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Extending the Study of Mass Transport Across the Gas-Liquid Interface by Reversed-Flow Gas Chromatography

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Highlights

- Gas chromatographic study of solutes giving weak signals requiring post-processing
- Various physicochemical parameters pertaining to mass transfer from gas to liquid
- Flexible uncertainty analysis showing sources of error in the estimated parameters
- The effect of the reverse liquid-to-gas mass transfer process is identified
- Successful comparisons were made with literature data

Abstract:

The transfer of dichlorodifluoromethane to water was utilized as model system to provide better insight on the determination of mass transport parameters across the gas-liquid interface. Weak signals by reversed-flow gas chromatography were recorded at various temperatures, from 320.7 to 344.3 K, by digitizing and smoothing the output of the flame ionization detector. A flexible uncertainty analysis distinguished the main sources of error in the determined parameters, suggesting improvements on the utilized experimental setup. Liquid diffusivities decreased with rising temperature (4.39 to 1.01 ×10⁻¹⁰ m² s⁻¹), approaching literature values at lower temperatures. The estimated liquid film thicknesses similarly decreased (1.8 to 1.0 ×10⁻⁴ m) and were one order of
magnitude larger than previous findings, due to the larger extent of evaporation permitted by the current experimental setup. A mass transfer coefficient was estimated, corresponding to the endothermic contribution of the reverse (liquid-to-gas) process, whose activation energy (43.4 ± 2.8 kJ mol⁻¹) matched the vaporization enthalpy of water in the studied temperature range. Successful comparisons were made with literature distribution coefficients and Henry’s law constants. The dissolution of CFC-12 in water was found to be exothermic, slightly spontaneous at lower temperatures and approaching equilibrium at higher ones (indicated by the small negative molar Gibbs free energy values), with negative entropy change values [average: –(190.7 ± 6.9) J K⁻¹ mol⁻¹], as expected for a process of increased order.

**Keywords:** Reversed-flow gas chromatography; Mass transfer coefficients; Diffusion coefficients; Two-film theory; Dichlorodifluoromethane; Physicochemical measurements

1. Introduction

Knowledge of mass transfer coefficients is very important for the proper modeling and design of several industrial and engineering processes, such as absorption, extraction, distillation, membrane filtration, evaporation and drying [1-3] Diffusion is often a limiting factor in rapid chemical reactions, whose rate depends on how quick the reactive molecules reach one another [4]. In addition, many processes occur in the natural environment which involve the exchange of chemicals between gas-liquid interfaces, including (but not limiting to) the uptake of gases in the Earth’s surface water bodies and the microdroplets within Earth’s atmosphere [5-8]. As a result, there is a need for determining diffusion coefficients of small molecules at infinite dilution.

Generally, the gas-liquid interface is a microscopic region of intense gradients which makes reliable mass transfer measurements of gases in liquids significantly difficult. The scales of such processes are far smaller than those associated with bulk ones on either side of the interface and consequently require novel theoretical and experimental approaches. This is clear by the fact that experimental and theoretically predicted values rarely achieve close agreement. Gas
chromatographic techniques have been widely employed to provide diffusion and mass transfer coefficient, based on the peak broadening factors of the van Deemter equation [9,10], relating the efficiency of a chromatographic column to the various flow and kinetic parameters.

Reversed-flow gas chromatography (RF-GC) is classified as an inverse gas chromatographic technique [11] due to the stationary (liquid or solid) phase being under investigation, unlike traditional GC techniques where only the mobile phase is under study [12]. In RF-GC, the migration of the injected solute is only due to its interaction with the stationary phase and the stagnant carrier gas. RF-GC is proficient in studying slow rate processes, since physicochemical measurements are not affected by the carrier gas flow velocity, and it has been used to determine a variety of parameters such as gaseous diffusion coefficients in binary and ternary mixtures [13-15], mass transfer coefficients across the gas-liquid interface [16-21], rate constants, activation parameters and various parameters of surface-catalyzed reactions [22-25], as well as parameters related to the energetics and topography of the active sites of heterogeneous adsorbents [12,26-34].

In a recent work, a new RF-GC methodology was developed, permitting the simultaneous determination of mass transfer coefficients and providing information on both phase equilibria and transport through the interface [20]. Moreover, the digitization of the chromatographic signal automated the whole experimental procedure and recording of the chromatographic signal, utilizing the computational power and connectivity capabilities of modern computers and microcontrollers [35,36].

In the present work, dichlorodifluoromethane (CFC-12) is used as a model solute. On one side, the interaction of chlorofluorocarbons with water attracts scientific interest due to the chemical stability of the former. This permits them to be transferred to high altitudes, where they associate with polar stratospheric clouds (PSCs), which facilitate ozone destruction [7]. Furthermore, they are useful tools for tracing and age-dating groundwater [5]. There is also a chromatographic perspective by using the (normally) more sensitive flame ionization detector (FID), as the CFC-12 molecule lacks carbon-hydrogen bonds, resulting in similarly weak signals to ones recorded by thermal conductivity detector (TCD). This leads to noisy signals, particularly at the end of the experiments
where the signal-to-noise ratio is small. Considering the demands of the mathematical model, the
digitization and subsequent post-processing of the chromatographic signal is imperative for more
reliable determinations of the various mass transfer parameters.

Mass transfer coefficients related to the interaction of CFC-12 with water at various
temperatures were experimentally determined for the first time: overall mass transfer coefficients
through the respective gas \((K_G)\) and liquid \((K_L)\) stagnant interfacial films, liquid diffusion
coefficients \((D_L)\), partition coefficients \((K)\) and Henry’s law constants \((\kappa_{\text{H}})\), as well as the
thermodynamic functions of dissolution. The subsequent uncertainty analysis enabled closer
examination of the experimental setup’s effect on the parameters, helpful in optimizing the
experimental setup for more reliable measurements in terms of uncertainty.

The liquid film thickness \((z_L)\) was also estimated, enabling the determination of a new
parameter \((K_v)\), describing the opposite liquid-to-gas mass transfer process. Another goal was to
investigate whether the present methodology is sensitive enough to determine physicochemical
parameters using experimental setups where the effect of solvent evaporation is amplified,
compared to previous studies. These mass transfer parameters were further compared with available
literature data and were used to extract general mechanistic information about mass transfer of
gases in liquids.

2. Experimental section

2.1 Materials

Dichlorodifluoromethane (99.8 % purity) was the injected solute gas (Huizhan Energy
Machinery Co. Ltd, China), while nitrogen (99.999% purity) was the carrier gas (Aerialco, Greece).
The liquid substance, constituting the stationary phase, was double-distilled (2d) water, while
hydrogen (99.999% purity, Aerialco, Greece) and dry air from a commercial compressor (AirBlock
Mini 50) were utilized for the operation of the flame ionization detector (FID).
2.2 Gas chromatographic apparatus

The main feature of the reversed-flow version of inverse gas chromatography is the utilization of a T-system of chromatographic columns, schematically illustrated in Figure 1 and applied to a conventional gas chromatograph (Shimadzu GC-14A, Japan).

Figure 1

An empty section of stainless-steel tubing (diffusion column) of length $L_1$ is placed perpendicularly in the middle of the traditional sampling column (of length $l + l'$) through a brass tee fitting. The carrier gas (nitrogen) flows continuously through the sampling column towards the flame ionization detector (FID), while it remains stagnant within the diffusion column. The other end of the diffusion column is connected through a brass fitting to a small glass bottle, which can be filled with a liquid phase (in this case pure water) up to a height $L_2$. The surface of the liquid sits below the injector port, where a gas solute (CFC-12) can be injected through a rubber septum.

The length of the empty section of the diffusion column ($L_1$) was measured with a conventional ruler (of accuracy 0.1 cm), while the much smaller height of the liquid phase ($L_2$) was measured accurately with a digital Vernier caliper (BGS 1930, Germany) with a resolution of 0.01 mm and accuracy of 0.02 mm. The uncertainty of $L_2$ values was determined by 25 repeated measurements and calculating the standard deviation of the mean. In addition, the volume of both sections of the diffusion column (empty, $V_G$, and filled, $V_L$) were determined by completely filling them with water of known density and weighing the columns with an analytical balance (of accuracy 0.01 g). All these details are provided in the supplementary material of this article.

It should be noted that, unlike previous experiments where the surface area ($a_L$) of the liquid phase was 0.221 cm$^2$, the present experimental setup utilized another glass bottle with a surface area
approximately nine times larger (2.01 cm$^2$). This difference should be considered when comparing the present results to literature values, as well as to those obtained by previous RF-GC studies [18,20].

2.3 Chromatographic procedure

Experiments were performed at six different temperatures, ranged from 320.7 to 344.3 K. Before each experiment, the glass bottle was emptied, cleaned and refilled with double distilled water until the top of the cylindrical section (at approximately 1.2 cm), whose exact height was measured with the digital caliper. The glass bottle was placed inside the chromatographic oven for at least 5 minutes for temperature equilibrium to be achieved. Then, 0.5 cm$^3$ of CFC-12 was introduced at atmospheric pressure into the glass bottle through a side injector port. Pressure drops in the system were not found because both diffusion and sampling columns were empty, and no restrictor/separation column was placed before the FID.

The output signal from the detector was continuously monitored by an analog-to-digital ISA expansion card (PCL-711B) and automatically logged to a Pentium PC at a sampling rate of 1 Hz (experimental points per second). The digitization of the output signal enables sampling of the physicochemical phenomena in an easier and accurate way, compared to the usual flow reversals procedure [20,35]. The temperature inside the chromatographic oven was simultaneously logged in a similar fashion using an external IC temperature sensor (LM35AH, Texas Instruments) with an uncertainty of ± 0.2 K.

As a small quantity of solute (CFC-12), corresponding to infinite dilution, is instantaneously introduced at the closed end of the diffusion column, the only phenomenon responsible for its displacement through the stagnant mobile phase (carrier gas), as well as the sole broadening factor of the resulting chromatographic peak, is longitudinal diffusion [16]. In the presence of a liquid phase, a small quantity of the injected solute gets diffused in it. Because the diffusional process is slower in the liquid phase, an equilibrium is slowly established between the concentration of the
solute in the liquid and gaseous phase (presented as a distribution coefficient which changes with temperature) [3].

Figure 2 clearly illustrates the difference between the semilogarithmic chromatographic signals (diffusion bands) in the absence of a stationary phase (where equilibrium is quickly established, and the resulting diffusion band is linear after the maximum) [15] and in the presence of a liquid phase, where a clear “break” in the linearity of the diffusion band is observed [20].

Figure 2

The presently-utilized RF-GC technique is a differential method of physicochemical rate measurements over an extended period, unlike other techniques utilizing integration methods for determining concentrations as functions of time. Therefore, unlike other GC techniques, it does not depend on retention volumes or other broadening factors. [37] This results in simpler mathematical analysis of the diffusion bands, which are utilized to measure physicochemical parameters pertaining to liquid diffusivity and/or overall mass transfer across the gas-liquid interface.

An important note should be made regarding the effect of digitization on the lower uncertainty of the various measured physicochemical quantities. Higher sampling rates allow post-processing of the resulting signal (e.g. smoothing) if it is deemed necessary (see dashed diffusion band of Figure 2). Also, due to the large amount of data points obtained per experiment, one experiment is enough to determine the standard deviation of the various physicochemical quantities with good confidence. This also negates the need for repeated lengthy experiments at identical conditions (as was the case in past studies), with the additional benefits of using up less consumables, reducing chemical waste and man hours in the laboratory [35].

Wherever literature data were available, usually at 298.2 K, the present experimental observations were extrapolated to the required temperature by utilizing the predict function of R
language, which takes the parameters of the linear regression model and a known list of \( x \) values and outputs a list of “fitted” \( y \) values, together with their respective uncertainties.

3. Theoretical

Whitman’s two film theory provides a physical model for the processes taking place in the gas-liquid interface [16,38]. The overall mass transfer coefficients \( K_L \) and \( K_G \) contain the partial resistances of the gas \((1/k_G)\) and the liquid \((1/k_L)\) stagnant films. The overall flux equation, based either on liquid or gas phase concentration gradient, is expressed as:

\[
\frac{1}{K_L} = \frac{1}{k_L} + \frac{K}{k_a} = \frac{K}{K_G} \tag{1}
\]

where \( K \) is the partition coefficient between the gas and liquid phase.

When the lower part \( L_2 \) of the diffusion column is filled with a liquid, the diffusion band gets distorted. The equation describing the descending part of the diffusion band is expressed as the sum of two exponential functions of time [20]:

\[
signal^{1/\mu} = N \left[ \left(1 + \frac{Z}{Y}\right) \exp \left(-\frac{X + Y}{2} t\right) + \left(1 - \frac{Z}{Y}\right) \exp \left(-\frac{X - Y}{2} t\right) \right] \tag{2}
\]

where:

\[
N = \frac{6 m D_a}{V L_i^2 \left(1 + 3 V_a / V_G \right)} \tag{3}
\]

\[
X = \frac{3 \beta + 72 K a V_L / V_G + 25 \pi^2 \left(1 + 3 V_G / V_a \right)}{\pi^2 \left(1 + 3 V_G / V_a \right)} \tag{4}
\]

\[
X^2 - Y^2 = \frac{300 a \left(\beta + 16 K a V_L / V_G \right)}{\pi^2 \left(1 + 3 V_G / V_a \right)} \tag{5}
\]

\[
Z = X - 50a \tag{6}
\]
where $M$ is the response factor (equal to unity in the case of flame ionization and thermal conductivity detectors), $m$ is the molar amount of injected solute, $D_G$ is the diffusivity of the solute into the carrier gas, $V_G$ and $V_G'$ are the respective gaseous volumes in sections $L_1$ and $L_2$ of the diffusion column, $\dot{V}$ is the volumetric flow rate of the carrier gas in the sampling column, $V_L$ is the volume of the liquid (usually equal to $V_G'$), $D_L$ is the diffusivity of the solute gas in the liquid, $K''$ is the ratio of the gas solute concentration at the interface to that in the gas phase and $\alpha$, $\beta$ are respective relations of liquid and gaseous diffusivities.

For estimating mass transfer coefficients, the respective auxiliary parameters $N$, $X$, $Y$ and $Z$ are instead expressed by the following relations [20]:

$$N = \frac{\pi m D_G}{2 V L_i^2} \quad (9)$$

$$X = \frac{\pi^2 D_G}{4 L_i^2} + \frac{2 K_G a_k}{V_G} + \frac{K_L a_k}{V_L} \quad (10)$$

$$Y = \left[ \left( \frac{\pi^2 D_G}{4 L_i^2} + \frac{2 K_G a_k}{V_G} + \frac{K_L a_k}{V_L} \right)^2 - \frac{\pi^2 D_G}{L_i^2} \frac{K_L a_k}{V_L} \right]^{1/2} \quad (11)$$

$$Z = \frac{\pi^2 D_G}{4 L_i^2} + \frac{2 K_G a_k}{V_G} - \frac{K_L a_k}{V_L} \quad (12)$$

where $K_G$ and $K_L$ are the respective overall mass transfer coefficients in the gas and the liquid phase, and $a_L$ is the free surface area of the liquid. A distribution coefficient $K$ can then be calculated from the ratio of the two overall mass transfer coefficients, $K = K_G / K_L \quad (12)$. 

## Appendix A

### Table A.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>Response Factor</td>
</tr>
<tr>
<td>$m$</td>
<td>Molar Amount of Injected Solute</td>
</tr>
<tr>
<td>$D_G$</td>
<td>Diffusivity of the Solute into the Carrier Gas</td>
</tr>
<tr>
<td>$V_G$</td>
<td>Gaseous Volume in Section $L_1$</td>
</tr>
<tr>
<td>$V_G'$</td>
<td>Gaseous Volume in Section $L_2$</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Volumetric Flow Rate of Carrier Gas</td>
</tr>
<tr>
<td>$V_L$</td>
<td>Volume of the Liquid</td>
</tr>
<tr>
<td>$D_L$</td>
<td>Diffusivity of the Solute Gas in the Liquid</td>
</tr>
<tr>
<td>$K''$</td>
<td>Ratio of Gas Solute Concentration at the Interface to that in the Gas Phase</td>
</tr>
<tr>
<td>$\alpha$, $\beta$</td>
<td>Relations of Liquid and Gaseous Diffusivities</td>
</tr>
<tr>
<td>$N$</td>
<td>Auxiliary Parameter</td>
</tr>
<tr>
<td>$X$</td>
<td>Auxiliary Parameter</td>
</tr>
<tr>
<td>$Y$</td>
<td>Auxiliary Parameter</td>
</tr>
<tr>
<td>$Z$</td>
<td>Auxiliary Parameter</td>
</tr>
<tr>
<td>$K_G$</td>
<td>Overall Mass Transfer Coefficient in the Gas Phase</td>
</tr>
<tr>
<td>$K_L$</td>
<td>Overall Mass Transfer Coefficient in the Liquid Phase</td>
</tr>
<tr>
<td>$a_L$</td>
<td>Free Surface Area of the Liquid</td>
</tr>
</tbody>
</table>

### Table A.2

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7)</td>
<td>$a = \frac{\pi^2 D_L}{4 L_i^2}$</td>
</tr>
<tr>
<td>(8)</td>
<td>$\beta = \frac{\pi^2 D_G}{4 L_i^2}$</td>
</tr>
<tr>
<td>(9)</td>
<td>$N = \frac{\pi m D_G}{2 V L_i^2}$</td>
</tr>
<tr>
<td>(10)</td>
<td>$X = \frac{\pi^2 D_G}{4 L_i^2} + \frac{2 K_G a_k}{V_G} + \frac{K_L a_k}{V_L}$</td>
</tr>
<tr>
<td>(11)</td>
<td>$Y = \left[ \left( \frac{\pi^2 D_G}{4 L_i^2} + \frac{2 K_G a_k}{V_G} + \frac{K_L a_k}{V_L} \right)^2 - \frac{\pi^2 D_G}{L_i^2} \frac{K_L a_k}{V_L} \right]^{1/2}$</td>
</tr>
<tr>
<td>(12)</td>
<td>$Z = \frac{\pi^2 D_G}{4 L_i^2} + \frac{2 K_G a_k}{V_G} - \frac{K_L a_k}{V_L}$</td>
</tr>
</tbody>
</table>

### Table A.3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>1.00</td>
</tr>
<tr>
<td>$m$</td>
<td>0.123</td>
</tr>
<tr>
<td>$D_G$</td>
<td>0.45</td>
</tr>
<tr>
<td>$V_G$</td>
<td>2.12</td>
</tr>
<tr>
<td>$V_G'$</td>
<td>2.34</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>0.98</td>
</tr>
<tr>
<td>$V_L$</td>
<td>3.21</td>
</tr>
<tr>
<td>$D_L$</td>
<td>0.56</td>
</tr>
<tr>
<td>$K''$</td>
<td>0.73</td>
</tr>
<tr>
<td>$\alpha$, $\beta$</td>
<td>0.50, 0.60</td>
</tr>
<tr>
<td>$K_G$</td>
<td>1.23</td>
</tr>
<tr>
<td>$K_L$</td>
<td>1.45</td>
</tr>
<tr>
<td>$a_L$</td>
<td>0.65</td>
</tr>
</tbody>
</table>
The regression analysis of the diffusion band provides the auxiliary parameters $N$, $X$, $Y$ and $Z$ (cf. eq. 2). The liquid diffusion coefficients $D_L$ are determined by the first set of equations (3-8), whereas the mass transfer and distribution coefficients ($K_G$, $K_L$ and $K$ respectively) are provided by the second set of equations (9-12).

The Henry’s law constant, $K^*_{H}$, is defined as the partial pressure of the gas $p$ divided by the concentration of the dissolved gas into the bulk liquid phase $c^*_{L} (K^*_{H} = p / c^*_{L})$ [16]. It expresses the volatility of the gas dissolved into the liquid phase [39] and it is calculated by the relation $K^*_{H} = RT / K$ (13), where $R$ is the gas constant and $T$ is the absolute temperature.

More details concerning the estimation of the various parameters can be found in the theoretical section and the supporting material of Ref. (20).

4. Results and Discussion

4.1 Uncertainty analysis and experimental design

A main feature of the present work is the more flexible determination of the estimated parameters’ uncertainties using Taylor’s error propagation rules, in contrast to previous ones utilizing a MS Excel plugin (ChemStat) [20]. The plugin did not allow real-time updating of the analysis results (it had to be re-run every time) and it was tedious to re-calculate uncertainties for each experiment. For the present study, auto-updating Excel functions were utilized, which allowed real-time determinations of the main sources of uncertainty and the effect of the instrumentation’s geometrical characteristics in the estimated parameters.

Before commenting on the bulk of the estimated physicochemical parameters, it would be useful to first focus on one indicative experiment, e.g. at 334.9 K., whose diffusion band is shown in Figure 3 and details about its calculation are provided in the supplementary material.

Figure 3
Gas chromatographic experiments featuring CFC-12 in large concentration usually utilize a thermal conductivity detector (TCD) [40-42] or an electron capture detector (ECD) wherever CFCs are present in trace concentrations [43]. The usual sensitivity advantage of the flame ionization detector (FID) is somewhat negated, as the molecules of the solute do not contain any carbon-hydrogen bonds. Despite that, the FID was still selected for the present study as it is more robust, reliable and outputs a less-noisy signal in measurements of organic substances [15]. Moreover, as operation of the TCD demands carrier gases of low molecular weights (helium or hydrogen), another advantage of the FID is its ability to operate with nitrogen (or synthetic air), better simulating environmental conditions.

An increased amount of noise was observed at longer experimental times, clearly seen in Figure 3, especially after $2 \times 10^4$ s. Consequently, a preliminary post-processing of the experimental data was carried out by Origin software, using Adjacent-Average smoothing method with 250 points of window. This was facilitated by the large amount (17334) of available experimental points thanks to the digitization of the output signal, increasing the degrees of freedom for the subsequent linear analysis and permitting lossless post-processing (smoothing) of the signal, if necessary. The smoothing procedure, in this case, did not affect the regression results, but significantly decreased their errors, particularly those pertaining to the noisier second linear section of the diffusion band (longer experimental times).

The relative uncertainties of the diffusion band’s linear regression results ($\ln A_i$, $b_i$) and the geometric details of the experimental setup are provided in the supplementary material. The uncertainties are generally less than 0.2%, indicating that the main sources of experimental uncertainty are the geometrical characteristics of the diffusion column (particularly lengths, $L_1$ and $L_2$, c.f. Figure 1). Consequently, these parameters should be carefully considered when designing the experimental setup. In fact, $L_2$ presents the largest relative uncertainty, significantly impacting the respective uncertainties of liquid diffusion coefficients, $D_L$ (cf. eq. 7). On the other hand, the rest
of the mass transfer coefficients depend on parameters whose relative uncertainties are all lower than 0.5%.

There are two ways to physically measure the height of the liquid phase \( (L_2) \). By far the easiest and quickest one is with a common ruler, but it leads to values with high relative standard uncertainties, \( \delta(L_2)/L_2 \) [for the indicative experiment of Figure 3, \( L_2 = (1.2 \pm 0.1) \text{ cm} \), \( \delta(L_2)/L_2 = 8.3\% \) and \( D_L = (2.3 \pm 0.4) \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \), \( \delta(D_L)/D_L = 17\% \)]. A tedious, but more accurate method is the one described in the Experimental section (using a digital Vernier caliper), which significantly improves the uncertainties \( [L_2 = (1.20 \pm 0.02) \text{ cm}, \delta(L_2)/L_2 = 1.7\% \) and \( D_L = (2.3 \pm 0.4) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}, \delta(D_L)/D_L = 3.3\% \)]. Another method for reducing the relative uncertainty of \( L_2 \) would be to increase its value (e.g. by using a taller glass bottle), in which case even measurements by ruler would offer satisfactory precision.

4.2 Mass transfer study

The experimental values of the mass transfer coefficients for the gaseous and liquid stagnant films, \( K_G \) and \( K_L \), respectively, together with the liquid diffusion coefficients \( (D_L) \) for the interaction of CFC-12 with water at various temperatures, are listed in Table 1. The standard deviations were calculated by applying the respective error propagation formulas on the calculation relations for each value.

**Table 1**

The mean relative uncertainties of the estimated parameters are small (3.3\% for the liquid diffusion coefficient and 1.3-1.6\% for the mass transfer coefficients), permitting reliable conclusions. However, any conclusions regarding the diffusivity measurements of the present study should be given in context of the relatively high uncertainties of the theoretical equations, ranging
from 5-10% [6]. Thus, the present results can be considered reliable and highlight the importance of accurate measurements of the column’s geometric details. On the other hand, the smaller uncertainties of the overall mass transfer coefficients are mainly due to the lower relative uncertainty of the diffusion column length, $L_1$.

The temperature variation of $D_L$, their respective experimental uncertainties and their subsequent weighted least square analysis are shown in Figure 4, together with the predicted diffusivities in the same temperatures (also listed in Table 1), using the Wilke-Chang equation with the original (2.6) association factor for water solvent [3].

**Figure 4**

It is apparent that the present experimental $D_L$ values decrease with rising temperature, contrary to the theoretical values for CFC-12 diffusion in water, as calculated by the Wilke-Chang equation. However, they are one order of magnitude lower, and their opposing trend reveals that, in fact, they are total diffusion coefficients from the gas to the liquid phase, following the respective descending trend of gaseous solubility inside the liquid phase. Furthermore, better agreement was observed by linearly extrapolating the present values to lower temperatures [298.2 K, $D_L^{\text{exp}} = (6.9 \pm 0.4) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$]. Comparing with the literature value ($10.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) [44], the observed deviation (36%) indicates the effect of the solvent’s volatilization and, as it decreases with lowering temperature, experimental diffusivities approach literature values.

It should be noted that the utilized Wilke-Chang equation gives reportedly overestimated values with high uncertainties (~10%), compared to experimental results [45], and nowadays it is largely superseded by other theoretical equations [2]. However, examination of the applicability of other equations is not the focus of the present study, as the experimental diffusivity values are only apparent. However, valuable information can be extracted about the mechanism of gas-to-liquid mass transport, simulating the conditions of many environmental processes. For true diffusivities to
be determined, it is important to ensure that liquid diffusion through the interface is the main broadening factor of the diffusion band. This can easily be achieved by stirring the liquid phase [18], where molecular diffusion resistance in the bulk phase becomes negligible.

From the values listed in Table 1, it becomes apparent that the overall mass transfer coefficients through the stagnant liquid phase, $K_L$, decrease with temperature similarly with liquid diffusion coefficients and in opposition to the values of the stagnant gas phase, $K_G$, which increase. Therefore, the respective resistance to mass transfer ($1/K_{G,L}$) is greater at the stagnant gas film and appears to be the rate-determining step in the overall gas-to-liquid process. At rising temperatures where the vapor pressure of the liquid solvent (H$_2$O) increases, mass transfer through the liquid phase is hindered, while the opposite process through the gaseous stagnant film is facilitated.

The liquid diffusivities indicate that the interfacial thickness ($z_L$) is changing with temperature and can be approximated experimentally from the ratio of $D_L$ to $K_L$ at each temperature. The effect of the dissolved gas’s evaporation can be approximated by dividing the deviation of the experimental $D_L$ values from theoretical ones ($\Delta D_L$) with calculated $z_L$ values. However, since comparisons between experimental and calculated data usually result in nonsensical results, a preliminary linear weighted least square fit was performed on both experimental $D_L$ and $K_L$ values. The regression results were used to estimate the necessary parameters ($\Delta D_L$ and $z_L$), which resulted in $K_v$, representing a mass transfer coefficient describing the overall reverse process from liquid to gas phase. The uncertainties of these parameters were predicted from the regression results, using the predict function of R language.

The stagnant liquid film’s thickness, its percentage change with temperature and the resulting overall liquid-to-gas mass transfer coefficient are all listed in Table 2. The design of the current experimental setup exaggerated the effect of evaporation on the determined parameters, simulating the environmental conditions present in gas transfer into large surface water bodies.

Table 2

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The experimentally determined \( z_{L} \) values decrease with rising temperature (44% within the studied temperature range) and are larger by one order of magnitude than previous values, determined by RF-GC: e.g. \( 6.7 \times 10^{-5} \) m for the dissolution of vinyl chloride in distilled water [18,20].

At this point, more information about the effect of the experimental setup design on the determined parameters can be extracted. Utilizing a glass bottle with a larger surface area (\( a_{L} \)) by one order of magnitude (nine times larger than previous studies), resulted in liquid diffusivities and liquid film thickness values differing by approximately one order of magnitude. The difference can be safely attributed to the greater extent of evaporation permitted by the current experimental setup, resulting in lower liquid diffusivities and therefore higher liquid film thickness values. If direct comparisons with other studies are desired, they should be normalized considering the ratio of \( a_{L} \) values.

The temperature variation of the experimentally determined overall mass transfer coefficients in the respective gas and liquid films, compared to the estimated mass transfer coefficient from the liquid to gas phase, are shown in section (a) of Figure 5.

**Figure 5**

It is observed that \( K_{v} \) values increase with temperature, as expected. The overall behavior of the studied process is compatible with the endothermic nature of vaporization. More details regarding their physical meaning can be extracted by the slope of the Arrhenius plot (\( \ln K_{v} \) vs \( 1/T \)), shown in section (b) of Figure 5. The resulting activation energy was \((43.4 \pm 2.8) \) kJ mol\(^{-1}\), almost identical within statistical error to the vaporization enthalpy of water in the studied temperature range \((\Delta H_{v} = 43.1-42.0 \) kJ mol\(^{-1}\)) [46].
The distribution coefficients ($K$) and respective Henry’s law constants ($K_{H}^\text{pc}$) are listed in Table 3:

**Table 3**

The distribution coefficients present an inverse relation to solubility (proportional to the increase of volatilization) as temperature increases. They are related to the distribution of the dissolved gas along the gas/liquid interface. More details can be extracted from the plots of Figure 6.

**Figure 6**

The extrapolated value of $K$ at 298.2 K ($0.026 \pm 0.003$) is of the same order of magnitude to the literature value of 0.052 [44]. The negative deviation is owing to the effect of the solvent’s (water) evaporation, which directly competes with and further decreasing the solubility of CFC-12.

The Henry’s law constants decrease with temperature, exhibiting a similar behavior to the decrease of solubility. Their values are of the same order of magnitude as literature values for dissolving various gases in water (e.g. $2.94 \times 10^3$ m$^3$ Pa mol$^{-1}$ for carbon dioxide, $7.81 \times 10^4$ m$^3$ Pa mol$^{-1}$ for oxygen and $1.62 \times 10^5$ m$^3$ Pa mol$^{-1}$ for nitrogen) [20], further supporting the reliability of the present methodology.

**4.3 Thermodynamic study**

The molar heat of solution ($\Delta H_s$) can be calculated from the slope of the $\ln K_{H}^\text{pc}$ vs. $1/T$ plot, shown in Figure 7.
The resulting enthalpy value $[-(65.6 \pm 2.3) \text{ kJ mol}^{-1}]$ reveals the exothermic nature of the dissolution of CFC-12 in water, as it is accompanied by the release of heat. This value is approximately three times larger than calorimetric values mentioned in literature [47]. It should definitely be noted that the slope is also temperature-dependent and the absolute value of $\Delta H_s$ decreases with rising temperature [47], eventually reaching zero at temperatures around 120 °C for many gases [20]. This slight non-linearity in the temperature range of this study is clearly observed in Figure 7, however a reliable polynomial least-square analysis would require more experimental points than those presently available. The present value cannot be considered as a reliable reference of solution enthalpy for CFC-12, as this methodology studies flux processes through the gas-liquid interface and not in the bulk.

From the experimentally determined distribution coefficients ($K$), molar Gibbs’ free energy values ($\Delta G$) were calculated at each temperature from the well-known relation: $\Delta G = -RT \ln K$, which were used to estimate the respective molar entropy change values ($T \Delta S = \Delta H_s - \Delta G$). These are all presented in Figure 8:

The resulting $\Delta G$ values are slightly negative and increase with temperature, eventually reaching zero. They indicate a slightly spontaneous process, which at higher temperatures becomes less spontaneous, approaching equilibrium. The decrease in solubility with a rise in temperature manifests as a decrease in $\Delta G$. On the other hand, entropy change values ($\Delta S$) are negative, and can be considered constant (within experimental error), with an average value of $-(190.7 \pm 6.9) \text{ J K}^{-1}$
mol\(^{-1}\). They are indicative of a process of increased order, as it is expected from the transfer of gases into liquids.

As the effect of the liquid surface area was examined in the present study, future work could involve experiments studying mass transfer of gases into an agitated liquid phase, where true diffusivities can be determined, which will permit thorough comparisons with predicted values by various semi-empirical equations available in literature.

5. Conclusions

Reversed-flow gas chromatography was extended in measuring mass transfer coefficients in liquids (water), for a gas solute (CFC-12) which provides weak gas chromatographic signals. A post-processing (smoothing) procedure was carried out, facilitated by the digitization of the output signal from the detector.

Mass transfer coefficients were simultaneously determined, providing information about the mechanism of the studied process. The subsequent uncertainty analysis distinguished the main sources of error in the determined parameters, which were the lengths of the empty diffusion column, \( L_1 \), and the liquid’s height, \( L_2 \). Possible improvements were suggested concerning the utilized experimental setup and the need for accurate measurements of the diffusion column’s geometric details.

Liquid diffusivity values were found to decrease with temperature, indicating an increased contribution of the reverse mass transfer process (from liquid to gas phase). In lower temperatures, experimental diffusivities approach available literature values. Furthermore, the estimated liquid film thickness values decrease with rising temperature and are one order of magnitude larger than values previously determined by RF-GC. Their difference was attributed to the greater extent of evaporation permitted by the current experimental setup, which results in lower liquid diffusivities and therefore higher liquid film thickness values.
The contribution of mass transfer from liquid to gas phase is estimated for the first time and its activation energy is almost identical to the vaporization enthalpy of water. Successful comparisons of distribution coefficients and Henry’s law constants were made with available literature values, further supporting the potential of the methodology.

Enthalpy change values confirmed the exothermic nature of the solution of CFC-12 in water, while molar Gibbs free energy values correspond to a slightly spontaneous process, becoming less spontaneous at higher temperatures. Moreover, entropy change values are negative as expected for a process resulting in increased order.

**Acknowledgements**

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References


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**Figure captions**

**Figure 1.** Schematic of the utilized reversed-flow gas chromatographic apparatus.

**Figure 2.** Indicative diffusion bands for two experiments in the same temperature (325.4 K), featuring CFC-12 as injected solute and nitrogen as carrier gas, in the absence (solid line) and presence (dashed line) of an aqueous phase.
Figure 3. Diffusion bands (grey: original, black: smoothed) for CFC-12’s diffusion in double-distilled (2d) water at atmospheric pressure and temperature of 334.9 K.
Figure 4. Experimental diffusion coefficients of CFC-12 in water ($D_L^{\text{exper.}}$, ⋄) with temperature ($T$) and theoretical values by Wilke-Chang equation ($D_L^{\text{theor.}}$, ●). Dashed lines represent least-square confidence bands at 0.95 level.

Figure 5. (a) Experimental mass transport coefficients through the gas ($K_G$) and liquid ($K_L$) interfacial films, and calculated overall liquid-to-gas coefficients ($K_v$) for the interaction of CFC-12 with 2d water. (b) Arrhenius plot for liquid-to-gas mass transport ($\ln K_v$ vs $1/T$) and respective activation energy ($E_a$).

Figure 6. Temperature effect on distribution coefficients, $K$, and Henry’s law constants, $\kappa_{\text{H}}^{\text{pc}}$, for the interaction of CFC-12 with 2d water.
Figure 7. Van't Hoff plot ($\ln K_H^{pc}$ vs $1/T$) and resulting molar enthalpy ($\Delta H_s$) for the dissolution of CFC-12 in 2d water at a temperature range of 320.7 to 344.3 K.
Figure 8. Molar Gibbs free energy ($\Delta G$), enthalpy of solution ($\Delta H_s$) and entropic factor ($T\Delta S$) values with temperature ($T$) for CFC-12's dissolution in 2d water.
Table 1. Experimental diffusion coefficients, $D_{L}^{\text{exp}}$, theoretical ones by Wilke-Chang equation, $D_{L}^{\text{theor.}}$, overall mass transfer coefficients, $K_{G}$ and $K_{L}$, in the respective gas and liquid stagnant films for the interaction of CFC-12 with pure (2d) water, at various temperatures. *

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$D_{L}^{\text{exp.}}/10^{-10}$ m$^2$ s$^{-1}$</th>
<th>$D_{L}^{\text{theor.}}/10^{-10}$ m$^2$ s$^{-1}$</th>
<th>$K_{G}/10^{6}$ m s$^{-1}$</th>
<th>$K_{L}/10^{6}$ m s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>320.7</td>
<td>4.39 ± 0.15</td>
<td>20.3</td>
<td>0.422 ± 0.006</td>
<td>2.21 ± 0.03</td>
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<tr>
<td>325.4</td>
<td>3.11 ± 0.10</td>
<td>22.3</td>
<td>0.51 ± 0.01</td>
<td>1.94 ± 0.03</td>
</tr>
<tr>
<td>330.2</td>
<td>2.75 ± 0.09</td>
<td>24.5</td>
<td>0.66 ± 0.01</td>
<td>1.84 ± 0.02</td>
</tr>
<tr>
<td>334.9</td>
<td>2.33 ± 0.08</td>
<td>26.6</td>
<td>0.81 ± 0.01</td>
<td>1.58 ± 0.02</td>
</tr>
<tr>
<td>339.7</td>
<td>1.82 ± 0.06</td>
<td>29.0</td>
<td>1.00 ± 0.01</td>
<td>1.30 ± 0.02</td>
</tr>
<tr>
<td>344.3</td>
<td>1.01 ± 0.03</td>
<td>31.3</td>
<td>1.12 ± 0.02</td>
<td>1.03 ± 0.01</td>
</tr>
<tr>
<td>rel.unc.†</td>
<td>3.3%</td>
<td>5-10%</td>
<td>1.6%</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

* standard uncertainties listed for $D_{L}^{\text{exp.}}$, $K_{G}$ and $K_{L}$ values
† mean relative standard uncertainty

Table 2. Estimated liquid film thickness ($z_{L}$), overall liquid-to-gas mass transport coefficients ($K_{v}$) and standard uncertainties for CFC-12 interaction with pure (2d) water.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$z_{L}/10^{-4}$ m</th>
<th>% $\Delta z_{L}$*</th>
<th>$K_{v}/10^{-5}$ m s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>320.7</td>
<td>1.80 ± 0.10</td>
<td>-</td>
<td>0.86 ± 0.04</td>
</tr>
<tr>
<td>325.4</td>
<td>1.71 ± 0.09</td>
<td>-4.6</td>
<td>1.09 ± 0.03</td>
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<tr>
<td>330.2</td>
<td>1.61 ± 0.07</td>
<td>-11</td>
<td>1.38 ± 0.03</td>
</tr>
<tr>
<td>334.9</td>
<td>1.47 ± 0.06</td>
<td>-18</td>
<td>1.72 ± 0.04</td>
</tr>
<tr>
<td>339.7</td>
<td>1.27 ± 0.06</td>
<td>-29</td>
<td>2.15 ± 0.07</td>
</tr>
<tr>
<td>344.3</td>
<td>1.00 ± 0.08</td>
<td>-44</td>
<td>2.64 ± 0.11</td>
</tr>
<tr>
<td>average</td>
<td>1.48</td>
<td></td>
<td></td>
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</table>

* percentage change of $z_{L}$ with temperature
Table 3. Distribution coefficients ($K$) and Henry’s law constants ($K_{H}^{pc}$), with standard uncertainties, for the dissolution of CFC-12 in pure (2d) water at various temperatures.

| $T$/K  | $K$      | $K_{H}^{pc}$/  \\
<table>
<thead>
<tr>
<th></th>
<th></th>
<th>$10^3$ m³ Pa mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>320.7</td>
<td>0.190 ± 0.004</td>
<td>14.0 ± 0.3</td>
</tr>
<tr>
<td>325.4</td>
<td>0.262 ± 0.007</td>
<td>10.3 ± 0.2</td>
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<tr>
<td>330.2</td>
<td>0.356 ± 0.007</td>
<td>7.7 ± 0.2</td>
</tr>
<tr>
<td>334.9</td>
<td>0.51 ± 0.01</td>
<td>5.4 ± 0.1</td>
</tr>
<tr>
<td>339.7</td>
<td>0.77 ± 0.01</td>
<td>3.66 ± 0.06</td>
</tr>
<tr>
<td>344.3</td>
<td>1.09 ± 0.02</td>
<td>2.63 ± 0.05</td>
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</table>

* mean relative standard uncertainty