

Matthias Linnemann, Jadran Vrabec

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# Vapor-Liquid Equilibria of Nitrogen + Diethyl Ether and Nitrogen + 1,1,1,2,2,4,5,5,5-Nonafluoro-4-(trifluoromethyl)-3-pentanone by Experiment, Peng-Robinson and PC-SAFT Equations of State

Matthias Linnemann and Jadran Vrabec\*

*Lehrstuhl für Thermodynamik und Energietechnik, Universität Paderborn, Warburger  
Straße 100, 33098 Paderborn, Germany*

E-mail: jadran.vrabec@upb.de

Phone: +49 (0)5251 602421. Fax: +49 (0)5251 603522

## Abstract

The saturated liquid line of the systems nitrogen ( $N_2$ ) + diethyl ether and  $N_2$  + 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone (Novec 649) is measured along three isotherms, i.e. 390 K, 420 K and 450 K; 360 K, 390 K and 420 K, respectively. The employed gas solubility apparatus, based on the synthetic method, allows to measure points up to the critical region of these mixtures. The experimental data are used to correlate the Peng-Robinson and PC-SAFT equations of state (EOS). For the parametrization of the system  $N_2$  + diethyl ether the Peng-Robinson EOS is combined with the Huron-Vidal mixing rule and the non-random two-liquid (NRTL) excess Gibbs energy model, for the system  $N_2$  + Novec 649 the quadratic mixing rule is used.

# Introduction

To make liquid fueled energy conversion processes more efficient, it is important to understand the often complex fluid phase behavior of liquids injected in form of droplets into combustion chambers, filled with supercritical gas. Transcritical jets undergo a sequence of thermodynamic phenomena, like mixing, vaporization and change of state in the supercritical regime with respect to the liquid.<sup>1</sup> These issues are investigated by the Collaborative Research Center Transregio 75 'Droplet Dynamics Under Extreme Ambient Conditions' (SFB-TRR75),<sup>2</sup> funded by Deutsche Forschungsgemeinschaft (DFG). In this context, the injection of acetone droplets<sup>3</sup> and of *n*-heptane droplets<sup>4</sup> into a nitrogen environment was studied in the past. For undertaking this task, our group contributed vapor-liquid equilibrium (VLE) data for the system nitrogen + acetone.<sup>5</sup> Subsequently, studies of the same kind for the systems nitrogen + diethyl ether and nitrogen + Novec 649 are underway in SFB-TRR75. Therefore, again VLE data of these systems are necessary, but not available in the literature. Hence, measurements in a broad temperature range up to the near-critical region were done in the present work for both systems. The employed apparatus operates with the synthetic method, measuring points on the saturated liquid line at temperatures of 390 K, 420 K and 450 K up to a maximum pressure of 24 MPa for the system nitrogen + diethyl ether and at temperatures of 360 K, 390 K and 420 K up to a maximum pressure of 19 MPa for the system nitrogen + Novec 649. Furthermore, the Peng-Robinson equation of state and the Perturbed Chain - Statistical Associating Fluid Theory (PC-SAFT) EOS were parametrized and compared for both systems. With these models, VLE data can be calculated over the entire range of interest.

# Experimental setup

## Apparatus

The main part of the present measuring apparatus was a high pressure view cell that was constructed for temperatures up to 600 K and pressures up to 70 MPa. The cell was located in a vacuum chamber and was electrically heated, which allows for an effective and precise temperature regulation. The temperature measurement was realized by calibrated platinum resistance thermometers with a basic resistance of 100  $\Omega$  (Pt100), which have a measuring error of  $\pm 0.04$  K.<sup>6</sup> The pressure in the cell was measured by a pressure transducer with a measuring scale of 70 MPa. The gaseous component was filled into the cell from a gas bottle, where the feed line was equipped with a pressure transducer with a measuring scale of 20 MPa. The liquid component was filled into the cell with a piston screw pump, with which the internal volume can be calculated from the knowledge of the axial piston position. The pressure of the fluid in the pump, that was also equipped with a platinum resistance thermometer, was determined by a pressure transducer with a measuring scale of 100 MPa. The pressure transducers were of the same model 'Super TJE' by 'Honeywell Test & Measurement' with a given accuracy of 0.1% of the full measuring scale. More details on the apparatus were described in a preceding work by Windmann et al.<sup>6</sup>

## Materials

The nitrogen had a volume fraction of 0.99999 (nitrogen 5.0) and was purchased from 'Air Liquide'. The liquid components, diethyl ether with a purity of  $\geq 99.7\%$  by 'Merck' and Novec 649 with a purity of  $\geq 99.8\%$  by '3M', were degassed under vacuum. The purity data were provided by the suppliers. The sample information are summarized in Table 1.

Table 1: Sample information

Fluid	CAS registry number	source	minimum purity
Nitrogen	7727-37-9	Air Liquide	99.999%
Diethyl ether	60-29-7	Merck	99.7%
Novec 649	756-13-8	3M	99.8%

## Measuring procedure

The evacuated cell, thermostatted slightly above ambient temperature, was filled with the gaseous component (nitrogen). Measuring temperature and pressure, the density was calculated with the highly accurate EOS by Span et al.<sup>7</sup> and with a known cell volume, the mass of nitrogen was calculated. Before and after filling the liquid component into the cell, its temperature, pressure and volume inside the piston screw pump was determined. Hence, the density was calculated with the EOS by Thol et al.<sup>8</sup> and by McLinden et al.<sup>9</sup> for diethyl ether and Novec 649, respectively. The mass of the liquid in the pump is then known and consequently, the mass of liquid component filled into the cell can be obtained from the properties of different pump piston positions. After forming a binary mixture, the cell was heated up to approximately 20 K above the desired measuring temperature. If there was still a two-phase system at this time, more liquid component was added into the cell until a homogeneous mixture was attained. Next, the cell was cooled down slowly until the first small vapor bubble appeared, and the VLE state was reached. If the temperature was above the desired measuring temperature, the cell was heated up again and a small amount of liquid component was added. After cooling down again, the temperature where the VLE state is achieved decreases. Typically, several repetitions were required until the first bubble appeared at the desired measuring temperature. By reaching this point, the saturated vapor pressure was measured with the pressure transducer. In the last step, the composition was calculated on the basis of the known masses of each component filled into the cell. More details on the procedure were described in a preceding work.<sup>6</sup>

# Modelling

## Peng-Robinson equation of state

The experimental data generated in this work were correlated with the Peng-Robinson EOS<sup>10</sup>

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}, \quad (1)$$

where the substance specific parameters  $a$  and  $b$  were defined as

$$a = \left(0.45724 \frac{R^2 T_c^2}{p_c}\right) \cdot \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) \left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2, \quad (2)$$

and

$$b = 0.07780 \frac{RT_c}{p_c}, \quad (3)$$

with the ideal gas constant  $R$ , the molar volume  $v$ , the critical temperature  $T_c$ , the critical pressure  $p_c$  and the acentric factor  $\omega$ . The pure component parameters are listed in Table 2. For describing mixtures with the Peng-Robinson EOS, a suitable mixing rule has to be found. In the present work the Huron-Vidal (HV) mixing rule<sup>11</sup> combined with the NRTL  $g^E$  model and the quadratic mixing rule<sup>12</sup> were adjusted for the systems nitrogen + diethyl ether and nitrogen + Novec 649, respectively. Applying the Huron-Vidal mixing rule in combination with the Peng-Robinson EOS, the pure substance parameters  $a$  and  $b$  are replaced by

$$a_m = b_m \left( \sum_i \frac{a_i}{b_i} x_i - \frac{g_\infty^E}{\Lambda} \right), \quad (4)$$

where

$$\Lambda = \frac{1}{2\sqrt{2}} \ln \left( \frac{2 + \sqrt{2}}{2 - \sqrt{2}} \right), \quad (5)$$

and

$$b_m = \sum_i x_i b_i. \quad (6)$$

For the calculation of the excess Gibbs free energy at infinite pressure  $g_\infty^E$ , a number of  $g^E$  models can be found in the literature. In this work, the NRTL model for strongly non-ideal mixtures<sup>13</sup> was used

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum_j A_{ji} \exp(-\alpha_{ji} A_{ji}/T) x_j / T}{\sum_l \exp(-\alpha_{li} A_{li}/T) x_l}, \quad (7)$$

and

$$\alpha_{ij} = \alpha_{ji}, \quad (8)$$

where  $A_{ij}$  and  $A_{ji}$  are adjustable interaction parameters and  $\alpha_{ij}$  is the non-randomness parameter. In this work,  $A_{ij}$  and  $A_{ji}$  were chosen to be linearly temperature dependent and  $\alpha_{ij} = 0.2$  was specified as a constant.

Table 2: Pure substance parameters of the Peng-Robinson EOS.

Fluid	$T_c$ K	$p_c$ MPa	$\omega$ -
Nitrogen <sup>14</sup>	126.2	3.394	0.04
Diethyl ether <sup>14</sup>	466.7	3.638	0.281
Novec 649 <sup>15</sup>	441.81	1.869	0.471

## PC-SAFT equation of state

In contrast to the Peng-Robinson EOS, the PC-SAFT EOS is based on theoretical principles accounting for molecular interactions.<sup>16</sup> In this work, the components were assumed to be non-associating, hence they were characterized by three pure component parameters. Table 3 lists the temperature independent segment diameter  $\sigma$ , the segment energy parameter  $\epsilon/k_B$

and the number of segments per chain  $m$ . Furthermore, the molar mass  $M$ , the absolute average deviation (AAD) of the the vapor pressure  $p_{\text{sat}}$  and of the molar volume  $v$  and also the temperature range of the underlying experimental data are given. The parameters for Novec 649 were fitted to vapor pressure and  $pvT$  data obtained from '3M'.<sup>15</sup> The pure fluid parameters for nitrogen and diethyl ether were taken from Gross and Sadowski.<sup>17</sup>

For the VLE calculation of mixtures, the PC-SAFT EOS contains one binary interaction parameter  $k_{ij}$  that can be adjusted to experimental data. In this work, a linear temperature dependence for  $k_{ij}$  was introduced for the system nitrogen + diethyl ether, for the mixture  $\text{N}_2$  + Novec 649 a constant  $k_{ij}$  value was sufficient. More details on the structure of the PC-SAFT EOS are given in the original paper by Gross and Sadowski.<sup>17</sup>

Table 3: Pure substance parameters of the PC-SAFT EOS.

Fluid	$M$ g/mol	$m$ -	$\sigma$ Å	$\epsilon/k_B$ K	$p_{\text{sat}}$ AAD/%	$v$ %	$T$ range K
Nitrogen <sup>17</sup>	28.01	1.2053	3.3130	90.96	0.34	1.5	63-126
Diethyl ether <sup>17</sup>	74.123	2.9686	3.5147	220.09	0.46	0.94	240-467
Novec 649	316.04	4.6109	3.6662	173.93	1.79	1.05	233-436

## Results and discussion

### Nitrogen + diethyl ether

The saturated liquid line of the binary system  $\text{N}_2$  + diethyl ether was measured at temperatures of 390 K, 420 K and 450 K up to the critical region of the mixture. The experimental data were used to parametrize the Peng-Robinson (PR-HV-NRTL) and the PC-SAFT EOS. The results are shown in Figure 1 and the numerical experimental data, together with their uncertainties  $u(x)$  that were calculated with the error propagation law, are listed in Table 4. The parameters  $A_{ij}$  and  $A_{ji}$  of the NRTL  $g^E$  model according to eq. (7) were specified to be

$$A_{ij} = -68.212 \frac{\text{J}}{\text{mol K}} \cdot T + 28382 \frac{\text{J}}{\text{mol}}, \quad (9)$$



and

$$A_{ji} = 61.787 \frac{\text{J}}{\text{mol K}} \cdot T - 23916 \frac{\text{J}}{\text{mol}}. \quad (10)$$

It can be seen that the results from calculations with the Peng-Robinson EOS are in good line with the experimental data in the region of small mole fractions  $x_{\text{N}_2}$  for all three isotherms. With increasing nitrogen content in the liquid, especially in the critical region and for high temperatures, the EOS overestimates the pressure for the system.

The binary interaction parameter  $k_{ij}$  of the PC-SAFT EOS was assumed to be linearly temperature dependent for the system  $\text{N}_2 + \text{diethyl ether}$

$$k_{ij} = -2.333 \cdot 10^{-4} \cdot T/\text{K} + 0.160. \quad (11)$$

At 390 K and 420 K, the results from PC-SAFT also agree well with the experimental data at small nitrogen mole fractions  $x_{\text{N}_2}$  and not differ much from the results of the PR-HV-NRTL model in this region. Again, the pressure at higher  $x_{\text{N}_2}$  is overestimated, particularly in the critical region. In case of the 450 K isotherm, the PC-SAFT EOS yields too high pressures over the whole mole fraction range. Hence, the Peng-Robinson EOS in combination with the Huron-Vidal mixing rule and the NRTL  $g^{\text{E}}$  model seems to be more suitable for the system nitrogen + diethyl ether due to the larger number of adjustable interaction parameters.

## **Nitrogen + Novec 649**

For the system  $\text{N}_2 + \text{Novec 649}$ , measurements of the saturated liquid line at temperatures of 360 K, 390 K and 420 K up to the critical region of the mixture were made. The Peng-Robinson EOS in combination with the quadratic mixing rule and a constant binary interaction parameter  $k_{ij} = 0.02417$ , and the PC-SAFT EOS with a constant binary interaction parameter  $k_{ij} = 0.08$  were parametrized. The results are shown in Figure 2 and the experimental data are listed in Table 4, including their uncertainties  $u(x)$  calculated

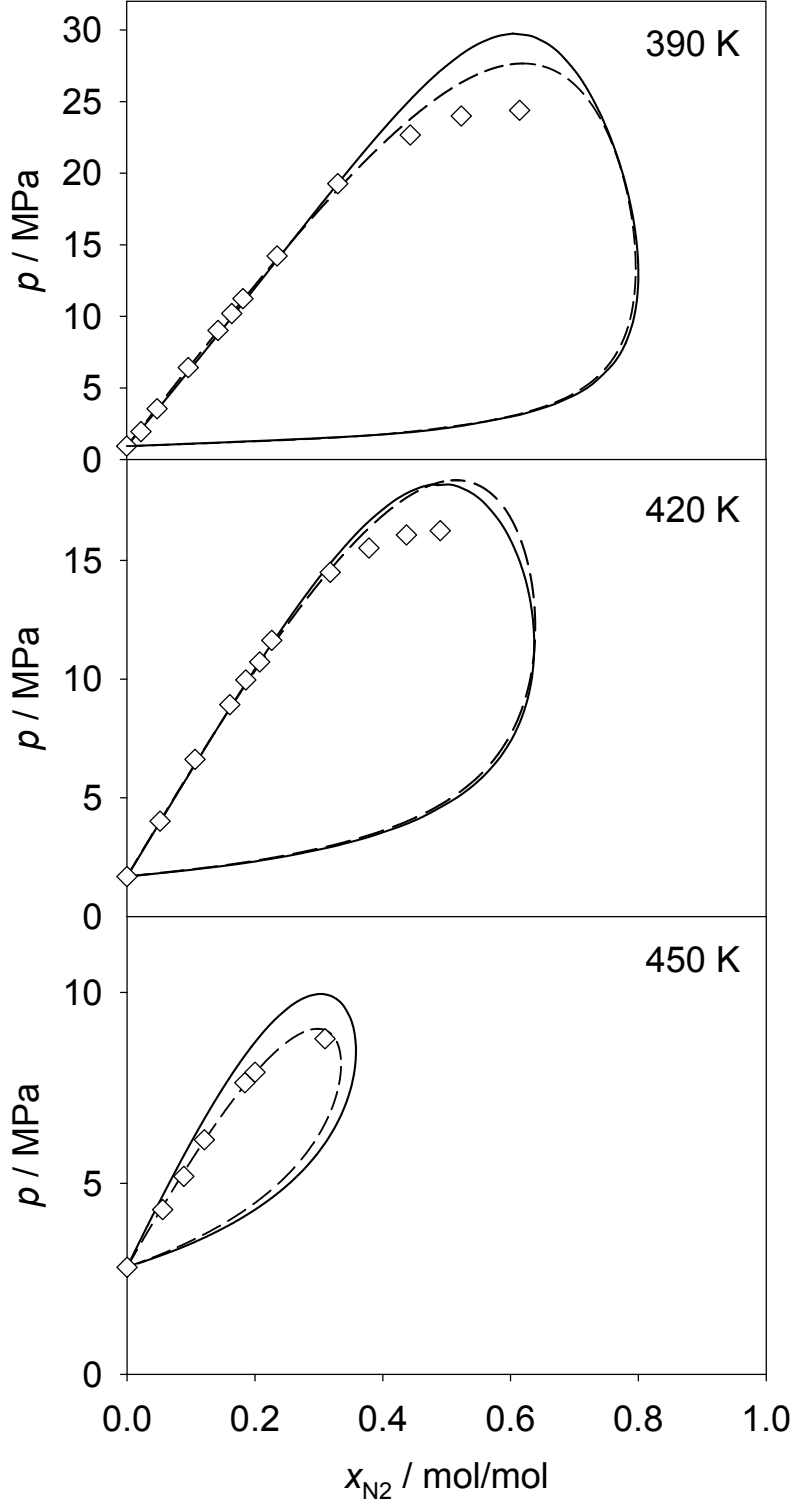


Figure 1: Vapor-liquid equilibrium of nitrogen + diethyl ether at 390 K, 420 K and 450 K, experimental data, this work:  $\diamond$ , PC-SAFT EOS: —, Peng-Robinson EOS (PR-HV-NRTL): - -.

with the error propagation law. Both EOS show a good agreement at small nitrogen mole fractions  $x_{\text{N}_2}$  for all three isotherms. The Peng-Robinson model overestimates the pressure at higher mole fractions, especially in the critical region. In case of nitrogen + Novec 649 the PC-SAFT EOS shows better results for all isotherms. However, while the calculated pressure in the critical region is too high at a temperature of 360 K, the model describes the 390 K and 420 K isotherms very accurately, even in the critical region.

## Conclusions

Data on the saturated liquid line for the systems nitrogen + diethyl ether and nitrogen + Novec 649 were measured with the synthetic method at three temperatures up to the near critical region of the mixture, respectively. The data were correlated with the Peng-Robinson and PC-SAFT EOS. For the system nitrogen + diethyl ether the Peng-Robinson EOS was combined with the Huron-Vidal mixing rule and the NRTL  $g^{\text{E}}$  model, where the binary interaction parameters were assumed to be linearly temperature dependent. Also, the binary interaction parameter of the PC-SAFT EOS was parametrized with a linear temperature dependence. It was found that the PR-HV-NRTL model is more suitable for this system. For nitrogen + Novec 649 the Peng-Robinson EOS together with the quadratic mixing rule and the PC-SAFT EOS were parametrized with a constant binary interaction parameter, respectively. In this case, particularly the results from the PC-SAFT EOS show a good agreement with the present experimental data.

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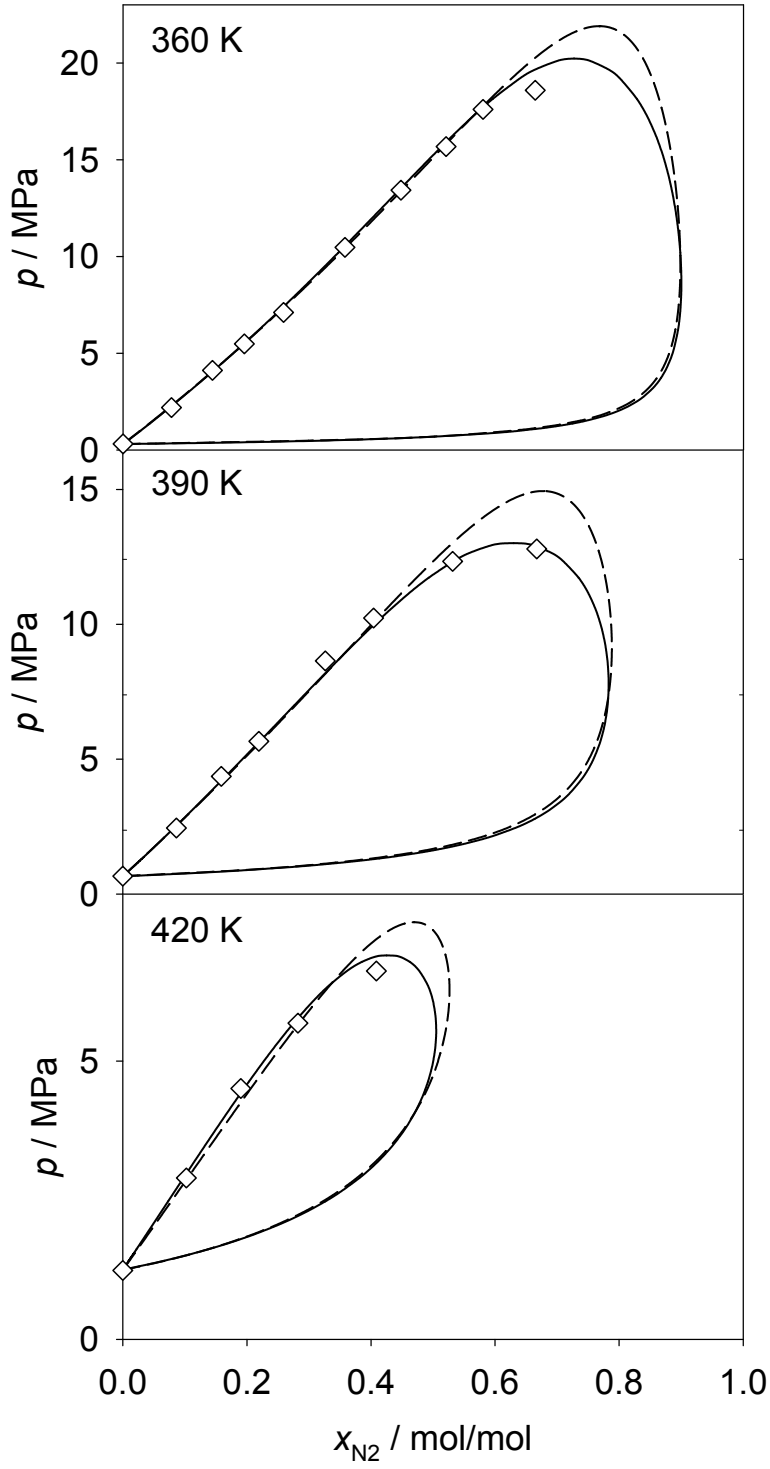


Figure 2: Vapor-liquid equilibrium of nitrogen + Novec 649 at 360 K, 390 K and 420 K, experimental data, this work:  $\diamond$ , PC-SAFT EOS: —, Peng-Robinson EOS: - -.

Table 4: Binary mixtures  $\text{N}_2$  + diethyl ether and  $\text{N}_2$  + Novec 649: Experimental data along the saturated liquid line for the vapor pressure  $p$  and the saturated liquid mole fraction of nitrogen  $x_{\text{N}_2}$ . The numbers in parantheses indicate the uncertainties  $u(x)$  in the last digit. The error of the temperature measurement is  $\pm 0.04$  K.

$\text{N}_2$ + diethyl ether			$\text{N}_2$ + Novec 649		
$T$	$p$	$x_{\text{N}_2}$	$T$	$p$	$x_{\text{N}_2}$
K	MPa	mol/mol	K	MPa	mol/mol
390	1.96 (7)	0.022 (1)	360	2.20 (7)	0.078 (2)
390	3.55 (7)	0.047 (2)	360	4.12 (7)	0.144 (4)
390	6.43 (7)	0.096 (4)	360	5.49 (7)	0.195 (6)
390	9.02 (7)	0.143 (6)	360	7.11 (7)	0.259 (8)
390	10.20 (7)	0.164 (7)	360	10.48 (7)	0.36 (1)
390	11.24 (7)	0.182 (7)	360	13.43 (7)	0.45 (1)
390	14.22 (7)	0.235 (9)	360	15.68 (7)	0.52 (2)
390	19.27 (7)	0.33 (1)	360	17.61 (7)	0.58 (2)
390	22.67 (7)	0.44 (1)	360	18.59 (7)	0.66 (2)
390	24.00 (7)	0.52 (1)	390	2.45 (7)	0.086 (3)
390	24.39 (7)	0.62 (1)	390	4.36 (7)	0.159 (5)
420	4.01 (7)	0.052 (3)	390	5.67 (7)	0.219 (7)
420	6.62 (7)	0.106 (5)	390	8.65 (7)	0.33 (1)
420	8.93 (7)	0.161 (7)	390	10.23 (7)	0.40 (1)
420	9.97 (7)	0.186 (7)	390	12.33 (7)	0.53 (2)
420	10.73 (7)	0.208 (8)	390	12.80 (7)	0.67 (2)
420	11.64 (7)	0.227 (8)	420	2.90 (7)	0.102 (3)
420	14.50 (7)	0.32 (1)	420	4.51 (7)	0.190 (6)
420	15.52 (7)	0.38 (1)	420	5.68 (7)	0.282 (8)
420	16.07 (7)	0.44 (1)	420	6.62 (7)	0.41 (1)
420	16.25 (7)	0.49 (1)			
450	4.31 (7)	0.056 (3)			
450	5.18 (7)	0.089 (4)			
450	6.14 (7)	0.121 (5)			
450	7.64 (7)	0.184 (7)			
450	7.91 (7)	0.200 (8)			
450	8.79 (7)	0.31 (1)			

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