# Measurement and Modeling of Hydrocarbon Dew Points for Five Synthetic Natural Gas Mixtures

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## Abstract

The dew points of five synthetic natural gas (SNG) mixtures were measured by using a custom made chilled mirror apparatus. The chilled mirror apparatus was designed to detect hydrocarbon dew points from low pressures up to the cricondenbar. The experimental temperature range was from 235 K to 280 K and the pressure range from 0.3 MPa to 10 MPa. The synthetic natural gases were comprised of methane and gravimetrically prepared fractions of ethane, propane, *i*-butane, *n*-butane and *n*-pentane. The experimental data were compared to calculations with the Soave-Redlich-Kwong (SRK) equation of state with classical mixing rule. However, considerable and increasing deviations between calculated and experimental dew points were observed as the pressure approached the cricondenbar. Therefore, a model based on the Redlich-Kwong (RK) equation of state with Mathias and Copeman (MC) temperature dependent term was utilized. An optimization procedure was employed to fit the Mathias and Copeman coefficients of methane to both pure component vapor pressures and experimental dew points. There is good agreement between experimental data and modeling results. For pressures higher than the pressure corresponding to the cricondetherm, the proposed model is better than the standard SRK equation of state. Good predictions with the model were obtained when comparing to dew point data from literature.

*Keywords*: Natural gas, experiment, dew point, modeling.

## Introduction

There is always a risk of hydrocarbon condensation in natural gas transmission pipelines. Hydrocarbon liquids from condensation will increase the pressure drop and introduce operational problems resulting from two phase flow. It is important to prevent condensation by keeping the natural gas temperature and pressure in the single phase region. Optimal control of the hydrocarbon dew point is therefore important for economical, operational and safety reasons.

Natural gas from the Norwegian continental shelf is transported to the European market through rich and dry gas pipelines. The gas is transported from offshore production installations as rich gas to onshore processing plants where liquids are extracted, and finally as dry gas to the European market. Rich gas is partially processed natural gas transported in a dense phase where the capacity of the pipelines is limited by the lowest possible arrival pressure (cricondenbar). Dry gas transport is the transport of fully processed natural gas. The lowest acceptable temperature is limited by the hydrocarbon dew point specification on sales gas (cricondentherm) and the requirement of no liquid hydrocarbon formation in the export pipelines. To utilize the natural gas production and transmission system optimal it is important to be able to predict the phase behaviour of natural gases both near the cricondentherm and cricondenbar.

The dew points of natural gas mixtures can be predicted using traditional equations of state; however, the predictions are often inaccurate [1], especially for pressures higher than the pressure corresponding to the cricondentherm [2].

Recent studies by Avila et al. [2] and Jarne et al. [3] indicate that the average absolute error in predicting dew point temperatures could be as large as 3.7 K. The demand for more accurate calculations of the natural gas dew points was apparent. It was therefore decided to perform a systematic study of hydrocarbon dew points of synthetic natural gases. The dew points of five synthetic natural gas mixtures comprised of light hydrocarbons (methane to *n*-pentane) were measured. The obtained experimental data was then simulated using an equation-of-state approach. Nasrifar et al. [1] compared the accuracy of 15 equations of state for predicting the dew points of synthetic and real natural gas mixtures. The comparisons revealed that the Soave-Redlich-Kwong (SRK) [4] equation of state, or one of its variants, can best predict the dew points of synthetic natural gases, especially near cricondentherm. Thus, the Redlich-Kwong (RK) equation of state [5], using the Mathias and Copeman temperature dependent term [6] and an optimization procedure were used to improve the accuracy in the calculations. The Mathias and Copeman coefficients of methane were fitted to both pure component vapor pressures and the experimental dew points measured in this work. The results using the RK equation of state with the Mathias and Copeman temperature dependent term (RKMC) and the new optimized parameters show improved accuracy both compared to using the SRK equation of state and also using the previous published parameters for Mathias and Copeman temperature dependent term.

## Experimental equipment

A custom made apparatus for measurement of hydrocarbon dew points of dry- and rich natural gasses has been built up in the Statoil R&D laboratories in

Trondheim, Norway. The apparatus was used without any modification to do the measurements of this work.

The experimental equipment consists of a piston circulating the sample back and forth between two equally large chambers. As the gas is circulated, it passes a mirror whose temperature is controlled by fitting a cooled copper rod to the back of it. The copper rod is cooled by a manually controlled liquid $CO_2$ cooling system. The cooling system allows dew point detection down to 230 K at pressures up to 40 MPa. The dew point mirror and cooling system are manufactured by Chandler Engineering [7].

The total volume of circulated gas is approximately 150 ml. The filling pressure of each experiment has varied, depending on the pressure of the synthetic natural gas sample. All external piping is heat traced to a temperature of 330 K. The rest of the equipment is held constant at 300 K. The layout of the experimental equipment is illustrated in Figure 1. The $CO_2$ cooling system is illustrated in Figure 2.

The temperature is measured by a Pt-100 element in direct contact with the back of the mirror. The temperature element is covered by heat conducting paste to enhance the heat flow. A Dostmann P655-EX is used to measure the temperature of the mirror. The uncertainty of the thermometer is ± 0.1 degrees in the region 170 K to 420 K.

The synthetic natural gasses used in the experimental series were all gravimetrically calibrated. The relative uncertainty in the compositional analysis is less than 0.5% for all components. The gas compositions were verified by GC-analysis following procedures in GPA 2286-95 and ASTM D5134/92 [8,9].

## Experimental procedure

The system was vacuumed at an ambient temperature of 320 K for a minimum of 12 hours. Then, the system was filled with the gas sample to the highest possible pressure (gas bottle pressure was typically 100-120 bar). The system was stabilized by circulating the gas between the two chambers for half an hour. The mirror was cooled while the gas was circulated at 400ccm/hour until a visually observable amount of hydrocarbon precipitated on the mirror. All of the measured dew points were detected visually. The mirror was then heated for the hydrocarbons to evaporate. The dew point temperature for the sample was set to the mean of the precipitation and the evaporation temperature. The difference in temperature where condensate was first observed and to that of total evaporation was always less than 1 K. The measurements started at highest possible pressure (close to the cricondenbar). The pressure of the sample was reduced in small steps by venting portions of the gas. Typically, twenty dew points were measured from high pressure to low pressure for each synthetic natural gas. All gasses were measured two times to check the repeatability of the measurements. The maximum deviation between two independent dew point measurements at any pressure was always less than 1 K.

## Experimental Results

The compositions and code names for the five SNG mixtures are given in Table 1. One mixture (SNG2) contains less than 85% methane while the other four mixtures contain at least 93% methane. In addition to methane, the gases consisted of ethane, propane, *i*-butane, *n*-butane and *n*-pentane. All gases were supplied by Yara, Norway

[10]. The claimed compositions for the gases by the supplier were validated in the Statoil R&D laboratory using gas chromatography. There were close agreement between the two measurements.

Using the procedure mentioned above, the dew point conditions for the five natural gas mixtures (SNG1-SNG5) were measured. Table 2 gives the dew point conditions for wide ranges of temperature and pressure. The temperature ranges from roughly 235 K to 280 K and pressure from 0.3 MPa to almost 10 MPa.

## Modeling with Equation of State

In order to describe the phase envelopes for the synthetic natural gas mixtures, the RK equation of state [5] with MC temperature dependent term [6] are used (RKMC). The *PVT* relationship for the RKMC equation of state may then be expressed by:

$$P = \frac{RT}{v - b} - \frac{a_C \alpha(T_r)}{v(v + b)} \tag{1}$$

with

$$b = 0.08664 \frac{RT_C}{P_C} \tag{2}$$

$$a_C = 0.42748 \frac{R^2 T_C^2}{P_C} \tag{3}$$

While the temperature dependent attractive term in the SRK equation of state is expressed by

$$\alpha(T_r) = \left[1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - \sqrt{T_r})\right]^2 \quad (4)$$

the temperature dependent term [6] in the RKMC equation is:

$$\alpha(T_r) = \left[1 + c1\left(1 - T_r^{0.5}\right) + c2\left(1 - T_r^{0.5}\right)^2 + c3\left(1 - T_r^{0.5}\right)^3\right]^2 \quad (5)$$

where subscripts *C* and *r* stand for the critical and reduced properties, respectively, *P* is the pressure, *R* is the universal gas constant, *T* is the temperature, *v* is the specific volume, *b* is the molar co-volume, $a_C$ is the attractive parameter at the critical point and $\omega$ the acentric factor. The coefficients c1, c2 and c3 are specific to each component and are normally determined by fitting the equation of state and the Mathias and Copeman temperature dependent term to the vapor pressure of pure compounds. In this work, however, with the exception of methane, the coefficients were taken from Nasrifar and Moshfeghian [11] and Nasrifar et al. [12]. For methane, the coefficients (c1, c2, c3) were adjusted by use of a nonlinear regression package [13] to minimize the following objective function:

$$\Omega = \sum_{i=1}^{np}\left|T_{cal,i}^{dew} - T_{exp,i}^{dew}\right| + \sum_{\text{Triple point}}^{\text{Critical point}}\left|P_{cal,CH4}^{s} - P_{exp,CH4}^{s}\right| / P_{exp,CH4}^{s} \quad (6)$$

where $\Omega$ is the objective function. The first summation runs over all the dew point measurements. The second summation ranges from the methane triple point temperature to the critical point temperature. The adjusted coefficients for methane and the coefficients for other components taken from literature are given in Table 3.

In order to apply Eq.(1) to a mixture, the van der Waals (vdW) mixing rules were used. The vdW mixing rules may be expressed by:

$$b = \sum_i x_i b_i \tag{7}$$

$$a = \sum_i \sum_j x_i x_j \sqrt{a_{C,i} a_{C,j} \alpha_i(T_r) \alpha_j(T_r)} \left(1 - k_{ij}\right) \tag{8}$$

where the summations run over all the components in the mixture. Because the binary interaction parameter, $k_{ij}$, is not appreciable between the binary pairs of the synthetic natural gas mixtures, we used $k_{ij} = 0$ for all pairs.

## Results and Discussion

The measured dew point pressures and temperatures for the five synthetic natural gas mixtures are plotted in Figure 3-Figure 7. Also shown in Figure 3-Figure 7 are the modeling results. For the sake of comparison, the dew point conditions predicted by the SRK equation of state [4] and the conventional RKMC equation of state are also shown. By writing conventional we emphasize on the use of literature values for the Mathias and Copeman temperature dependent term. Figure 3-Figure 7 show that the predictions adequately describe the experimental values from low temperature to the cricondentherm. However, at pressures higher than the pressure corresponding to the cricondentherm, the SRK equation of state in general underestimates the experimental values. Compared to the SRK equation of state, the conventional RKMC is in better agreement with experimental data at high pressures. The RKMC equation of state significantly describes the mixtures SNG3, SNG4 and SNG5 for the whole experimental data range. When the model is compared to the other models, it in general estimates higher pressures. Our modeling reproduces the experimental dew points for the mixtures SNG3, SNG4 and SNG5 very well. It is also predicts the experimental dew points of the mixtures SNG1 and SNG2 good and slightly better than the alternatives for high pressures. One may argue that we have fitted the experimental data using the procedure outlined above. Hence, we obtained a good fit of data. It is, however, worth stressing that with the exception of methane, the literature values of Mathias and Copeman coefficients were used for other components. Besides, for methane, in minimizing the objective function, we also included the vapor pressure of methane from the triple point to the critical point. As a consequence, we preserved the actual characteristics of the Mathias and Copeman coefficients by including vapor pressure. In general, the Mathias and Copeman coefficients are solely obtained using pure component vapor pressures.

Interestingly, using the optimization, the obtained coefficients for methane does not significantly change the accuracy of the RKMC equation of state when predicting the vapor pressure. In Figure 8 we see a deviation plot for predicting the vapor pressures of methane for the whole temperature range by use of the SRK equation of state, the RKMC with the coefficients in literature [11] and the RKMC with the coefficients optimized in this work. Figure 8 reveals that optimization of coefficients for methane leads to predicted vapor pressures with accuracies between the SRK and conventional RKMC equation of state. The average absolute deviation in predicting the vapor pressure of methane is within 1% for the RKMC equation of state, while it is 1.5% for the SRK equation of state and 0.8% for the conventional RKMC equation of state.

As a final test, as illustrated in Figure 9, using the coefficients obtained for methane, the dew point conditions for a synthetic natural gas mixture containing 89% $CH_4$ + 7% $C_2H_6$ + 4% $n$-$C_4H_{10}$ were predicted and compared with experimental data given in literature [15]. Again, the same characteristics were obtained, the model estimates higher dew points compared to the SRK and conventional RKMC equations of state and it is in better agreement with experimental data than the two others.

## Conclusion

The dew point temperatures and pressures of five synthetic natural gas mixtures were measured using a chilled mirror apparatus. The experimental data were compared to the predictions with the original SRK equation of state and to the predictions with the Mathias and Copeman modification of the RK equation of state with previous published parameters. The evaluations showed that results from the SRK equation of state can be improved if literature values of Mathias and Copeman coefficients are used. Even better agreement was obtained when the Mathias and Copeman coefficients for methane were optimized using the measured dew point data and the vapor pressure of methane from the triple point to the critical point. The improvement was most significant at relatively high pressures, and especially in the region near the cricondenbar. Comparisons with experimental data from literature reveal that the proposed model is more accurate in predicting dew point conditions.

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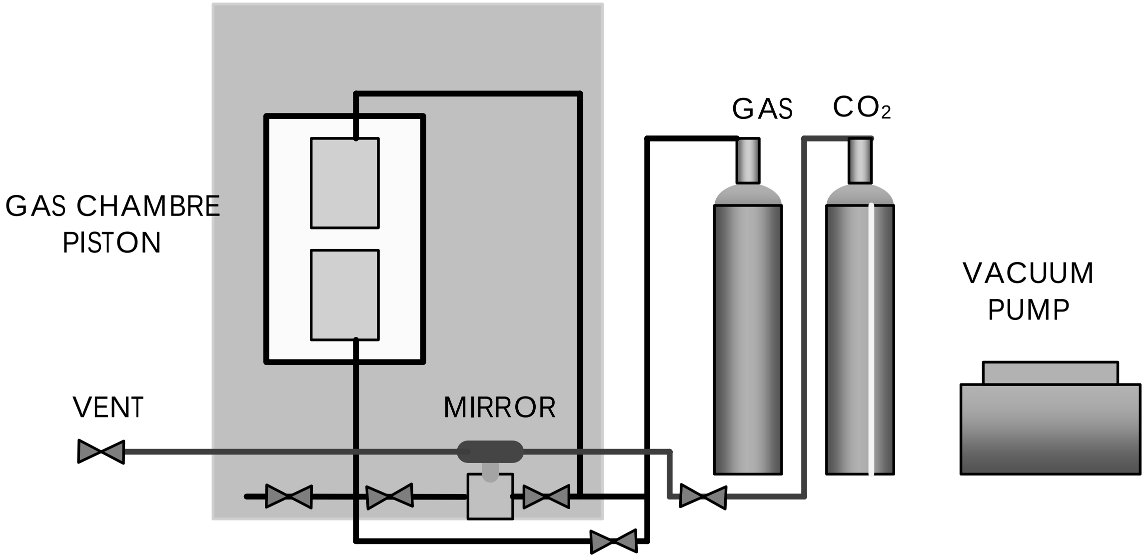

**Figure 1** **The dew point rig**

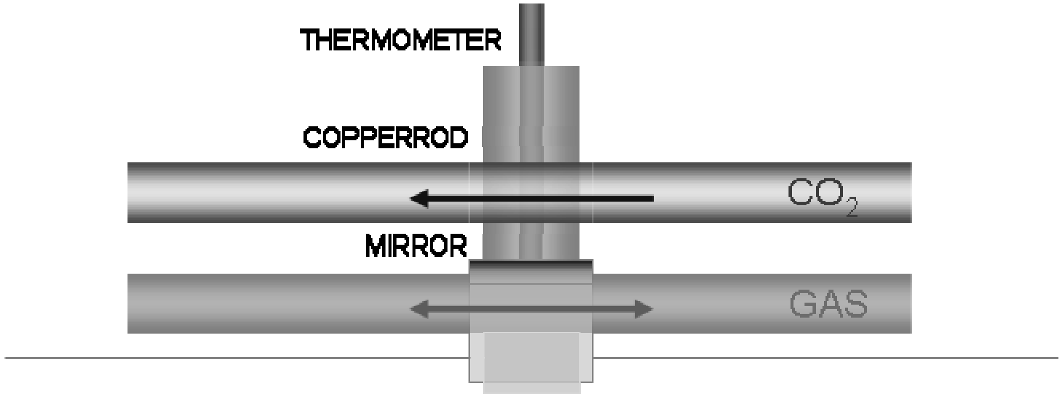

**Figure 2** Cooling of the chilled mirror

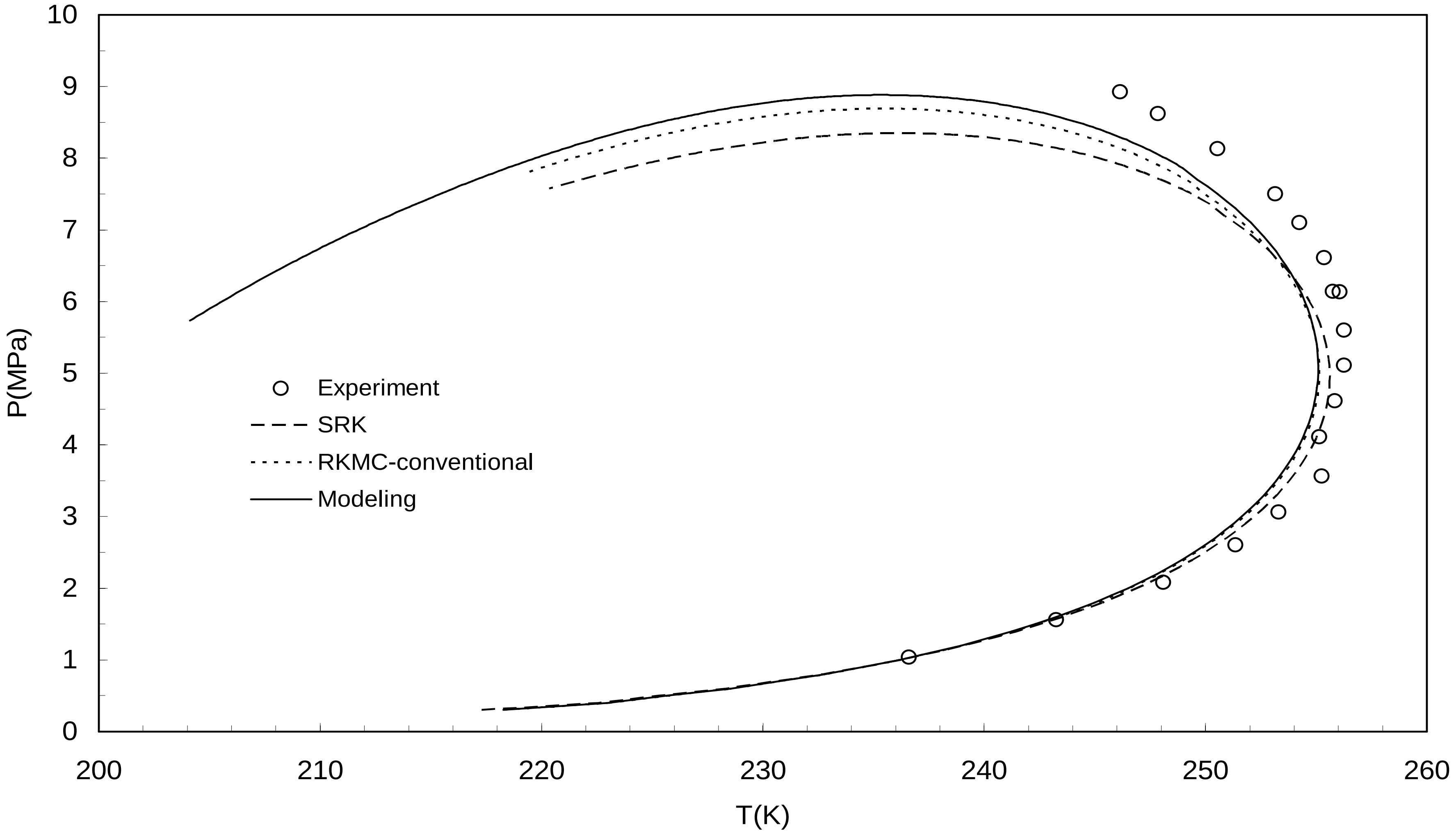

**Figure 3** Experimental and predicted dew points for the mixture SNG1

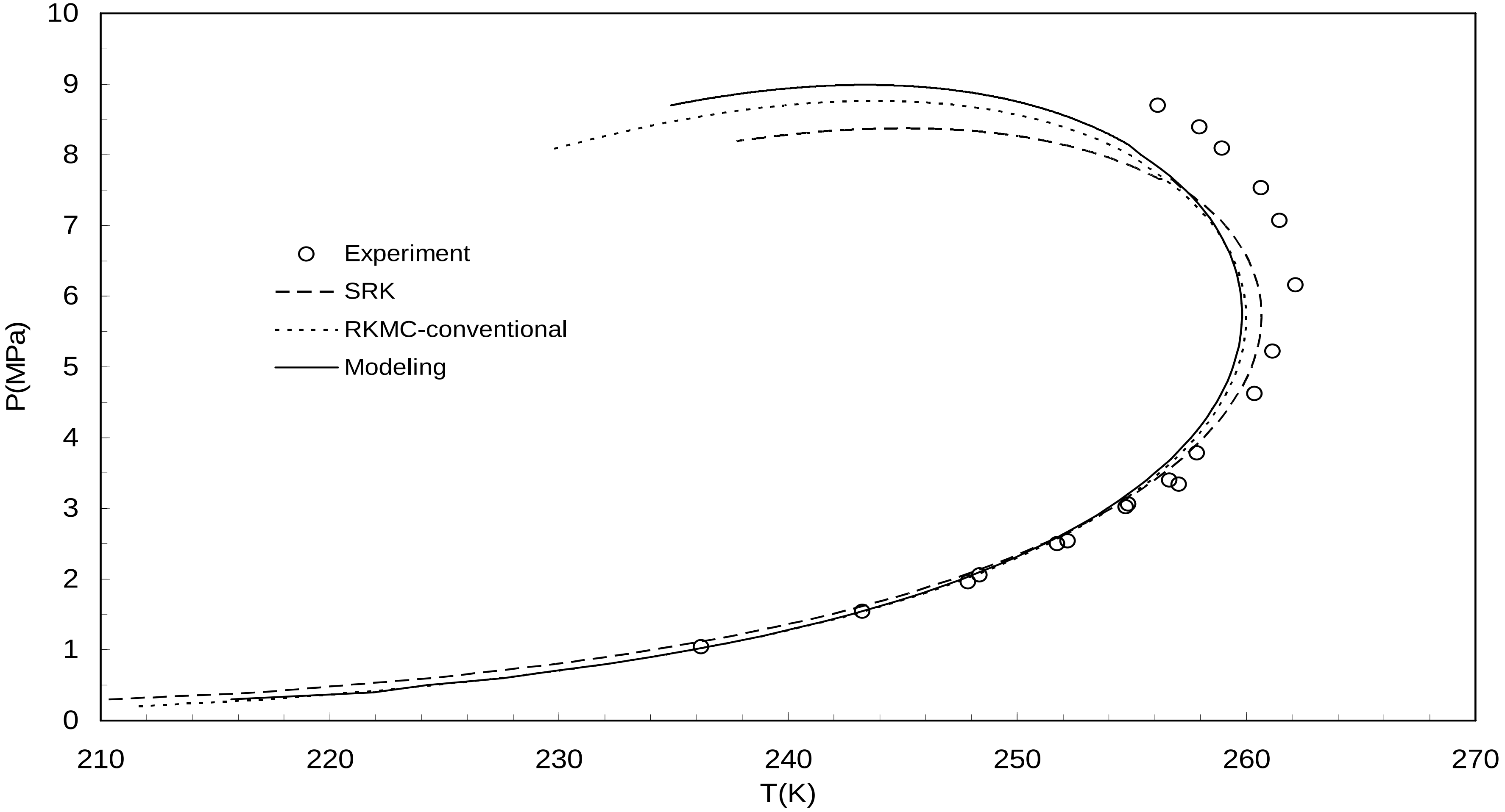

**Figure 4** Experimental and predicted dew points for the mixture SNG2

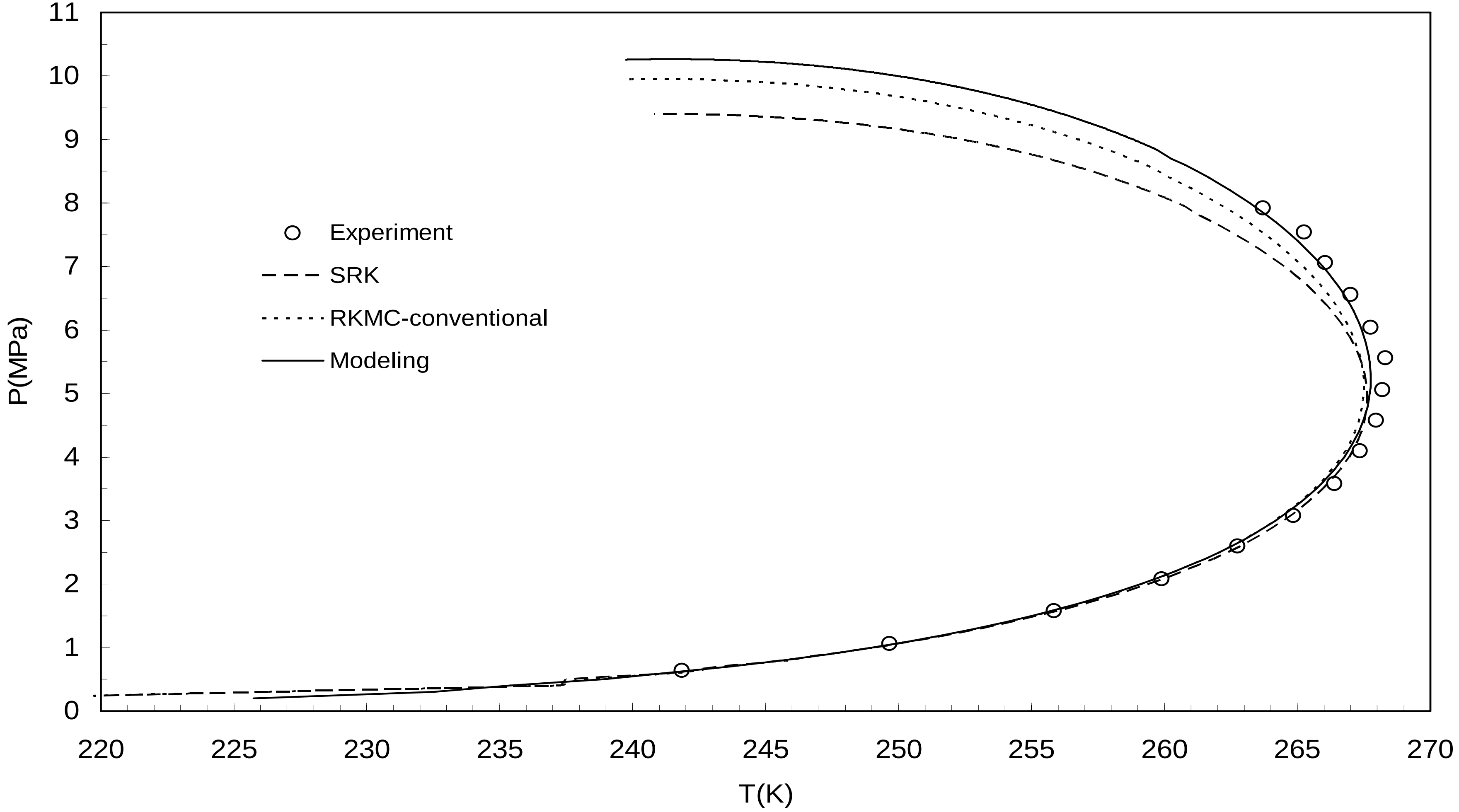

**Figure 5** Experimental and predicted dew points for the mixture SNG3

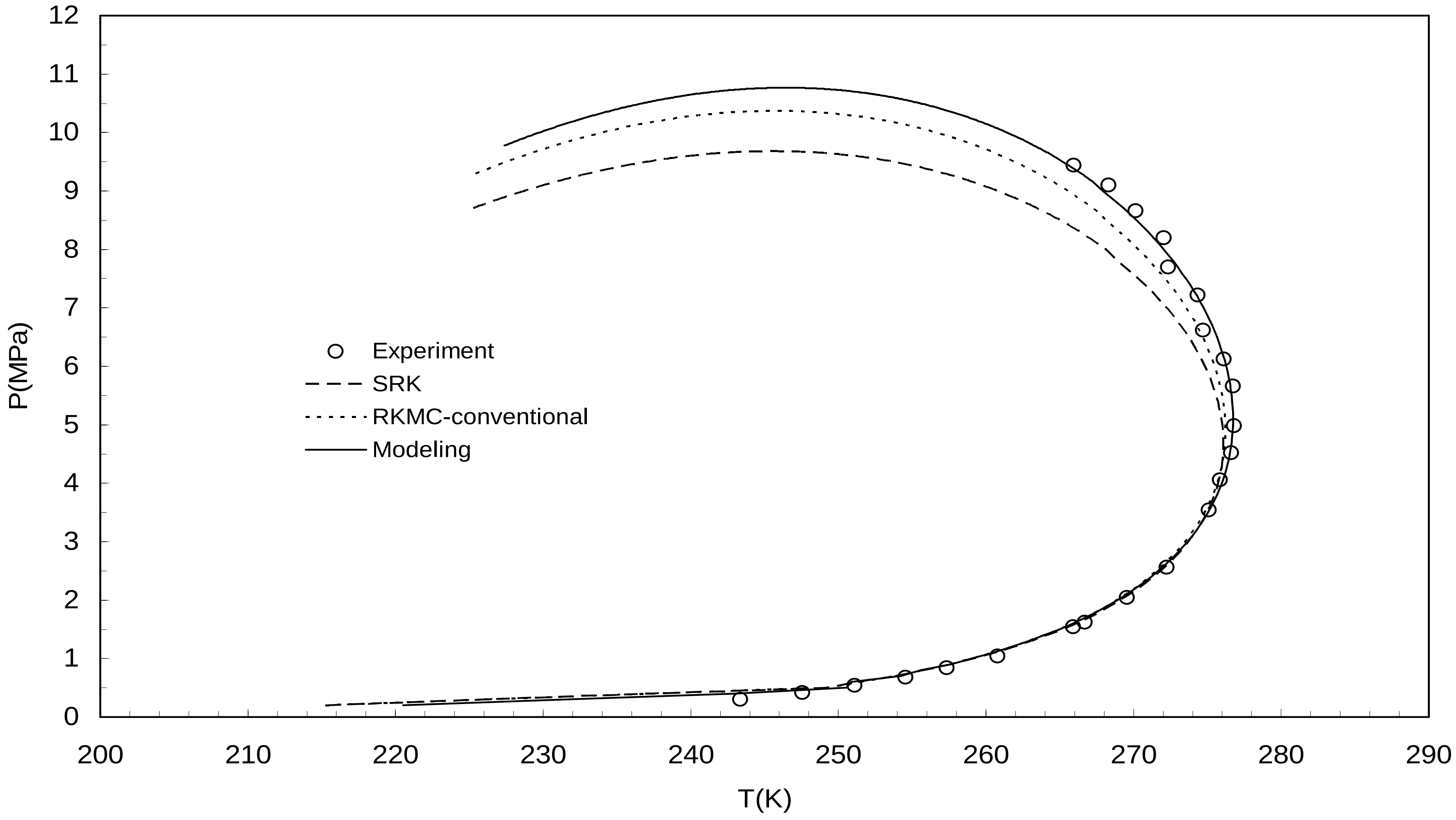

**Figure 6** Experimental and predicted dew points for the mixture SNG4

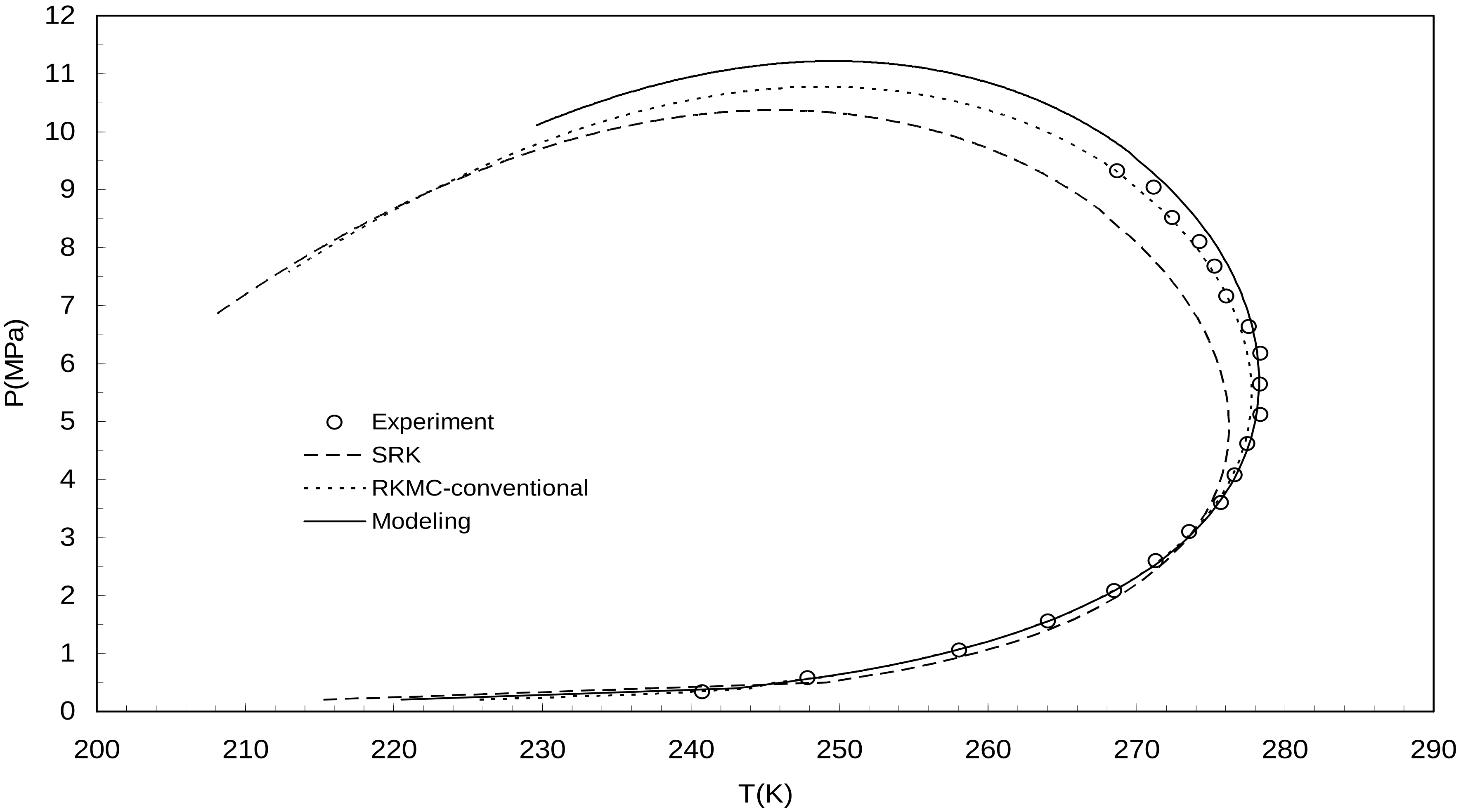

**Figure 7** **Experimental and predicted dew points for the mixture SNG5**

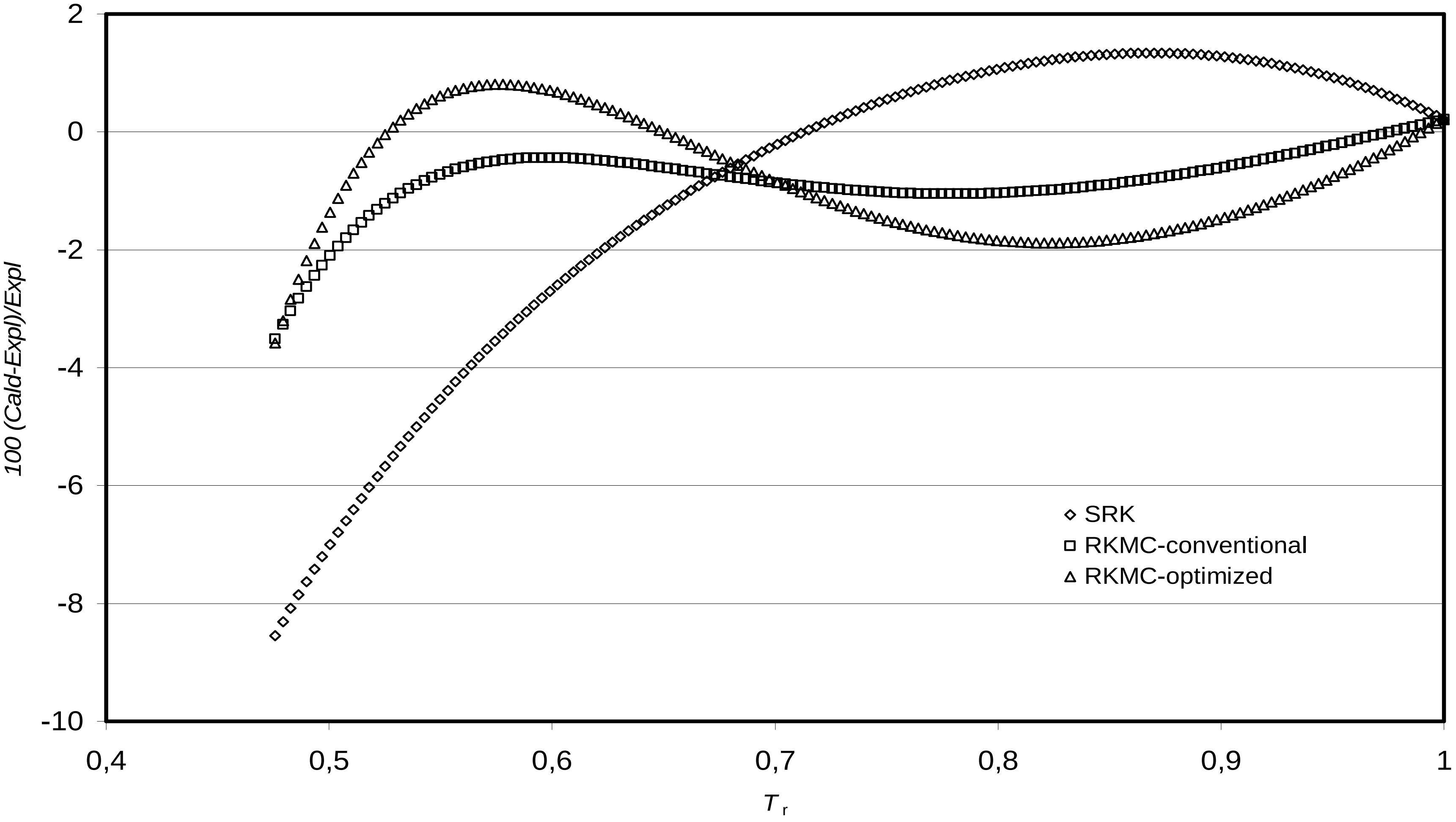

**Figure 8** **Deviation plot for predicting the vapor pressure of methane from the triple point to the critical point (experimental data from [14])**

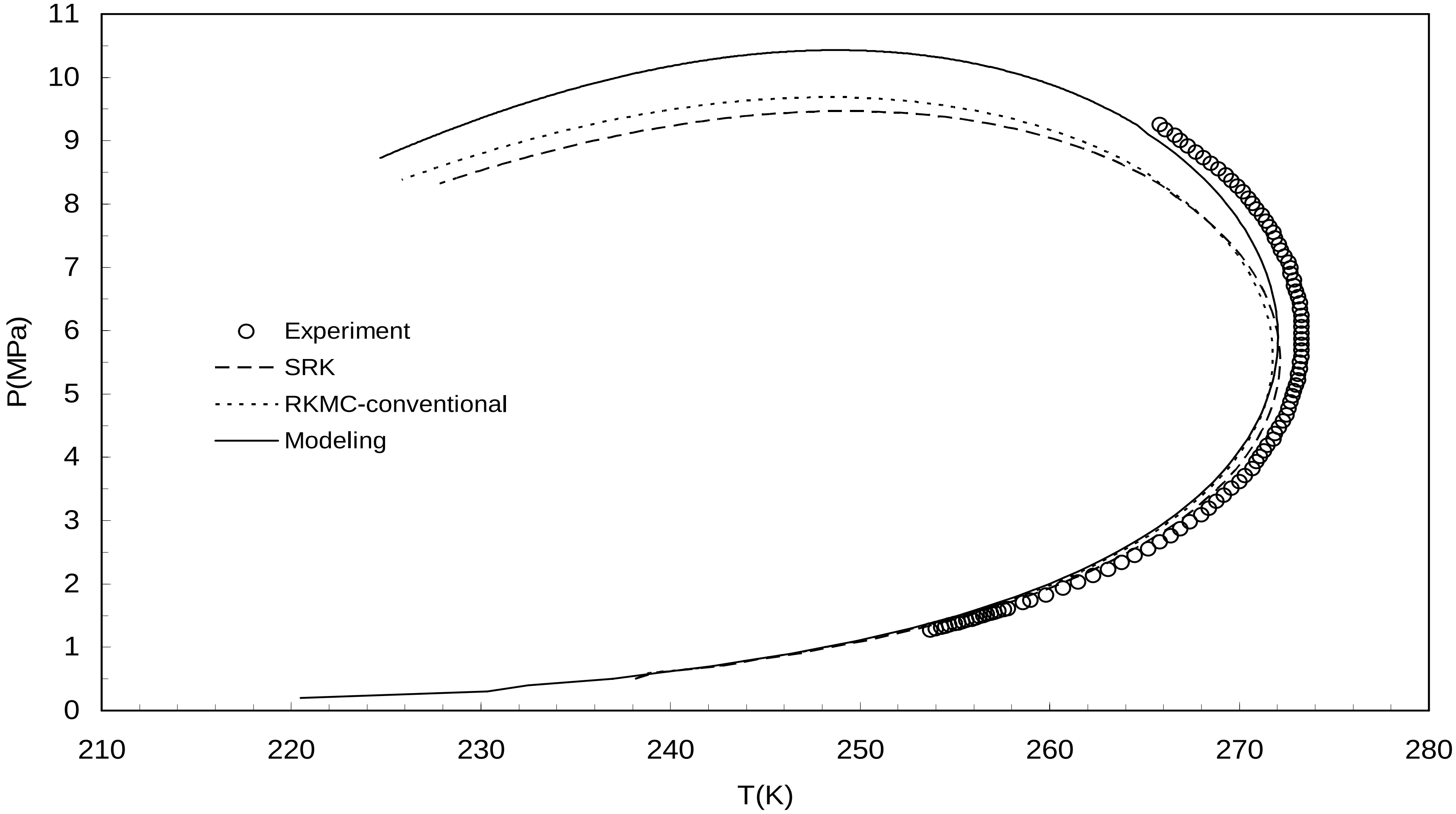

**Figure 9** Experimental and predicted dew points for the natural gas mixture [15] containing 89% $CH_4$ + 7% $C_2H_6$ + 4% *n*-$C_4H_{10}$

**Table 1**
**Code names and compositions for the synthetic natural gas mixtures**

| Component | SNG1 | SNG2 | SNG3 | SNG4 | SNG5 |
|---|---|---|---|---|---|
| $C_1$ | 0.93505 | 0.84280 | 0.96611 | 0.94085 | 0.93600 |
| $C_2$ | 0.02972 | 0.10067 | - | 0.04468 | 0.02630 |
| $C_3$ | 0.01008 | 0.04028 | - | - | - |
| $i$-$C_4$ | 0.01050 | 0.00597 | 0.01527 | - | 0.01490 |
| $n$-$C_4$ | 0.01465 | 0.01028 | 0.01475 | - | 0.01490 |
| $n$-$C_5$ | - | - | 0.00385 | 0.014470 | 0.00795 |

**Table 2**

**Dew point temperature and pressure for the synthetic natural gas mixtures**

| SNG1 | | SNG2 | | SNG3 | | SNG4 | | SNG5 | |
|---|---|---|---|---|---|---|---|---|---|
| T(K) | P(MPa) | T(K) | P(MPa) | T(K) | P(MPa) | T(K) | P(MPa) | T(K) | P(MPa) |
| 246,2 | 8,92 | 256,2 | 8,7 | 263,7 | 7,92 | 266,0 | 9,44 | 268,7 | 9,32 |
| 247,9 | 8,62 | 258,0 | 8,39 | 265,3 | 7,54 | 268,3 | 9,1 | 271,2 | 9,04 |
| 250,6 | 8,13 | 259,0 | 8,09 | 266,1 | 7,06 | 270,2 | 8,66 | 272,4 | 8,52 |
| 253,2 | 7,5 | 260,7 | 7,53 | 267,0 | 6,56 | 272,1 | 8,2 | 274,3 | 8,1 |
| 254,3 | 7,1 | 261,5 | 7,07 | 267,8 | 6,04 | 272,4 | 7,7 | 275,3 | 7,68 |
| 255,4 | 6,61 | 262,2 | 6,16 | 268,3 | 5,56 | 274,4 | 7,22 | 276,1 | 7,16 |
| 256,1 | 6,13 | 261,2 | 5,22 | 268,2 | 5,06 | 274,7 | 6,62 | 277,6 | 6,64 |
| 255,8 | 6,14 | 260,4 | 4,62 | 268,0 | 4,58 | 276,1 | 6,12 | 278,4 | 6,18 |
| 256,3 | 5,6 | 257,9 | 3,78 | 267,4 | 4,1 | 276,8 | 5,66 | 278,3 | 5,64 |
| 256,3 | 5,11 | 256,7 | 3,4 | 266,4 | 3,58 | 276,8 | 4,98 | 278,4 | 5,12 |
| 255,9 | 4,61 | 254,8 | 3,02 | 264,9 | 3,08 | 276,6 | 4,52 | 277,5 | 4,62 |
| 255,2 | 4,11 | 251,8 | 2,5 | 262,8 | 2,6 | 275,9 | 4,06 | 276,6 | 4,08 |
| 255,3 | 3,56 | 247,9 | 1,96 | 259,9 | 2,08 | 275,1 | 3,54 | 275,7 | 3,6 |
| 253,3 | 3,06 | 254,9 | 3,06 | 255,9 | 1,58 | 272,3 | 2,56 | 273,6 | 3,1 |
| 251,4 | 2,6 | 252,2 | 2,54 | 249,7 | 1,06 | 269,6 | 2,04 | 271,3 | 2,6 |
| 248,1 | 2,08 | 248,4 | 2,06 | 241,9 | 0,64 | 266,7 | 1,62 | 268,5 | 2,08 |
| 243,3 | 1,56 | 243,3 | 1,54 | | | 265,9 | 1,54 | 264,1 | 1,56 |
| 236,6 | 1,04 | 236,2 | 1,04 | | | 260,8 | 1,04 | 258,1 | 1,06 |
| | | | | | | 257,4 | 0,84 | 247,9 | 0,58 |
| | | | | | | 254,6 | 0,68 | 240,8 | 0,34 |
| | | | | | | 251,1 | 0,54 | | |
| | | | | | | 247,6 | 0,42 | | |
| | | | | | | 243,4 | 0,3 | | |

**Table 3**
**Mathias and Copeman coefficients for the components in the synthetic natural gas mixtures [11,12]**

| Components | c1 | c2 | c3 |
|---|---|---|---|
| $C_1$ [*] | 0.6296 | -1.1333 | 2.1659 |
| $C_1$ | 0.5857 | -0.7206 | 1.2899 |
| $C_2$ | 0.7178 | -0.7644 | 1.6396 |
| $C_3$ | 0.7863 | -0.7459 | 1.8454 |
| *i*-$C_4$ | 0.8288 | -0.8285 | 2.3201 |
| *n*-$C_4$ | 0.8787 | -0.9399 | 2.2666 |
| *n*-$C_5$ | 0.9820 | -1.1695 | 2.7523 |

[*] Parameters fitted in this work