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Homogeneous nucleation rates for n-pentanol from expansion wave tube experiments

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Within the scope of joint experiments by the international Nucleation Workshop Group, nucleation experiments on n-pentanol were carried out using a pulse-expansion wave tube. Data were obtained for nucleation at temperatures between 240 K and 260 K. Total pressures of the carrier gas (heium) during nucleation varied from 89 to 109 kPa. The results are presented in tabular form, to facilitate future comparison. Our results are consistent with existing data by Hruby et al. Comparisons are made to the Kinetic Classical Theory (KCT) as well as to the semiphenomenological theory by Kalikmanov and Van Dongen (KvD–SPT). Although both theories predict nucleation rates that are apparently too low in the temperature range of interest, the KvD–SPT is approximately two orders of magnitude closer to the experimental results. © 1997 American Institute of Physics.

I. INTRODUCTION

During the last few decades, the emphasis in experimental research on nucleation has shifted from the determination of critical supersaturations (onset activities) to measurements of quantitative nucleation rates. The latter have become possible due to the development of several methods to separate the nucleation and growth stages, which together constitute the process of homogeneous condensation. An excellent review of experimental techniques is provided by Heist and He.1

On the other hand, theoretical modelling of the nucleation process is still in progress. Several routes to describe the formation of critical nuclei out of a vapor consisting of a distribution of (subcritical) clusters have been developed until now.2,3

Comparison of the experimentally determined nucleation rates to these models still meets considerable problems, since severe discrepancies exist between data sets obtained by different experimental groups. These are first of all caused by the use of different substances for nucleation studies. Second, every setup has its own limiting range of operating conditions (pressures, temperatures and activities), which constitutes another source of scatter. An additional problem, the use of different physico-chemical parameters even when the same compounds are studied, might be overcome by recalculation of results, provided that “raw” data are available. For example, nucleation temperatures and supersaturations for an expansion-type experiment might be recalculated afterwards, using alternative equations of state or alternative vapor pressure equations. However, in order to do this, the measured pressure history has to be available, which is not always the case. Finally (but certainly most interesting), the use of different measurement principles should be mentioned.

In order to verify the results of the varying experimental techniques, the other sources of scatter have to be eliminated. To achieve this, an international cooperation has been initiated during the Workshop on Nucleation Experiments in Prague, June 1995. The criteria for choosing the substance, and the conditions under which it should be studied, can be found elsewhere.4 One agreed on the choice of n-pentanol at temperatures of 240, 250 and 260 K, in the presence of helium with a pressure of approximately 100 kPa as a carrier gas.

The present paper constitutes our contribution to the Workshop project. We present data in the full range of conditions mentioned above, obtained using our pulse-expansion wave tube. A detailed description of this method can be found elsewhere;5,6 in the next section we merely summarize the principles. After presenting the results in tabular and graphical form, they are compared to existing data by Hruby et al.7 and Smolik.8 Comparisons will also be made to the Kinetic Classical Theory2 and to the semi-phenomenological model by Kalikmanov and Van Dongen.3 The latter is based on the Fisher model for the cluster distribution and a radius-dependent form for the microscopic surface tension.

II. WAVE TUBE EXPERIMENTS

In our expansion wave tube setup (see Fig. 1), extensively described in Refs. 5 and 6, the separation of nucleation and droplet growth stages in time is accomplished by the well-known nucleation pulse method. The pulse-like pressure history is obtained at the endwall of the high pressure section (HPS) in the following way. After rupture of the membrane by electrically heating it, an expansion wave travels in the direction of the HPS endwall. The shock wave, travelling in the reverse direction, generates another small expansion at a local widening in the tube, followed by a weak recompression. When these waves reach the HPS endwall, an effective nucleation pulse is obtained. After the pulse, the pressure remains approximately constant until the shock reflection from the LPS endwall returns. During this period, droplet growth is observed using Constant Angle Mie Scattering (CAMS) under 90°. The time-resolved radius is used to calculate time-resolved extinction efficiencies. These
are in their turn used to evaluate the droplet density from the attenuated transmission signal. Division by the duration of the nucleation pulse (approximately 0.3 ms) yields the nucleation rate. Typical recorded signals of one experiment are shown in Fig. 2.

In order to perform reproducible measurements in this way, great care has to be taken in preparing a well-defined mixture of the \( n \)-pentanol vapor and the carrier gas. Therefore, the preparation stage of our experiment consists of the following steps. First, after mounting a membrane, the HPS is evacuated during 1 h in order to remove all residual gas and foreign particles. Then, the pentanol vessel is separately pumped for 1 min. This is done in order to remove any residual air that might have leaked into the vessel from the outside. After assuring in this way the purity of the \( n \)-pentanol vapor in the vessel, it is opened until the desired vapor pressure \( p_{v,0} \) (measured using an Edwards 600 AB static pressure transducer) is reached in the test section. Due to wall adsorption, it takes typically 45 min for the vapor pressure to stabilize. The measured vapor pressure is corrected for the small leakage of ambient air into the system—at a rate of 0.015 Pa/min—during the stabilization period. At this stage, the helium is added, up to the desired initial pressure \( p_0 \) (obtained from a Druck PDCR81 transducer). Homogeneity of composition is restored by applying a circulation pump for 15 min, after which the mixing circuit valves are closed. Now, the initial temperature \( T_0 \) is read from a Keithley 871A thermocouple, and the experiment is started.

Besides the nucleation rate, the thermodynamic conditions during nucleation have to be measured or calculated. These are obtained from the initial conditions described above, and the pressure history. The latter is recorded from a Kistler 603B, in combination with a Kistler 5001 charge amplifier. The experimental temperature \( T \) and pressure \( p \) are measured using an Edwards 600 AB transducer. The temperature due to this approximation can be shown to be slightly with temperature, we used the value \( \gamma_0 = 1.07 \) as an average value during the expansion. The error in nucleation temperature due to this approximation can be shown to be smaller than \( 10^{-2} \) K, which is clearly within the total uncertainty in \( T \).

$$
\gamma_{\text{mix}} = c_{p, \text{mix}} / c_v, \text{mix}
$$

where \( c_v, \text{mix} \) is calculated according to

$$
g_{\text{mix}} = 1 + \left( \frac{1}{\gamma_g - 1} \right)^{-1} - \left( \frac{1}{\gamma_g - 1} \right)^{-1}, \tag{1}
$$

based on weighed averaging of the mixture’s isochoric heat capacity \( c_v \). Although the heat capacity of \( n \)-pentanol varies slightly with temperature, we used the value \( \gamma_0 = 1.07 \) as an average value during the expansion. The error in nucleation temperature due to this approximation can be shown to be smaller than \( 10^{-2} \) K, which is clearly within the total uncertainty in \( T \). This uncertainty equals 0.5 K, and is largely

### Table I. Physico-chemical properties of \( n \)-pentanol used in this work. All values were collected by Žďámal and Smolík for collective use by the Nucleation Workshop Group.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (units)</th>
</tr>
</thead>
</table>
| Molar mass        | 0.08815 kg mol
| Liquid density    | 1.13324 g cm
| Surface tension   | 0.02684 J cm
| Vapor pressure    | 133.324 Pa
| Adiabatic parameter | 1.07  |
| Refraction index  | 1.41          |

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caused by the uncertainty in the dynamic pressure measurement. For helium, the ideal value $\gamma_g = 5/3$ is used.

In order to obtain the experimental supersaturation ratio, one needs the nucleation temperature and the partial vapor pressure $p_{v,exp}$. The latter is obtained from the initial vapor pressure $p_{v,0}$ and the ratio of total nucleation pressure to total initial pressure. Supersaturations are accordingly calculated from the expression

$$S = \frac{p_{v,exp}}{p_{sat,exp}} = \frac{p_{v,exp}}{p_0} \times \frac{p_{exp}}{p_{sat}(T_{exp})}.$$  \hspace{1cm} (2)

The correlation to be used for the saturated vapor pressure $p_{sat}$ has been agreed to be the one by Schmeling and Strey,$^9$ given in Table I. All other listed correlations were also taken according to the agreements of the Nucleation Workshop Group.$^{10}$

III. RESULTS AND DISCUSSION

Since the main objective of this paper is to provide nucleation data for future comparison, we summarize all measured values in Table II.

Values of the experimental nucleation rate as a function of the $n$-pentanol supersaturation (which, of course, equals the $n$-pentanol activity in this case) are represented in Fig. 3. In this graph, only the data points of the 240, 250 and 260 K series are plotted. For one typical point at each experimental
temperature, representative error bars are included in both directions. The nucleation rate is measured with an accuracy better than 30%. The error in the supersaturation stems largely from the uncertainty in experimental temperature. Since the latter equals 0.5 K, errors in the supersaturation can be calculated to yield approximately 1.7, 1.1 and 0.6 at 240, 250 and 260 K, respectively. Even within the rather large uncertainty, the data at 260 K seems to give a steeper $S$-dependence than expected. This might be associated with problems of vapor depletion and heat release, since the embryonic droplets grow very fast at the higher temperatures and rates.\(^7\) Due to this rapid growth, only one out of twelve experiments was successful at 260 K.

During recent years, it has become clear that the number of molecules in the critical cluster can be derived from experimental data, \textit{independently} of any nucleation model, by applying the so-called nucleation theorem.\(^11\) For low density vapors, it can be written in the form\(^7\)

$$n^* = \frac{\partial \ln J(S,T)}{\partial \ln S} - 1.$$  \hspace{1cm} (3)

In view of the relatively large scatter in the supersaturation—obviously caused by the very low saturated vapor pressures of \textit{n}-pentanol at the present temperatures—and the number of experiments for each series, we believe that application of the nucleation theorem to our data only makes sense for the large set of 250 K data. This results in an estimated critical cluster size of 22 molecules for a nucleation rate of \(10^{10} \text{ cm}^{-3} \text{s}^{-1}\).

In Fig. 3, theoretical curves for the temperatures of interest are included for the semiphenomenological theory of Kalikmanov and Van Dongen.\(^3\) It finds its basis in the Fisher classical theory. The nucleation rate can be written as

$$J_{\text{KCT}} = \frac{2\sigma M}{\pi N_\text{A} \rho_s^2 T^2} \frac{1}{S} \exp\left(-\frac{16\pi M^2}{3N_\text{A} \rho_s^2 k_\text{B} T^2 \ln^2 S}\right).$$  \hspace{1cm} (4)

where $k_\text{B}$ and $N_\text{A}$ have their usual meanings and other properties can be found in Table I. Results of the KCT are left out in Fig. 3, because its values are up to 5 orders of magnitude lower than experimental data. This result seems to be in contradiction with the results by Hrubý \textit{et al.},\(^7\) who report a rather satisfactory agreement between experiment and classical theory. The difference has to do with their inclusion of the factor $\exp(\Theta)$ into classical theory, $\Theta$ being a dimensionless surface tension. We prefer to omit this factor, since its physical basis is somewhat questionable, as was recently pointed out by McClurg and Flagan.\(^12\) We did include, however, the $1/S$ factor into the classical prefactor, which is generally believed to be more consistent.\(^3,12\)

In Fig. 4, we compare our experimental results to predictions of both theories mentioned. We deduce from the graph that the KCT underestimates the measured nucleation rates by approximately four to five orders of magnitude, whereas the KvD–SPT underestimates it by only two orders of magnitude.

In Fig. 5, some representative data points by Hrubý \textit{et al.}\(^7\) —also obtained in an expansion chamber setup—are presented in the same fashion. It is important to stress, that the results by Hrubý are measured at nucleation rates about three orders of magnitude lower than the present ones. Within the uncertainty of the data points in Fig. 4 (approximately one order of magnitude, largely caused by the uncertainty in the theoretical rate due to the error in $S$), we conclude that our results are consistent with the data by Hrubý.
In Fig. 5, we also included recent measurements by Smolík,\(^8\) summarized as one single point. This data was measured at nucleation rates near 1 cm\(^{-3}\) s\(^{-1}\), while ours are higher by about ten orders of magnitude. Since both nucleation models are applied over the whole range of rates—and critical cluster sizes—it is rather remarkable that the ratio between experiment and theory does not vary strongly than reported here. Still, this does not exclude the possibility that the deviation is partly caused by the use of different measuring principles, since the data by Smolík was measured in a Thermal Diffusion Cloud Chamber. Recently, the quality of diffusion cloud chamber data has become subject of discussion, due to the possible occurrence of buoyancy driven convection.\(^13\)

We would like to stress at this point, that the above comparisons to theoretical models are first of all meant as a guideline for mutual comparison of both presently available data series and future measurements. We believe that comprehensive discussions about the validity of nucleation models for this system are more meaningful if additional data, in a larger range of nucleation rates, will have been provided by other members of the Workshop Group on Homogeneous Nucleation.

**IV. CONCLUSIONS**

We have presented a comprehensive data series on homogeneous nucleation of \(n\)-pentanol in a carrier gas of helium. Results were obtained using an expansion wave tube setup, at temperatures varying from 240 K to 260 K and total pressures between 89 and 109 kPa. Nucleation rates varied from \(10^6\) to \(10^{11}\) cm\(^{-3}\) s\(^{-1}\). Our measurements constitute part of an international program of nucleation studies on \(n\)-pentanol, as agreed on by the Workshop Group on Nucleation in Prague, June 1995.

Dividing measured nucleation rates by theoretical predictions of two nucleation models, yields the following general picture. The semiphenomenological theory by Kalikmanov and Van Dongen underestimates the experimental rates by about two orders of magnitude. For the (kinetic) Classical Theory, experiment is underestimated by four to five orders of magnitude. Comparing the results in this way to existing data at lower nucleation rates, obtained by Hruby et al. using a similar expansion chamber-like setup, indicates that both data series are mutually consistent. Experimental nucleation rates at 260 K by Smolík, obtained at supersaturations \(S \approx 8\) using a Thermal Diffusion Cloud Chamber, are about ten orders of magnitude lower than ours at \(S \approx 12\). Lack of data in the intermediate range inhibits an unambiguous check of mutual consistency at this moment.

The main objective of the present paper has been to offer new data for future comparison to results obtained with other devices. When measurements will be available over a larger range of nucleation rates, the problem of mutual consistency can be more fully addressed. Not until that time, an assessment can be made of the quality of various existing nucleation models for the present system.

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