Homogeneous water nucleation and droplet growth in methane and carbon dioxide mixtures at 235 K and 10 bar

Citation for published version (APA):

Holten, V., & Dongen, van, M. E. H. (2010). Homogeneous water nucleation and droplet growth in methane and carbon dioxide mixtures at 235 K and 10 bar. *Journal of Chemical Physics*, 132(20), 204504-1/8. [204504]. <https://doi.org/10.1063/1.3432623>

DOI:

[10.1063/1.3432623](https://doi.org/10.1063/1.3432623)

Document status and date:

Published: 01/01/2010

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Homogeneous water nucleation and droplet growth in methane and carbon dioxide mixtures at 235 K and 10 bar

V. Holten^{a)} and M. E. H. van Dongen^{b)}

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513,
5600 MB Eindhoven, The Netherlands

(Received 16 March 2010; accepted 4 May 2010; published online 25 May 2010)

Homogeneous nucleation rates and droplet growth rates of water in pure methane and mixtures of methane and carbon dioxide were measured in an expansion wave tube at 235 K and 10 bar. The nucleation rate in pure methane is three orders of magnitude higher than literature nucleation rates of water in low-pressure helium or argon. Addition of carbon dioxide to the carrier gas mixture increases the rates even more. Specifically, rates in a mixture of methane and 3% carbon dioxide are a factor of 10 higher than the rates in pure methane. With 25% carbon dioxide, the rates are four orders of magnitude higher than the rates in pure methane. An application of the nucleation theorem shows that the critical cluster consists of 22 water molecules and 5 methane molecules, for nucleation in pure methane. Growth rates of water droplets were measured in methane and in methane-carbon dioxide mixtures at 243 K and 11.5 bar. At equal temperature, pressure and water vapor fraction, the growth rate of the squared droplet radius is about 20% lower in the mixture with 25% carbon dioxide than in pure methane. The lower growth rate is caused by a smaller diffusion coefficient of water in the mixture with carbon dioxide; the difference of the diffusion coefficients is qualitatively reproduced by the empirical Fuller correlation combined with Blanc's law.

© 2010 American Institute of Physics. [doi:10.1063/1.3432623]

I. INTRODUCTION

Knowledge of the nucleation and droplet growth behavior of water in mixtures of methane and carbon dioxide is relevant for the natural gas industry. For example, it is useful for the design of devices that separate water from natural gas containing carbon dioxide. Previously, nucleation rates and droplet growth rates of water in methane at 10, 25, and 40 bar have been measured by Peeters *et al.*^{1,2} Nucleation in a sample of real natural gas was studied by Luijten *et al.*,³ but their sample did not contain water vapor, as it had been removed before the experiments. The effect of carbon dioxide on water nucleation has not been studied until now. Carbon dioxide is expected to influence nucleation rates because of its solubility in water at low temperatures (e.g., at 235 K and 1 bar, the equilibrium molar fraction of CO₂ in liquid water is about 0.01). This article presents the first report of the influence of carbon dioxide on the nucleation and droplet growth rates of water in methane. A comparison is made of water nucleation and droplet growth in (1) pure methane, (2) a mixture of 97% methane and 3% carbon dioxide, and (3) a mixture of 75% methane and 25% carbon dioxide. All nucleation experiments take place at 235 K and 10 bar, and the droplet growth is measured at 243 K and 11.4 bar.

II. EXPERIMENTAL METHOD

The experimental setup of this study has been described before,⁴ and a summary will be given. Experiments were

performed in a so-called expansion wave tube,⁵ which is a modified shock tube (see Fig. 1) in which the nucleation pulse principle is implemented. The high-pressure section (HPS) serves as a test section in which nucleation occurs. It contains the mixture of water vapor and the carrier gases methane and carbon dioxide, which is produced in a dedicated mixture preparation device.¹ The purchased gases (Linde Gas) had a purity of 99.995% or better, with no more than 5 ppm (by volume) water content. The water was purchased from Merck (GR grade) and had a resistivity of at least 1 MΩ cm at 25 °C. The molar fraction of water vapor was varied between 240 and 340 ppm. The initial total pressure in the HPS was 25.0 bar. A diaphragm separates the HPS from the low-pressure section (LPS) that contains a carrier gas without water, at a pressure of about 11 bar. Prior to the experiment, the HPS is flushed at 25 bar for 1 h with the test mixture, to ensure adsorption equilibrium with the walls. The experiment is started by isolating the HPS from the flushing circuit and rupturing the diaphragm with an electric current. The waves caused by pressure equilibration lead to expansion and cooling down of the test mixture at the plane of observation. The widening in the LPS (Fig. 1) causes an additional pressure dip or pulse in the HPS, occurring immediately after the main expansion. During the pulse, the temperature and pressure reach their lowest value (235 K and 10 bar), and the high supersaturation results in a large droplet formation rate (3×10^{13} – 3×10^{17} m⁻³ s⁻¹). At the end of the pulse, the mixture is slightly recompressed, so that the formation of new droplets stops. A state of supersaturation is maintained, so that the existing small droplets can grow to optically detectable sizes.

^{a)}Electronic mail: v.holten@alumnus.tue.nl.

^{b)}Electronic mail: m.e.h.v.dongen@tue.nl.

FIG. 1. Schematic top view of the expansion wave tube setup. MPD: mixture preparation device supplying the mixture of water vapor, methane and carbon dioxide; HPS: high-pressure section containing the test mixture; LPS: low-pressure section; P: location of pressure transducers; W: widening; D: diaphragm; UPC: upstream pressure controller; PD: photodiode measuring the transmitted light; and PM: photomultiplier measuring the 90° scattered light. The arrows indicate the direction of flushing.

The pressure at a position of 5 mm from the HPS end wall is measured by a piezoelectric pressure transducer (Kistler 603B) and a piezoresistive transducer (Kistler 4073A50). The piezoelectric transducer has a fast response, but measures relative pressure changes only. The piezoresistive transducer measures absolute pressures and is used to calibrate the piezoelectric one *in situ*.

The initial temperature of the gas mixture is taken equal to the temperature of the HPS walls, which is measured before the start of the experiment with resistance thermometers accurate to 0.04 K. During the experiment, the temperature of the gas mixture changes so rapidly that it cannot be measured. However, the duration of the expansion is so short (2 ms) that the heat flow from the walls to the gas only influences the thermal boundary layers, and leaves the core to be adiabatic. The temperature can then be computed from the initial temperature and the pressure history, using a suitable equation of state (EOS). We selected the GERG-2004 EOS^{6,7} for this purpose. As an accuracy test, pulse temperatures for the experiments in pure methane were also computed with the EOS by Sychev *et al.*,⁸ the differences with GERG-2004 were at most 0.01 K.

Close to the end wall of the HPS, the size and number density of droplets is determined by a combination of constant angle Mie scattering at 90° and extinction measurements of a laser beam with a wavelength of 532 nm. The growth of the droplets is monitored during a period of 40 ms after the pulse. The minimum observable droplet radius is about 0.17 μm, and the radius at the end of the observation period is at most 0.5 μm. Finally, the nucleation rate is found as the ratio of the droplet density and the pulse duration.

Taking into account real-gas behavior, the supersaturation of water in a high-pressure carrier gas mixture is given by⁹

$$S = \frac{y}{y_{\text{eq}}} = \frac{yP}{f_e p_e} \quad (1)$$

Here y is the experimental molar vapor fraction of water and y_{eq} is its value at vapor-liquid equilibrium. Furthermore, p is the total pressure, f_e is the so-called enhancement factor, and p_e is the equilibrium vapor pressure. For the binary water-methane system, y_{eq} and f_e are functions of p and T only. For the ternary system with carbon dioxide, y_{eq} and f_e can be

FIG. 2. Nucleation rate of water in methane and carbon dioxide at 10 bar and 235 K, as a function of the supersaturation. Series were performed in the order of A to D. The composition of the carrier gas is given in parentheses.

expressed as functions of p , T , and the carbon dioxide molar fraction y_c . The value of f_e was computed with a suitable EOS, as explained in the Appendix.

III. NUCLEATION RATES

Figure 2 shows nucleation rates as a function of the supersaturation in the nucleation pulse. All data was obtained at approximately 235 K and 10 bar, with standard deviations of 0.7 K and 0.1 bar. The results have been corrected for the deviations of the nucleation temperature from the average.¹⁰ The average temperature and pressure of each series is listed as $\bar{T}$ and $\bar{p}$ in Table I. Tables with experimental data are available as supplementary material.¹¹

Four series of experiments were performed to study the effect of carbon dioxide, labeled A to D in Fig. 2. The first series (A) consists of nucleation experiments in pure methane. In the next series (B), nucleation took place in a carrier gas mixture of 3% carbon dioxide and 97% methane (the percentages are molar). Compared to the pure-methane data, the 3% carbon dioxide was found to increase the nucleation rate by about a factor of 10. To verify the reproducibility of the experiments, several experiments in pure methane and with 3% carbon dioxide were alternated.

After a 3-month break, the mixture preparation device was calibrated for experiments with a carrier gas mixture of 25% carbon dioxide and 75% methane. The reproducibility was then checked by performing an experiment with pure methane. The result deviated significantly from the earlier series A. After ruling out possible errors in the water vapor fraction and in measurements of pressure, temperature and nucleation rate,¹² a new series with pure methane was performed (C). Finally, the effect of 25% carbon dioxide was studied by alternating several experiments with 25% carbon dioxide (D) and pure methane (C). The influence of 25% carbon dioxide on the nucleation rate is quite large. As a result, the only supersaturation common to series C and D is $S \approx 9$. At that supersaturation, the 25% carbon dioxide increases the nucleation rate by about four orders of magnitude.

In Fig. 3, the nucleation rate is plotted versus the reduced partial pressure, which is the ratio of the partial pres-

TABLE I. Nucleation conditions and critical cluster size.

a	y_c	$\bar{T}$ (K)	$\bar{p}$ (bar)	$\bar{S}^b$	n_w^*		σ (mN/m) ^c	f_e^c
					Expt. ^c	Eq. (3) ^d		
A	0	235.0	10.09	11.77	22 ± 2	32 ± 3	80.00	1.11
C	0	235.5	10.11	10.91	20 ± 1	34 ± 4	79.92	1.11
B	0.03	235.4	10.07	10.70	22 ± 1	34 ± 4	78.92	1.16
D	0.25	235.5	10.12	7.80	22 ± 1	40 ± 9	72.35	1.56

^aLetters A to D refer to the labels of the series in Fig. 2.

^bThe average of S is calculated from the mean of $\ln S$, that is, $\bar{S} \equiv e^{(\ln S)}$.

^cThe uncertainty of the experimental n_w^* is the 90% confidence interval.

^dThe uncertainty of the theoretical n_w^* is a standard deviation, taking into account the uncertainties of the surface tension σ and the enhancement factor f_e .

^eValues of the surface tension σ and enhancement factor f_e are predictions (see the Appendix). At 235 K, the surface tension of pure water is estimated at 82.90 mN/m.

sure of water and the saturated vapor pressure. The reduced partial pressure is commonly used as an approximation of the supersaturation at low total pressure, where the effect of the carrier gas on the vapor-liquid equilibrium is negligible. At 10 bar, however, the enhancement factor [f_e in Eq. (1)] is significantly higher than unity, and must be taken into account. If it is not, like in Fig. 3, the effect of carbon dioxide appears smaller than it really is. The same result was obtained by Luijten *et al.*¹³ for water nucleation in nitrogen from 10 to 40 bar: if the nucleation rates are plotted versus the reduced partial pressure instead of S , the dependence on the carrier gas pressure apparently diminishes. Luijten *et al.* assumed that this effect is caused by a partial compensation of the two carrier gas influences: vapor pressure enhancement and surface tension reduction. In our case, at a fixed water vapor fraction, an increase of the carbon dioxide fraction lowers the supersaturation because it increases f_e (which decreases the nucleation rate) and decreases the surface tension (which increases the nucleation rate). The mutual compensation results in the near-overlap of series A to D in Fig. 3. Estimates of the surface tension and enhancement factor at our nucleation conditions are listed in Table I.

IV. CRITICAL CLUSTER COMPOSITION

The number of water molecules in the critical cluster, n_w^* , can be obtained from experimental J - S data using the nucleation theorem,¹⁴

FIG. 3. Nucleation rate of water in methane and carbon dioxide at 10 bar and 235 K, as a function of the reduced partial pressure of water.

$$n_w^* = \left(\frac{\partial \ln J}{\partial \ln S} \right) - 1, \quad (2)$$

where J is the nucleation rate. As can be seen in the double-logarithmic plot of Fig. 2, all four experimental series have nearly the same slope, so the critical cluster size is also similar. Indeed, application of Eq. (2) yields sizes of about 22 molecules; see Table I. Only series B has a slightly smaller slope. A theoretical prediction of the critical cluster size is given by the Gibbs–Thomson equation¹⁵

$$n_w^* = \frac{32\pi\sigma^3 v_l^2}{3(kT \ln S)^3}, \quad (3)$$

where σ is the surface tension, v_l is the molecular volume of liquid water and k is Boltzmann's constant. A comparison of the theoretical and experimental values (Table I) shows that Eq. (3) overpredicts the critical size by 10 to 18 molecules. However, the Gibbs–Thomson equation holds for clusters containing water molecules only. For the experiments in pure methane, we show below that there are about five methane molecules in the critical cluster. For such cluster compositions, Eq. (3) does not hold.

The amount of methane molecules in the critical cluster n_g^* can be obtained with an extended version of the nucleation theorem, derived by Oxtoby and Laaksonen¹⁶ and modified by Luijten *et al.*¹³ Applied to the water-methane system, it reads

$$\left(\frac{\partial \ln J}{\partial \ln p} \right)_{S,T} = \left(\frac{pv_w^l}{kT} - x_m^{\text{eq}} \right) n_w^* + Z_m \Delta n_m^* + 2 \ln f_e, \quad (4)$$

where v_w^l is the molecular volume of pure liquid water, x_m^{eq} is the equilibrium molar fraction of dissolved methane in the liquid, Z_m is the compressibility factor of methane, and f_e is the enhancement factor in equilibrium. Furthermore, Δn_m^* is the excess number of methane molecules; that is, the number of methane molecules in the cluster minus the number of methane molecules in one critical cluster volume in the gas phase. A different form of the nucleation theorem was derived by Kalikmanov and Labetski;¹⁷ it is given by

FIG. 4. Effect of carrier gas pressure on the nucleation rate of water at 235 K. For water in methane, the two measurement series at 10.1 bar from this work are shown, as well as the data of Peeters *et al.* (Ref. 1) at 10 bar and 25 bar. For low carrier gas pressures, fits to the data from Holten *et al.* (Ref. 4) and Wölk and Strey (Ref. 18) are given.

$$\left(\frac{\partial \ln y}{\partial \ln p}\right)_{J,T} = -\frac{1}{n_w^* + 1} \left(\frac{p \bar{V}_w^{\text{gas}}}{RT} \Delta n_w^* + Z_m \Delta n_m^* + \ln f_e + 1 \right), \quad (5)$$

where $\bar{V}_w^{\text{gas}}$ is the partial molar volume of water vapor in the gas phase and R is the gas constant.

To apply Eq. (4) or Eq. (5), measurements of the nucleation rate at different pressures are required. In Fig. 4, a collection of water nucleation rates at 235 K and several pressures is presented. Peeters *et al.*¹ obtained nucleation rates in methane at 10 bar—as in this work—and at 25 bar. Note that the 10 bar results of Peeters *et al.* are approximately between our two series, which supports the validity of the data. At lower pressures, nucleation rates in helium by Holten *et al.*⁴ and rates in argon by Wölk and Strey¹⁸ are shown. Of course, the pressure nucleation theorem is intended to be used for measurements with the same carrier gas, but at low total pressures (1 bar or less) the effect of the carrier gas is expected to be small. For the following analysis, the data with helium or argon will therefore be treated as measurements in methane at 1 bar.

To determine the methane content of the critical cluster with Eq. (4) at 10 bar, the nucleation rate at a supersaturation of $S=11.25$ was taken, for all three available pressures. That value of S corresponds to the middle of the 10 bar data; to evaluate the nucleation rate at 25 bar, the 25 bar fit (Fig. 4) was extrapolated to $S=11.25$. In Fig. 5(a), the resulting nucleation rates are plotted as a function of the methane pressure. A quadratic interpolation through the points was used to obtain the derivative $(\partial \ln J / \partial \ln p)_{S,T} = 5 \pm 1$ at $S=11.25$, which was substituted in Eq. (4). The evaluation of the other quantities is described in the Appendix. Finally, the excess number of methane molecules in the critical cluster was found to be $\Delta n_m^* = 5 \pm 1$. Peeters *et al.*¹ found the value $\Delta n_m^* = 5 \pm 2$ using a slightly different evaluation.

To apply Eq. (5), supersaturations were taken at a nucleation rate of $3 \times 10^{15} \text{ m}^{-3} \text{ s}^{-1}$, which lies in the middle of our measurement range. The supersaturation values were then converted to vapor fractions with the help of Eq. (1), that is, $y = S f_e p_e / p$. For the low-pressure argon and helium

FIG. 5. Effect of carrier gas pressure on water nucleation at 235 K. *Left*: Nucleation rate as a function of methane pressure, for a constant supersaturation of 11.25. *Right*: Water vapor fraction as a function of methane pressure, for a constant nucleation rate of $3 \times 10^{15} \text{ m}^{-3} \text{ s}^{-1}$. Error bars are smaller than the symbol size.

data, an enhancement factor of $f_e=1$ was taken. The vapor fractions were plotted versus the pressure [Fig. 5(b)], and a quadratic interpolation was employed again to find the derivative $(\partial \ln y / \partial \ln p)_{J,T} = -1.1 \pm 0.1$. The evaluation of the partial molar volume $\bar{V}_w^{\text{gas}}$ is described in the Appendix. Finally, the excess number of methane molecules in the critical cluster was found to be $\Delta n_m^* = 6 \pm 2$, which agrees with the result obtained by Eq. (4).

The actual number of methane molecules in the cluster is the sum of the excess number of methane molecules and the number of methane molecules in the gas phase that occupy a cluster volume. For our conditions (10 bar and 235 K) the actual number is about 0.3 molecules higher than the excess number. Taking into account the uncertainties of ± 1 and ± 2 in the results for the excess number, the absolute number of methane molecules can be taken equal to the excess number. This means that at the mentioned conditions and a supersaturation of about 11, the critical cluster consists of approximately 22 water molecules and five methane molecules. Accordingly, the liquid fraction of methane is about 0.2, whereas the equilibrium methane fraction is 2×10^{-3} , 100 times smaller (see the Appendix).

For our experiments in methane and carbon dioxide, we expect that the critical cluster contains not only methane, but also carbon dioxide molecules. However, the number of carbon dioxide molecules cannot be evaluated from our current experiments, because the nucleation theorems [Eqs. (4) and (5)] are applicable to binary systems only. Therefore, to obtain the carbon dioxide content of critical water clusters, measurements of water nucleation rates in pure carbon dioxide at different pressures are required.

V. COMPARISON WITH THEORY

For carrier gases that do not enter the nucleating clusters significantly, the classical nucleation theory can be adjusted for the two influences of the carrier gas: vapor fraction enhancement and surface tension change. The influence of enhancement is also taken into account in the definition of the supersaturation, Eq. (1). With this definition, Luijten and van Dongen¹⁹ obtained the following expression for the nucleation rate:

FIG. 6. Comparison of experiment and theory: nucleation rates of water in methane and carbon dioxide at 10 bar and 235 K. The points are the measurements; the lines represent the theoretical nucleation rate from Eq. (6).

$$J = \left(\frac{f_e p_e}{Z_g k T} \right)^2 \left(\frac{2 \sigma M}{\pi N_A} \right)^{1/2} \frac{S}{\rho_l} \exp \left[- \frac{16 \pi M^2 \sigma^3}{3 (N_A \rho_l \ln S)^2 (k T)^3} \right]. \quad (6)$$

Here Z_g is the compressibility factor of the carrier gas ($Z_g \equiv p/(\rho k T)$, with p , the total pressure and ρ , the number density of the carrier gas), ρ_l is the density of liquid water, M is its molar mass, and N_A is the Avogadro constant. It is worth stressing that Eq. (6) does not treat the carrier gases as inert; it is only required that the carrier gas fraction in the clusters is small. Detailed validity conditions are given in Luijten and van Dongen¹⁹ and Peeters *et al.*¹

To find the enhancement factor f_e and the surface tension σ at our nucleation conditions, an EOS was selected and fitted to experimental data (see the Appendix). The resulting values of f_e and σ are listed in Table I. In Fig. 6, the theoretical nucleation rates are compared with the experimental results. There is a large discrepancy, of about four orders of magnitude, between the nucleation experiments and theory. On the other hand, the shift in supersaturation resulting from the carbon dioxide addition is predicted fairly well.

However, for the nucleation in pure methane, we found in Sec. IV that the methane fraction in the cluster is about 0.2, which is 100 times as large as in equilibrium. For such a carrier gas fraction, Eq. (6) cannot be expected to yield accurate results. A theory that aims to reproduce the experimental results should predict such a high fraction of methane (and also carbon dioxide, if it is present) in clusters. Probably, a modified form of binary nucleation theory is required, in which the carrier gas absorption and adsorption and their dependence on cluster size and composition are taken into account.

VI. DROPLET GROWTH RATES

The nature of droplet growth depends on the ratio of the mean free path of vapor molecules and the diameter of the droplet. For our nucleation experiments in methane at 10 bar, the molecular mean free path is about 5 nm, according to gas kinetic theory.²⁰ In our setup, droplets can be observed when their diameter becomes larger than about 340 nm. Therefore, all observable droplets are much larger than the mean free path; for such droplets, the growth is controlled by diffusion of the vapor molecules through the carrier gas. In the case of

diffusion-controlled growth, the square of the droplet radius is proportional to time, as long as no significant depletion of vapor molecules occurs. If depletion does occur, the growth can be described by the model of Muijens *et al.*,²¹ which assumes constant temperature and pressure. In this model, the growth law (which gives the time t at which a droplet reaches a radius r) can be written as

$$t - t_0 = \frac{2r_m^2}{c} G \left(\frac{r}{r_m} \right), \quad (7)$$

where t_0 is the time at which the droplet growth starts, r_m is the maximum droplet radius (at which droplet growth stops), and $c \equiv dr^2/dt|_{t=t_0}$ is the initial growth rate of the squared radius. The function G is given by²¹

$$G(x) = \int_0^x \frac{x'}{1-x'^3} dx' = \frac{1}{\sqrt{3}} \left[\frac{\pi}{6} - \arctan \left(\frac{1+2x}{\sqrt{3}} \right) \right] + \frac{1}{6} \ln \left[\frac{1+x+x^2}{(1-x)^2} \right]. \quad (8)$$

For each experiment, the quantities t_0 , c , and r_m were obtained by least-squares fitting of the growth law to the experimental optical signals.¹¹

Before discussing the experimental growth rates, let us review the expected dependence on the water vapor fraction. At the beginning of the droplet growth, depletion is negligible, so the growth rate of the squared radius dr^2/dt is approximately constant in time. Theoretically, it is given by^{2,22}

$$\frac{dr^2}{dt} = \frac{2\rho_g D}{x\rho_l} (y - y_{eq}), \quad (9)$$

where ρ_g and ρ_l are molar densities of the gas mixture and the liquid, respectively, D is the diffusion coefficient of water in the gas mixture, x is the water liquid fraction, y is the water vapor fraction, and y_{eq} is the equilibrium vapor fraction of water at the droplet growth conditions. According to Eq. (9), the initial growth rates c of different experiments are a linear function of the water vapor fraction in the experiments, as long as the other quantities are held constant.

As expected, in Fig. 7 a linear trend is observed for experiments with the same carbon dioxide fraction. The presence of 25% carbon dioxide clearly decreases the growth rate. The growth rates of the experiments with 3% carbon dioxide are also slightly lower than the pure-methane ones, but the effect is small compared to the scatter. A remarkable result is the agreement of the growth rates of the two series with pure methane, series A and C. This agreement implies that the vapor fractions of both series are consistent, so the discrepancy in nucleation rates between the series (Fig. 2) cannot be due to an incorrect vapor fraction.

It is seen in Fig. 7 that the uncertainty of the growth rate is larger for experiments with a higher water fraction. In those experiments, depletion is important, and the strong decrease of the growth rate in time results in a less accurate value for the initial growth rate. Conversely, most experiments with water fractions below 280 ppm have negligible depletion and accurate growth rates.

FIG. 7. Initial growth rate of the squared droplet radius vs the initial water vapor fraction, at approximately 243 K and 11.5 bar, in methane and methane-carbon dioxide mixtures. The lines are least-squares fits which are *not* forced through the equilibrium vapor fraction y_{eq} at $dr^2/dt=0$. Tables with droplet growth data are available as supplementary material (Ref. 11).

Growth rates in the methane-water system (without carbon dioxide) have been measured earlier by Peeters *et al.*² Their measurements agree with the values from this work to within the experimental uncertainties.

From the experimental growth rates, the diffusion coefficients were determined in the manner described by Peeters *et al.*,² which proceeds as follows. A straight line is fitted to measurements in Fig. 7 with a constant carbon dioxide fraction. According to Eq. (9), the slope of the line is equal to $2\rho_g D/(x\rho_l)$, so D can be obtained when ρ_g , ρ_l , and x are known or estimated. If the equilibrium water vapor fraction y_{eq} is also known, the accuracy of the fit can be improved by forcing the line through the y_{eq} on the horizontal axis, at which the growth rate is zero [Eq. (9)]. In our case, y_{eq} was computed with a suitable EOS. Quantities from Eq. (9) are listed in Table II; sources are given in the Appendix.

The resulting fits are given as solid lines in Fig. 8, and the diffusion constants are listed in Table II. The fits through y_{eq} agree with the experiments fairly well, although for the experiments without carbon dioxide the slope deviates somewhat; the slope of the constrained fit is 17% higher than the slope of the unconstrained fit. In fact, the slope of the unconstrained fit is so small that extrapolation down to $dr^2/dt=0$ yields $y_{eq}=10\pm 7$. Such a value corresponds to an enhancement factor of about 0.2, which is impossible, given the

FIG. 8. Growth rate of the squared droplet radius vs the initial water vapor fraction, at approximately 243 K and 11.5 bar, for different carbon dioxide fractions. Error bars smaller than $\pm 0.2 \mu\text{m}^2/\text{s}$ are not shown. The solid lines are least-squares fits that are forced through the equilibrium vapor fraction y_{eq} at $dr^2/dt=0$. Because of the enhancement effect, y_{eq} increases with increasing carbon dioxide fraction. The dashed lines are predictions, with slopes given by the Fuller correlation and Blanc's law, Eqs. (9)–(11). From top to bottom, the three dashed lines pertain to the mixtures with 0%, 3%, and 25% carbon dioxide, respectively. The same order holds for the three solid lines. The dotted line is fitted to the pure-methane data, without constraining it to equilibrium (it is one of the fits shown in Fig. 7).

known behavior of the methane-water system. In view of this inaccuracy, it is clear that a fit through y_{eq} results in a more reliable value for the diffusion constant. The constrained fits were therefore used to determine the diffusion constants.

A. Comparison with Fuller correlation

The Fuller correlation²³ provides reliable estimates of binary diffusion coefficients. Here, the version modified by Luijten²⁴ is used, which reads

$$D_{AB} = \frac{0.0143T^{0.75}}{[(\Sigma_v)_A^{1/3} + (\Sigma_v)_B^{1/3}]^2} \left(\frac{1/M_A + 1/M_B}{2 \times 10^3} \right)^{1/2} \frac{M_A}{\rho_A R}, \quad (10)$$

with Σ_v the diffusion volume of a component (listed in Ref. 23), M the molar mass in kg/mol, ρ the mass density of the gas in kg/m³, R the gas constant in J mol⁻¹ K⁻¹, and subscripts A and B referring to the carrier gas and the condensing component, respectively.

The Fuller correlation can only be used for binary mixtures, such as the water-methane system. For diffusion of

TABLE II. Droplet growth conditions.

y_c	T (K)	p (bar)	D (mm ² /s)		ρ_g (mol/m ³)	x_m (%) ^a	x_c (%) ^a	$\Delta\rho_l$ (%) ^b	y_{eq} (ppm)
			Expt.	Fuller/Blanc					
0	243.3	11.53	1.37 ± 0.02	1.5 ± 0.2	594.0	0.15	0.00	−0.2	49.7
0.03	242.9	11.41	1.37 ± 0.03	1.5 ± 0.2	589.4	0.15	0.17	−0.3	50.2
0.25	241.7	11.23	1.14 ± 0.04	1.4 ± 0.2	589.4	0.13	1.41	−1.4	58.6

^aThe values x_m and x_c are the computed molar liquid fractions of methane and carbon dioxide, respectively (see the Appendix for details).

^b $\Delta\rho_l = (\rho_l/\rho_w) - 1$, with ρ_l the molar density of the liquid and ρ_w the molar density of pure water at the same temperature and pressure (see the Appendix for details).

water in a homogeneous mixture of methane and carbon dioxide, the effective diffusion coefficient can be approximated with Blanc's law,²³

$$D_w = \left(\frac{y_c}{D_{cw}} + \frac{1-y_c}{D_{mw}} \right)^{-1}, \quad (11)$$

where y_c is the molar fraction of carbon dioxide and D_{cw} and D_{mw} are the diffusion coefficients of water in pure carbon dioxide and methane, respectively, evaluated at the same pressure and temperature as the mixture.

The resulting diffusion constants are listed in Table II. In addition, purely theoretical growth rate lines are shown dashed in Fig. 8. These lines intersect the computed equilibrium point and have a slope given by Eq. (9) with the Fuller/Blanc diffusion constant. Clearly, the Fuller/Blanc approximation overpredicts the experimental values. In the case of 25% carbon dioxide, the deviation is 26%, which is larger than the expected uncertainty of about 10% of the Fuller method.²³ On the other hand, the qualitative behavior of lower growth rates with increasing carbon dioxide fraction is reproduced.

VII. CONCLUSION

We have measured nucleation rates of water at 235 K and 10 bar in methane and in mixtures of methane and carbon dioxide. Compared to the rates in pure methane, 3% of carbon dioxide increases the nucleation rate by a factor of 10; 25% carbon dioxide increases the rate by four orders of magnitude. The slope of the nucleation isotherms in the J - S diagram is unaffected by carbon dioxide; therefore, the number of water molecules in the critical cluster is also independent of the carbon dioxide concentration. In the case of nucleation in pure methane, the critical cluster contains 22 water molecules and five methane molecules, as an application of the pressure nucleation theorem shows. Remarkably, the methane fraction in the critical cluster is a hundred times as large as it is in the water-methane system in equilibrium. The nucleation rates in pure methane are three orders of magnitude higher than literature nucleation rates of water in low-pressure helium or argon.

Nucleation theory reproduces the influence of carbon dioxide qualitatively. The increase in nucleation rate is explained by the reduction in the water surface tension by methane and carbon dioxide. It is estimated that in the mixture with 25% carbon dioxide, the surface tension is 13% lower than the pure-water value; conversely, in pure methane at our conditions, it is 3.5% lower than the pure-water value.

The influence of carbon dioxide is not only visible in the nucleation rates, but also in the growth rates. At equal temperature, pressure and water vapor fraction, the growth rate of the squared droplet radius is about 20% lower in the mixture with 25% carbon dioxide than in pure methane. Since the molar densities of liquid and gas are nearly independent of the carbon dioxide concentration, the lower growth rate is mainly caused by a smaller diffusion coefficient in the mixture with carbon dioxide. The decrease of the diffusion coefficient with increasing carbon dioxide concentration is qualitatively reproduced by the Fuller correlation in combi-

nation with Blanc's law. Quantitatively, the experimental diffusion coefficient in the mixture with 25% carbon dioxide is 20% lower than the Fuller/Blanc prediction.

ACKNOWLEDGMENTS

We thank the Dutch technology foundation STW for their support of part of this research.

APPENDIX: PHYSICAL PROPERTIES

To predict the vapor-liquid phase equilibrium in the water-methane and water-methane-carbon dioxide systems, an EOS is required. We selected the "cubic plus association" (CPA) EOS,²⁵ implemented in the PE2000 program by Pfohl *et al.*²⁶ We fitted the EOS to experimental literature data on phase equilibrium of the three pure substances²⁷⁻²⁹ and the three binary systems water-methane,³⁰ water-carbon dioxide,³¹ and methane-carbon dioxide.³² The reference equations for methane²⁸ and carbon dioxide²⁹ were evaluated with the NIST webbook.³³ The literature data on water vapor fractions in the two binary systems with water is inaccurate and inconsistent, and the CPA prediction of the enhancement factor (Table I) is accurate to 5%, at best. On the other hand, the solubility of methane or carbon dioxide in water is reproduced well.

Another quantity that is required for the prediction of the nucleation rate is the surface tension of water, and the influence of methane and carbon dioxide on that quantity. Literature data³⁴⁻³⁷ were collected and summarized by empirical fits that are accurate to 0.5% in the range of experimental data. The equilibrium vapor pressure of water was taken from Murphy and Koop.³⁸ For the evaluation of the nucleation rate of Eq. (6), the liquid density of Malila and Laaksonen³⁹ was used.

For evaluating Eq. (4), x_m^{eq} and f_e were computed with the CPA EOS. The compressibility factor of methane was taken from the NIST webbook,³³ and v_w^l was computed from the liquid density of Malila and Laaksonen.³⁹ For evaluating Eq. (5), the partial molar volume of water vapor in methane was calculated using the GERG-2004 EOS^{6,7} and the relation $\bar{V} = V + (\partial V / \partial y)_{T,p}$, with $\bar{V}$ the partial molar volume, V the molar volume, and y the water vapor fraction, valid for $y \ll 1$.

Quantities from Eq. (9), listed in Table II, were obtained as follows. The molar density of pure methane was taken from Ref. 28 and the density of the methane-carbon dioxide mixture from the GERG-2004 EOS.^{6,7} The liquid fractions of methane, carbon dioxide and water were computed with the CPA EOS. The density of the liquid could not be taken directly from the CPA model because it is unable to reproduce the temperature dependence and the maximum of the density of water, as noted by Lundström *et al.*⁴⁰ The CPA can, however, be used to approximate the relative density change caused by the solution of methane and carbon dioxide into water. This value was combined with the IAPWS (Ref. 27) density of pure water to obtain the density of the mixture.

¹P. Peeters, J. Hrubý, and M. E. H. van Dongen, *J. Phys. Chem. B* **105**, 11763 (2001).

- ²P. Peeters, G. Pieterse, J. Hrubý, and M. E. H. van Dongen, *Phys. Fluids* **16**, 2567 (2004).
- ³C. C. M. Luijten, R. G. P. van Hooy, J. W. F. Janssen, and M. E. H. van Dongen, *J. Chem. Phys.* **109**, 3553 (1998).
- ⁴V. Holten, D. G. Labetski, and M. E. H. van Dongen, *J. Chem. Phys.* **123**, 104505 (2005).
- ⁵K. N. H. Looijmans, P. C. Kriesels, and M. E. H. van Dongen, *Exp. Fluids* **15**, 61 (1993); K. N. H. Looijmans and M. E. H. van Dongen, *ibid.* **23**, 54 (1997).
- ⁶O. Kunz, R. Klimeck, W. Wagner, and M. Jaeschke, *The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures*, GERG Technical Monograph 15, Vol. 557, Fortschritt-Berichte VDI Energieerzeugung (VDI, Düsseldorf, 2007), http://www.gerg.info/publications/tm15_04.pdf.
- ⁷W. Wagner, Software package for the Calculation of Thermodynamic Properties from the GERG-2004 Wide-Range Reference Equation of State for Natural Gases and Other Mixtures, Ruhr-Universität Bochum, Fakultät für Maschinenbau, Lehrstuhl für Thermodynamik, Bochum (2007), version 11.05.2007.
- ⁸V. V. Sychev, A. A. Vasserman, V. A. Zagoruchenko, A. D. Kozlov, G. A. Spiridonov, and V. A. Tsymarny, *Thermodynamic Properties of Methane* (Hemisphere, Washington, 1987).
- ⁹C. C. M. Luijten, K. J. Bosschaart, and M. E. H. van Dongen, *J. Chem. Phys.* **106**, 8116 (1997).
- ¹⁰The correction is based on Eq. (15) of Ref. 13; in the correction of the current work, not only the temperature dependence of the surface tension but also the temperature dependence of the liquid density was also into account.
- ¹¹See supplementary material at <http://dx.doi.org/10.1063/1.3432623> for tables with experimental nucleation and droplet growth data.
- ¹²Any of the following deviations is sufficient to explain the discrepancy between series A and C: a 7% error in the water vapor fraction, 0.4 bar in initial HPS pressure, 1.3% in the pressure transducer sensitivity, or 1 K in initial temperature. Our investigation resulted in the following maximum possible deviations: 2% in vapor fraction, 0.01 bar in initial pressure, 0.08% in pressure transducer sensitivity, and 0.05 K in initial temperature.
- ¹³C. C. M. Luijten, P. Peeters, and M. E. H. van Dongen, *J. Chem. Phys.* **111**, 8535 (1999).
- ¹⁴D. Kashchiev, *J. Chem. Phys.* **76**, 5098 (1982); D. W. Oxtoby and D. Kashchiev, *J. Chem. Phys.* **100**, 7665 (1994).
- ¹⁵*Nucleation*, edited by A. C. Zettlemoyer (Dekker, New York, 1969); D. Kashchiev, *Nucleation: Basic Theory with Applications* (Butterworth-Heinemann, Oxford, 2000).
- ¹⁶D. W. Oxtoby and A. Laaksonen, *J. Chem. Phys.* **102**, 6846 (1995).
- ¹⁷V. I. Kalikmanov and D. G. Labetski, *Phys. Rev. Lett.* **98**, 085701 (2007).
- ¹⁸J. Wölk and R. Strey, *J. Phys. Chem. B* **105**, 11683 (2001).
- ¹⁹C. C. M. Luijten and M. E. H. van Dongen, *J. Chem. Phys.* **111**, 8524 (1999).
- ²⁰P. W. Atkins, *Physical Chemistry*, 6th ed. (Oxford University Press, Oxford, 1998).
- ²¹M. J. E. H. Muijtens, V. I. Kalikmanov, M. E. H. van Dongen, and A. Hirschberg, *Rev. Inst. Fr. Pet.* **49**, 63 (1994).
- ²²P. Peeters, G. Pieterse, and M. E. H. van Dongen, *Phys. Fluids* **16**, 2575 (2004).
- ²³B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th ed. (McGraw-Hill, New York, 2001).
- ²⁴C. C. M. Luijten, "Nucleation and droplet growth at high pressure," Ph.D. thesis, Technische Universiteit Eindhoven, 1998.
- ²⁵G. M. Kontogeorgis, M. L. Michelsen, G. K. Folas, S. Derawi, N. von Solms, and E. H. Stenby, *Ind. Eng. Chem. Res.* **45**, 4855 (2006); **45**, 4869 (2006).
- ²⁶O. Pföhl, S. Petkov, and G. Brunner, *Ind. Eng. Chem. Res.* **39**, 4439 (2000); "PE 2000 for Windows," (September 2002), version 2.99a, <http://www.tu-harburg.de/v8/gruppe-prof-smirnova/veroeffentlichungen/pe-2000.html>.
- ²⁷W. Wagner and A. Prüss, *J. Phys. Chem. Ref. Data* **31**, 387 (2002); See also IAPWS, Release on the IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use (September 1996), <http://www.iapws.org/relguide/IAPWS95-Rev.pdf>.
- ²⁸U. Setzmann and W. Wagner, *J. Phys. Chem. Ref. Data* **20**, 1061 (1991).
- ²⁹R. Span and W. Wagner, *J. Phys. Chem. Ref. Data* **25**, 1509 (1996).
- ³⁰Z. Duan and S. Mao, *Geochim. Cosmochim. Acta* **70**, 3369 (2006).
- ³¹L. W. Diamond and N. N. Akinfiev, *Fluid Phase Equilib.* **208**, 265 (2003); C. R. Coan and A. D. King, Jr., *J. Am. Chem. Soc.* **93**, 1857 (1971); P. C. Gillespie and G. M. Wilson, "Vapor-liquid and liquid-liquid equilibria: Water-methane, water-carbon dioxide, water-hydrogen sulfide, water-n-pentane, water-methane-n-pentane," Gas Processors Association, Tulsa, OK, Research Report No. RR-48, 1982.
- ³²J. Davalos, W. R. Anderson, R. E. Phelps, and A. J. Kidnay, *J. Chem. Eng. Data* **21**, 81 (1976); M. S.-W. Wei, T. S. Brown, A. J. Kidnay, and E. D. Sloan, *ibid.* **40**, 726 (1995).
- ³³E. W. Lemmon, M. O. McLinden, and D. G. Friend, in *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, edited by P. J. Linstrom and W. G. Mallard (National Institute of Standards and Technology, Gaithersburg MD, 2009), <http://webbook.nist.gov/chemistry/fluid>.
- ³⁴P. T. Hacker, "Experimental values of the surface tension of supercooled water," National Advisory Committee for Aeronautics Technical Report No. 2510, 1951, <http://naca.central.cranfield.ac.uk/reports/1951/naca-tn-2510.pdf>.
- ³⁵B.-S. Chun and G. T. Wilkinson, *Ind. Eng. Chem. Res.* **34**, 4371 (1995).
- ³⁶A. Hebach, A. Oberhof, N. Dahmen, A. Kögel, H. Ederer, and E. Dinjus, *J. Chem. Eng. Data* **47**, 1540 (2002).
- ³⁷W. Sachs and V. Meyn, *Erdöl Erdgas Kohle* **111**, 119 (1995).
- ³⁸D. M. Murphy and T. Koop, *Q. J. R. Meteorol. Soc.* **131**, 1539 (2005).
- ³⁹J. Malila and A. Laaksonen, in *Proceedings of the 15th International Conference on the Properties of Water and Steam*, edited by R. Span and I. Weber (VDI, Düsseldorf, 2008), <http://www.icpws15.de/proceedings.htm>.
- ⁴⁰C. Lundström, M. L. Michelsen, G. M. Kontogeorgis, K. S. Pedersen, and H. Sørensen, *Fluid Phase Equilib.* **247**, 149 (2006).