 1.021 | 1.025 | 1.028 | 1.031 | 0.6 | 0.9 |
| 100 | 150 | 1.001 | 1.002 | 1.005 | 1.008 | 1.011 | 1.014 | 1.017 | 1.020 | 1.023 | 1.025 | 0.4 | 0.6 |
| 110 | 60 | 1.003 | 1.009 | 1.018 | 1.028 | 1.039 | 1.050 | 1.061 | 1.071 | 1.082 | 1.091 | 1.5 | 3.3 |
| 110 | 70 | 1.002 | 1.008 | 1.015 | 1.024 | 1.033 | 1.043 | 1.054 | 1.063 | 1.073 | 1.082 | 1.5 | 3.2 |
| 110 | 80 | 1.002 | 1.006 | 1.013 | 1.020 | 1.029 | 1.038 | 1.047 | 1.056 | 1.065 | 1.073 | 1.4 | 2.9 |
| 110 | 90 | 1.001 | 1.005 | 1.011 | 1.018 | 1.025 | 1.034 | 1.042 | 1.050 | 1.058 | 1.065 | 1.3 | 2.7 |
| 110 | 100 | 1.001 | 1.005 | 1.010 | 1.016 | 1.022 | 1.030 | 1.037 | 1.044 | 1.051 | 1.058 | 1.1 | 2.4 |
| 110 | 110 | 1.001 | 1.004 | 1.008 | 1.014 | 1.020 | 1.026 | 1.033 | 1.039 | 1.045 | 1.050 | 1.0 | 2.0 |

| Temperature (°C) | Outlet pressure (bar) | Pressure drop (bar) | | | | | | | | | | Percent difference from ideal gas | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | Average | Maximum |
| 110 | 120 | 1.001 | 1.004 | 1.007 | 1.012 | 1.017 | 1.023 | 1.028 | 1.034 | 1.039 | 1.044 | 0.9 | 1.7 |
| 110 | 130 | 1.001 | 1.003 | 1.006 | 1.010 | 1.015 | 1.020 | 1.025 | 1.029 | 1.033 | 1.037 | 0.7 | 1.3 |
| 110 | 140 | 1.001 | 1.003 | 1.006 | 1.009 | 1.013 | 1.017 | 1.021 | 1.025 | 1.028 | 1.031 | 0.6 | 1.0 |
| 110 | 150 | 1.001 | 1.002 | 1.005 | 1.008 | 1.011 | 1.014 | 1.018 | 1.021 | 1.024 | 1.026 | 0.4 | 0.7 |
| 120 | 60 | 1.003 | 1.009 | 1.017 | 1.027 | 1.037 | 1.047 | 1.056 | 1.067 | 1.076 | 1.085 | 1.3 | 2.7 |
| 120 | 70 | 1.002 | 1.007 | 1.014 | 1.022 | 1.031 | 1.040 | 1.049 | 1.059 | 1.068 | 1.076 | 1.2 | 2.6 |
| 120 | 80 | 1.002 | 1.006 | 1.012 | 1.019 | 1.027 | 1.035 | 1.044 | 1.052 | 1.060 | 1.068 | 1.1 | 2.4 |
| 120 | 90 | 1.001 | 1.005 | 1.010 | 1.016 | 1.023 | 1.031 | 1.039 | 1.046 | 1.054 | 1.060 | 1.0 | 2.2 |
| 120 | 100 | 1.001 | 1.004 | 1.009 | 1.014 | 1.021 | 1.027 | 1.034 | 1.041 | 1.047 | 1.054 | 0.9 | 2.0 |
| 120 | 110 | 1.001 | 1.004 | 1.008 | 1.013 | 1.018 | 1.024 | 1.030 | 1.036 | 1.042 | 1.047 | 0.8 | 1.7 |
| 120 | 120 | 1.001 | 1.003 | 1.007 | 1.011 | 1.016 | 1.021 | 1.026 | 1.032 | 1.037 | 1.042 | 0.7 | 1.5 |
| 120 | 130 | 1.001 | 1.003 | 1.006 | 1.010 | 1.014 | 1.018 | 1.023 | 1.028 | 1.032 | 1.036 | 0.6 | 1.2 |
| 120 | 140 | 1.001 | 1.002 | 1.005 | 1.008 | 1.012 | 1.016 | 1.020 | 1.024 | 1.028 | 1.031 | 0.5 | 0.9 |
| 120 | 150 | 1.001 | 1.002 | 1.004 | 1.007 | 1.010 | 1.014 | 1.017 | 1.020 | 1.024 | 1.027 | 0.4 | 0.7 |
| 130 | 60 | 1.002 | 1.009 | 1.017 | 1.026 | 1.035 | 1.045 | 1.054 | 1.062 | 1.072 | 1.080 | 1.0 | 2.3 |
| 130 | 70 | 1.002 | 1.007 | 1.014 | 1.021 | 1.030 | 1.038 | 1.047 | 1.055 | 1.064 | 1.072 | 1.0 | 2.2 |
| 130 | 80 | 1.002 | 1.006 | 1.011 | 1.018 | 1.025 | 1.033 | 1.041 | 1.049 | 1.056 | 1.064 | 0.9 | 2.0 |
| 130 | 90 | 1.001 | 1.005 | 1.010 | 1.016 | 1.022 | 1.029 | 1.036 | 1.043 | 1.050 | 1.057 | 0.9 | 1.9 |
| 130 | 100 | 1.001 | 1.004 | 1.008 | 1.013 | 1.019 | 1.025 | 1.032 | 1.038 | 1.044 | 1.050 | 0.8 | 1.7 |
| 130 | 110 | 1.001 | 1.003 | 1.007 | 1.012 | 1.017 | 1.022 | 1.028 | 1.034 | 1.039 | 1.045 | 0.7 | 1.5 |
| 130 | 120 | 1.001 | 1.003 | 1.006 | 1.010 | 1.015 | 1.020 | 1.025 | 1.030 | 1.035 | 1.039 | 0.6 | 1.3 |
| 130 | 130 | 1.001 | 1.003 | 1.005 | 1.009 | 1.013 | 1.017 | 1.022 | 1.026 | 1.031 | 1.035 | 0.5 | 1.1 |
| 130 | 140 | 1.001 | 1.002 | 1.005 | 1.008 | 1.011 | 1.015 | 1.019 | 1.023 | 1.027 | 1.030 | 0.4 | 0.9 |
| 130 | 150 | 1.001 | 1.002 | 1.004 | 1.007 | 1.010 | 1.013 | 1.017 | 1.020 | 1.023 | 1.026 | 0.4 | 0.7 |
| 140 | 60 | 1.002 | 1.008 | 1.016 | 1.025 | 1.034 | 1.043 | 1.052 | 1.060 | 1.068 | 1.077 | 0.9 | 1.9 |
| 140 | 70 | 1.002 | 1.007 | 1.013 | 1.021 | 1.029 | 1.037 | 1.045 | 1.052 | 1.061 | 1.068 | 0.8 | 1.8 |
| 140 | 80 | 1.002 | 1.005 | 1.011 | 1.017 | 1.024 | 1.032 | 1.039 | 1.046 | 1.054 | 1.060 | 0.8 | 1.7 |
| 140 | 90 | 1.001 | 1.005 | 1.009 | 1.015 | 1.021 | 1.027 | 1.034 | 1.041 | 1.047 | 1.054 | 0.7 | 1.6 |
| 140 | 100 | 1.001 | 1.004 | 1.008 | 1.013 | 1.018 | 1.024 | 1.030 | 1.036 | 1.042 | 1.048 | 0.7 | 1.4 |
| 140 | 110 | 1.001 | 1.003 | 1.007 | 1.011 | 1.016 | 1.021 | 1.026 | 1.032 | 1.037 | 1.042 | 0.6 | 1.3 |
| 140 | 120 | 1.001 | 1.003 | 1.006 | 1.010 | 1.014 | 1.018 | 1.023 | 1.028 | 1.033 | 1.038 | 0.5 | 1.1 |
| 140 | 130 | 1.001 | 1.002 | 1.005 | 1.008 | 1.012 | 1.016 | 1.021 | 1.025 | 1.029 | 1.033 | 0.4 | 0.9 |
| 140 | 140 | 1.001 | 1.002 | 1.004 | 1.007 | 1.011 | 1.014 | 1.018 | 1.022 | 1.026 | 1.029 | 0.4 | 0.8 |
| 140 | 150 | 1.001 | 1.002 | 1.004 | 1.006 | 1.009 | 1.013 | 1.016 | 1.019 | 1.023 | 1.026 | 0.3 | 0.6 |
| 150 | 60 | 1.002 | 1.008 | 1.016 | 1.024 | 1.033 | 1.042 | 1.050 | 1.058 | 1.065 | 1.074 | 0.8 | 1.7 |
| 150 | 70 | 1.002 | 1.006 | 1.013 | 1.020 | 1.028 | 1.035 | 1.043 | 1.050 | 1.057 | 1.065 | 0.7 | 1.6 |
| 150 | 80 | 1.001 | 1.005 | 1.010 | 1.017 | 1.023 | 1.030 | 1.037 | 1.044 | 1.051 | 1.058 | 0.7 | 1.5 |
| 150 | 90 | 1.001 | 1.004 | 1.009 | 1.014 | 1.020 | 1.026 | 1.032 | 1.039 | 1.045 | 1.051 | 0.6 | 1.3 |
| 150 | 100 | 1.001 | 1.004 | 1.007 | 1.012 | 1.017 | 1.023 | 1.028 | 1.034 | 1.040 | 1.046 | 0.6 | 1.2 |
| 150 | 110 | 1.001 | 1.003 | 1.006 | 1.011 | 1.015 | 1.020 | 1.025 | 1.030 | 1.036 | 1.041 | 0.5 | 1.1 |
| 150 | 120 | 1.001 | 1.003 | 1.006 | 1.009 | 1.013 | 1.018 | 1.022 | 1.027 | 1.031 | 1.036 | 0.4 | 0.9 |
| 150 | 130 | 1.001 | 1.002 | 1.005 | 1.008 | 1.012 | 1.015 | 1.019 | 1.024 | 1.028 | 1.032 | 0.4 | 0.8 |
| 150 | 140 | 1.001 | 1.002 | 1.004 | 1.007 | 1.010 | 1.014 | 1.017 | 1.021 | 1.025 | 1.028 | 0.3 | 0.7 |
| 150 | 150 | 1.000 | 1.002 | 1.004 | 1.006 | 1.009 | 1.012 | 1.015 | 1.019 | 1.022 | 1.025 | 0.3 | 0.5 |

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