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A new method for determining binary diffusion coefficients in dilute condensable vapors

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Abstract—A new method for determining binary diffusion coefficients in dilute condensable vapors is outlined. The method is based on condensational droplet growth. It can be used in a large range of pressures and temperatures, even below the freezing point of the condensing vapor. Results are obtained for the mixtures water–nitrogen and water–helium in the pressure range 11–44 bar. The product of pressure and diffusivity is found to be constant. New temperature correlations for the binary diffusion coefficient are proposed, valid for the range 235–375 K. For water–nitrogen the temperature dependence is significantly stronger than predicted by the Fuller correlation; for water–helium, it is weaker. © 1997 Elsevier Science Ltd.

1. INTRODUCTION

The binary diffusion coefficient is one of the key transport properties of a gas mixture. According to Fick's first law it is defined as the proportionality constant between molecular flux and concentration gradient of a species. In industrial chemical processes, mass transfer rates are often governed by diffusion equations. The spreading of air polluting waste gases into the atmosphere is an application of environmental interest, closely related to the field of meteorology. Even in astronomy, diffusion processes can readily be identified.

A wide range of techniques exists to determine diffusion coefficients in binary mixtures of dilute gases. An extensive review was provided by Marrero and Mason [1], who also summarized and evaluated about all of the reported data up to 1968.

Some reported techniques make use of unsteady droplet evaporation. We present here what could be considered as the opposite of this principle: a method based on the condensational growth of liquid droplets. One advantage of this technique is that it can be used to determine binary diffusion coefficients in a wide range of Knudsen numbers (*Kn*) by varying the total pressure. As we will point out in the next section, especially small Knudsen number systems are suitable for diffusion coefficient determination. Very small *Kn* values are easily obtained with the present method. Another useful aspect of the presented technique is its ability to determine binary diffusion coefficients at supercooled conditions (below the freezing point of the condensable vapor).

Droplet growth rates, which form the basis of the method, are determined using an expansion wave tube designed by Looijmans *et al.* [2]. The particular advantage of this setup is that droplet formation (nucleation) and droplet growth stages can be separated in time, which greatly facilitates both nucleation rate and growth rate measurements.

We illustrate our method using a measurement series of the binary diffusion coefficient of supercooled water in nitrogen and in helium. The validity of extrapolating existing correlations to lower temperatures will be investigated. Since measurements were performed at three different pressures of approximately 11, 27 and 44 bar, the influence of pressure on the diffusion coefficient is also discussed.

2. CONDENSATIONAL DROPLET GROWTH

In order to derive a diffusion coefficient from a condensation experiment, a growth model is needed. The model used in this study is described in detail by Gyarmathy [3]. It takes into account the whole range of Knudsen numbers, from very large (free molecular flow) down to very small (usually referred to as the continuum regime). In the latter, case, droplet growth is controlled by diffusion and can accurately be described by:

$$\frac{\mathrm{d}r_{\mathrm{d}}^{2}}{\mathrm{d}t} = 2\mathscr{D}_{12}\frac{\rho_{\mathrm{g}}}{\rho_{\mathrm{l}}}(y_{\mathrm{v}}-y_{\mathrm{v,eq}}). \qquad (1)$$

The Knudsen number is defined here as the ratio of the mean free path of a vapor molecule to the droplet diameter, $Kn = l/(2r_{\mathrm{d}})$. It is readily verified that under typical experimental conditions in this work, the Knudsen number is very small indeed: l ranges from 10^{-8} m at 10 bar to 10^{-9} m at 40 bar and r_{d} lies typically between 10^{-6} m at 10 bar and 10^{-7} m at 40 bar.

Although the model covers the entire range of Knudsen numbers—as do our calculations—we men-

NOMENCLATURE

$\mathscr{D}_{12}$	binary diffusion coefficient
Kn	Knudsen number
l	mean free path
n	index of refraction
p	pressure
r_d	droplet radius
t	time
T	temperature
x	position
y	vapor fraction.

Greek symbols

ρ	density
θ	scattering angle
δ	scattering angle
λ	wavelength of laser.

Subscripts

12	binary
d	droplet
eq	equilibrium
exp	experimental
g	gas
l	liquid
v	vapor.

tion the continuum limit because of several reasons. Firstly, our growth experiments are clearly in the continuum regime. Using the continuum approximation throughout our calculations would yield only small deviations (up to about 6%). However, for a quantitative determination of diffusion coefficient values, one should be as accurate as possible and thus use the complete set of implicit equations. Secondly, the continuum limit provides considerable insight into diffusion-controlled droplet growth. Using the complete model—covering the whole range of Knudsen numbers—is correct, of course, but does not provide a clear interpretation. As a last point, the continuum limit is important because of its generality. Several droplet growth models exist, which differ considerably in describing the transition regime for intermediate Knudsen numbers [3, 4]; however, for small Kn values they all coincide to the same continuum limit. Therefore, our results for $\mathscr{D}_{12}$ are only weakly dependent on the particular form of the growth model used.

Besides the small Knudsen numbers, there is an additional advantage of our experiments being in the continuum regime: the experimental temperatures at which the droplets are growing, are very well defined. The droplet temperature T_d differs from the far field gas temperature T_g by at most 1.4K for the lowest pressures used in this work. Therefore, the choice of the interpolation method, that calculates the experimental diffusion temperature from T_d and T_g, is of minor importance.

3. EXPERIMENTAL METHOD

3.1. *Growth rates*

In our expansion wave tube, separation of nucleation and droplet growth stages is accomplished by means of a local widening in the low pressure section (LPS). Figure 1 shows a schematic drawing of the setup.

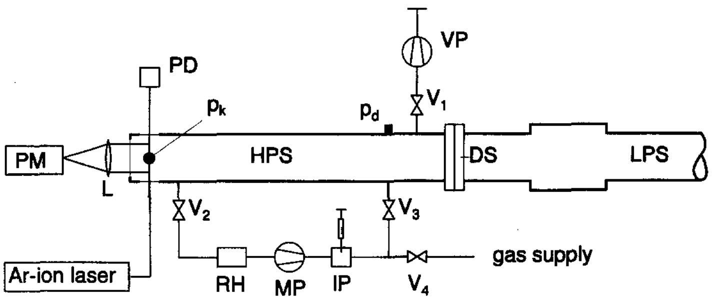
The preparation stage of the experiment involves several steps. Firstly, the tube is evacuated to a residual pressure below 10^{-2} Pa. Secondly, liquid water is injected, after which evaporation and wall adsorption stabilize the vapor pressure within half an hour. Thirdly, the carrier gas is let in and the mixture is homogenized by the circulation pump MP. Homogeneity is monitored by the humidity sensor RH, whose signal oscillates to an equilibrium value—typically in 10 min.

A condensation experiment proceeds in the following way. Following rupture of the membrane, an expansion wave travels into the high pressure section (HPS). At the same time, a shock wave travels into the LPS. It is reflected at the local widening as another small expansion, followed by a weak recompression as it reaches the narrowing. An x–t-diagram of the wave propagation is shown in Fig. 2, together with the resulting pressure history at the HPS endwall (calculations were done using the Random Choice Method, described by Smolders *et al.* [5]).

The temperature follows a similar pattern, since the process can be considered as isentropic. Latent heat release due to condensation does not violate this assumption: the amount of heat is negligible in view of the large heat capacity of the carrier gas at the high pressures concerned. The gasdynamic aspects are discussed in more detail in Ref. [6].

Due to the particular form of the temperature pattern, the saturation ratio S—defined as the ratio of vapor pressure to saturated vapor pressure at a given temperature—peaks during the pressure dip. Because of the extreme sensitivity of nucleation rates on S, significant nucleation only takes place during the small period of lowest pressure. After this so-called 'nucleation pulse', the saturation ratio decreases, but is still larger than unity. Therefore, the new droplets grow to macroscopic sizes.

An optical setup monitors the growth process. 90° light scattering is used for time-resolved radius determination, whereas measurement of the transmitted intensity yields the droplet concentration. In Fig. 3, both theoretical and experimental scattering patterns



HPS	high pressure section	$V_{1,\ldots,4}$	valves
LPS	low pressure section	VP	vacuum pump
DS	diaphragm section	MP	mixing pump
PM	photomultiplier	IP	injection point
PD	photodiode	p_d	static pressure (Druck PDCR 200)
L	lens	p_k	dynamic pressure (Kistler 603 B)
RH	humidity (Vaisala HMP 124B)		

Fig. 1. Schematic drawing of the expansion wave tube setup. The point of observation is situated at the endwall of the high pressure section (HPS)

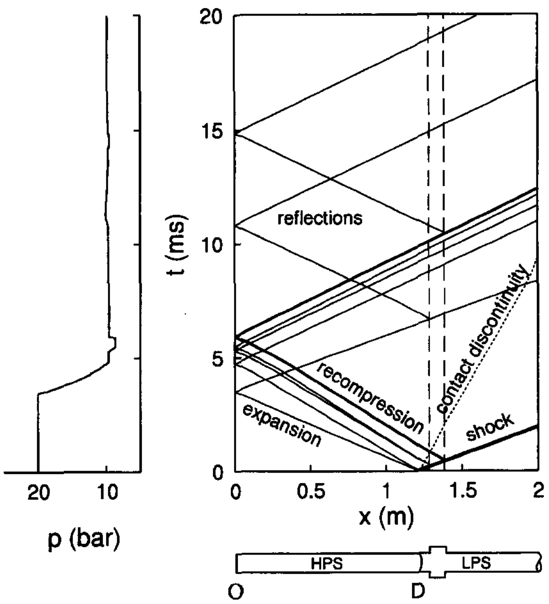


Fig. 2. x–t diagram of wave propagation in the pulse expansion tube with schematic tube configuration and pressure history at the HPS endwall. Calculations were performed using the Random Choice Method.

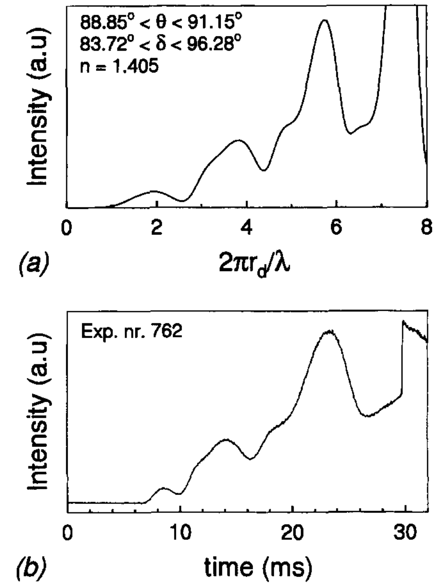


Fig. 3. (a) Theoretical Mie-pattern and (b) corresponding experimentally measured Mie-pattern.

are shown for a typical experiment. The resemblance is striking: the radius can be determined accurately as a function of time by simple pattern recognition. Both peaks and valleys are used as reference points.

3.2. *Vapor fractions*

By comparison of measured and theoretical growth rates, the diffusion coefficient $\mathscr{D}_{12}$ is obtained. From equation (1) it is clear that vapor fractions must be known in order to calculate theoretical growth rates. Since the tube is operated at high total pressures, special effort is required to measure the water content of the mixture.

We used a Vaisala Humicap 124B humidity transducer, based on changes in capacitance of a polymer film as it absorbs water. Since the absorption process is influenced by ambient pressure, the device was calibrated with both humidity and pressure as independent variables. In this way, it can be used for high pressure humidity determination; however, the relative error is estimated to be no smaller than 5%.

The saturated vapor fraction is obtained from the Wagner equation, described in the book by Reid *et al.* [7].

3.3. *Calculation of* $\mathscr{D}_{12}$

The experimental diffusion coefficient is defined as the particular value for which experimental and theoretical growth patterns coincide. In this section, the calculation method will be described in some detail.

Only part of the recorded pressure signal is used for the growth calculation, starting from the middle of the 'nucleation pulse' (where all droplets are assumed to be formed) up to the reflection of the shock wave from the LPS endwall (which heats the mixture and forces the droplets to evaporate). This period consists of roughly 150 pressure samples.

The temperature and density in the middle of the pulse are calculated from the pressure, using isentropic relations and real gas equations of state, proposed by Sychev *et al.* [8, 9]. Continuing from this starting point, variations of temperature and density at each sample point are calculated using the ideal gas law, to save computational cost. This causes no significant error, since the pressure fluctuations during the growth stage are only very slight. In all these calculations, the influence of the water vapor—with a molar fraction of about 10^{-4}—is neglected.

Once the temperature is known, an existing correlation for the diffusion coefficient as a function of temperature is used as an 'Ansatz' to calculate the growth pattern. To this end, the correlation according to Fuller is chosen [7]. Then the 'Ansatz' value for $\mathscr{D}_{12}$ is multiplied by a correction factor. It is this correction factor that is fitted to match theory with experiment.

As a last step (total) pressure and temperature during the growth period are averaged. The corrected diffusion coefficient value is assigned to the average temperature and pressure.

4. RESULTS AND DISCUSSION

In Figs. 4 and 5, typical experimental growth patterns are shown (markers). Also represented are the calculated curves using the 'Ansatz' diffusion coefficient (dashed lines) and the fitted theoretical curves (solid lines). Clearly, the growth model yields qualitatively correct results: correcting the diffusion coefficient with a constant factor yields an almost perfect match between theory and experiment. The alternate positive and negative deviations from the best fit (for valleys and peaks, respectively) can be understood by taking the background of the scattered signal into account. Such considerations show that this effect introduces no systematic error: one should indeed use the least squares fit for a correct interpretation.

All the correction factors $\mathscr{D}_{\text{exp}}/\mathscr{D}_{\text{Ansatz}}$ were between 0.8 and 1.2, demonstrating that extrapolation of the Fuller correlation is accurate within 20% for the water–nitrogen and water–helium systems. The results of our experiments are summarized in Table 1. Average values for $p\mathscr{D}_{12}$ are given for each pressure range studied, together with the numbers of experimental runs on which these averages are based.

Finally, our results are plotted in Figs. 6 and 7. It is clear from the table that no significant pressure dependence of the product $p\mathscr{D}_{12}$ can be deduced from the present results; therefore, each triplet of data in Table 1 is averaged to a single point in Figs. 6 and 7. Also represented are data for water–nitrogen from O'Connell [10], obtained between 280K and 380K, and recommended by Marrero and Mason [1]. For water–helium, data from Schwertz and Brow [11] and Lee and Wilke [12] are indicated. The 'Ansatz' correlations are shown, as well as new correlations, which are based on the combined new and existing data. For the binary diffusion coefficient of water–nitrogen, the improved correlation reads:

$$p\mathscr{D}_{12} = 1.13\times10^{-5}(T\mathrm{K}^{-1})^{2.159} \quad (\mathrm{Pa\,m^2\,s^{-1}}), \quad 235\mathrm{K} < T < 355\mathrm{K}. \quad (2)$$

For water–helium, the best fit to new and existing data is given by

$$p\mathscr{D}_{12} = 4.35\times10^{-3}(T\mathrm{K}^{-1})^{1.338} \quad (\mathrm{Pa\,m^2\,s^{-1}}), \quad 235\mathrm{K} < T < 375\mathrm{K}. \quad (3)$$

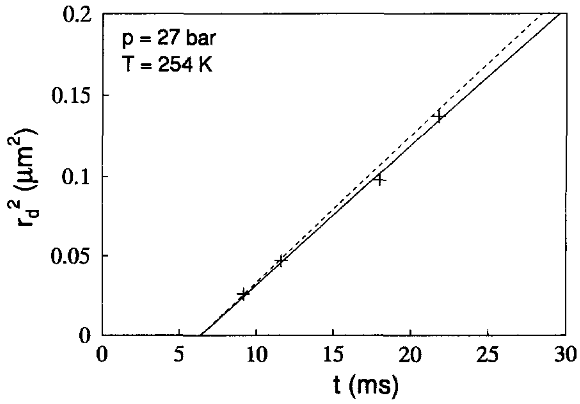


Fig. 4. Experimental droplet growth curve (markers) for water droplets in nitrogen. Also shown is the theoretical pattern using the Fuller correlation for $\mathscr{D}_{12}$ (dashed line), and the least squares fit using the corrected value of the diffusion coefficient (solid line).

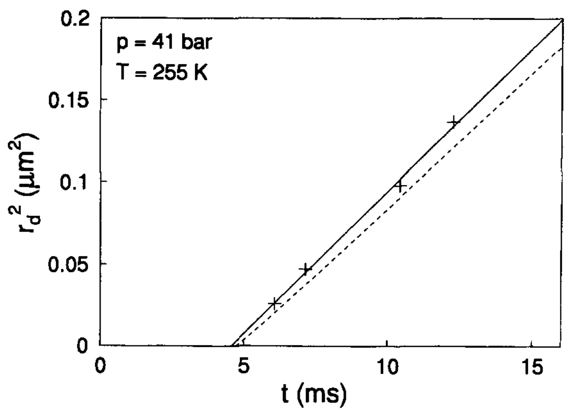


Fig. 5. Experimental droplet growth curve (markers) for water droplets in helium. Also shown is the theoretical pattern using the Fuller correlation for $\mathscr{D}_{12}$ (dashed line), and the least squares fit using the corrected value of the diffusion coefficient (solid line).

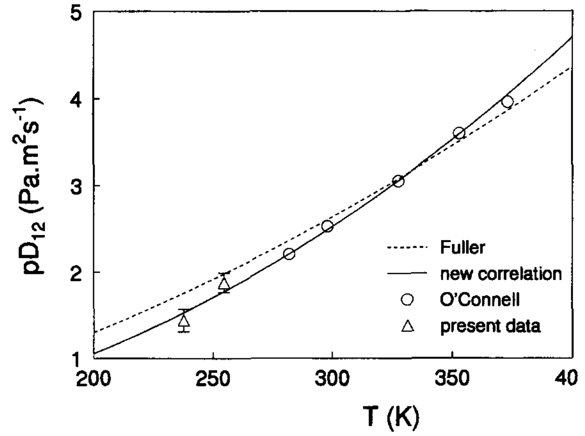


Fig. 6. Diffusion coefficient of water–nitrogen as a function of temperature. Dashed line is the correlation according to Fuller [7]. Solid line is the new correlation.

Table 1. Binary diffusion coefficient data obtained in this study. For each series of experiments, the average result over the indicated number of runs is given. The uncertainty in temperatures is smaller than 1K; the spreading in pressures is approximately 1 bar

2nd comp.	p (bar)	T (K)	$p\mathscr{D}_{12}$ (Pa m² s⁻¹)	No. of runs
He	11.0	239.7	7.0±0.4	1
He	26.6	235.8	6.3±0.6	3
He	43.6	238.8	6.2±0.4	3
N_2	11.2	237.5	1.5±0.1	3
N_2	27.9	237.1	1.4±0.1	4
N_2	44.9	238.3	1.4±0.1	5
He	10.7	255.9	7.6±0.4	2
He	26.5	255.8	7.4±0.4	5
He	42.1	255.6	7.3±0.7	5
N_2	10.6	255.2	1.9±0.1	6
N_2	26.7	254.6	1.9±0.1	5
N_2	43.0	254.2	1.8±0.1	4

Looking carefully at Figs. 6 and 7, two conclusions can be drawn.

Firstly, our data are fairly in line with the recommended data from other experimentalists, obtained at higher temperatures. This is an important argument of support for the reliability of our new method. Unfortunately, we cannot reproduce the data at temperatures above room temperature, because our method is based on isentropic cooling of the gas mixture, starting from room temperature.

Secondly, the Fuller correlation—for which $p\mathscr{D}_{12} \propto T^{1.75}$—does not accurately describe the temperature dependence of the product $p\mathscr{D}_{12}$. This observation can be made only now, with our low temperature data included in the picture; at higher temperatures, the deviations from the Fuller relation seem to be hardly significant, especially for water–helium.

5. CONCLUSIONS

A new method, based on condensational droplet growth, has been introduced to determine binary diffusion coefficients for mixtures of a condensable vapor and a gas at small Knudsen numbers. A pulse expansion wave tube setup was applied for measuring droplet growth rates.

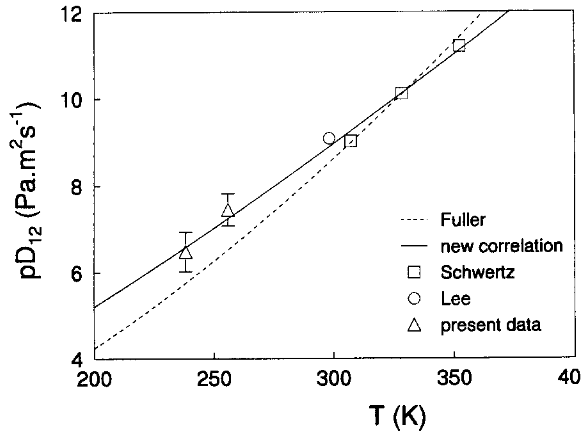


Fig. 7. Diffusion coefficient of water–helium as a function of temperature. Dashed line is the Fuller correlation [7]. Solid line is the new correlation.

The method can be used across large ranges of pressures and temperatures, even below the freezing point of the condensable vapor. Its relative uncertainty (estimated to be 5% in the present work) depends largely on the accuracy of vapor fraction measurement, which requires special techniques at high pressures.

The method was illustrated with measurements in the systems water–helium and water–nitrogen in the pressure range 11–44 bar. A significant pressure dependence of the product of diffusion coefficient and pressure could not be identified. The obtained diffusion coefficient data, obtained at temperatures near 237K and 255K, showed to be fairly in line with available data, obtained at higher temperatures. This result can be expected to hold for other mixtures as well.

The Fuller correlation, describing the temperature dependence of the product of pressure and diffusivity, was found to be significantly in error for the present mixtures. Therefore, improved correlation coefficients were proposed, providing a better accuracy over an extended temperature range (down to 235K).

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