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Homogeneous nucleation rates of 1-pentanol

Kristina Iland, Jan Wedekind, and Judith Wölk
Institut für Physikalische Chemie, Universität zu Köln, Luxemburger Str. 116, D-50939 Köln, Germany

Paul E. Wagner
Institut für Experimentalphysik, Universität Wien, Boltzmanngasse 5, 1090 Wien, Austria

Reinhard Strey
Institut für Physikalische Chemie, Universität zu Köln, Luxemburger Str. 116, D-50939 Köln, Germany

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We have measured isothermal homogeneous nucleation rates J for 1-pentanol vapor in two different carrier-gases, argon, and helium, using a two-valve nucleation pulse chamber. The nucleation rates cover a range of $10^5 < J/\mathrm{cm}^{-3}\,\mathrm{s}^{-1} < 10^9$ at temperatures between $235 < T/\mathrm{K} < 265$. We observed no influence of the carrier gas on location and slope of the nucleation rate isotherms. These measurements are part of an international effort to examine 1-pentanol using various experimental techniques, which was initiated in Prague in 1995. In the present paper nucleation rate data obtained by several groups are compared to each other and to the classical nucleation theory. As expected, the classical theory is not able to quantitatively predict the experimental results. Nevertheless, relating the experimental data to the classical theory provides a suitable way to compare data of widely differing nucleation rates obtained by different experimental techniques. This comparison helps judging mutual support of the data and, at the same time, provides a rather interesting insight into the accuracy of the individual experimental techniques. [DOI: 10.1063/1.1809115]

I. INTRODUCTION

A number of different devices and methods have been developed to investigate homogeneous gas–liquid nucleation and a variety of chemical compounds has been studied (e.g., Refs. 1–13). Each experiment is working in different regimes of temperature and pressure. Consequently, different measuring windows of nucleation rates are covered.[14] In addition, diverse physicochemical constants where often used to deduce the data—comparisons between these different methods were often complicated. Therefore, at the *Workshop on Nucleation Experiments—State of the Art and Future Developments* in 1995 in Prague it was decided to perform a joint experiment on homogeneous nucleation of 1-pentanol in helium at temperatures of 240 K, 250 K, and 260 K using a variety of different techniques.[15] To preserve comparability, all groups where encouraged to use 1-pentanol from one and the same lot (Lot No. K21223075518, Merck, Germany). A GC/MS analysis of this material made by Rudek *et al.* attested a purity of >99% 1-pentanol.[16] The total experimental pressure was chosen to be approximately 100 kPa and the purity of the carrier gas has been specified to be ⩾99.999%. For reduction of the data a common set of physicochemical properties like surface tension, equilibrium pressure, and density was provided by Zdímal and Smolík (see Table I).[17]

The combined measuring window of the methods used for this joint experiment covers almost 20 orders of magnitude, starting from nucleation rates of $J=10^{-3}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ measured by thermal diffusion cloud chambers up to $J=10^{17}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ reachable with supersonic nozzles. Figure 1 is an overview containing the different methods and their measurable nucleation rates.

The measurements presented in this paper were made in a two-valve nucleation pulse chamber. Its measuring window is reaching from $J=10^5\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$ to $10^9\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$, lying in the middle of the nucleation rates reachable in this joint experiment. We have measured nucleation rate isotherms of 1-pentanol in argon for temperatures from 235 K to 265 K in 5 K steps. In an earlier paper, Strey and Wagner found no influence of the carrier gas on measurements made with a two-piston expansion chamber,[18] which we consider to be a general result for all nucleation pulse chambers. Nevertheless, measurements at 240 K, 250 K, and 260 K were repeated using helium as carrier gas to fulfill the requirements of the joint experiment. The excess number of molecules in the critical cluster was calculated for both carrier gases as a function of temperature. We compared the data with earlier results of Strey and Wagner[18] and Hrubý *et al.*[19] In the scope of the joint experiment the data was also compared to pulse expansion wave tube data by Luijten *et al.*,[20] thermal diffusion cloud chamber data by Rudek *et al.*,[16] piston-expansion wave tube data by Graßmann and Peters[21] and data measured in laminar flow diffusion chambers by Anisimov *et al.*[22] and Lihavainen *et al.*[12] By reducing the experimental data with the classical nucleation theory (CNT), a comparison of all experimental results is possible over a wide range of temperatures and nucleation rates.

TABLE I. Physicochemical constants for 1-pentanol as used in this work. The values where provided by Zdímal and Smolík for use in the joint experiment.

Molar mass/kg mol^{-1}	$m=0.088\,15$	
Specific heat ratio	$\kappa_g=1.1$	
Equilibrium pressure/Pa	$p_e=133.324\exp(90.079\,043-9788.384/T-9.9\ln T)$	
Liquid density/kg m^{-3}	$\rho=\sum_{i=0}^{5} a_i\left(1-\frac{T}{588.15}\right)^{1/3}$	
	$a_0=270$	$a_3=19\,226.001$
	$a_1=1930.229$	$a_4=-18\,559.303$
	$a_2=-8414.762$	$a_5=6555.718$
Surface tension/N m^{-1}	$\sigma=0.026\,854\,69-7.889\times10^{-5}(T-273.15)$	

II. EXPERIMENTAL TECHNIQUE

The experimental setup and the measuring procedure have been described in detail by Strey *et al.*,[23] so just the fundamental issues will be repeated here.

The vapor–carrier-gas mixture is adiabatically expanded to a lower pressure p_{exp} and consequently to a lower temperature T_{exp} well inside the metastable regime. Nuclei form in the supersaturated vapor phase. After a short period of time ($\Delta t\sim 1$ ms), we slightly recompress the mixture, which abruptly stops nucleation while still retaining a supersatured vapor phase. Thus, the already formed nuclei are still able to grow: nucleation and growth are decoupled. The growing droplets are then "counted" using constant-angle-Mie-scattering,[24] i.e., the number density N in the scattering volume is determined. A typical pressure pulse and the corresponding light scattering signal for a 1-pentanol experiment is shown in Fig. 2.

Since nucleation and growth are decoupled, the nucleation time is limited to the length Δt of the plateau of the pressure pulse, which can be determined geometrically. The nucleation rate is then easily calculated as

$$J=\frac{N}{\Delta t}. \tag{1}$$

The corresponding supersaturation S is defined as the ratio of the actual vapor pressure p_v and the equilibrium vapor pressure p_e at the given temperature T_{exp},

$$S=\omega\frac{p_{\mathrm{exp}}}{p_e(T_{\mathrm{exp}})}=\frac{p_v}{p_e(T_{\mathrm{exp}})}, \tag{2}$$

where ω is the ratio of vapor pressure to carrier-gas pressure. It is also worth mentioning, that the optical detection system has been thoroughly recalibrated between the helium and the argon measurements. Also, the piezo-pressure transducer was calibrated after every temperature change of the chamber.

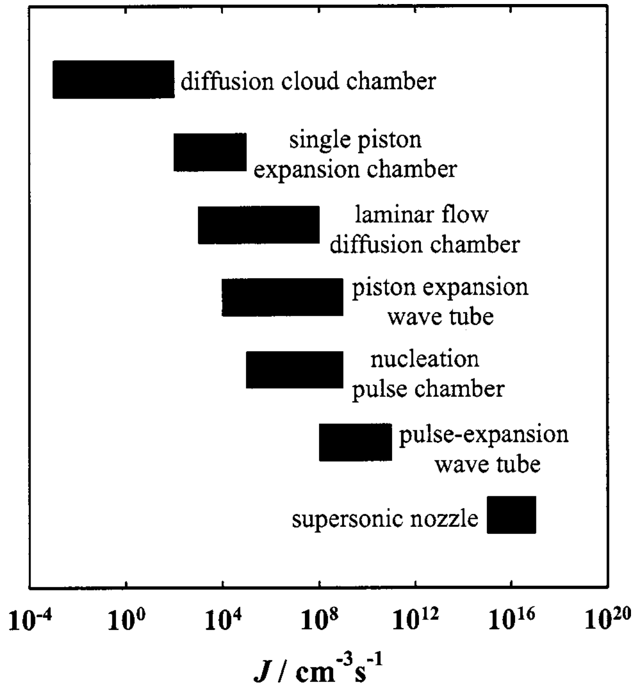

FIG. 1. Different techniques for homogeneous nucleation experiments and their respective ranges in nucleation rates J.

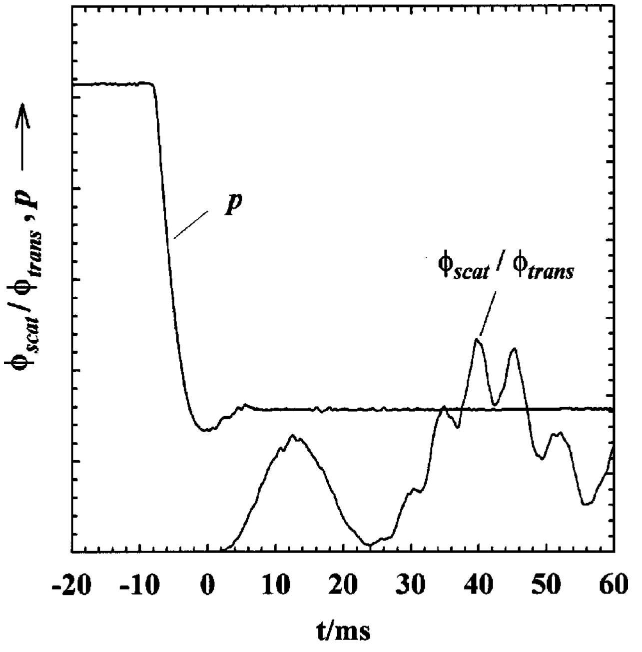

FIG. 2. Typical nucleation pulse and corresponding light scattering signal for a 1-pentanol experiment.

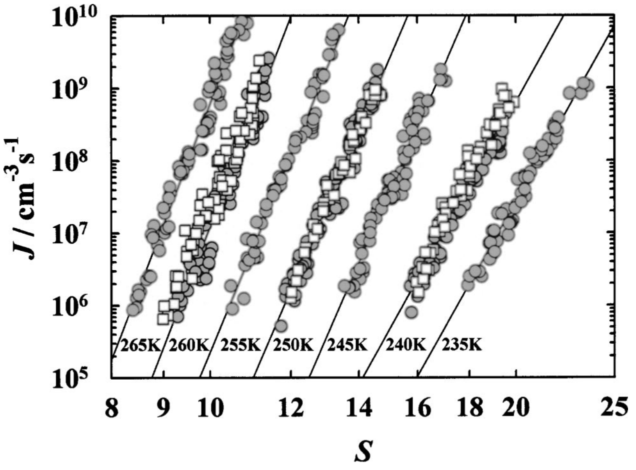

FIG. 3. Nucleation rates J of 1-pentanol as a function of supersaturation S for nucleation temperatures T_{exp} from 235 K to 265 K using argon (filled circles) or helium (empty squares) as carrier gas. The solid lines are straight line fits to the data produced in argon as carrier gas.

III. NUCLEATION OF 1-PENTANOL IN ARGON AND HELIUM

The experimental data for measurements on 1-pentanol in argon and 1-pentanol in helium is available online.[25] In Fig. 3 the nucleation rates J determined are plotted as a function of supersaturation S.

The data for the nucleation of 1-pentanol in argon (filled circles) coincides with the data of 1-pentanol in helium (empty squares) within experimental error considering the scatter of data points. This finding is in perfect agreement with the results of Strey and Wagner,[18] who made the first measurements of 1-pentanol in a two-piston expansion chamber, a former version of the two-valve chamber used in this work. They used argon, helium and nitrogen as carrier gases for nucleation experiments at temperatures around 250 K and 270 K. The lines in Fig. 3 are straight line fits for the 1-pentanol in argon data. The lines for the 1-pentanol in helium cases were left out to retain lucidity. The slopes of these lines yield the excess number n^*_{exp} of molecules in the critical cluster according to the nucleation theorem by Kashchiev,[26]

$$n^*_{\mathrm{exp}} \approx \left(\frac{\partial \ln J}{\partial \ln S} \right)_T . \tag{3}$$

The $(\ln J/\ln S)_T$ dependence will generally not correspond to a straight line. Nevertheless, for the comparatively small experimental window of our experimental data the deviations from a straight line fit are negligible. Thus, we feel (and tested) that a more elaborate fitting method (as used by some groups) serves no purpose, at least when it comes to the determination of critical cluster sizes. The determined critical cluster sizes n^*_{exp} for the given experimental temperature T_{exp} (averaged over the whole isotherm) can be found in Table II.

TABLE II. Averaged temperatures T_{exp} of the measured isotherms, supersaturation S_0 where the experimental nucleation rate equals 10^7 cm^{-3} s^{-1} and experimentally determined critical nuclei sizes n^*_{exp}.

Carrier gas	T_{exp}/K	ΔT_{exp}/K	S_0	n^*_{exp}
Ar	264.98	0.12	9.0	37
Ar	260.03	0.06	9.9	36
Ar	255.05	0.05	11.2	34
Ar	250.05	0.05	12.6	33
Ar	245.01	0.05	14.4	32
Ar	240.08	0.05	16.9	25
Ar	235.00	0.05	19.2	25
He	260.06	0.05	9.7	33
He	250.07	0.05	12.7	32
He	240.09	0.06	16.8	28

The value ΔT_{exp} is the standard deviation of experimental temperature. Also given is the value S_0 where the experimental nucleation rate equals 10^7 cm^{-3} s^{-1}. We estimate the error of n^*_{exp} to be ±10% and of S_0 to be ±4% due to the straight line fit and the data scatter. Taking this into account the values of n^*_{exp} are in agreement with the ones found by Hrubý *et al.*,[19] while the slopes of the isotherms presented in this work are based upon 10 times more measurements each.

In Fig. 4 the critical cluster sizes n^*_{exp} are compared to the sizes n^*_{GT} predicted by the Gibbs–Thomson equation using the supersaturation S_0 at $J = 10^7$ cm^{-3} s^{-1},

$$n^*_{\mathrm{GT}} = \frac{32\pi}{3} \frac{v^2 \sigma^3}{(kT \ln S_0)^3} . \tag{4}$$

Here, σ is the bulk surface tension and v is the volume of a single molecule (in the liquid phase) calculated from the liquid density ρ. The dashed line in Fig. 4 corresponds to a perfect agreement between experiment and theory.

The critical cluster sizes for both carrier gases agree within the error range. For the higher temperatures the experimental values are lying close to the prediction, except for the highest temperature measured with helium as carrier gas. For the lower temperatures and correspondingly smaller

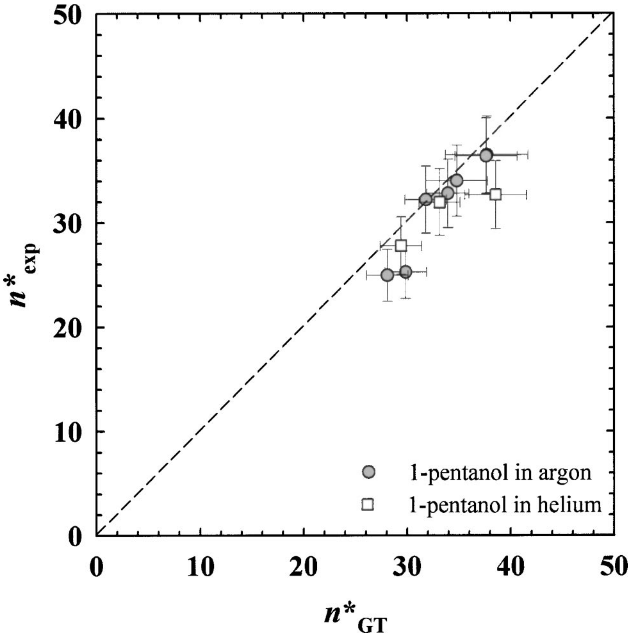

FIG. 4. Comparison of the experimentally determined critical cluster sizes n^*_{exp} to the sizes n^*_{GT} calculated with help of Gibbs–Thomson equation.

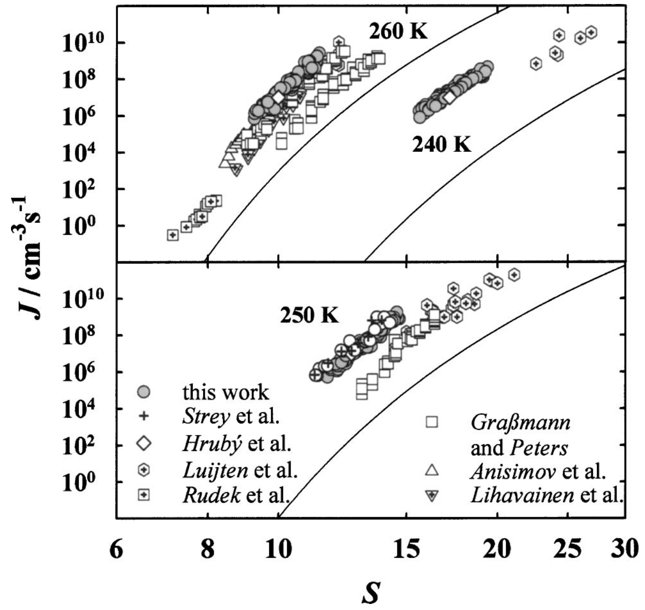

FIG. 5. Nucleation rates determined of this work (filled circles) for 240 K and 260 K (upper plot) and 250 K (lower plot) using argon as a carrier gas in comparison with other data from the international joint experiment. The solid lines show the predictions by the CNT.

cluster sizes the agreement gets worse, even though the difference is still astonishingly small considering the capillarity approximation inherent in the Gibbs–Thomson equation.

IV. COMPARISONS IN THE SCOPE OF THE JOINT EXPERIMENT

The demands of the international joint experiment on 1-pentanol were to perform nucleation experiments at temperatures of 240 K, 250 K, and 260 K using helium as carrier gas. Unfortunately, not all research groups where able to fulfill these conditions due to their individual experimental setup. For example, not all of them used helium as carrier gas. While we could show that the carrier gas does not have an influence on nucleation rates measured with the nucleation pulse chamber, this is not necessarily the case for other devices, e.g., the thermal diffusion cloud chamber.[27] For some devices it turned out that not all the preferred temperatures are lying in their given measuring window, so some of them were measured at more suitable temperatures. Figure 5 shows all up to now available experiments performed in the scope of the joint experiment for 240 K and 260 K (upper figure) and 250 K (lower figure).

We decided to include our data for 1-pentanol in argon (filled circles) to provide consistency with Fig. 5. It can be seen that our data agrees well with the data of Hrubý *et al.*[19] (empty diamonds) and Strey and Wagner[18] (empty circles). The data of Strey and Wagner plotted here is the combined data for the three different carrier gases they used (argon, helium, and nitrogen). Their data was measured in a former version of the nucleation pulse chamber and due to a missing separate mixing unit not measured isothermally. They used a different vapor-pressure equation to calculate the experimental supersaturation, rather than the one used in this work. For comparison, their data was converted using the equation given in Table I. As already mentioned, the data of Hrubý *et al.* is not based on such an abundant number of data points for each isotherm as the data presented in this work. Thus, the agreement is quite satisfactory. Luijten *et al.*[20] used a pulse-expansion wave tube to make measurements at all three demanded temperatures (crossed hexagons) using helium as carrier gas. Their measuring window is lying above the one reachable with the nucleation pulse chamber, just giving an overlap at 260 K, where they measured slightly lower nucleation rates than the ones presented in this work. Graßmann and Peters[21] delivered data measured with a piston-expansion wave tube using nitrogen as a carrier gas (empty squares). At 250 K their nucleation rates are approximately one order of magnitude lower than the data from this work. At 260 K they made three different experimental series using two different values for initial temperature T_0 and pressure p_0. The two series starting from the same temperature (297.7 K) but different pressures are just lying slightly below the data given in this paper, while the difference to the third series with a higher starting temperature (310.1 K) is approximately one order of magnitude. At 260 K, two datasets taken from laminar flow diffusion chamber experiments using helium as carrier gas are also plotted. The data given by Anisimov *et al.*[22] (empty triangles) shows good agreement with the data from this work, while the data by Lihavainen *et al.*[12] (turned crossed triangles) tends to deviate to lower nucleation rates at lower supersaturations. The data given by Rudek *et al.*[16] was measured using a thermal diffusion cloud chamber and helium as a carrier gas and therefore lies at much lower nucleation rates and supersaturations than the data presented in this work.

The solid lines in Fig. 5 represent the predictions of the CNT by Becker and Döring[28] for the given temperatures,

$$J_{\mathrm{CNT}}=K_{\mathrm{CNT}}\exp\left\{-\frac{\Delta G^*_{\mathrm{CNT}}}{kT}\right\}, \tag{5}$$

$$K_{\mathrm{CNT}}=\sqrt{\frac{2\sigma}{\pi m}}\,v_l N_1^2, \tag{6}$$

$$\Delta G^*_{\mathrm{CNT}}=\frac{16\pi}{3}\,\frac{v_l^2\sigma^3}{(kT)^2(\ln S)^2}. \tag{7}$$

Here σ is the surface tension, m and v the molecular mass and volume, T the temperature, and N_1 the actual monomer number concentration calculated from the vapor pressure and the ideal gas law. Figure 5 allows a direct comparison of the experimental results measured with different devices at the certain temperatures demanded by the international joint experiment. However, most of the experimental series already mentioned span greater or different temperature ranges. As these measuring windows differ substantially with respect to nucleation rates and supersaturations, a direct comparison in the form of a $\ln J/\ln S$ plot is not suitable. The CNT can act as a common base for comparison between the different experiments. The ratio $J_{\mathrm{exp}}/J_{\mathrm{CNT}}$ of experimental nucleation rates and nucleation rates predicted by CNT is calculated for all available experimental data. Then, the average is taken over all values corresponding to one measur-

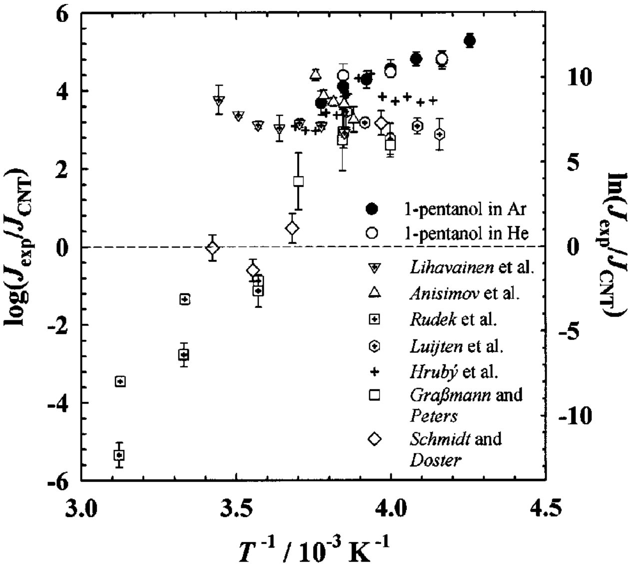

FIG. 6. Ratio of experimental nucleation rates J_{exp} and nucleation rates J_{CNT} predicted by CNT as a function of inverse temperature T.

ing series and one nucleation temperature. This way we are able to compare all experiments in a single diagram.

In Fig. 6 the experimental data reduced in the above mentioned way is plotted as function of inverse temperature. All nucleation rates measured by different groups and their discrepancy to CNT can be compared as well as the temperature dependence of the reduced data. The dashed line in Fig. 6 would mean perfect agreement of experiment and theory.

Altogether, Fig. 6 shows a rather ‘‘chaotic’’ picture. The results just coincide around 260 K, but show a different dependence on temperature. For higher or lower temperature, they diverge and show discrepancies of up to four orders of magnitude. Let us try to sort the different results.

The data by Schmitt and Doster[29] (empty diamonds) was measured in an expansion cloud chamber using argon as carrier gas. Although there is no quantitative agreement between their measurements and the ones by Rudek *et al.*[16] (crossed squares), the temperature dependence is similar. They predict agreement between theory and experiment at a temperature around 280 K. Recently, Fergusson *et al.*[30] made a recalculation of the data by Rudek *et al.* using a new model, which takes the wall heating of the thermal diffusion cloud chamber into account. They found that their results at 320 K are shifted by about two orders of magnitude, while this shift gets weaker to lower temperatures—the data at 260 K is nearly unaffected. This would result in a much weaker slope of their reduced nucleation rates. Also, a weaker temperature dependence is shown by the data from this work (filled circles) and the data measured by Graßmann and Peters[21] (empty squares), so that based on these data the temperature of agreement between experiment and CNT is expected to lie at much higher temperatures. The data measured by Lihavainen *et al.*[12] (turned crossed triangles) and Luijten *et al.*[20] (crossed hexagons) are also lying parallel in respect to each other, but now with an inverted slope compared to results already mentioned. Anisimov *et al.*[22] also found this inverted temperature dependence, but with a steeper slope. In summary, we find a positive slope with a too strong temperature dependence of theory for the data of the nucleation pulse chamber, the expansion cloud chamber, the thermal diffusion cloud chamber and the piston-expansion wave tube. A negative slope is found for data produced by laminar flow diffusion chamber experiments and the experiments made with the expansion wave tube.

In an attempt to analyze the fundamental background, we assume that our experimental nucleation rates J_{exp} can be described correctly by a Boltzmann ansatz similar to the one for classical nucleation rate J_{CNT} [Eq. (5)]. A similar approach has already been made by Kacker and Heist.[4] By dividing the experimental nucleation rate by the CNT we get

$$\ln\frac{J_{exp}}{J_{CNT}}=\ln\frac{K_{exp}}{K_{CNT}}+\frac{\Delta G^*_{CNT}-\Delta G^*_{exp}}{kT}. \tag{8}$$

Here K is the kinetic prefactor and ΔG^* is the formation free energy of the critical nucleus. The indices ‘‘exp’’ and ‘‘CNT’’ represent the experimental and theoretical values, respectively. Equation (8) suggests, that the ratio $\ln(J_{exp}/J_{CNT})$ should be a linear function of $(1/T)$ (under the mild assumption that the logarithm of ratio of the experimental and the classical prefactor is temperature independent[31,32]) and we can express it in the simple form of[31]

$$\ln\frac{J_{exp}}{J_{CNT}}=A+\frac{B}{T}, \tag{9}$$

with

$$A=\ln\frac{K_{exp}}{K_{CNT}}+\frac{\Delta\overline{S}^*_{exp}-\Delta\overline{S}^*_{CNT}}{k}$$

and

$$B=\frac{\Delta H^*_{CNT}-\Delta H^*_{exp}}{k}.$$

From a least squares fit to our data we find these parameters to be $A=-39$ and $B=15\,643$ K. This finding seems to confirm the suggestion made by McGraw and Laaksonen, that the CNT can be effectively corrected by one single temperature dependent parameter.[33] A deeper understanding of the origin, the significance and the numerical magnitude of these parameters remains a task for future work in nucleation research.

V. SUMMARY AND CONCLUSION

Homogeneous nucleation rates of 1-pentanol have been measured for temperatures $235\,\mathrm{K}<T<265\,\mathrm{K}$ in steps of 5 K using argon as a carrier gas. The measurements at 240 K, 250 K, and 260 K were repeated using helium as a carrier gas. In accordance with the measurements of Strey and Wagner[18] we found no influence of the carrier gas to our experimental results. Quantitatively, there is good agreement of the data presented in this work with older data measured with the nucleation pulse chamber.[18,19] At 260 K our data is lying on top or just slightly above the data measured with laminar flow diffusion chambers,[12,22] expansion wave tube,[20] and piston-expansion tube.[21] A further comparison exhibits significant differences in the temperature dependence of the data measured by different techniques. If anything, these joint experiments on homogeneous nucleation seem to raise even more questions about the quality of the different techniques than in 1995. Recently, Wölk *et al.* showed that their empirically determined function to calculate nucleation rates of water is in good agreement with results over a range of 20 orders of magnitude.[31] This function is based on measurements performed with the same nucleation pulse chamber we used in this work, spanning just four orders of magnitude in terms of nucleation rates. This unique finding adds confidence to the data we present in this work.

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[25] See EPAPS Document No. E-JCPSA6-121-010444 for experimental data for nucleation of 1-pentanol in argon and helium. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.
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