PREDICTION OF NATURAL GAS MIXTURES PHASE BEHAVIOUR USING EIGHT EOS FUNCTIONS WITH VAN DER WALL AND WONG SANDLER MIXING RULES

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CERTIFICATION OF APPROVAL

**Prediction of Natural Gas Mixtures Phase Envelope using Eight EOS Functions
with Van der Wall and Wong Sandler Mixing Rules**

by

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Approved by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the reference and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MUHAMAD LUKMAN BIN MANSHOR

ABSTRACT

Prediction of natural gas phase behaviour is important and crucial in hydrocarbon processing industries. This paper main objective is to predict phase envelope of natural gas mixtures by using eight equations of state functions and hence to look at its applicability by comparing the predictions of temperature and pressure from the experimental values conducted for 24 set of natural gas mixtures that comprise of lean natural gases or synthetic natural gases. Hence, the studies of Van der Wall (VDW) and Wong Sandler (WS) mixing rules used with EOS functions are discussed in terms of its significant and validity of the equations to the calculated results. The resulted calculation values of T and P was calculated by using Prode add in Microsoft Excel simulator. For a conclusion, it is found that Soave-Redlich-Kwong (SRK) families with VDW mixing rules have wide applications and are superb in predicting phase behaviours of different mixtures with 83% dominant level compared to Peng-Robinson (PR) families with WS mixing rules when tested for 24 set of natural gas mixtures data. PR-WS is superb at predicting phase behaviours of natural gas mixtures with 25.91% carbon dioxide content, 1.56% of nitrogen and 0.11% of n-hexane. Hence, PR-VDW is superior at predicting synthetic natural gas mixture with 0.77% nitrogen, 1.75% of carbon dioxide, 84.45% of methane, and 0.05% of n-hexane. Thus, the application of PR families is limited for several mixtures only and requires some modification of the EOS parameters. For the effect of different mixing rules used in this study, VDW mixing rules is best described the phase envelopes of natural gas mixtures with different heavies content as heavy as n-octane and its dominated 24 set of mixtures as high as 95% over WS mixing rule. Therefore, it is conclusive that no single EOS provides reliable predictions of bubble point line and dew point line of all 24 set of natural gas mixtures used in this study and application of VDW mixing rules is reasonable over WS mixing rules, and it is recommended that RK families with Soave temperature functions have wider applications over PR families for this 24 set of natural gas mixtures.

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LIST OF ABBREVIATIONS

AAD	→	Average Arithmetic Deviation
API	→	American Petroleum Institute
BIP	→	Binary Interaction Parameter
BWR	→	Benedict-Webb-Rubin
CPA	→	Cubic Plus Association
DEV	→	Deviation
EOS	→	Equation of State
EOS/G^E	→	EOS+Gibbs Free Energy
EXP	→	Experiment
EXT	→	Extended
HV	→	Huron-Vidal
LLE	→	Liquid Liquid Equilibrium
MPa.a	→	Megapascal Absolute
MHV2	→	Mansoori –Huron-Vidal Two Parameters
MIX	→	Mixture
NRTL	→	Non-Random Two Liquid
PR	→	Peng-Robinson
P&R	→	Panagiotopoulos-Reid
PRSV	→	Peng-Robinson-Stryjek-Vera
PVT	→	Pressure Volume Temperature
RK	→	Redlich-Kwong

SNG	→	Synthetic Natural Gases
SRK	→	Soave-Redlich-Kwong
SWP	→	Sako-Wu-Prausnitz
STP	→	Standard Temperature Pressure
UNIQUAC	→	Universal Quasi Chemical
VLE	→	Vapour-Liquid-Equilibrium
VDW	→	Van der Walls
WS	→	Wong-Sandler
ZM	→	Zhong-Masuoka

LIST OF SYMBOLS

General Symbols

A	$\rightarrow$	Helmholz free energy
g^E	$\rightarrow$	Gibbs free Energy
P	$\rightarrow$	Pressure
R	$\rightarrow$	Gas constant, 0.08314 bar dm^3/mol.K
T	$\rightarrow$	Temperature,K
K	$\rightarrow$	Kelvin
V	$\rightarrow$	Molar volume, dm^3
X^A	$\rightarrow$	Mole fraction of the molecule not bonded at site A
a	$\rightarrow$	Activity coefficient/Attractive constant in EOS
a(T)	$\rightarrow$	Temperature function in an EOS
a_0	$\rightarrow$	Parameter in the energy term, bar-dm^6/mol^2
b	$\rightarrow$	Covolume parameter/Repulsive constant in EOS, dm^3/mol
c	$\rightarrow$	Volume translation
k*ij*, l*ij*	$\rightarrow$	Binary interaction parameters
n	$\rightarrow$	Mole number
x	$\rightarrow$	Mole fraction

Greek Symbols

α $\rightarrow$ Coefficients in generalized cubic EOS

$\alpha(Tr)$ $\rightarrow$ Residual temperature function in an EOS

β $\rightarrow$ Association volume parameter, dimensionless

ε $\rightarrow$ Association/ Interaction energy parameter,$bar.dm^3/mol$

ρ $\rightarrow$ Molar density, mol/dm^3

ω $\rightarrow$ Accentric factor

Subscripts/Superscripts

0      $\rightarrow$ Standard state

c $\rightarrow$ Critical function

i,j $\rightarrow$ Components in a mixture

m $\rightarrow$ Molar property

r $\rightarrow$ Residual function

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1: An Overview

Oils and natural gases naturally occur within the earth at high pressure and temperature. The industry focuses on the extraction and processing of petroleum mixtures to satisfy the energy demands of today's modern society. Hence, the needs of understanding phase behaviour of petroleum fluids are the key for profitable extraction, production, and processing had captured interest for the industry. Natural gas chemical compositions are depending on the origins of the reservoir as it comprises of light hydrocarbons, heavier hydrocarbons and non hydrocarbon mixtures like carbon dioxide, hydrogen sulphide and asphalthene. Typical compositions of natural gas comprise of 20 to 50 mol% of light hydrocarbons like methane gases and certain heavies (Ayala, 2006). As said earlier, typical compositions of natural gas depending on nature of the originate natural gas. Where actually gas releases from the expanding of oil droplet as the pressure is reduced.

Natural gas has widely used in chemical processing industries and as a fuel for boiler in a petrochemical plant. It does widely used to produce varieties of products, and nowadays with improvements in technology had governed many companies to invest into research and development in understanding its behaviour. It is unlikely to have more than 10% of carbon dioxide mixtures in the original natural gas mixtures, but it is not possible to have the kinds of compositions where much of the processing natural gas comes clean with almost no heavies.

The concentration of carbon dioxide gases can be increased by a process of Synthesis Natural Gas (SNG) and it can be applied to the industry based on their purpose of synthesizing the gas in the first place. Some of the companies will use synthetic natural gas for enhanced oil recovery technique. For example if the natural gas obtained from the multiple distillation stage, what left in the natural gas mixtures is the chemical compositions with no interest to the companies and to

further separate the mixtures are determined as non valuable and not economic. Then those mixtures can be sending to the boiler as a heating fuel. What happened if the mixtures are produced at the offshore? And considering transportation of the light hydrocarbons considered not economical? It is a breakthrough if the "lights" can further be processed and maybe injected back into the reservoir as a new enhanced oil recovery technique. Theoretically it can be implemented and yet had been implemented by injecting the lights hydrocarbon which called immiscibility displacement. The improved oil recovery techniques; like water injection had been used for decades to improve companies' recovery factor. To implement the idea, the prediction of phase behaviour at reservoir conditions is a necessity.

It is a headache when water handling issues are discussed that could increase corrosion rates and sand problem. These problems had been faced and challenged enough for the operator where it had increased their CAPEX and eventually OPEX too. Strictly speaking, immiscibility displacement by natural gas mixtures with high inorganic content like carbon dioxide and nitrogen gases are possible to replace water injection technique and the behaviour of the mixtures needs to be investigated further.

As we deplete the readily accessible reserves, we will need to obtain natural gas from conditions that are both more severe and more remote. And gases that were previously thought to be uneconomical, such as those containing non-combustible components of nitrogen, carbon dioxide and hydrogen sulphide, will also be explored. And previously mentioned topics related to water handling issue, CAPEX and OPEX rises and also immiscibility displacement; are actually very connected to the importance of phase behaviour of natural gas mixtures. This is actually the needs of this study where fluid phase equilibria is crucial to predict as not all equation of state are capable of predicting phase behaviour of the mixtures. Hence, the needs of testing different cubic equation of state at different natural gas mixtures compositions will gives and understanding to the engineers and companies in predicting natural gaseous phase behaviour.

1.2: Background of Study

One of the most useful phase behaviour visualisations is the pressure-temperature (P-T) diagram or normally called a phase envelope. Each envelope represents a thermodynamic boundary separating the two-phase conditions from the single-phase region. This paper's attention is to discuss the complexities of the phase behaviour of the natural gas with and without non-hydrocarbon with different concentrations by using eight equations of state. The needs to use many equations in this study are to test the validity of the equations to the experimental studies that had been done by previous researchers. The objectives and scope of study are given below.

1.3: Objectives

The study of natural gas mixtures phase behaviour prediction governs in this paper are based on the following objectives;

1. To study the applicability of EOS functions; CPA-PR-VDW, CPA-SRK-VDW, PR-VDW, SRK-VDW, PR-UNIQUAC-WS, PR-NRTL-WS, SRK-EXT-VDW and PR-WS on the natural gas mixtures using different mixing rules.
2. To calculate %AAD of temperature and pressure of different EOS equation used.
3. To study the effect of two types of mixing rules used in EOS equations; Van-der-Walls and Wong-Sandler in predicting phase envelopes.

1.4: Scope of Study

In supporting objectives above, the results will be generated based on the following scope of studies given below:

1. Generate phase envelope at standard temperature and pressure, 273.15K and 101325 Pa.
2. Using eight EOS functions as described above to perform phase equlibria calculations by using an excel simulator PRODE add in.
3. Tested EOS models from SRK families and PR families with WS mixing rule and VDW mixing rules.

CHAPTER 2

LITERATURE REVIEW

2.1: Introduction

This chapter describes previous works that had been done in the phase equilibria, theoretical concept of thermodynamics, and application of the EOS in the industry. Predicting phase behaviour of the natural gas mixtures has been done on many concentrations by using different mixing rules and different types of EOS. EOS can be divided into cubic and non cubic equation of states. Non cubic equations of state better describe the volumetric behaviour of pure substance but may not be suitable for complex hydrocarbon mixtures. Cubic EOSs are better and commonly used in oil and gas industries as it better describes the Pressure Volume Temperature (PVT) and Vapour Liquid Equilibrium (VLE) of pure substances. No matter which EOS that is to be used, it is the needs for the engineers and scientists to associate functions with the mixing rules, as in our case for multi-component systems; each parameter is defined by its mixing rule and quite at best arbitrary. In this chapter, associate theory regarding to the phase envelope calculations on natural gas mixtures at low temperature conditions is discussed with some fundamental concepts from previous works that had been done.

2.2 Natural Gas

Natural gases are composed of hydrocarbon and non-hydrocarbon mixtures. It consists largely of methane, ethane, propane, butane, higher alkane, nitrogen, oxygen, carbon dioxide, hydrogen sulphide and helium. It is reported that typical natural gas compositions for methane would be greater than 85%, ethane around 3-8%, propane 1-2%, butane and pentane would be less than 1%, carbon dioxide around 1-2%, hydrogen sulphide less than 1%, nitrogen gases around 1-5% and helium less than 0.5% (Ibrahim, 2000). It is found that most of natural gas brought to surface from the reservoir conditions has less than 20% of carbon dioxide. The carbon dioxide concentrations are meant to be increasing when the natural gas meant to be synthesized into synthetic natural gas known as SNG (Bakar et al., 2010).

Bakar describes that in a modern technology, a machine called digesters is used to turn organic material like plants, animal waste, etc into SNG, that could replaces waiting of thousands of years for the gas to form naturally and simultaneously overcome the depletion of natural gas resources. Hence, this study on calculating phase behaviour of natural gas in high carbon dioxide content is feasible to be conducted as the companies and industries are looking for a new alternative to harnessing energy from waste. In coming chapter, we will see on EOSs models capabilities in predicting 90% carbon dioxide concentration in SNG mixtures. The research on natural gas dew points and bubble points at different concentrations and conditions had been done for many years and they are using SNG (Nasrifar et al., 2005).

Actually, petroleum reservoir fluids comprise of five categories; black oil, volatile oils, retrograde gases, wet gases and dry gases (Ayala, 2006). The difference between each fluid characterization is depending on their degree API and composition of the heavies' fractions (Ayala, 2006). Ayala had described that the location of the critical point and fluid phase envelope is a function of fluid composition and in general, phase envelopes tend to shift to the right when the relative proportion of heavies' component (C7+) increases (Turek et al., 1980), which in the other hand, the mixture is said to behave as a natural gas phase behaviour.

For the confirmation of the equation of interest to the applicability of SNG that had been used to study phase equilibria, the same EOS functions will be used to test with the experimental data conducted by several researches. Nasrifar (Nasrifar et al., 2004) had presented fifteen EOS functions in describing and predicting dew points of SNG natural gases, but due to the limited time constraint, this research will used only eight EOS by using the experimental values conducted by many literatures and as can be seen in chapter four with the EOS parameters in terms of the PVT relations coming from the standard practices from the industry.

The idea is that, not all EOSs are applicable in modelling phase behaviours to be used for every mixtures of the natural gas. This is true when Turek mentioned in his paper that if a generalized equation of state can match experimental data, then it can be used in a reservoir simulator to calculate the phase equilibria necessary for the

prediction of fluid compositions, densities, and viscosities during a displacement process (Turek et al., 1980). The phrase gives an idea that the more general the equation which turns out to be more simpler form of the EOS, the better the result would yield in terms of the percentage absolute average deviation between experimental values and calculated values. That is the idea of testing eight EOS functions for different sets of constituent's mixture.

2.3 Applications of the EOS in the Industry

If an equation of state is to represent the PVT behaviour of both liquids and vapour, it must encompass a wide range of temperatures and pressures. Yet it must not be so complex as to prevent excessive numerical or analytical difficulties in application. Polynomial equations that are cubic in molar volume offer a compromise between generality and simplicity that is suitable for many purposes (Smith et al., 2005).

Non cubic EOS used widely for describing volumetric behaviour and its application are not suitable for complex hydrocarbon mixtures (Ashour et al., 2011). In his paper, he presented that if VLE calculations are involving by using modified Benedict-Webb-Rubin equation for the PVT description of pure substances, it is accurate enough with less percentage AAD compared two cubic EOS of Peng-Robinson. But it turns out that using Peng-Robinson EOS for describing hydrocarbon mixtures gives significantly accurate results compared to Benedict-Webb-Rubin (BWR) (Ashour et al., 2011). That is one of the reasons on why these papers choose to study EOS models from PR families.

The application of BWRS are less accurate for computing VLE of hydrocarbon mixtures as it requires high volume and large numbers that actually a measured of the complexity of the equations and hence not suitable for reservoir fluids studies where many sequential equilibrium calculations are required (Ashour et al., 2011). So, in calculating phase envelope of natural gas mixtures, the cubic equation of state will be used with associating parameters of mixing rule.

The mixing rules are simply a means of calculation mixture parameters equivalent to pure substance and actually cubic EOS are developed and derived only for pure fluids and extended to mixtures through the use of mixing rules as stated by Ibrahim Ashour (Ashour et al., 2011). In this study, eight equations of state will be used. There are CPA-PR-VDW, CPA-SRK-VDW, PR-VDW, SRK-VDW, PR-UNIQUAC-WS, PR-NRTL-WS, SRK-EXT-VDW, and PR-WS.

After Van der Walls equation of state had been introduced in 1873, Valderama describes that many attempts had been introduced to improve VDW EOS in terms of the predictions of volumetric, thermodynamic, and phase equilibrium properties. (Valderama, 2003). It is actually regarded as a "hard sphere term + attractive term" equation of state that was composed from the contribution of repulsive and attractive intermolecular forces interactions, and the first equation capable of representing vapour liquid coexistence that describe by Sadus (Sadus, 1994).

Realizing the limitations of the VDW, in 1994, Redlich and Kwong (RK) succeed in formulated two parameter cubic equation of state that improving hard sphere term and attractive term equation by proposing temperature dependence for the attractive term (Ashour et al., 2011). Hence, many investigators got interest in the EOS limitations by improving and modify VDW equations and improving RK equations, for example Soave in late 1972 and Peng-Robinson in 1976 proposed additional modifications for the RK equation to make the phase equilibria predictions are more accurate in order to predict vapour pressure, liquid density, and K-values or known as equilibrium ratios (Velderama, 2003). Since then, many works and experimental values had been done and more additional theory to prove the existence theorem of hydrogen bonding have been developed, for example thermodynamic perturbation theory (TPT) that was proposed by Wertheim in late 1987 (Velderama, 2003).

In 1980, Van Konyenburg and Scott successfully demonstrated the most critical equilibria exhibited by binary mixtures that could be qualitatively predicted by the VDW EOS that is fully limited and rarely accurate for describing critical properties and phase equilibria calculations as explained by Velderama (Velderama, 2003). Five examples of cubic equations of state on the VDW equations are listed in Figure 2.1.

Reference	Equations of state
Redlich-Kwong (1949)	$p = \dfrac{RT}{V-b} - \dfrac{a}{V(V+b)T^{0.5}}$
Soave-Redlich-Kwong (1972)	$p = \dfrac{RT}{V-b} - \dfrac{a(T)}{V(V+b)}$
Peng-Robinson (1976)	$p = \dfrac{RT}{V-b} - \dfrac{a(T)}{V(V+b)+b(V-b)}$
Stryjek-Vera-Peng-Robinson (1986)	$p = \dfrac{RT}{V-b} - \dfrac{a(\theta,T)}{V(V+b)+b(V-b)}$
Patel-Teja (1982)	$p = \dfrac{RT}{V-b} - \dfrac{a(T)}{V(V+b)+c(V-b)}$

Figure 2. 1: Five Examples of Improved Cubic EOS from the VDW EOS

(Velderama, 2003)

From figure 2.1, RK EOS equation is quite similar to the SRK, except that Soave introduced new constant for replacing the term $a/T^{0.5}$ with a general temperature dependent term $a(T)$ as in the SRK equations above and he also introduces an accentric factor. The validity of the SRK fitted well with the experimental that had been done by him and several researches like Zheng and Daubert in predicting phase behaviour of mixtures in the critical region using mixtures of hydrocarbons in estimating their critical properties (Velderama, 2003). From here, it is clear that RK-EOS cannot predict the critical properties of the phase equilibria mixtures and only suitable for moderate temperatures and pressures. Yet the fundamentals introduction of the accentric terms gives an improvement in fluid equilibria predictions in hydrocarbon mixtures.

For the PR EOS, in late 1976, they slightly improve the predictions of fluid volumes and critical compressibility factor and Ashour reported that PR-EOS functions is excellent in characterizing non hydrocarbon components like hydrogen and nitrogen containing mixtures (Ashour et al., 2011). Ashour in his paper explains that PR-EOS gives good result in obtaining a relatively accurate, non-iterative and computationally efficient correlation of high pressure mixtures used in gas turbines and rocket engines. Ashour also states in his paper that SRK EOS fails to predict liquid compressibility accurately and comparisons of vapour pressure calculation

that had been done shows small error in both equations when comparing with the experimental results He added that PR-EOS enjoys more simplicity and reliability than other EOS functions but both PR and SRK break down at C10 to C11 and heavier compounds (Ashour et al., 2011). However, the successes of both EOS are restricted to the estimation of phase equilibria pressure as depicted in figure 2.2. Figure 2.2 describes that, for the mixture's property calculation, none single EOS are capable in the prediction and calculation mixture's property where the calculated saturated liquid volumes are not been improvised and tend to be higher than the experimental data.

As years by years, there are many complex and accurate EOS have been introduced and published for better understanding in PVT properties and VLE. Velderama outlined in his article that summarized some basic rules that should be observed for developing molecular based EOS as in Figures 2.2 and 2.3 below. It can be concluded from here that the mixtures polarity by means of non hydrocarbon and hydrocarbon mixtures and equilibrium condition give a very significant impact on the calculation of the VLE and mixtures phase equilibria. Not all EOS functions can be applied. From Figure 2.3, most of the recommendations lead to SRK, PR, and PTV as the best EOS functions in describing the fluid behaviour. Thus, this is one of the reasons on why this study trying to use SRK and PR for describing phase envelope with varies natural gas mixtures with different non-hydrocarbon compositions.

property	comments	recommendations
gas volume at moderate/ high pressure	most cubic EoS with two or three parameters	SRK, PR, PTV
gas volume at low temperature, moderate/high pressure	most cubic EoS with two or three parameters adjusted using low-temperature data	SRK, PR
saturated vapor volume	most cubic equations	SRK, PR, PT
saturated liquid volume for nonpolar fluids	three-parameter equations seem to be better	PTV, PT, but empirical correlations should be preferred
saturated liquid volume for polar fluids	two- or three-parameter equations with parameters adjusted for polar fluids	PT, but empirical correlations should be preferred
compressed liquid volume	none of the cubic equations	empirical correlations or specific equations for a given fluid should be used
volume near the critical point	most cubic EoS fail in this region, but three-parameter equations should be preferred	PTV or other three-parameter EoS with parameters adjusted using near-critical data
vapor pressure for nonpolar fluids	most cubic EoS, although those that use more involved $a(T)$ functions give better results	SRK, PR, PTV, but prefer $\alpha(T)$ with specific parameters for polar fluids, such as Soave-polar[28]
vapor pressure for polar fluids	most cubic equations, although those that use specific parameters for polar fluids should be preferred	PR, PTV with complex $\alpha(T)$ function, such as that of Twu[169]
vapor pressure for associating fluids	none of the cubic equations	noncubic equations specially developed for this type of fluid should be preferred
enthalpy and entropy of liquids	none of the cubic equations give accurate results	specific equations, usually polynomial, should be preferred
enthalpy and entropy of gases at low pressure	most cubic equations, although those that use specific parameters for polar fluids should be preferred	SRK, PR, PTV, but prefer $\alpha(T)$ with specific parameters
enthalpy and entropy of gases at moderate/ high pressure	most cubic equations, although those that use specific parameters for polar fluids should be preferred	PR and PTV with $\alpha(T)$ with specific parameters; noncubic equations are also good

Figure 2. 2: Recommendations on Suitability of Modelling Mixtures by EOS

(Velderama, 2003)

type of mixture	EoS	temp function	mixing rule
low pressure (<10 atm)			
nonpolar + nonpolar	SRK, PR, PTV	Soave[26]	P&R, WS
nonpolar + polar	SRK, PR, PTV	Soave-polar[28]	P&R, WS
polar + polar	SRK, PR, PTV	Soave-polar,[28] Mathias[163]	WS
asymmetric mixtures	SRK, PR, PTV	Twu	P&R, MWS-1P
polymer solutions	SRK, PR, SWP	Soave,[26] Mathias[163]	HV, MWS-1P, ZM
moderate and high pressures (>10 atm.)			
nonpolar + nonpolar	SRK, PR	Soave[26]	vdW-1 or -2
nonpolar + polar	SRK, PR, PTV	Soave-polar[28]	vdW-1 or -2
polar + polar	SRK, PR	Soave-polar,[28] Mathias[163]	vdW-2, P&R
nonpolar + nonpolar	SRK, PR	Soave[26]	vdW-1 or -2
reservoir fluids	SRK, PR, PTV	Soave[26]	vdW-1 or -2
polymer solutions	SRK, PR, SWP	Soave,[26] Mathias[163]	WS, ZM
one supercritical component	PR, PTV	Soave,[26] Twu[169]	P&R, WS-2P, WS-3P

Figure 2.3: Recommendation on General EOS and Mixing Rule for Different Types

of Liquid-Vapor Mixtures (Velderama, 2003)

mixing/combining rule	formulas
van der Waals one parameter: k_{ij} two parameters: k_{ij}, l_{ij}	$a = \sum_i \sum_j x_i x_j a_{ij}$ $\qquad b = \sum_i \sum_j x_i x_j b_{ij}$ $a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$ $\qquad b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij})$
Panagiotopoulos−Reid (PR) two parameters: k_{ij}, k_{ji} three parameters: k_{ij}, k_{ji}, l_{ij}	$a_{ij} = \sqrt{a_i a_j}[1 - k_{ij} + (k_{ij} - k_{ji})x_i]$ $b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij})$
general nonquadratic (GNQ) two parameters: δ_i, δ_j three parameters: $\delta_i, \delta_j, \beta_i$	$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$ $\qquad k_{ij} = \delta_i x_i + \delta_j x_j$ $b_{ij} = 0.5[b_i(1 - \beta_i) + b_j(1 - \beta_j)]$ $\beta_i \neq 0$ for all solutes and $\beta_j = 0$ for all solvents
Kwak−Mansoori (KM) three parameters: $k_{ij}, \beta_{ij}, l_{ij}$	$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$ $\qquad b_{ij} = 0.5(b_i^{1/3} + b_j^{1/3})^3(1 - \beta_{ij})$ $d_{ij} = 0.5(d_i^{1/3} + d_j^{1/3})^3(1 - l_{ij})$
Kwak−Mansoori modification 1 (KM-1) three parameters: k_{ij}, l_{ij}, β_i (one solute)	$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$ $\qquad b_{ij} = 0.5[b_i(1 - \beta_i) + b_j(1 - \beta_j)]$ $d_{ij} = 0.5(d_i^{1/3} + d_j^{1/3})^3(1 - l_{ij})$ $\beta_i \neq 0$ for all solutes and $\beta_j = 0$ for all solvents
Kwak−Mansoori modification 2 (KM-2) three parameters: $\delta_i, \delta_j, \beta_i$ (one solute)	$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$ $\qquad d_{ij} = 0.5(d_i^{1/3} + d_j^{1/3})^3$ $k_{ij} = \delta_i x_i + \delta_j x_j$ $\qquad b_{ij} = 0.5[b_i(1 - \beta_i) + b_j(1 - \beta_j)]$ $\beta_i \neq 0$ for all solutes and $\beta_j = 0$ for all solvents
Kurihara et al. (KTK) three parameters: η_1, η_2, η_3	$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} - (\tau - \phi)g^E_{RES}/\ln[(b - \phi)/(b - \tau)]$ $b = \sum_i \sum_j x_i x_j b_{ij}, \quad b_{ij} = \frac{1}{2}(b_i + b_j) \quad g^E_{RES} = RTx_1 x_2[\eta_1 + \eta_2(x_1 - x_2) + \eta_3(x_1 - x_2)^2]$
Wong−Sandler one parameter: k_{ij} two parameters: k_{ij}, l_i (one solute)	$b = \sum\sum x_i x_j (b - a/RT)_{ij}/[1 - \sum x_i a_i/b_i RT - A^E_x(x)/\Omega RT]$ $a = b[\sum x_i a_i/b_i - A^E_x(x)/\Omega]$ $(b - a/RT)_{ij} = 0.5[b_i(1 - l_i) + b_j] - (a_i a_j)^{0.5}(1 - k_{ij})/RT$ $l_i \neq 0$ for all solutes and $l_j = 0$ for all solvents

Figure 2.4: Selected Mixing Rule and Combining Rules Used In Two-Constant
Cubic EOS (Velderama, 2003)

It is said by Ashour that the most applicable EOS functions in fluid characterization in terms of phase equilibria is RK-EOS, SRK-EOS and PR-EOS because both SRK and PR introduced accentric factor as the third parameter to obtain parameter *a* in their equations (Ashour et al., 2011).

The list of different mixing rules that can be used in EOS functions are presented in Figure 2.4. The recommendations presented in figure 2.3 above is an indication that for the fluid mixtures used in this study, most hydrocarbon phase equilibria calculations will be predicted accurately by using SRK, PRSV, PR and by using VDW mixing rule of one parameter or two parameter binary interactions as shown in Figure 2.4. As can be seen from Tables 4.1 to 4.2, the compositions used in this study ranging from a mixtures of a polar and non polar components which depicted that another possible mixing rule to be used as indicated in Figure 2.3 and 2.4 which is WS mixing rule that is recommended to be applicable at low pressure of less than 10 atm. The risk is worth taking on trying to use WS mixing rules by using the cubic EOS functions in getting an understanding of the outcomes result.

With regards to the natural gas mixtures discussed earlier in this studies, Hartono describes that for modelling systems with non-polar and slightly polar compounds, a new concept has evolved in recent years with the introduction of EOS abbreviated CPA (Cubic Plus Association) presented by Kontogeorgis in 1996 that used for modelling VLE for alcohol-hydrocarbon system in correlating LLE for this mixtures. CPA models are actually combining the physical effects from the classical models and a chemical contribution (Hartono et al., 2004).

Kontogeorgis describes that CPA is the combination of the physical term and the association term. The physical terms characterized as repulsive forces and attractive forces and can be calculated by using simple EOS models like SRK and PR. The association term accounts for the hydrogen bonding and calculated from the Weirtheim perturbation theory (Kontogeorgis et al., 1996). He added that perturbation theory are complex and endless that depending on the nature of the system. That is why the needs of reference state, approximations and simple methods are needed in account for the perturbation theory (Kontogeorgis et al., 2010).

Kontogeorgis and his friends added the term "pseudo-association" which refered as previously mention reference system for accounting the limitations of the perturbation theory. They pointed that for strongly dipolar molecules like acetone or a quadrupolar like carbon dioxide, these molecules are treated using the concept of pseudo-association that actually being able to act as associating compounds (Kontogeorgis et al., 1996, 2010). This approach renders CPA to be reliable to such compounds without the need of extra terms to account for polar or quadropolar interactions. And for the needs of understanding, it is worth evaluating phase behaviour of natural gas by using CPA EOS models.

The use of non quadratic mixing rules for the prediction of VLE in polar organic binary solutions, which had been discussed in details by Vahid. His research used the combination of cubic EOS and excess free Gibbs energy mixing rules in representing the behaviour of highly polar solutions. Vahid states that the combined EOS and free Gibbs energy models need to reproduce the excess Gibbs free energy models as closely as possible in order to represent low pressure VLE of polar mixtures accurately and to make vapor liquid predictions at higher temperatures and pressures accurate using only low pressure information. In his work, the introduction of two

models Gibbs free energy is used which were UNIQUAC and NRTL models and both models are in good association only with WS mixing rules where NRTL model has weak predictive capabilities due to the limitation in temperature-dependent variables and UNIQUAC has better approximations for prediction of polar organic mixtures (Vahid, 2004).

Velderama in his papers describes that quadratic mixing rules are usually sufficient for the correlation of phase equilibrium in simple systems. Velderama describes that, to treat more complex systems, there is a modifications by previous researcher that introduced a second interaction parameter by making the binary interaction parameter concentration dependent, thus transforming mixing rule in a non-quadratic form (Velderama, 2003)

He also added that EOS + Gibbs Free energy seems to be the most appropriate for modelling mixtures with highly asymmetric components which had been applied in Huron and Vidal that modelling the combination of EOS and Gibbs free energy to modelling a mixtures of low and high pressure vapor liquid mixtures, to liquid-liquid equilibrium, and gas solid equilibria, with the important contribution of mixing rules such as WS. Velderama shared an important predictions of the WS mixing rule, where this mixing rule has been the focus of several studies, and among all the mixing rule that had been tested by several authors that combining NRTL and UNIQUAC models for the excess Gibbs free energy and the study shows that for strongly polar-non-polar mixtures, the combination of WS + NRTL gives the best results and the combination of WS + UNIQUAC models give best results in strongly polar + strongly polar mixtures. This gives an early estimation that EOS +Gibbs Energy+ mixing rule are not capable in predictions of any hydrocarbon mixtures (Velderama, 2003).

In relevance of the introduction of CPA-EOS-NRTL-mixing rule into this studies by combining equation of state of PR and RK families is that the capabilities of the equation in modelling mixtures of varies pressure range and also a temperature dependence and expected that some equations introduced in this study that use CPA+EOS+mixing rule and EOS+ Gibbs free energy mixing rule like CPA-PR-VDW, CPA-SRK-VDW, PR-UNIQUAC-WS and PR-NRTL-WS will gives an

interesting results in modelling natural gas mixtures phase behaviours. Some general formulations on each EOS models described are presented in Table 2.1.

Table 2. 1: Summaries of the General Formalism of Eight EOS Models

Abbreviation [a,b,c,]	General Formalism[a,b,c,]	a[a,b,c,]	b [a,b,c,]	a(T)[a,b,c,]	Mixing Rule[a,b,c,]	
PR-VDW	$P = RT/(V-b) + a_c\alpha(Tr)/(V(V+b))$	$0.45724(R^2(Tc)^2)/Pc$	$0.07780RTc/Pc$	$[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1-(Tr)^{1/2})]^2$	$a = \sum\sum xixjaij$; $aij = \sqrt{((aiaj)(1-kij))}$	$b = \sum\sum xixjbij$; $bij = \frac{1}{2}(bi + bj)(1-\beta ij)$
PR-WS	$P = RT/(V-b) + a_c\alpha(Tr)/(V(V+b))$	$0.45724(R^2(Tc)^2)/Pc$	$0.07780RTc/Pc$	$[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1-(Tr)^{1/2})]^2$	$a = b[\sum xiai/bi - A_\infty^E(x)/\Omega]$	$b = \sum\sum xixj(b - a/RT)ij/[1 - \sum xiai/biRT - A_\infty^E(x)/\Omega RT]$
SRK-VDW	$P = RT/(V-b) + a_c\alpha(Tr)/(V(V+b))$	$0.42748(R^2(Tc)^2)/Pc$	$0.08664RTc/Pc$	$[1 + (0.480 + 1.574\omega - 0.176\omega^2)(1-(Tr)^{1/2})]^2$	$a = \sum\sum xixjaij$; $aij = \sqrt{((aiaj)(1-kij))}$	$b = \sum\sum xixjbij$; $bij = \frac{1}{2}(bi + bj)(1-\beta ij)$
SRK-EXT-VDW	$P = RT/(V-b) + a_c\alpha(Tr)/(V(V+b))$	$0.42748(R^2(Tc)^2)/Pc$	$0.08664RTc/Pc$	$[1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1-(Tr)^{1/2})]^2$	$a = \sum\sum xixjaij$; $aij = \sqrt{((aiaj)(1-kij))}$	$b = \sum\sum xixjbij$; $bij = \frac{1}{2}(bi + bj)(1-\beta ij)$
CPA-PR-VDW	$P = RT/(V-b) - (a/(V(V+b)) + (RT/V) p\sum[1/X^A - 0.5][\partial X^A/\partial p]$	$0.45724(R^2(Tc)^2)/Pc$	$0.07780RTc/Pc$	$[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1-(Tr)^{1/2})]^2$	$a = \sum\sum xixjaij$; $aij = \sqrt{((aiaj)(1-kij))}$	$b = \sum\sum xixjbij$; $bij = \frac{1}{2}(bi + bj)(1-\beta ij)$
CPA-SRK-VDW	$P = RT/(V-b) - (a/(V(V+b)) + (RT/V) p\sum[1/X^A - 0.5][\partial X^A/\partial p]$	$0.42748(R^2(Tc)^2)/Pc$	$0.08664RTc/Pc$	$[1 + (0.480 + 1.574\omega - 0.176\omega^2)(1-(Tr)^{1/2})]^2$	$a = \sum\sum xixjaij$; $aij = \sqrt{((aiaj)(1-kij))}$	$b = \sum\sum xixjbij$; $bij = \frac{1}{2}(bi + bj)(1-\beta ij)$

		a	b		a	b
PR-NRTL-WS	$P = RT/(V-b)$ $+a_c\alpha(Tr)/(V(V+b))$	$a=b[g^E_0/A_1 +\sum x_1(a_i/b_i)+RT/A_i\sum x_i\ln(b/b_i)]$	$b=\sum b_i x_i$	$[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1-(Tr)^{1/2})]^2$	$a = b[\sum x_i a_i/b_i - A_\infty^E(x)/\Omega]$	$b = \sum\sum x_i x_j(b - a/RT)_{ij}/[1 -\sum x_i a_i/b_i RT - A_\infty^E(x)/\Omega RT]$
		$0.45724(R^2(Tc)^2)/Pc$	$0.07780RTc/Pc$		$(b - a/RT)_{ij} = 0.5[b_i(1 - l_i) + b_j] - (a_i a_j)0.5(1 - k_{ij})/RT$; $l_i \neq 0$ for all solutes and $l_j=0$ for all solvents	
PR-UNIQUAC-WS	$P = RT/(V-b)$ $+a_c\alpha(Tr)/(V(V+b))$	$a=b[g^E_0/A_1 +\sum x_1(a_i/b_i)+RT/A_i\sum x_i\ln(b/b_i)]$	$b=\sum b_i x_i$	$[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1-(Tr)^{1/2})]^2$	$a = b[\sum x_i a_i/b_i - A_\infty^E(x)/\Omega]$	$b = \sum\sum x_i x_j(b - a/RT)_{ij}/[1 -\sum x_i a_i/b_i RT - A_\infty^E(x)/\Omega RT]$
		$0.45724(R^2(Tc)^2)/Pc$	$0.07780RTc/Pc$		$(b - a/RT)_{ij} = 0.5[b_i(1 - l_i) + b_j] - (a_i a_j)0.5(1 - k_{ij})/RT$; $l_i \neq 0$ for all solutes and $l_j=0$ for all solvents	

[a] Kontogeorgis et al., 1996

[b] Velderama, 2003

[c] Velderama et al., 2003

[d] Diamantonis et al., 2013

2.4: About PRODE software in Microsoft Excel Simulation

The attention for using simulator is an added advantage in testing different sets of natural gas mixtures phase envelope by using EOS models. The idea is that, engineers should be able to choose which equation is right for modelling thermodynamic properties and phase envelope of the mixtures, and by using simulator like Prode properties is another way of conducting, validating and testing each EOS models for different sets of mixture. Another reasons on why testing EOS models by using Prode is that most of the engineers and students should use the equations for application of the industrial usage that was developed an invented by previous scientist and mathematician. It was many EOS models that were developed these days and very few of the usage limitation of each equation are reported and their applicability and efficiency for certain mixtures is still questionable.

Prode properties includes a comprehensive collection of procedures that used to solve problems related to physical properties data, heat and material balance, process simulation, process control, equipment design, phase envelope calculations, flash calculation, separations, instrument design and more.

The technical features overview of the Prode Properties includes direct access from Windows applications that includes Microsoft Excel and Visual Studio applications that includes MATLAB, MathCad and more. The properties of this software support for up to 500 different streams up to 100 components per stream.

In relation to the thermodynamic properties calculation, a Prode property includes several compilations of chemical data and Binary Interaction Parameters (BIPs) are available. A comprehensive set of thermodynamic models likes Regular, Wilson, NRTL, UNIQUAC, UNIFAC, Soave-Redlich-Kwong, Peng-Robinson, BWRS, Steam Tables (IAPWS 1995), Lee Kesler Plocker , AGA (ISO 20765); GERG (ISO 18453); GERG (2008); Hydrates (VDW-Platteeuw), models which include association contribute CPA SRK, CPA PR, PC-SAFT, EOS models with different mixing rules like Van der Waals, Huron Vidal and Wong Sandler are also available for the ease of industrial applications.

The software also have a functions for thermodynamic calculation such as enthalpy and entropy and also coded built ins models for industrial applications in performing

a set of flash operations at isothermal, isobaric, isochoric and adiabatic. In relation to the modeling mixtures of different compositions in performing phase envelope calculations, Prode properties include functions for calculating specific properties of mixtures that includes critical point, cricodentherm, cricondenbar, and cloud point.

Here after, the limitation of this software is that the developer doesn't share on details about the coding built in for generation of the calculation that similarly observed as others commercial software such as PVTi, VLE flash and HYSYS.

CHAPTER 3

METHODOLOGY

3. 1: Introduction

Procedure identification of this studies are modelling phase envelopes of various sets of data that comprise of twenty four contextual mixtures by using excel simulator Prode add in. The procedure in this modelling is simple and tested 200 equations of state is not a problem, but the idea is that which existing equations of state are capable of characterizing natural gas mixtures with and without non-hydrocarbon components with a minimum percentage AAD.

3. 2: Procedure

The steps involve in this modelling is the same as we do modelling in every other software like PVTi, VLE and HYSYS. As described in chapter two, twenty four mixtures of natural gases will be modelled by using this simulator and the resulted temperature and pressure of the modelled phase envelope are compared with the experimental pressure and temperature obtain from the literature. Then, all sets of data in terms of deviation pressure calculated and temperature calculated to the experimental values are calculated and presented in terms of the average arithmetic deviation or AAD. In this case, two types of percentage AAD will be presented which is percentage AAD due to temperature and pressure. The significance of calculating both percentages AAD is that, most of the EOSs are good at predicting and modelling phase envelope with respect to temperature deviation, but for pressure deviation, it entirely varies.

Due to lots of data calculated for temperature and pressure and for matching between calculated values to the experimental values, the easiest way is to use excel formulae as equation 3.5 and the matching values were used to calculate percentage deviation. The calculated percentage deviation formulae used for temperature and pressure deviation are as equation 3.1, 3.2 and for percentage AAD by using equation 3.3 and 3.4.

$$\% \, Dev = 100 \left[\frac{abs(calculated \, P - experimental \, P)}{experimental \, P} \right] \qquad (3.1)$$

$$\% \, Dev = 100 \left[\frac{abs(calculated \, T - experimental \, T)}{experimental \, T} \right] \qquad (3.2)$$

$$\% AAD \, (T) = \left(\frac{100}{n} \right) \sum_{i=1}^{n} \left(\frac{abs(calculated \, T - experimental \, T)}{experimental \, T} \right) \qquad (3.3)$$

$$\% AAD \, (P) = \left(\frac{100}{n} \right) \sum_{i=1}^{n} \left(\frac{abs(calculated \, P - experimental \, P)}{experimental \, P} \right) \qquad (3.4)$$

INDEX(E:E,MATCH(MIN(ABS(E:E-C3)),ABS(E:E-C3),0)) (3.5)

Where;

E and C = Excel Column

ABS =Absolute

MIN =Minimum

3.3: Procedure Summary

Summaries of the steps involve for calculation of the phase behaviours for 24 natural gas mixtures as in Table 4.1 and 4.2 by using eight EOSs models are listed below:

1. One EOS model and natural gas mixture had defined in the Prode add in simulator; note that only a mixture and one EOS models could be tested at the same time.

2. Particular isothermal conditions for simulation were defined where in this case at STP.

3. The simulation should be running after all the parameters and natural gas composition had defined and resulted graph of phase envelope with its calculated values of temperature and pressure are analysed.

4. Then, the resulted temperature and pressure values together with the experimental values will be match in the excel file by using equation 3.5.

5. The values match for temperature and pressure are used to calculate percentage deviation by using equation 3.1 and 3.2.

6. Percentage AAD of T and P from the step 5 were calculated by using equation 3.3 and 3.4 for that particular mixture.

7. The calculated values of T and P from step 3 together with experimental values were plotted on the same graphs.

8. Step 1 to step 6 were repeated for another 7 EOS models for same mixtures in this study.

9. Steps 1 to 7 were repeated for another 23 natural gas mixtures.

10. The resulted percentage AAD of T and P calculated were compared and analysed in choosing the most applicable EOS models for modelling that particular natural gas mixture.

11. Resulted graph generated will be 192 graphs as shown in the appendices.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1: Introduction

There are twenty four types of natural gas mixtures used in this, study with different component compositions. These can be divided into different sets of analysis which is set 6, set 9, set 15, set 18, set 19 and set 20. The different sets of the mixtures composition were obtain from the literature studies conducted previously by different authors that modelling and investigating various thermodynamics calculation theories for different types of equations of state. The summaries of different sets of data are presented as in Tables 4.1 and 4.2.

There are 192 graphs of natural gas mixture's phase envelope generated for different equation of states and presented in the appendix. But for the ease of presentation and comparing, the graphs is combine and yielded 24 phase envelope graphs as shown below and table summarizes of the experimental values, calculated values and the percentage AAD for temperature and pressure presented in Tables 4.3 to 4.8. The resulted graph presented in this chapter will be briefly discussed.

Table 4. 1: Summaries of Composition of Natural Gas Mixtures Used In This Study

component mixture	SET 6 [a]			SET 9[b]	SET 15[c]							
	SNG 2	SNG 3	SNG 4	GAS 1	GAS 1	GAS 2	GAS 3	SNG 1	SNG 2	SNG 3	SNG 4	SNG 5
nitrogen	1.70%	1.71%	-	1.70%	-	6.90%	0.75%	-	-	-	-	-
carbon dioxide	1.71%	1.70%	-	1.70%	-	0.51%	3.91%	-	-	-	-	-
methane	89.99%	89.98%	90.00%	89.98%	89.00%	88.19%	70.20%	93.51%	84.28%	96.61%	94.09%	93.60%
ethane	3.15%	2.86%	4.57%	3.01%	7.00%	2.72%	9.22%	2.97%	10.07%	-	4.47%	2.63%
propane	1.58%	1.43%	2.24%	1.51%	-	0.85%	2.76%	1.01%	4.03%	-	-	-
iso-butane	0.78%	0.71%	1.14%	0.75%	-	0.17%	0.66%	1.05%	0.60%	1.53%	-	1.49%
n-butane	0.79%	0.72%	1.15%	0.75%	4.00%	0.32%	0.98%	1.47%	1.03%	1.48%	-	1.49%
iso-pentane	0.15%	0.45%	0.45%	0.30%	-	0.09%	0.40%	-	-	0.39%	1.45%	0.80%
n-pentane	0.15%	0.45%	0.45%	0.30%	-	0.09%	0.42%	-	-	-	-	-
n-hexane	-	-	-	-	-	0.12%	0.82%	-	-	-	-	-
n-heptane	-	-	-	-	-	0.03%	9.87%	-	-	-	-	-
n-octane	-	-	-	-	-	0.02%	-	-	-	-	-	-
SUM/ % Mol	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%

[a] Atilhan et al., 2011

[b] Atilhan et al., 2011

[c] Nasrifar et al., 2006

Table 4. 2: Summaries of Composition Natural Gas Mixtures Used In This Study

component mixture	SET 18[d]					SET 19[e]		SET 20[f]				
	SNG 1	SNG 2	SNG 3	SNG 4	SNG 5	GAS 1	GAS 2	MIXTURE A	MIXTURE B	MIXTURE C	MIXTURE D	MIXTURE E
nitrogen	1.56%	0.31%	0.77%	6.90%	5.65%	-	-	-	-	0.86%	0.80%	0.60%
carbon dioxide	25.91%	0.20%	1.70%	0.51%	0.28%	95%	99%	-	-	-	-	-
methane	69.11%	90.48%	84.45%	88.19%	83.35%	-	-	85.34%	75.44%	75.70%	74.27%	90.07%
ethane	2.62%	8.04%	8.68%	2.72%	7.53%	-	-	7.90%	15.40%	13.59%	16.51%	6.54%
propane	0.42%	0.80%	3.30%	0.85%	2.01%	5%	-	4.73%	6.95%	6.74%	6.55%	2.20%
iso-butane	0.11%	0.08%	0.29%	0.17%	0.31%	-	-	0.85%	0.98%	1.34%	0.84%	0.29%
n-butane	0.10%	0.12%	0.59%	0.32%	0.52%	-	1%	0.99%	1.06%	1.33%	0.89%	0.28%
iso-pentane	0.03%	0.01%	0.08%	0.09%	0.12%	-	-	0.10%	0.09%	0.22%	0.07%	0.01%
n-pentane	0.02%	0.01%	0.09%	0.09%	0.14%	-	-	0.09%	0.08%	0.22%	0.07%	0.01%
n-hexane	0.11%	0.00%	0.05%	0.12%	0.07%	-	-	-	-	-	-	-
n-heptane	-	0.00%	-	0.03%	0.01%	-	-	-	-	-	-	-
n-octane	-	-	-	0.02%	0.01%	-	-	-	-	-	-	-
SUM/ % Mol	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%

[d] Nasrifar, et al.; 2005

[e] Gil, et al.; 2006

[f] Nasrifar, et al.; 2002

Table 4. 3: Comparison Table of Different EOS and Their Percentage AAD to the Experimental Values for Set 6

Type of EOS	MIXTURE	Experimental T Range (K)	Experimental P Range (MPa)	Calculated T Range (K)	Calculated P Range (MPa)	%AAD/P	%AAD/T
CPA-PR-VDW	SNG2	224.81 to 245.28	7.51179 to 1.57178	205.069 to 211.32	0.1013 to 6.4087	2.84%	0.13%
	SNG3	239.31 to 270.6	9.68088 to 3.3032	214.202 to 211.236	0.1013 to 6.5889	5.40%	0.91%
	SNG4	265.6 to 274.23	11.76229 to 1.59253	241.89 to 245.64	0.101327 to 0.532805	89.12%	12.84%
CPA-SRK-VDW	SNG2	224.81 to 245.28	7.51179 to 1.57178	207.319 to 217.883	0.10132 to 7.194	2.37%	0.33%
	SNG3	239.31 to 270.6	9.68088 to 3.3032	217.36 to 218.06	0.101327 to 7.423	1.78%	0.18%
	SNG4	265.6 to 274.23	11.76229 to 1.59253	218.81 to 226.13	0.101327 to 8.02	6.15%	0.68%
PR-VDW	SNG2	224.81 to 245.28	7.51179 to 1.57178	204.718 to 211.651	0.10132 to 6.711	2.94%	0.19%
	SNG3	239.31 to 270.6	9.68088 to 3.3032	213.82 to 211.73	0.101327 to 6.92	3.47%	0.70%
	SNG4	265.6 to 274.23	11.76229 to 1.59253	215.66 to 219.36	0.101327 to 7.52	7.41%	1.63%
SRK-VDW	SNG2	224.81 to 245.28	7.51179 to 1.57178	207.0907 to 212.077	0.10132 to 6.8308	3.04%	0.27%
	SNG3	239.31 to 270.6	9.68088 to 3.3032	217.48 to 211.74	0.101327 to 7.00	2.29%	0.32%
	SNG4	265.6 to 274.23	11.76229 to 1.59253	218.74 to 252.59	0.101327 to 9.80	6.74%	0.98%
PR-UNIQUAC-WS	SNG2	224.81 to 245.28	7.51179 to 1.57178	209.449 to 205.79	0.10132 to 4.093	8.28%	0.64%
	SNG3	239.31 to 270.6	9.68088 to 3.3032	217.67 to 207.59	0.101327 to 4.01	19.66%	2.53%
	SNG4	265.6 to 274.23	11.76229 to 1.59253	219.75 to 213.14	0.101327 to 3.90	21.47%	4.41%
PR-NRTL-WS	SNG2	224.81 to 245.28	7.51179 to 1.57178	204.698 to 231.4953	0.10132 to 6.5224	7.44%	1.49%
	SNG3	239.31 to 270.6	9.68088 to 3.3032	215.36 to 226.82	0.101327 to 6.76	17.28%	3.62%
	SNG4	265.6 to 274.23	11.76229 to 1.59253	216.48 to 243.62	0.101327 to 6.56	21.05%	6.19%
SRK-EXT-VDW	SNG2	224.81 to 245.28	7.51179 to 1.57178	206.256 to 217.049	0.10132 to 7.149	2.33%	0.17%
	SNG3	239.31 to 270.6	9.68088 to 3.3032	216.74 to 217.37	0.101327 to 7.39	2.03%	0.19%
	SNG4	265.6 to 274.23	11.76229 to 1.59253	217.99 to 226.28	0.101327 to 8.03	6.40%	0.80%
PR-WS	SNG2	224.81 to 245.28	7.51179 to 1.57178	209.460 to 226.8026	0.10132 to 6.555	6.90%	1.08%

| | SNG3 | 239.31 to 270.6 | 9.68088 to 3.3032 | 217.56 to 243.33 | 0.101327 to 6.15 | 22.05% | 3.21% |
| | SNG4 | 265.6 to 274.23 | 11.76229 to 1.59253 | 220.33 to 233.88 | 0.101327 to 6.77 | 18.05% | 5.46% |

Table 4. 4: Comparison Table of Different EOS and Their Percentage AAD to the Experimental Values for Set 9

Type of EOS	MIXTURE	Experimental T Range (K)	Experimental P Range (MPa)	Calculated T Range (K)	Calculated P Range (MPa)	%AAD/P	%AAD/T
CPA-PR-VDW	GAS 1	230.96 to 259.89	198.3 to 274.8	210.330774 to 211.243033	0.101327 to 6.494981	3.43%	0.43%
CPA-SRK-VDW	GAS 1	230.96 to 259.89	198.3 to 274.8	211.869254 to 247.291510	0.101327 to 9.056496	0.66%	0.21%
PR-VDW	GAS 1	230.96 to 259.89	198.3 to 274.8	209.953530 to 211.642000	0.101327 to 6.807748	1.95%	0.38%
SRK-VDW	GAS 1	230.96 to 259.89	198.3 to 274.8	213.169809 to 211.872919	0.101327 to 6.911106	0.68%	0.15%
PR-UNIQUAC-WS	GAS 1	230.96 to 259.89	198.3 to 274.8	214.096582 to 206.587089	0.101327 to 4.050863	15.11%	1.79%
PR-NRTL-WS	GAS 1	230.96 to 259.89	198.3 to 274.8	209.516326 to 239.659577	0.101327 to 4.244432	18.51%	3.19%
SRK-EXT-VDW	GAS 1	230.96 to 259.89	198.3 to 274.8	212.396532 to 217.160417	0.101327 to 6.049359	1.13%	0.27%
PR-WS	GAS 1	230.96 to 259.89	198.3 to 274.8	213.548040 to 239.166622	0.101327 to 6.274874	16.53%	2.71%

Table 4. 5: Comparison Table of Different EOS and Their Percentage AAD to the Experimental Values for Set 15

Type of EOS	MIXTURE	Experimental T Range (K)	Experimental P Range (MPa)	Calculated T Range (K)	Calculated P Range (MPa)	%AAD/P	%AAD/T
CPA-PR-VDW	GAS 1	253.7 to 265.8	1.27 to 9.25	209.848257 to 220.772086804371	0.101327 to 7.237094	4.31%	0.81%
	GAS 2	247.7 to 211.6	0.19 to 6.79	239.542266 to 199.378710046142	0.101327 to 5.808732	7.17%	0.32%
	GAS 3	313.5 to 371.6	45.02 to 46.68	111.666960 to 315.111540993529	0.101327 to 18.96125	58.80%	7.96%
	SNG 1	246.2 to 236.6	8.92 to 1.04	200.565822 to 210.919424	0.101327 to 6.277544	2.90%	0.51%
	SNG 2	256.2 to 236.2	8.7 to 1.04	198.441894 to 229.216766	198.441894 to 229.216766	4.17%	0.46%
	SNG 3	263.7 to 241.9	7.92 to 0.64	211.435928 to 210.708285911528	0.101327 to 6.808647	2.47%	0.85%
	SNG 4	266 to 243.4	9.44 to 0.3	222.576170 to 222.658277553349	0.101327 to 8.046678	3.09%	0.52%
	SNG 5	268.7 to 240.8	9.32 to 0.34	218.412315 to 243.935164	0.101327 to 9.27768	3.37%	0.69%
CPA-SRK-VDW	GAS 1	253.7 to 265.8	1.27 to 9.25	209.939661 to 226.779416920867	0.101327 to 7.953985	3.90%	0.03%
	GAS 2	247.7 to 211.6	0.19 to 6.79	239.712413 to 204.953307553279	0.101327 to 6.479749	5.55%	0.35%
	GAS 3	313.5 to 371.6	45.02 to 46.68	111.453599 to 329.199694950395	0.101327 to 20.08734	56.35%	4.94%
	SNG 1	246.2 to 236.6	8.92 to 1.04	200.693555 to 230.375502	0.101327 to 0.737535	79.46%	8.44%
	SNG 2	256.2 to 236.2	8.7 to 1.04	198.562958 to 246.524635	0.101327 to 8.473739	3.09%	0.18%
	SNG 3	263.7 to 241.9	7.92 to 0.64	212.488238 to 228.277494914328	0.101327 to 8.7619	2.89%	0.11%

	SNG 4	266 to 243.4	9.44 to 0.3	222.944058 to 243.863860	0.101327 to 9.554254	2.32%	0.20%
	SNG 5	268.7 to 240.8	9.32 to 0.34	219.336352 to 249.997078642019	0.101327 to 10.00667	3.44%	0.15%
PR-VDW	GAS 1	253.7 to 265.8	1.27 to 9.25	209.377856 to 221.012225327231	0.101327 to 7.58861	4.07%	0.53%
	GAS 2	247.7 to 211.6	0.19 to 6.79	238.871196 to 200.382984997653	0.101327 to 6.166527	6.14%	0.31%
	GAS 3	313.5 to 371.6	45.02 to 46.68	111.963259 to 319.448343724951	0.101327 to 19.11443	58.47%	6.98%
	SNG 1	246.2 to 236.6	8.92 to 1.04	200.272725 to 211.097814	0.101327 to 6.56872	2.04%	0.36%
	SNG 2	256.2 to 236.2	8.7 to 1.04	198.128163 to 229.537440	0.101327 to 7.637711	3.81%	0.29%
	SNG 3	263.7 to 241.9	7.92 to 0.64	211.117508 to 237.531133	0.101327 to 9.098834	2.64%	0.67%
	SNG 4	266 to 243.4	9.44 to 0.3	222.138750 to 225.940583665357	0.101327 to 8.638277	2.54%	0.47%
	SNG 5	268.7 to 240.8	9.32 to 0.34	218.058221 to 243.102217	0.101327 to 9.703952	3.51%	0.53%
SRK-VDW	GAS 1	253.7 to 265.8	1.27 to 9.25	210.539680 to 210.853081472523	0.101327 to 6.452288	6.86%	0.15%
	GAS 2	247.7 to 211.6	0.19 to 6.79	243.506657 to 197.90430016099	0.101327 to 5.855365	5.51%	0.30%
	GAS 3	313.5 to 371.6	45.02 to 46.68	112.007316 to 319.610495448242	0.101327 to 20.37991	55.72%	6.96%
	SNG 1	246.2 to 236.6	8.92 to 1.04	202.235513 to 211.489804	0.101327 to 6.658122	1.72%	0.08%
	SNG 2	256.2 to 236.2	8.7 to 1.04	199.796500 to 230.225994	0.101327 to 0.725226	76.55%	9.52%
	SNG 3	263.7 to 241.9	7.92 to 0.64	211.368312 to 243.778944	0.101327 to 9.26641	2.37%	0.47%
	SNG 4	266 to 243.4	9.44 to 0.3	223.541944 to 241.575983	0.101327 to 9.618063	2.69%	0.24%
	SNG 5	268.7 to 240.8	9.32 to 0.34	218.519439 to 237.883364013621	0.101327 to 9.64333	3.16%	0.43%

PR-UNIQUAC-WS	GAS 1	253.7 to 265.8	1.27 to 9.25	209.284936 to 213.072633	0.101327 to 3.949091	4.05%	4.25%
	GAS 2	247.7 to 211.6	0.19 to 6.79	238.362582 to 195.737554	0.101327 to 4.111135	19.52%	2.69%
	GAS 3	313.5 to 371.6	45.02 to 46.68	120.565810 to 261.448214	0.101327 to 6.075115	86.80%	23.42%
	SNG 1	246.2 to 236.6	8.92 to 1.04	203.915777 to 204.773596	0.101327 to 4.054188	7.69%	1.82%
	SNG 2	256.2 to 236.2	8.7 to 1.04	201.663906 to 218.070725	0.101327 to 4.039414	7.29%	1.14%
	SNG 3	263.7 to 241.9	7.92 to 0.64	216.791374 to 201.917936	0.101327 to 3.984572	5.05%	2.73%
	SNG 4	266 to 243.4	9.44 to 0.3	221.829542 to 234.907551	0.101327 to 6.151763	10.08%	3.84%
	SNG 5	268.7 to 240.8	9.32 to 0.34	221.886422 to 207.266725	0.101327 to 3.913619	8.83%	2.87%
PR-NRTL-WS	GAS 1	253.7 to 265.8	1.27 to 9.25	209.178004 to 227.884067	0.101327 to 6.518905	5.37%	5.08%
	GAS 2	247.7 to 211.6	0.19 to 6.79	238.090734 to 210.835327	0.101327 to 6.413986	17.42%	3.07%
	GAS 3	313.5 to 371.6	45.02 to 46.68	120.427847 to 315.628774	0.101327 to 6.600051	85.66%	7.89%
	SNG 1	246.2 to 236.6	8.92 to 1.04	200.928784 to 226.304969	0.101327 to 0.623112	82.65%	10.06%
	SNG 2	256.2 to 236.2	8.7 to 1.04	198.637403 to 235.752759	0.101327 to 6.640566	6.05%	1.90%
	SNG 3	263.7 to 241.9	7.92 to 0.64	208.303488 to 232.794057	0.101327 to 6.106699	6.40%	5.66%
	SNG 4	266 to 243.4	9.44 to 0.3	221.695771 to 231.396188	0.101327 to 6.378342	9.27%	4.56%
	SNG 5	268.7 to 240.8	9.32 to 0.34	215.982544 to 240.213065	0.101327 to 6.283101	9.94%	5.43%
SRK-EXT-VDW	GAS 1	253.7 to 265.8	1.27 to 9.25	209.904742 to 218.299366044065	0.101327 to 7.07514	5.75%	0.03%
	GAS 2	247.7 to 211.6	0.19 to 6.79	242.380502 to 202.722830762698	0.101327 to 6.220538	5.57%	0.38%

	GAS 3	313.5 to 371.6	45.02 to 46.68	111.456353 to 320.501011194739	0.101327 to 20.57214	55.30%	6.79%
	SNG 1	246.2 to 236.6	8.92 to 1.04	201.360192 to 216.790974	0.101327 to 7.016825	1.89%	0.07%
	SNG 2	256.2 to 236.2	8.7 to 1.04	198.963126 to 246.410078	0.101327 to 8.477509	3.17%	0.20%
	SNG 3	263.7 to 241.9	7.92 to 0.64	210.576199 to 241.714707	0.101327 to 9.301485	2.93%	0.28%
	SNG 4	266 to 243.4	9.44 to 0.3	222.944058 to 243.863860	0.101327 to 9.554254	2.32%	0.42%
	SNG 5	268.7 to 240.8	9.32 to 0.34	217.831886 to 235.15041697764	0.101327 to 9.289856	4.10%	0.25%
PR-WS	GAS 1	253.7 to 265.8	1.27 to 9.25	209.203415 to 238.405462	0.101327 to 6.823677	5.20%	5.01%
	GAS 2	247.7 to 211.6	0.19 to 6.79	221.011809 to 226.346863	0.101327 to 6.038113	20.10%	4.87%
	GAS 3	313.5 to 371.6	45.02 to 46.68	120.427845 to 289.749196	0.101327 to 6.198233	86.53%	15.13%
	SNG 1	246.2 to 236.6	8.92 to 1.04	202.624761 to 221.445302	0.101327 to 6.485643	7.06%	2.99%
	SNG 2	256.2 to 236.2	8.7 to 1.04	200.379370 to 236.292221	0.101327 to 6.700871	6.23%	1.65%
	SNG 3	263.7 to 241.9	7.92 to 0.64	215.629861 to 234.077065	0.101327 to 6.061801	5.93%	4.26%
	SNG 4	266 to 243.4	9.44 to 0.3	221.715410 to 235.795108	0.101327 to 6.069642	10.42%	4.50%
	SNG 5	268.7 to 240.8	9.32 to 0.34	217.831886 to 235.15041697764	0.101327 to 9.289856	8.74%	3.88%

Table 4. 6: Comparison Table of Different EOS and Their Percentage AAD to the Experimental Values for Set 18

Type of EOS	MIXTURE	Experimental T Range (K)	Experimental P Range (MPa)	Calculated T Range (K)	Calculated P Range (MPa)	%AAD/P	%AAD/T
CPA-PR-VDW	SNG1	213.6 to 246.4	0.12 to 6.02	181.958304 to 232.602920	0.101327 to 7.979895	6.74%	0.21%
	SNG2	205.8 to 211.6	0.25to 6.27	175.319163 to 218.376649	0.101327 to 5.774435	5.17%	1.44%
	SNG3	217.9 to 244.5	0.12 to 8.18	212.597546 to 225.097799	0.101327 to 7.065975	5.25%	0.36%
	SNG4	247.7 to 211.6	0.19 to 6.79	215.584449 to 202.624697	0.101327 to 6.153122	8.85%	3.20%
	SNG5	258.3 to 215.7	0.2 to 7.42	208.265858 to 231.744026	0.101327 to 7.66834	5.57%	3.93%
CPA-SRK-VDW	SNG1	213.6 to 246.4	0.12 to 6.02	181.958304 to 232.602920	0.101327 to 9.056496	6.74%	0.21%
	SNG2	205.8 to 211.6	0.25to 6.27	175.543055 to 223.020263	0.101327 to 6.354389	3.81%	0.56%
	SNG3	217.9 to 244.5	0.12 to 8.18	212.597546 to 225.097799	0.101327 to 7.065975	5.25%	0.36%
	SNG4	247.7 to 211.6	0.19 to 6.79	221.377315 to 205.237296	0.101327 to 6.461588	6.46%	2.70%
	SNG5	258.3 to 215.7	0.2 to 7.42	208.228260 to 236.351681	0.101327 to 8.271359	3.27%	3.20%
PR-VDW	SNG1	213.6 to 246.4	0.12 to 6.02	181.958304 to 232.602920	0.101327 to 7.979895	6.74%	0.21%
	SNG2	205.8 to 211.6	0.25to 6.27	175.195994 to 220.330570	0.101327 to 6.009801	4.78%	1.22%
	SNG3	217.9 to 244.5	0.12 to 8.18	212.252744 to 225.515670	0.101327 to 7.427102	4.04%	0.34%
	SNG4	247.7 to 211.6	0.19 to 6.79	221.200149 to 200.650191	0.101327 to 6.1421232	8.81%	2.24%
	SNG5	258.3 to 215.7	0.2 to 7.42	207.916397 to 233.610809	0.101327 to 8.05633	3.95%	3.75%

SRK-VDW	SNG1	213.6 to 246.4	0.12 to 6.02	181.958304 to 232.602920	0.101327 to 7.979895	6.74%	0.21%
	SNG2	205.8 to 211.6	0.25to 6.27	173.768548 to 214.394976	0.101327 to 5.731945	5.96%	2.75%
	SNG3	217.9 to 244.5	0.12 to 8.18	213.909879 to 221.112419	0.101327 to 7.047848	5.04%	0.36%
	SNG4	247.7 to 211.6	0.19 to 6.79	222.883363 to 199.185179	0.101327 to 5.977344	8.13%	1.90%
	SNG5	258.3 to 215.7	0.2 to 7.42	209.893396 to 211.120386	0.101327 to 6.761969	4.97%	3.84%
PR-UNIQUAC-WS	SNG1	213.6 to 246.4	0.12 to 6.02	181.958304 to 232.602920	0.101327 to 7.979895	6.74%	0.21%
	SNG2	205.8 to 211.6	0.25to 6.27	176.250486 to 221.485669	0.101327 to 5.596609	6.96%	1.23%
	SNG3	217.9 to 244.5	0.12 to 8.18	212.627893 to 214.868019	0.101327 to 4.113537	11.31%	1.00%
	SNG4	247.7 to 211.6	0.19 to 6.79	220.847764 to 214.868019	0.101327 to 4.130955	19.79%	5.19%
	SNG5	258.3 to 215.7	0.2 to 7.42	208.151801 to 229.211759	0.101327 to 4.130955	12.72%	6.10%
PR-NRTL-WS	SNG1	213.6 to 246.4	0.12 to 6.02	207.940176 to 239.659577	0.101327 to 7.497602	6.24%	0.29%
	SNG2	205.8 to 211.6	0.25to 6.27	191.114861 to 197.670888	0.101327 to 3.752208	8.01%	1.64%
	SNG3	217.9 to 244.5	0.12 to 8.18	212.281379 to 231.954207	0.101327 to 6.68215	9.66%	1.44%
	SNG4	247.7 to 211.6	0.19 to 6.79	220.651968 to 209.748583	0.101327 to 6.328076	19.21%	5.81%
	SNG5	258.3 to 215.7	0.2 to 7.42	201.770045 to 235.245807	0.101327 to 5.904307	14.00%	7.01%
SRK-EXT-VDW	SNG1	213.6 to 246.4	0.12 to 6.02	216.281802 to 234.180958	0.101327 to 7.792258	8.39%	0.37%
	SNG2	205.8 to 211.6	0.25to 6.27	172.718769 to 216.792232	0.101327 to 5.92354	5.06%	2.29%
	SNG3	217.9 to 244.5	0.12 to 8.18	212.538137 to 225.646641	0.101327 to 7.289261	4.42%	0.33%
	SNG4	247.7 to 211.6	0.19 to 6.79	221.411983 to 203.342098	0.101327 to 6.253115	8.05%	1.88%

	SNG5	258.3 to 215.7	0.2 to 7.42	208.660124 to 219.189033	0.101327 to 7.322935	5.40%	4.26%
PR-WS	SNG1	213.6 to 246.4	0.12 to 6.02	217.031883 to 251.073439	0.101327 to 8.248001	5.89%	0.40%
	SNG2	205.8 to 211.6	0.25to 6.27	176.153551 to 222.095658	0.101327 to 5.547751	6.46%	1.30%
	SNG3	217.9 to 244.5	0.12 to 8.18	212.496343 to 250.518500	0.101327 to 4.012318	10.94%	1.40%
	SNG4	247.7 to 211.6	0.19 to 6.79	220.721038 to 213.824063	0.101327 to 6.226488	19.74%	5.74%
	SNG5	258.3 to 215.7	0.2 to 7.42	208.025218 to 222.195591	0.101327 to 6.607029	12.22%	6.83%

Table 4. 7: Comparison Table of Different EOS and Their Percentage AAD to the Experimental Values for Set 19

Type of EOS	MIXTURE	Experimental T Range (K)	Experimental P Range (MPa)	Calculated T Range (K)	Calculated P Range (MPa)	%AAD/P	%AAD/T
CPA-PR-VDW	GAS 1	198.3 to 274.8	0.12 to 3.49	212.652516 to 365.252978	0.101327 to 4.314516	3.22%	2.23%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.494499 to 368.618737	0.101327 to 4.089688	4.75%	4.70%
CPA-SRK-VDW	GAS 1	198.3 to 274.8	0.12 to 3.49	222.736576 to 370.671501	0.101327 to 4.576448	3.58%	2.20%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.049334 to 373.350708	0.101327 to 4.389156	4.58%	4.58%
PR-VDW	GAS 1	198.3 to 274.8	0.12 to 3.49	212.973203 to 366.774594	0.101327 to 4.48467	3.25%	2.20%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.293397 to 370.373227	0.101327 to 4.232301	4.75%	4.65%
SRK-VDW	GAS 1	198.3 to 274.8	0.12 to 3.49	216.104228 to 364.800043	0.101327 to 4.347441	3.13%	2.24%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.609128 to 370.596833	0.101327 to 4.254033	4.91%	4.72%
PR-UNIQUAC-WS	GAS 1	198.3 to 274.8	0.12 to 3.49	218.892230 to 363.792834	0.101327 to 4.257795	3.13%	2.24%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.293397 to 370.373227	0.101327 to 4.232301	4.76%	4.65%
PR-NRTL-WS	GAS 1	198.3 to 274.8	0.12 to 3.49	218.892230 to 363.792834	0.101327 to 4.257795	3.13%	2.24%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.273825 to 370.527868	0.101327 to 4.244432	4.76%	4.65%
SRK-EXT-VDW	GAS 1	198.3 to 274.8	0.12 to 3.49	217.727253 to 370.223935	0.101327 to 4.603517	3.51%	2.20%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.293397 to 370.373227	0.101327 to 4.232301	4.76%	4.65%
PR-WS	GAS 1	198.3 to 274.8	0.12 to 3.49	226.249086 to 365.856787	0.101327 to 4.25394	3.52%	2.22%
	GAS 2	192.6 to 274.5	0.13 to 3.49	232.293397 to 370.373227	0.101327 to 4.232301	4.76%	4.65%

Table 4. 8: Comparison Table of Different EOS and Their Percentage AAD to the Experimental Values for Set 20

Type of EOS	MIXTURE	Experimental T Range (K)	Experimental P Range (MPa)	Calculated T Range (K)	Calculated P Range (MPa)	%AAD/P	%AAD/T
CPA-PR-VDW	MIX A	110 to 130	0.0787 to 0.321	113.515268 to 228.835587	0.101327 to 7.482849	17.41%	1.89%
	MIX B	110 to 125	0.0723 to 0.2153	114.820031 to 249.093249	0.101327 to 8.188404	20.67%	2.29%
	MIX C	110 to 130	0.1155 to 0.3744	111.688196 to 251.057236	0.101327 to 9.473044	9.57%	2.05%
	MIX D	110 to 135	0.1158 to 0.2853	112.068549 to 252.065442	0.101327 to 9.151403	11.53%	2.13%
	MIX E	115 to 130	0.1456 to 0.3698	111.381827 to 211.198370	0.101327 to 5.922366	11.76%	1.90%
CPA-SRK-VDW	MIX A	110 to 130	0.0787 to 0.321	113.363522 to 233.638267	0.101327 to 8.065472	17.35%	1.91%
	MIX B	110 to 125	0.0723 to 0.2153	114.638112 to 254.102754	0.101327 to 8.810461	20.61%	2.24%
	MIX C	110 to 130	0.1155 to 0.3744	111.488677 to 260.485417	0.101327 to 10.38745	9.61%	1.93%
	MIX D	110 to 135	0.1158 to 0.2853	111.856484 to 258.840011	0.101327 to 9.931922	11.55%	2.13%
	MIX E	115 to 130	0.1456 to 0.3698	111.242941 to 216.472486	0.101327 to 6.577725	12.06%	1.82%
PR-VDW	MIX A	110 to 130	0.0787 to 0.321	113.345744 to 227.465490	0.101327 to 7.709621	17.30%	1.92%
	MIX B	110 to 125	0.0723 to 0.2153	114.637846 to 249.071839	0.101327 to 8.609445	20.57%	2.23%
	MIX C	110 to 130	0.1155 to 0.3744	111.609332 to 252.763091	0.101327 to 10.03412	9.67%	1.98%
	MIX D	110 to 135	0.1158 to 0.2853	111.973424 to 249.198012	0.101327 to 9.429675	11.57%	2.13%
	MIX E	115 to 130	0.1456 to 0.3698	0.101327 to 6.577725	0.101327 to 6.204181	12.34%	1.81%
SRK-VDW	MIX A	110 to 130	0.0787 to 0.321	113.748155 to 236.305447	0.101327 to 0.70316	23.22%	2.74%
	MIX B	110 to 125	0.0723 to 0.2153	114.603874 to 244.373946	0.101327 to 8.29514	20.41%	2.18%
	MIX C	110 to 130	0.1155 to 0.3744	111.706480 to 249.604196	0.101327 to 9.818784	9.93%	1.99%
	MIX D	110 to 135	0.1158 to 0.2853	111.721259 to 115.118774	0.101327 to 0.129073	12.79%	1.29%
	MIX E	115 to 130	0.1456 to 0.3698	111.619149 to 210.948057	0.101327 to 6.178393	13.08%	1.90%
PR-UNIQUAC-	MIX A	110 to 130	0.0787 to 0.321	114.234212 to 218.029259	0.101327 to 5.93874	17.49%	1.78%
	MIX B	110 to 125	0.0723 to 0.2153	116.213527 to 230.594827	0.101327 to 6.096456	20.83%	2.84%

WS	MIX C	110 to 130	0.1155 to 0.3744	114.909270 to 233.095733	0.101327 to 6.274074	10.13%	1.99%
	MIX D	110 to 135	0.1158 to 0.2853	115.099629 to 233.381954	0.101327 to 6.255438	11.62%	2.39%
	MIX E	115 to 130	0.1456 to 0.3698	112.007375 to 206.919149	0.101327 to 5.517862	12.29%	2.10%
PR-NRTL-WS	MIX A	110 to 130	0.0787 to 0.321	114.236423 to 233.128935	0.101327 to 6.536331	17.50%	1.78%
	MIX B	110 to 125	0.0723 to 0.2153	116.183326 to 246.680304	0.101327 to 1.044302	28.14%	3.83%
	MIX C	110 to 130	0.1155 to 0.3744	114.875646 to 257.173352	0.101327 to 6.859932	10.22%	1.99%
	MIX D	110 to 135	0.1158 to 0.2853	115.060364 to 255.906975	0.101327 to 6.834363	11.66%	2.37%
	MIX E	115 to 130	0.1456 to 0.3698	112.010511 to 215.468166	0.101327 to 6.004569	12.25%	2.10%
SRK-EXT-VDW	MIX A	110 to 130	0.0787 to 0.321	113.247810 to 228.153094	0.101327 to 7.556242	17.35%	1.93%
	MIX B	110 to 125	0.0723 to 0.2153	114.134575 to 248.882739	0.101327 to 8.439479	20.59%	2.17%
	MIX C	110 to 130	0.1155 to 0.3744	111.357781 to 253.222221	0.101327 to 9.831298	9.63%	1.86%
	MIX D	110 to 135	0.1158 to 0.2853	111.374633 to 114.410687	0.101327 to 0.125401	11.98%	1.22%
	MIX E	115 to 130	0.1456 to 0.3698	111.175210 to 214.042937	0.101327 to 6.34667	12.13%	1.79%
PR-WS	MIX A	110 to 130	0.0787 to 0.321	114.250956 to 229.509708	0.101327 to 6.457865	17.50%	1.78%
	MIX B	110 to 125	0.0723 to 0.2153	116.220665 to 251.909523	0.101327 to 6.82033	20.84%	2.85%
	MIX C	110 to 130	0.1155 to 0.3744	114.928904 to 257.873660	0.101327 to 6.82033	10.71%	2.00%
	MIX D	110 to 135	0.1158 to 0.2853	115.111452 to 255.195632	0.101327 to 6.811601	11.95%	2.40%
	MIX E	115 to 130	0.1456 to 0.3698	112.024051 to 214.481862	0.101327 to 6.013233	11.65%	2.11%

4.2: Resulted Calculation for SET 6
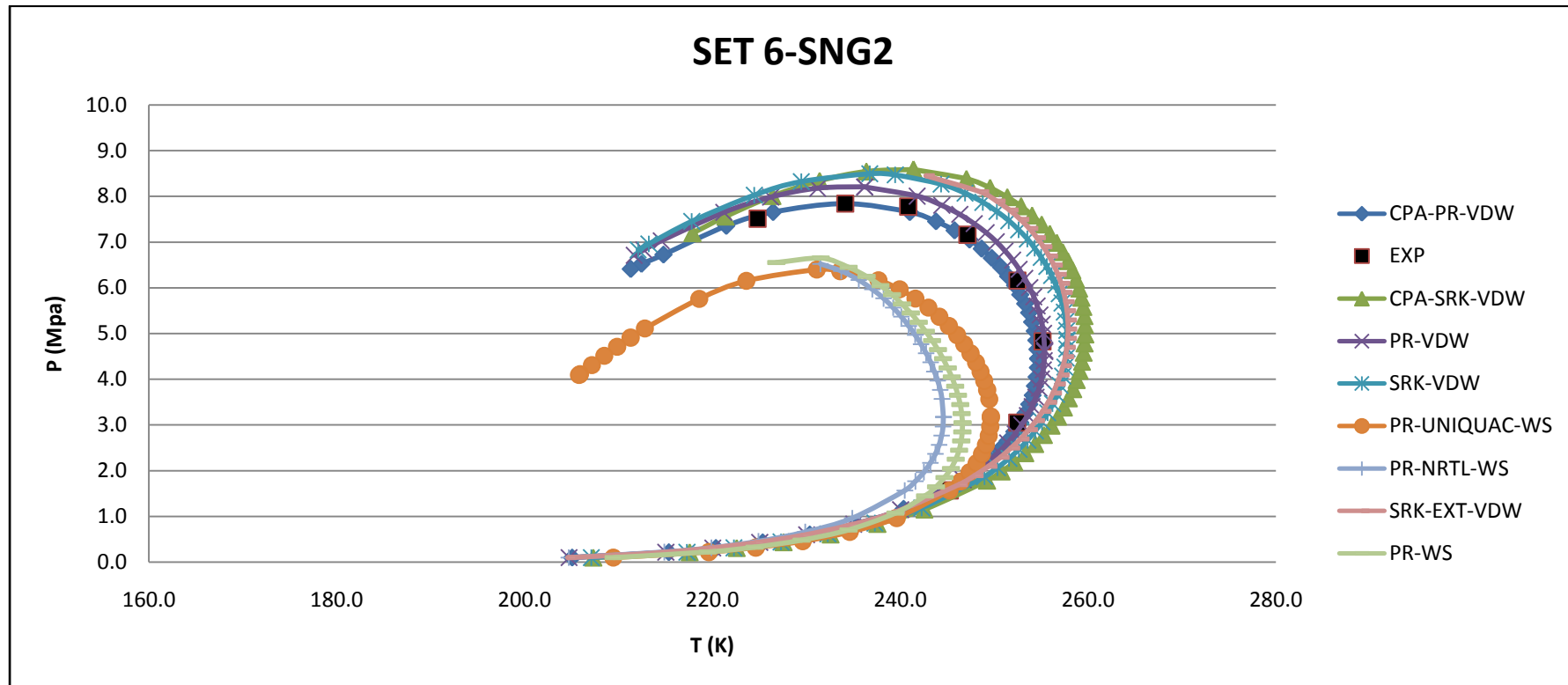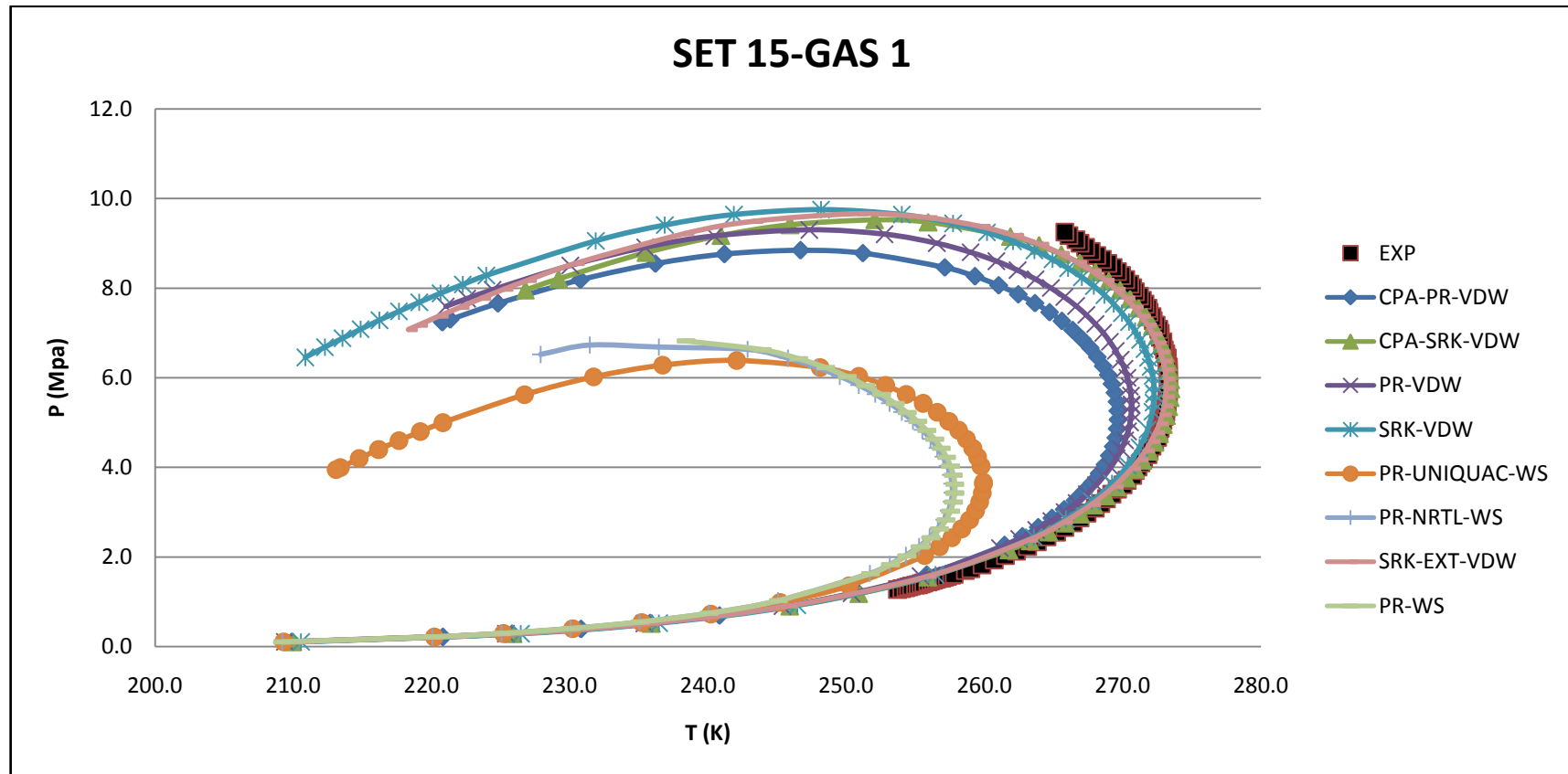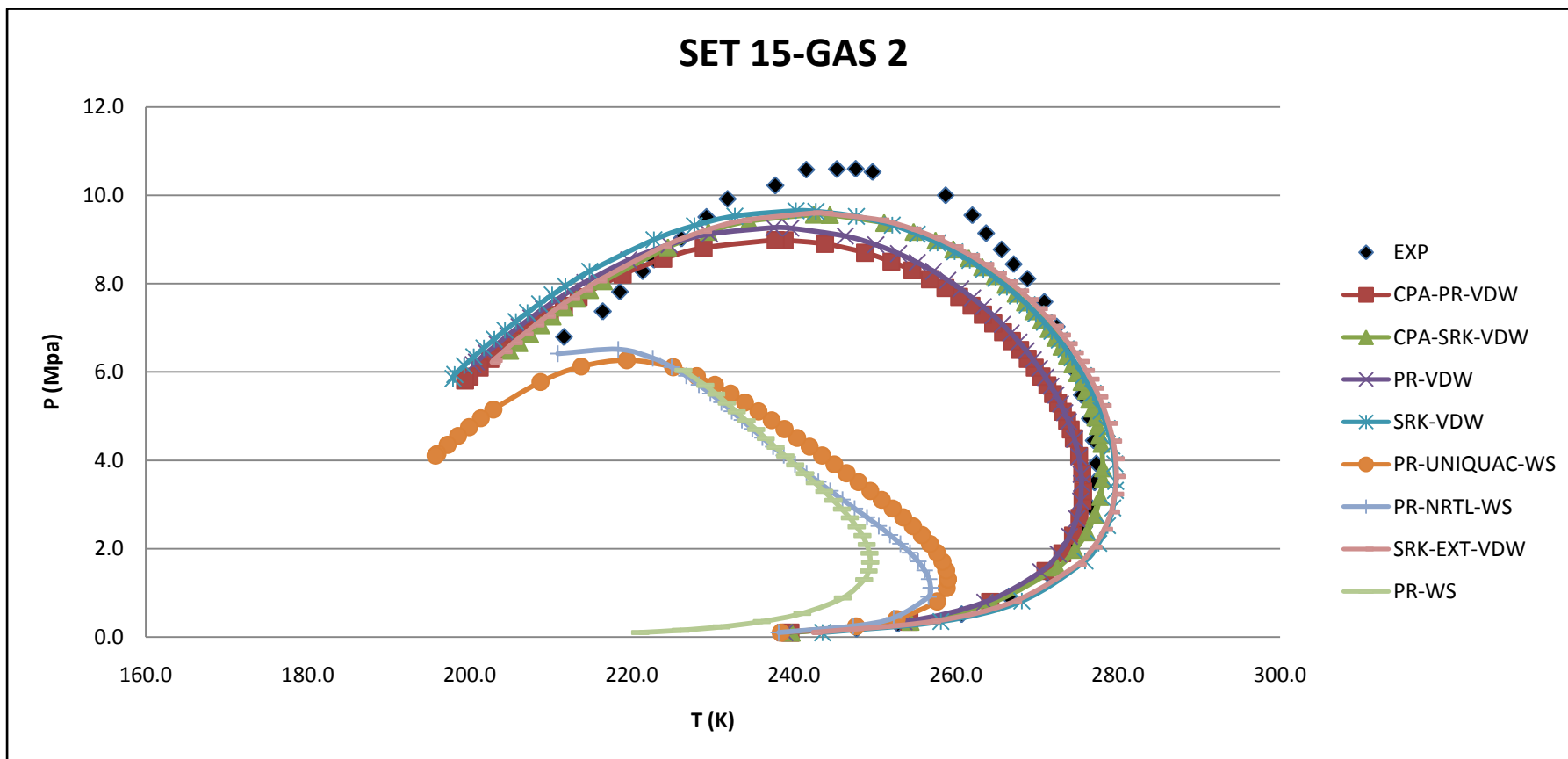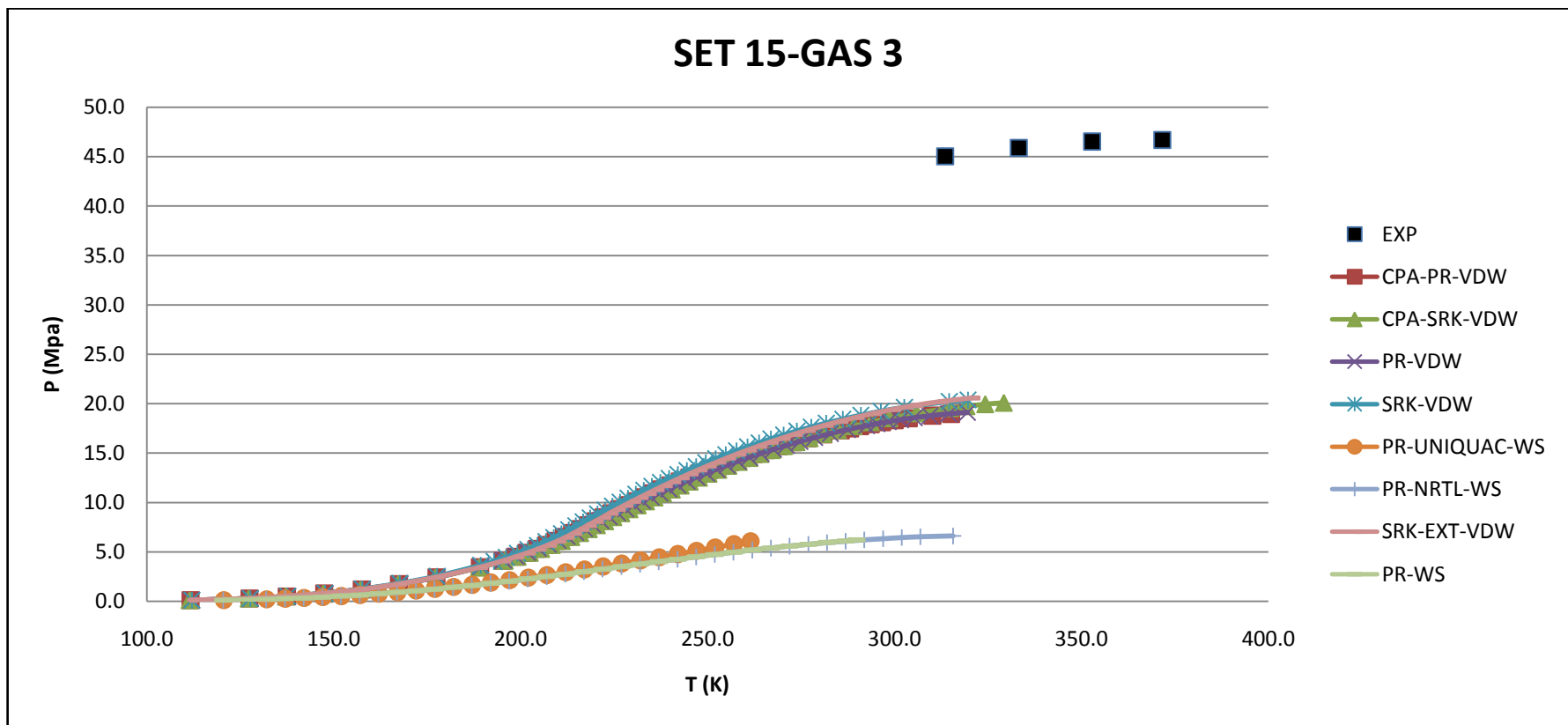

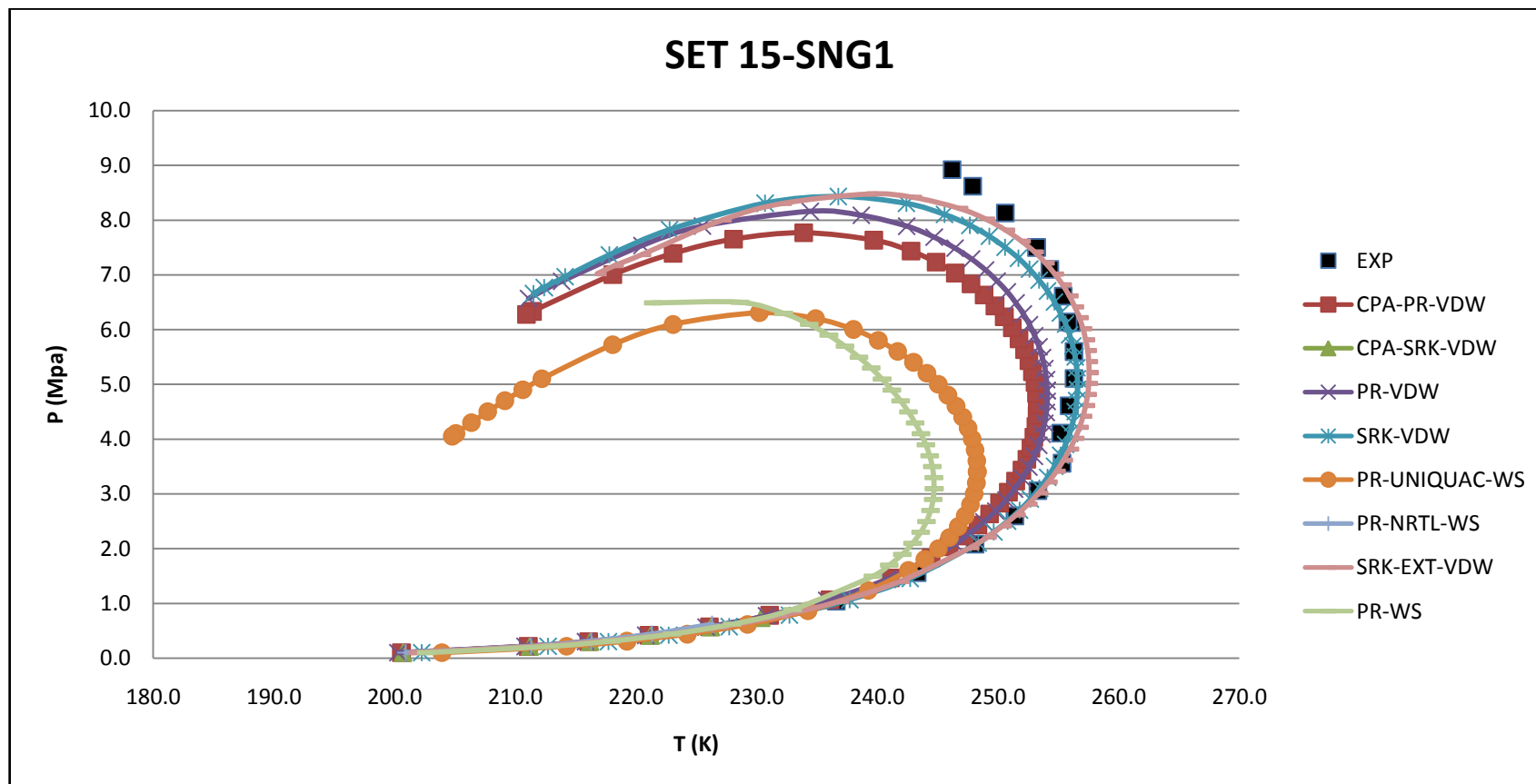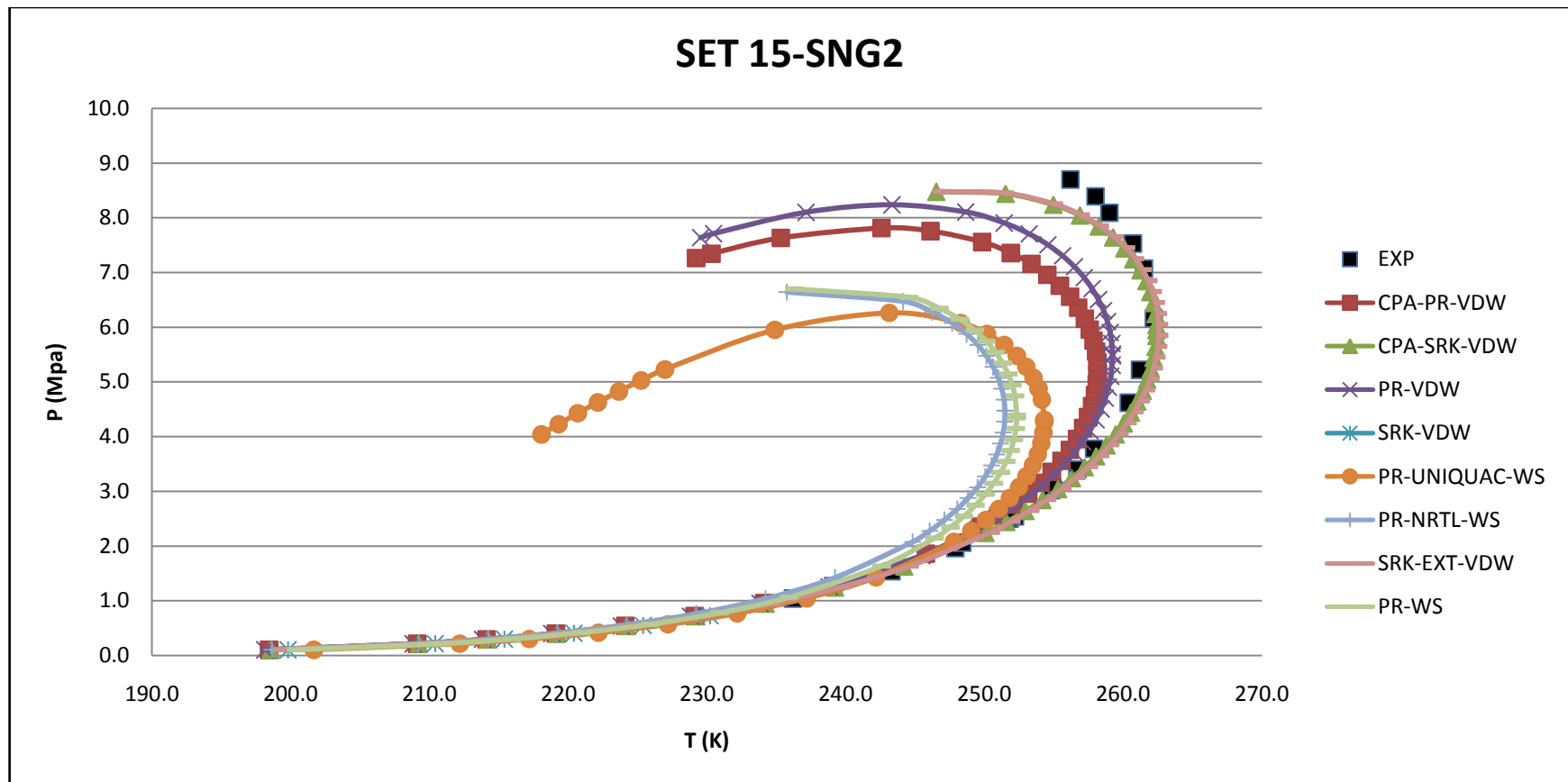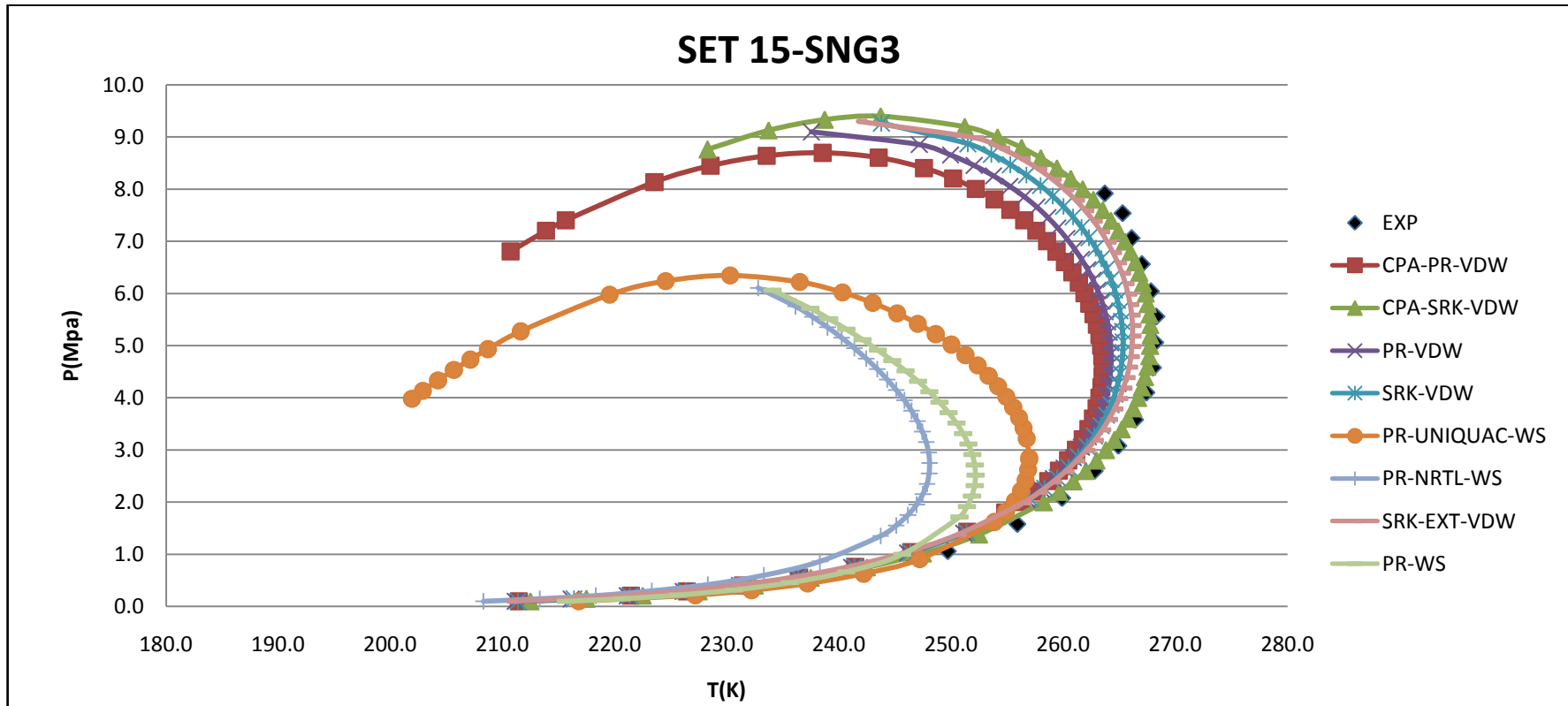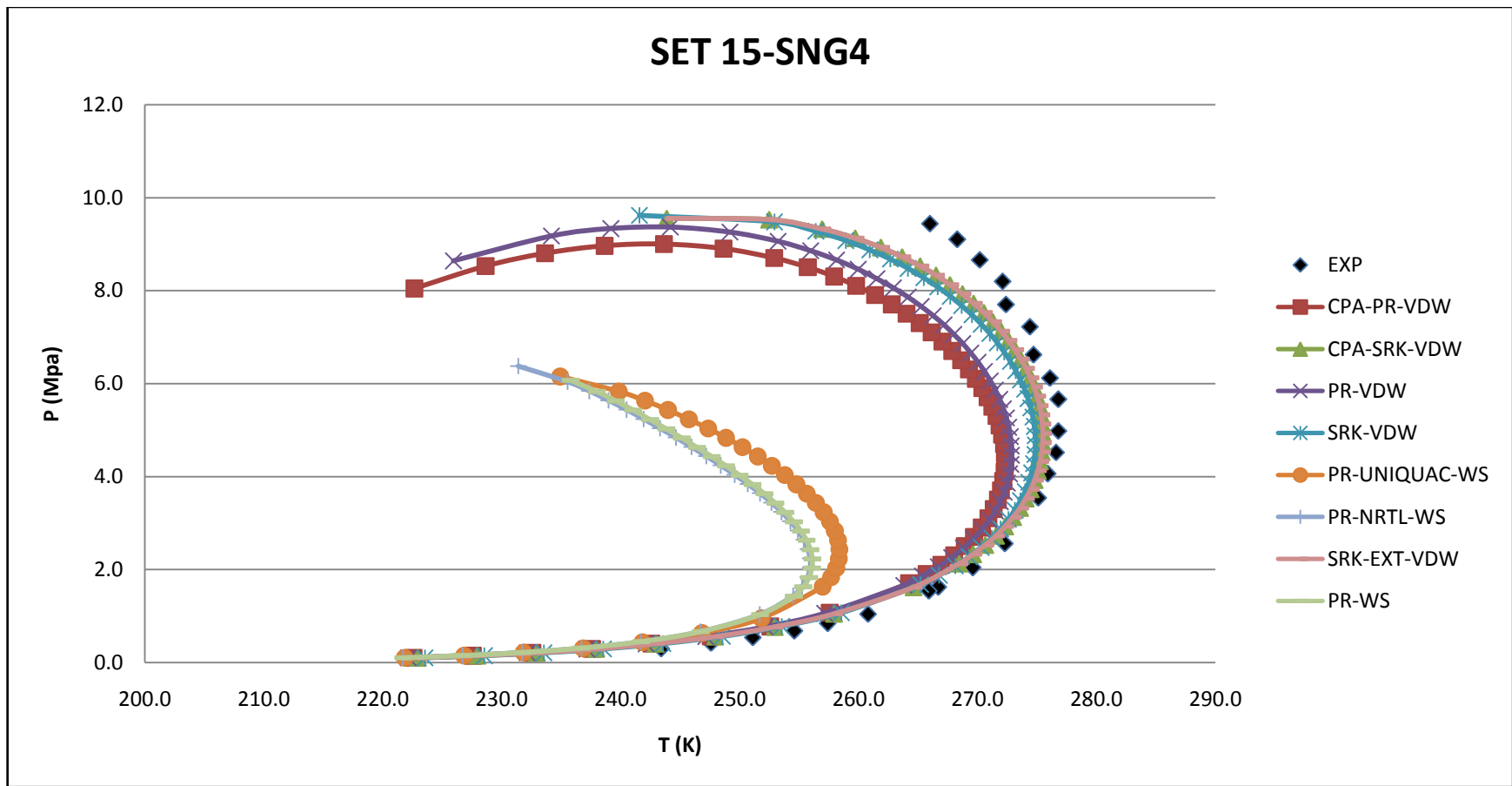Figure 4. 1: Phase Envelope Generated from Different EOS and Experimental Values for Set 6-SNG 2
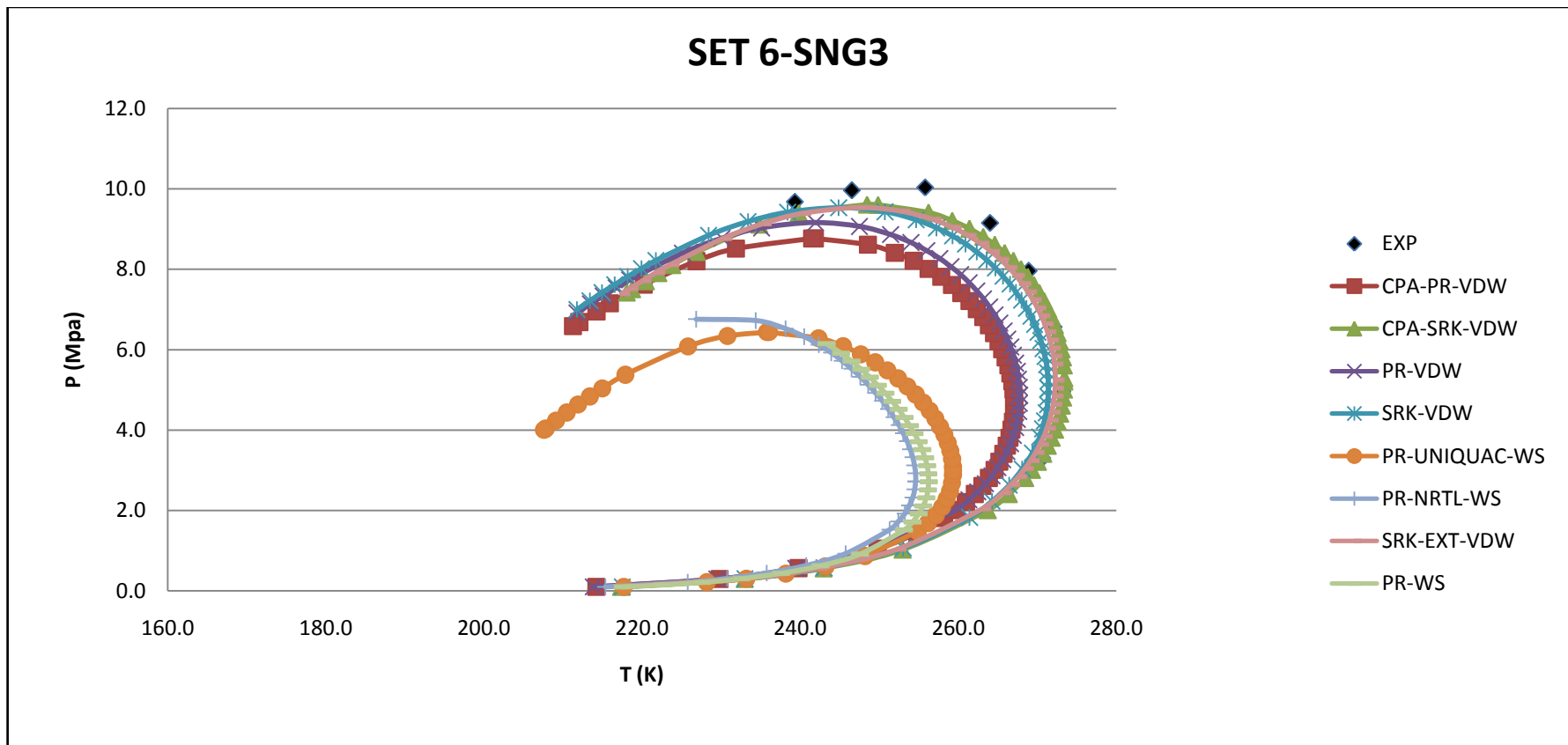
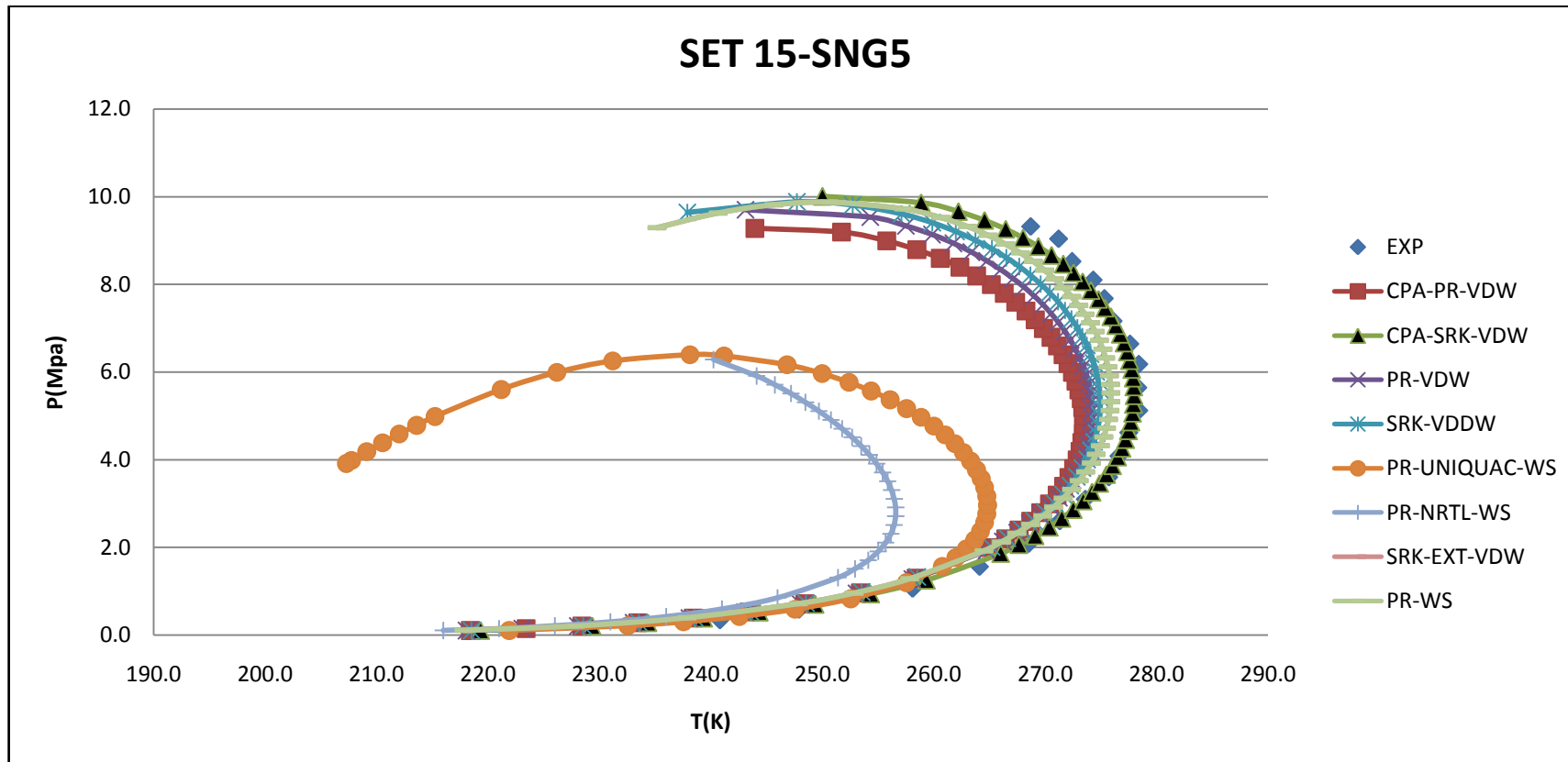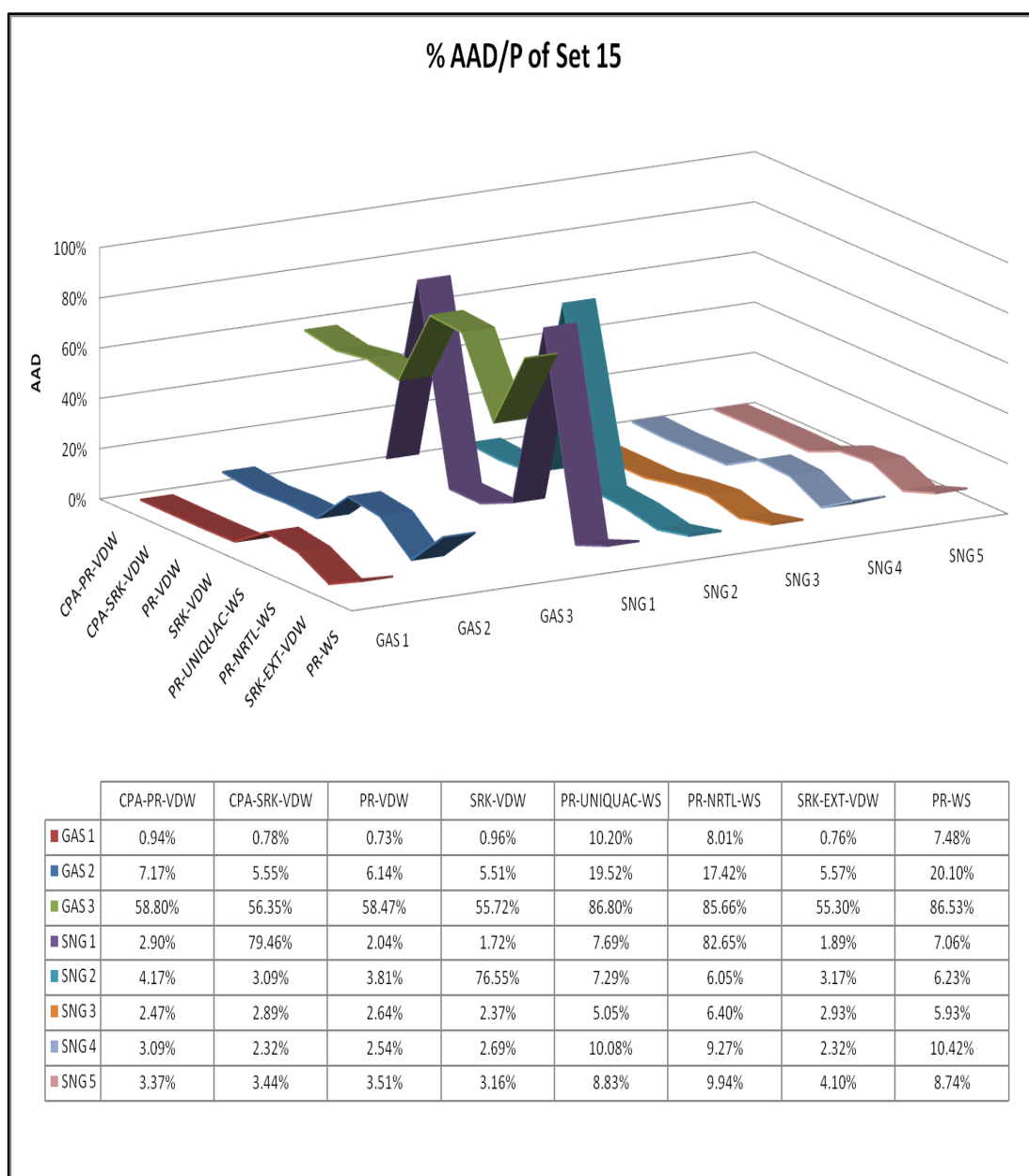Figure 4. 2: Phase Envelope Generated from Different EOSs and Experimental Values for Set 6-SNG
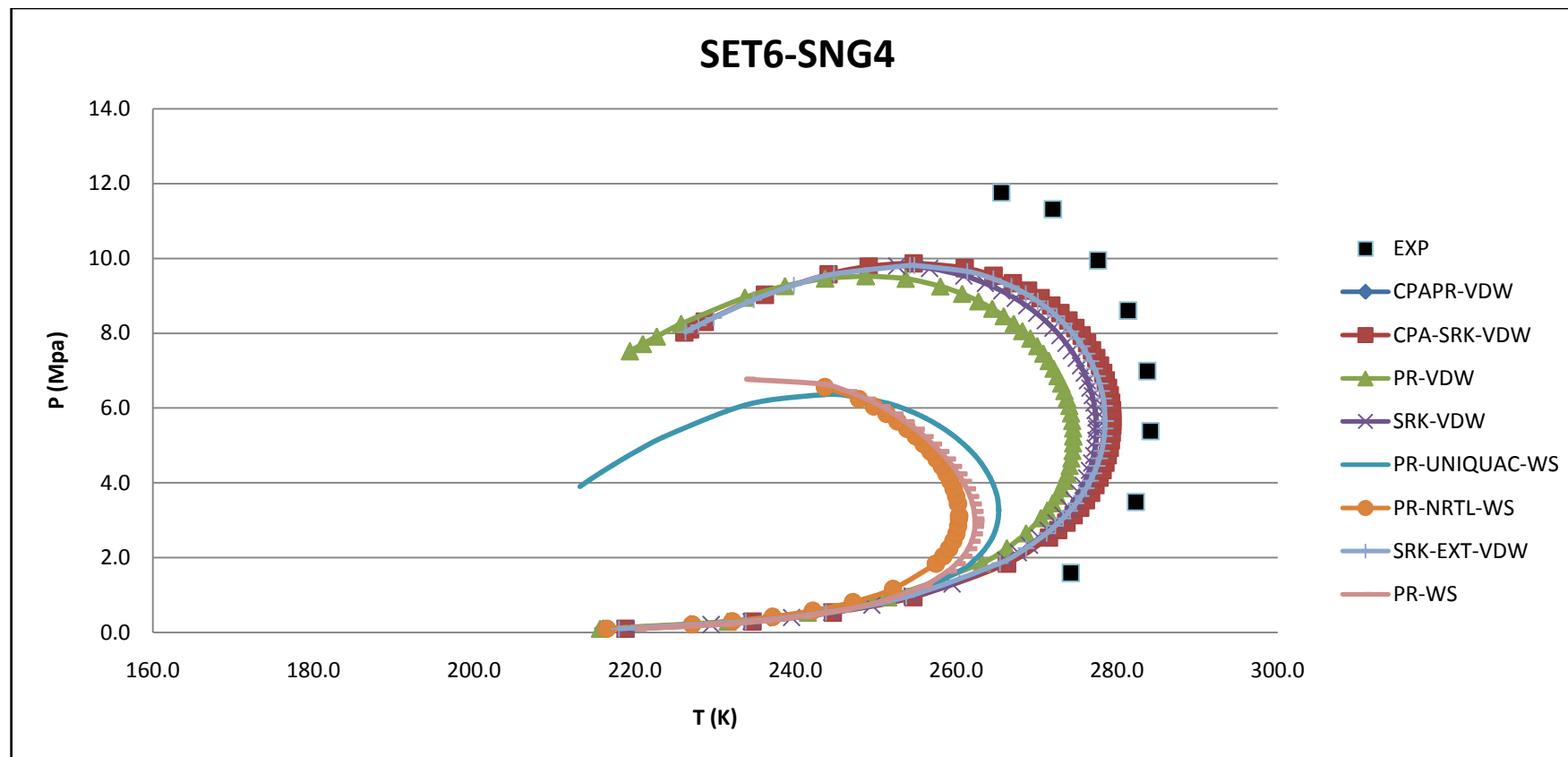
Figure 4. 3: Phase Envelope Generated from Different EOSs and Experimental Values for Set 6-SNG 4
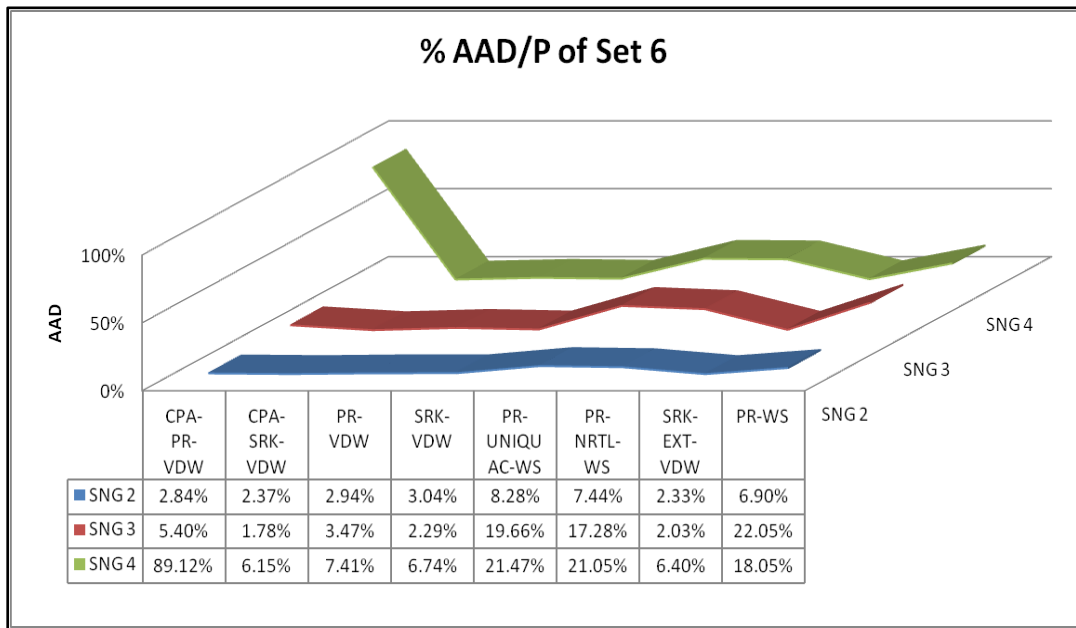
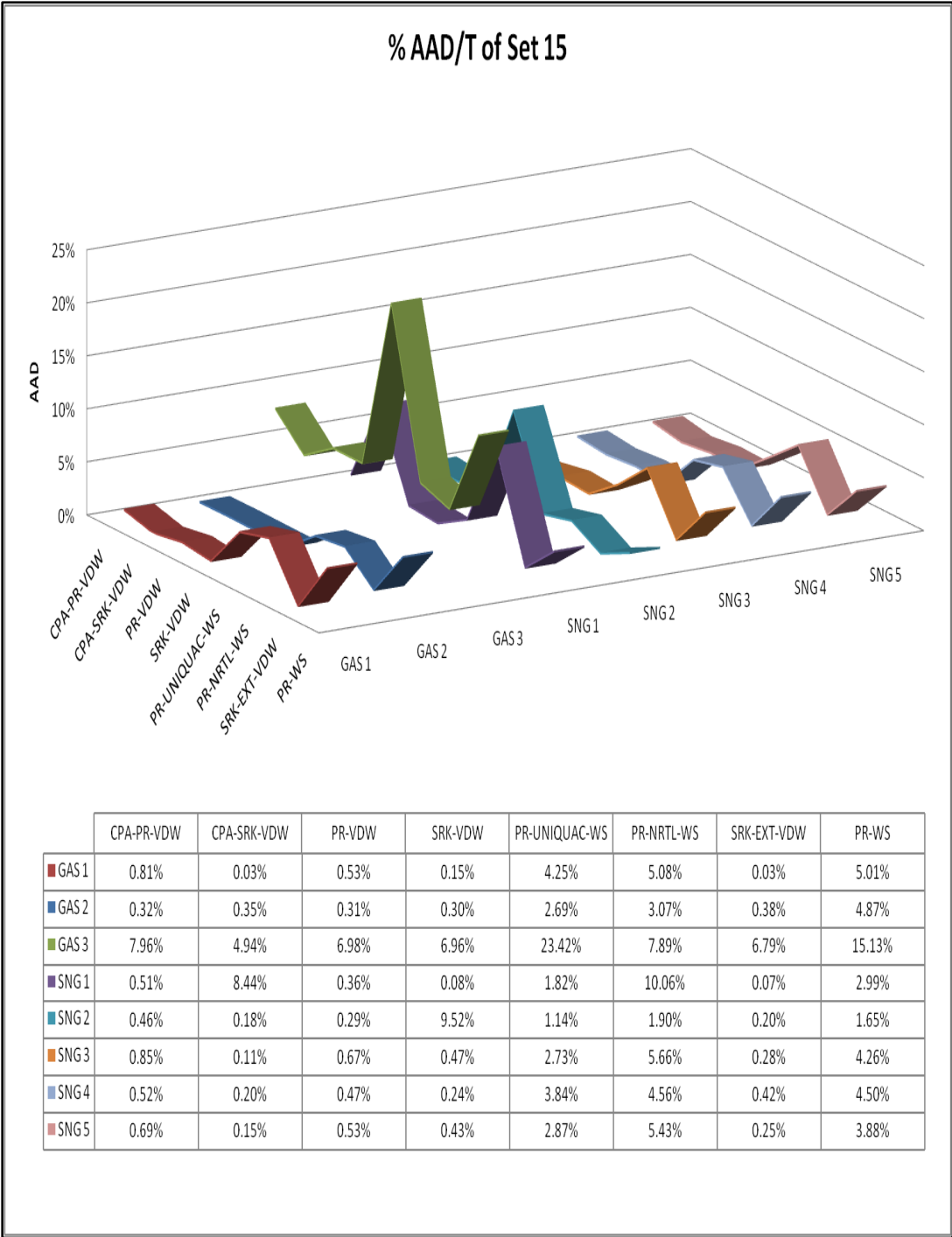Figure 4. 4: Percentage AAD/P Calculated from Different EOSs and Experimental Values for Set 6

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
SNG 2	2.84%	2.37%	2.94%	3.04%	8.28%	7.44%	2.33%	6.90%
SNG 3	5.40%	1.78%	3.47%	2.29%	19.66%	17.28%	2.03%	22.05%
SNG 4	89.12%	6.15%	7.41%	6.74%	21.47%	21.05%	6.40%	18.05%
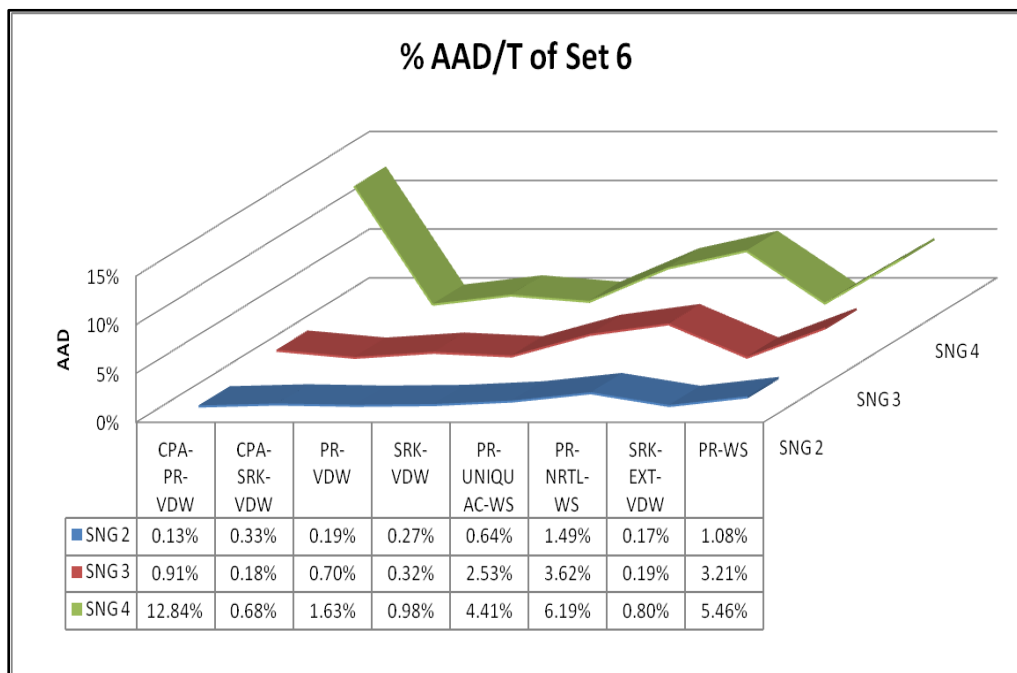
Figure 4. 5: Percentage AAD/T Calculated from Different EOSs and Experimental Values for Set 6

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
SNG 2	0.13%	0.33%	0.19%	0.27%	0.64%	1.49%	0.17%	1.08%
SNG 3	0.91%	0.18%	0.70%	0.32%	2.53%	3.62%	0.19%	3.21%
SNG 4	12.84%	0.68%	1.63%	0.98%	4.41%	6.19%	0.80%	5.46%

Figures 4.1 to 4.3 show phase envelope generated from different EOS model and experimental values for temperature and pressure that obtain from the literature (Table 4.1). For the average deviation of pressure and temperature that illustrated in

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figure 4.4 and 4.5, we can see that the average deviation obtain for all equation of states for all the compositional mixtures of synthetic natural gas mixtures at various composition molar fractions of set 6 are varies. The individual phase envelopes for mixture SNG 2, 3 and 4 are presented in the Appendix A.

For an ease of description, in the predictions of the phase envelope by CPA-PR-VDW for SNG 2, the resulted phase envelope is as the typical phase envelope as shown in Appendix A1, but the calculation by this model had produce % AAD of 2.84% for pressure and 0.13% for temperature deviation and comparing to the A2 figure, modelling SNG 2 mixtures by using CPA-SRK-VDW almost perfect phase envelope but the predictions of the dew point to the modelled phase envelope resulting a deviation of 0.33% for temperature and 2.19% for pressure. Overall, the predictions of the phase envelope modelled by using WS mixing rule unable to produce a closed loop of phase envelope as can be seen in Appendices A5, A6, and A8. This causes a high deviation of temperature and pressure for the dew point when modelled with WS mixing rule.

The reasons of high % AAD calculated for SNG 3 mixtures by using CPA-PR-VDW is that this model is unable to predict dew point pressure with 5.4 % compared to second EOS model as can be seen in Appendices A9 and A10. For SNG 3 mixture, the modelled phase envelope of using WS mixing rule is again unable to generate phase envelope as the typical phase envelope (A13) but in fact tend to overestimate bubble point pressure line as in Appendix A16.

Surprisingly, all EOS model unable to produce less than 1% of percentage deviation in pressure for dew point predictions as can be seen in Table 4.11 and Appendices A19 to A24 though the compositions of methane gases in the mixture is almost the same as in SNG 3 and 4. From Figure 4.3, variations in deviation of temperature compared to experimental that have less % AAD among all EOS models is CPA-SRK-VDW with 0.68%. It comes to an early conclusion that EOS models entirely good at predictions of temperature only and not pressure due to the temperature dependant variables developed for all EOS models.

In terms of the mixing rule associate with EOS, WS mixing rule is unable to accurately calculate and generate phase envelope as VDW mixing rule as shown in Appendices A21 and A22, but a good modelled of phase envelope had been

generated by using PR-WS but with high percentage AAD of temperature and pressure. It comes to an idea that EOS model combining with WS mixing rule and Gibbs free energy is unable to predict phase envelope as typical phase envelope and for three sets of data, all modelled phase envelope is incomplete.

SNG 2, 3 and 4 comprise of large mole fractions of methane approximately 90 mol %, and less than 2 percent of carbon dioxide and nitrogen gas as showed in Table 4.1. For SNG 2 mixtures, mostly all EOS used in this modelling gives reasonable AAD/T that less than 1 percent except that for the PR-NRTL-WS and PR-WS. It means that for high compositional mixtures of methane, VDW mixing rules are able to predict accurate experimental temperature.

For SNG 3 and 4, as the singe carbon number of the mixtures mole percent composition is increasing for ethane, butane and pentane as can be seen in SNG 4, the percentage AAD of pressure and temperature are increasing about 1% as obviously seen for WS mixing rule compared to VDW mixing rule. It is said from the literatures that VDW mixing rule with one or two parameters are adequate at giving good comparing results to the experimental values of the non polar systems. Wei et al in their analysis and studies discussed that Voros and Tassios had compared six mixing rules that involve one and two parameters of Van der Walls mixing rules; two based on excess Gibbs free energy model which is MHV2 and WS and they concluded that the VDW mixing rules gives best results for non polar systems (Wei et al., 2000). That is why PR-NRTL-WS and PR-UNIQUAC-Ws is unable to produce good AAD of temperature for SNG 2, 3 and especially SNG 4 where the error of the deviations is increasing to 4.41 % and 6.69 % when modelled with PR-NRTL-WS and PR-UNIQUAC-WS, due to the fact that the system mixtures of the SNG 4 is strongly non polar.

It is true when Velderama explained in his paper that for the mixtures of non polar and non polar system and reservoir fluid systems, he recommends that the best EOS used for predictions of the phase envelope of the mixtures is by using PR-WS, SRK-WS with temperature function from the Soave at low pressure conditions. He also suggest that PR-VDW and SRK-VDW gives good average deviations of these mixtures which is reservoir fluids and mixtures of nonpolar and nonpolar by using soave temperature function as can be seen in Figure 4.4, SRK based and PR based

EOS with VDW mixing rules gives stable AAD as the percentage of methane gaseous is increasing. The SRK-EXT-VDW, CPA-PR-VDW, CPA-SRK-VDW, PR-VDW and SRK-VDW give reasonable percentage AAD of temperature with less than one percent when modelled for SNG 2 and SNG 3. And yet some of these equations of states are reliable and proven to be useful in modelling phase envelope with high methane gas compositions of 90 % and gives less percentage AAD of 1 %. The EOS describe is SRK-EXT-VDW, SRK-VDW, and CPA-SRK-VDW.

The SRK EOS as described by Velderama is that, SRK based families equation is best used for the gas mixtures and modifications of the temperature dependence parameters and accentric factor gives and accurate results as Redlich and Kwong were very much concerned about the limiting behaviour of the EOS and introduction of the Cubic Plus Association (Velderama, 2003) and EOS like in this case CPA-SRK-VDW gives best results for the SNG 2, 3 and 4 and stable percentage deviations of less than 1 %. Regarding to SNG 4, CPA-SRK-VDW gives less percentage AAD compared to SRK-VDW. The fact that CPA-SRK-VDW is stable at high methane compositions is that this model explicitly takes into account the interactions encountered in mixtures of associating components and normally used for describing the physical interactions with Wertheim's first order perturbation theory as described by Folas (Folas et al., 2009).

4.2: Resulted Calculation for SET 9
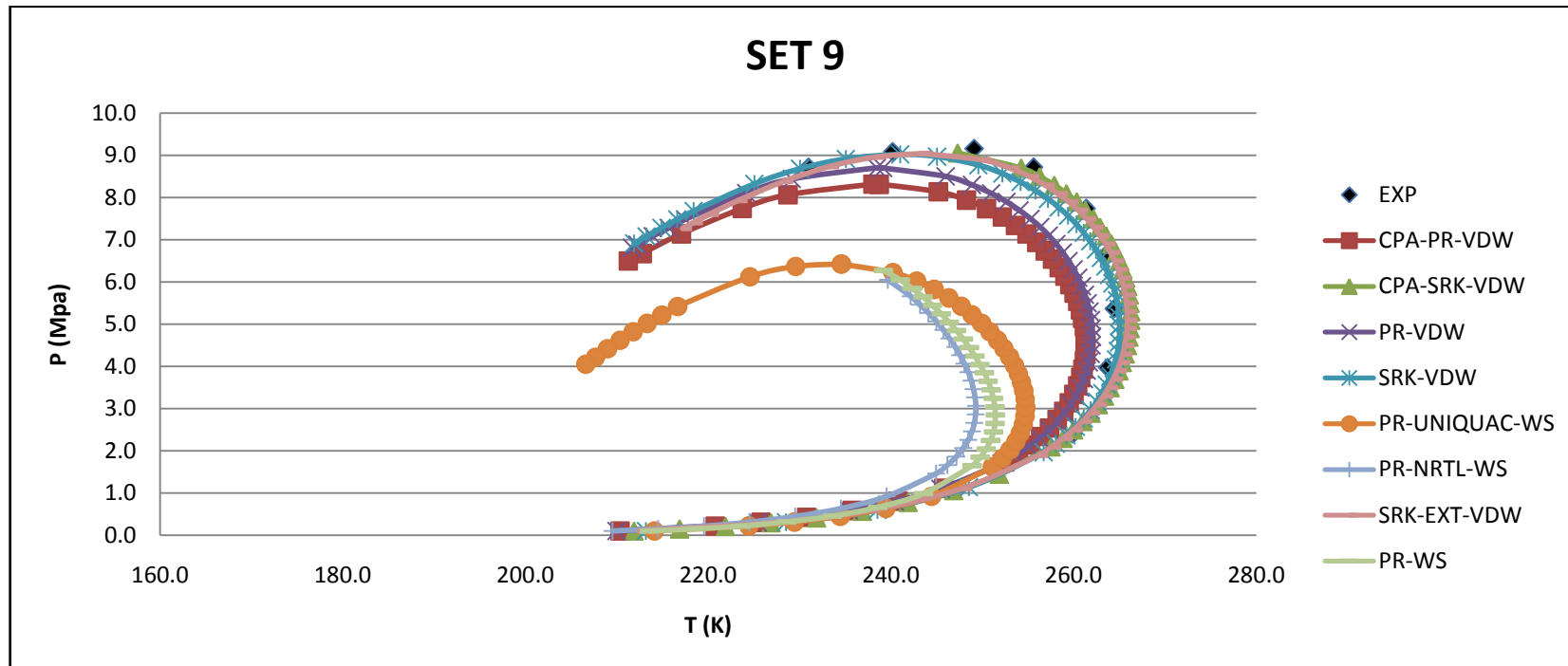
Figure 4. 6: Phase Envelope Generated from Different EOSs and Experimental Values for Set 9-Gas 1
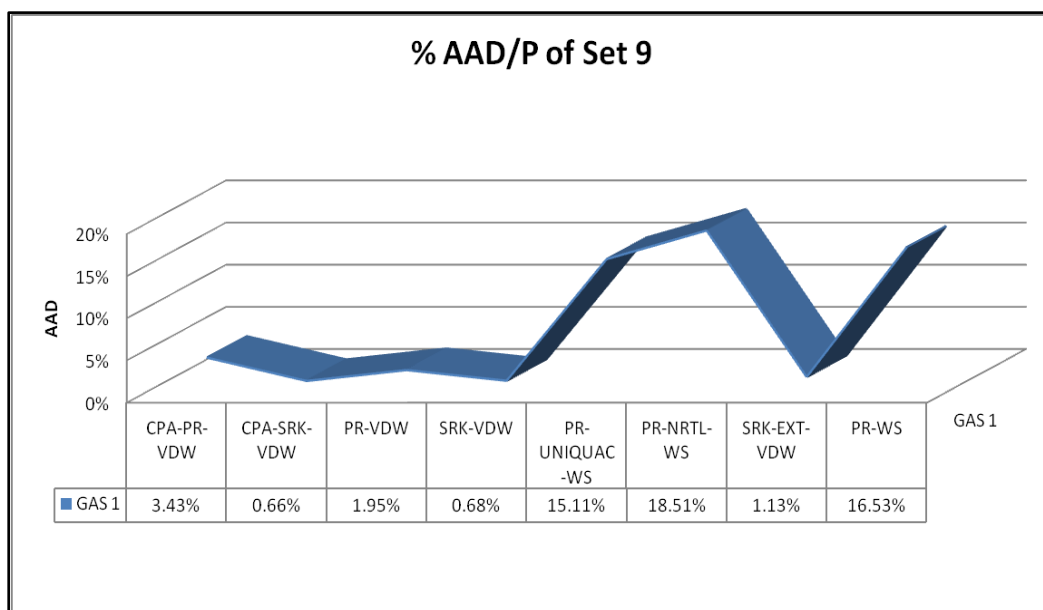
Figure 4. 7: Percentage AAD/P Calculated from Different EOSs and Experimental Values for Set 9
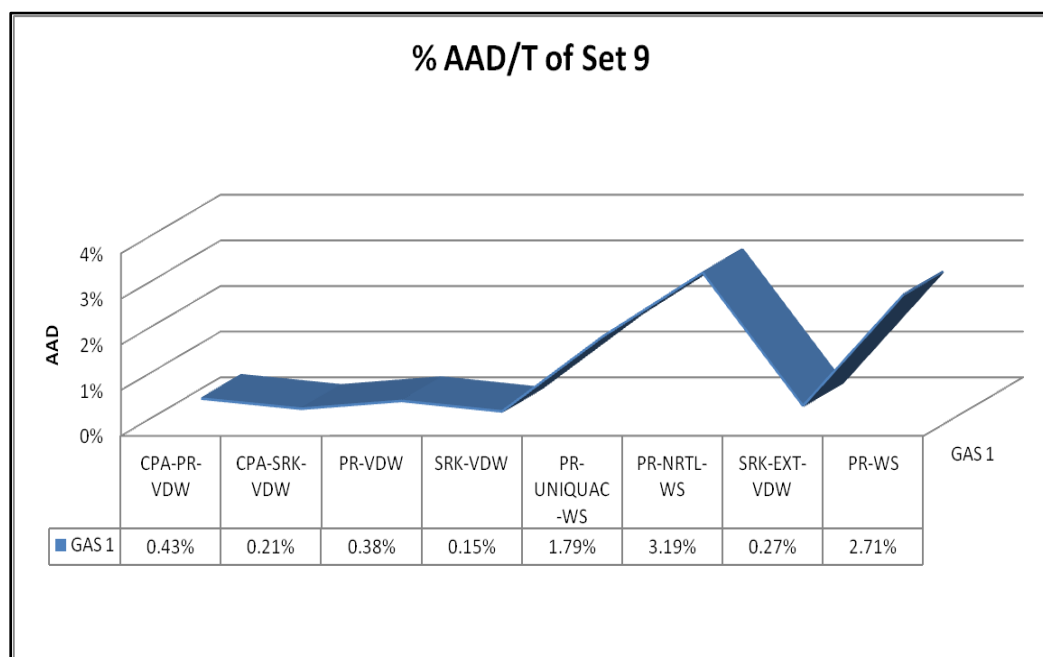
Figure 4. 8: Percentage AAD/T Calculated from Different EOSs and Experimental Values for Set 9

For gas mixture of set 9, the composition molar fraction of the chemical components is almost the same as set 6. For this case, the headache for the description of such variations is still uncertain. The given experimental values that conducted by Atilhan

and his fellow friends differs significantly with the experimental values conducted by him as in set 6 and presented in Table 4.3. He pointed out that the different measurement of experimental apparatus yielded different results of the experimental values and the effects of mixture composition on phase envelopes reveal that a small fractional increase in the components such as ethane, propane, butane and pentane produces a remarkable change in the cricondenthem region and near the cricondenbar. (Atilhan et al., 2011)

In the Appendix B, calculated phase envelope by using PR-NRTL-WS and PR-WS as in Appendices B6 and B8, resulting an over prediction of bubble point line and in Appendix B5, the predictions of the phase envelope is incomplete. It comes to an early conclusion that modelling phase envelope by using WS mixing rules yield and inaccurate predictions of bubble point line and dew point line that explains such high percentage AAD in temperature and pressure as tabulated in Figures 4.7 and 4.8.

As presented in Figures 4.7 and 4.8, obviously the modelling of phase envelope of gas 1 mixture yielded good percentage deviations of pressure and temperature when modelled with the CPA-SRK-VDW as in set 6. Though the experimental values given is far increase in terms of pressure and temperature compared to set 6, it is found that SRK-VDW gives lowest percentage AAD for both temperature and pressure at given higher experimental values that leads to the same explanation as previously discussed by Velderama (Velderama, 2003).

He suggest that for moderate and high pressure of the reservoir fluids, the gas mixtures is best modelled with VDW mixing rule with Soave temperature function and SRK and PR equation of states. At this stage, the compositional mixture of ethane and pentane use in this analysis had increase in a very small amount of about 0.15% from set 6 of SNG 2 and SNG 3 and yielded different experimental values of dew points that actually govern to the different approach of the EOS that can be used to model this gas mixture. For less than 1 % percentage AAD of temperature, VDW mixing rules with PR and SRK equation of states yielded the least percentage deviations compared to EOS functions associating with WS mixing rule as shown in Figures 4.7 and 4.8.
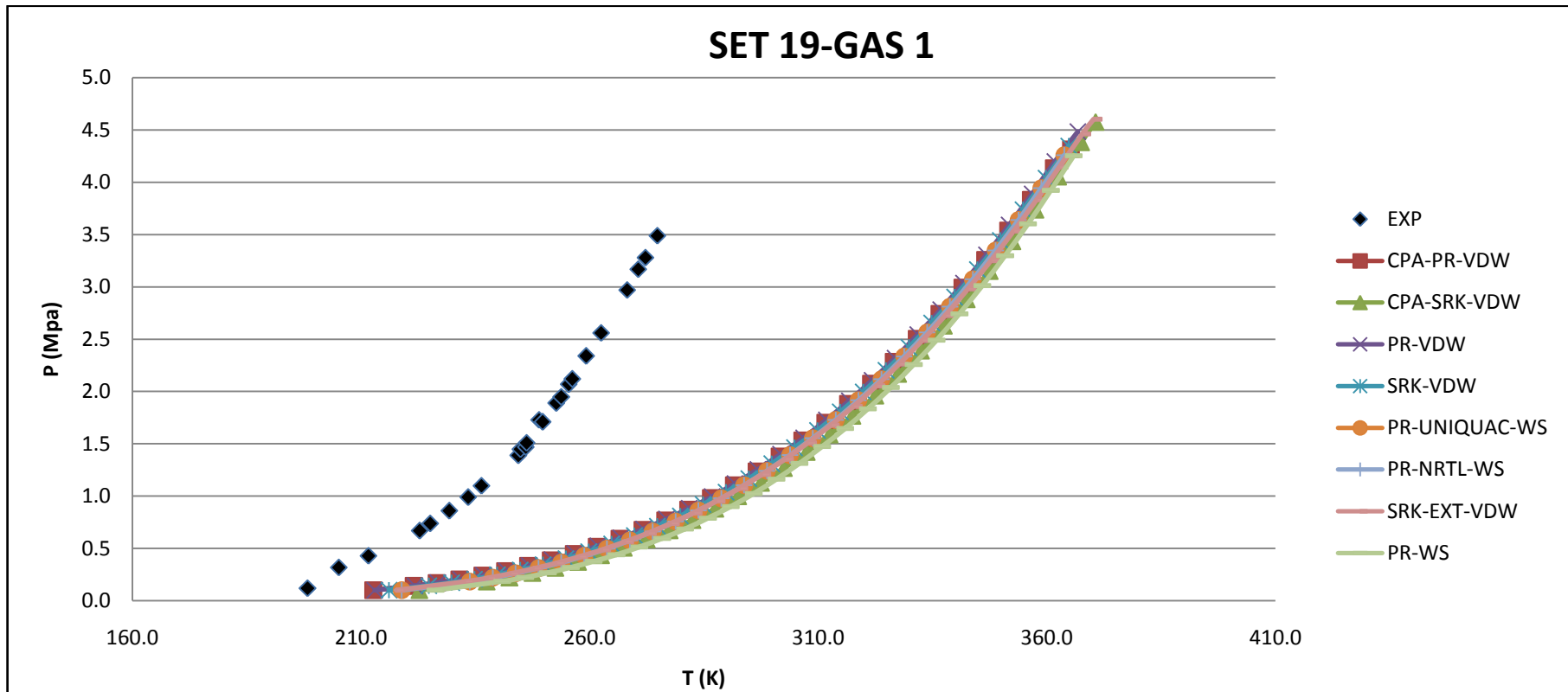
4.4: Resulted Calculation for SET 15

Figure 4. 9: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-Gas 1

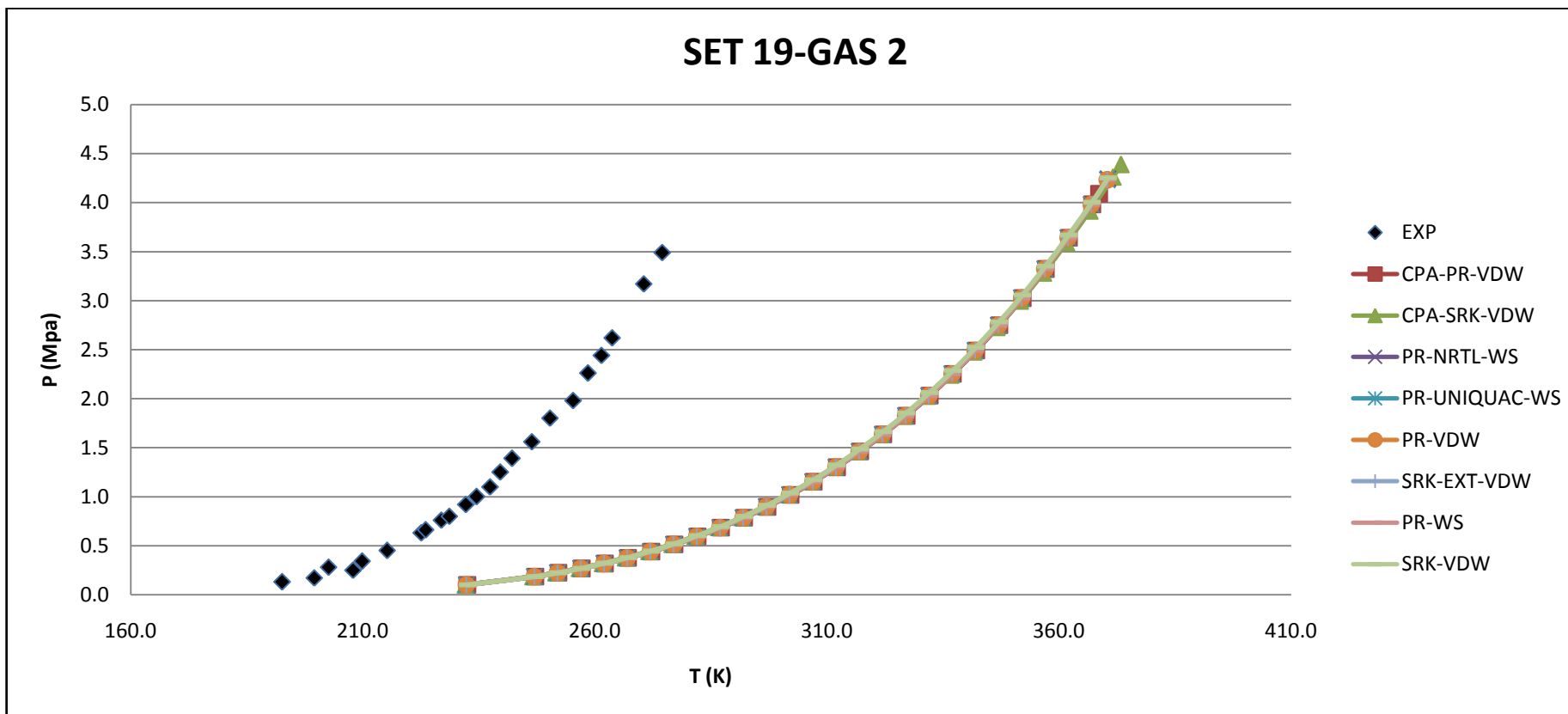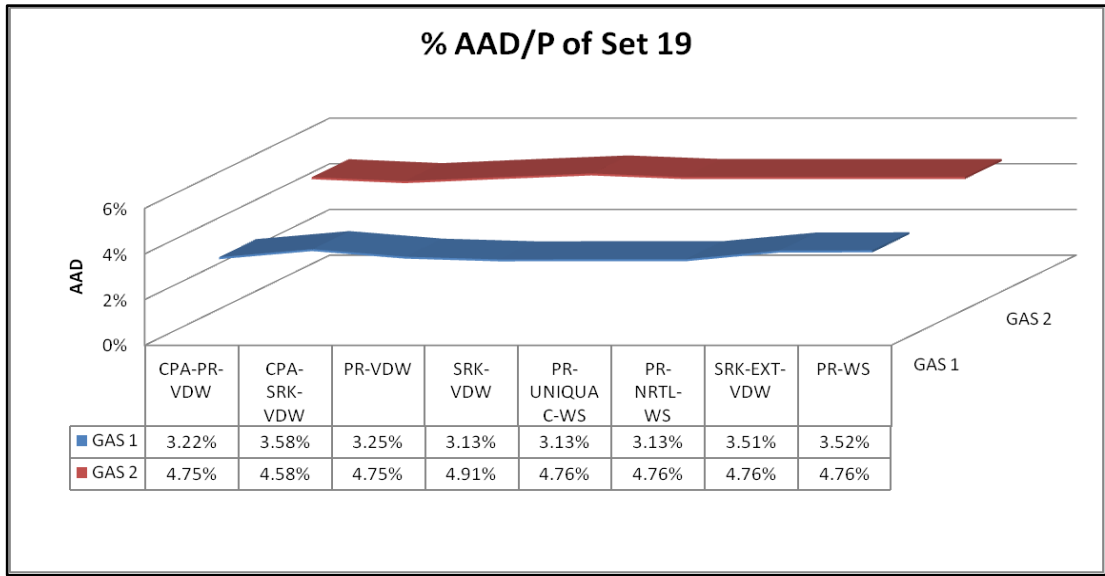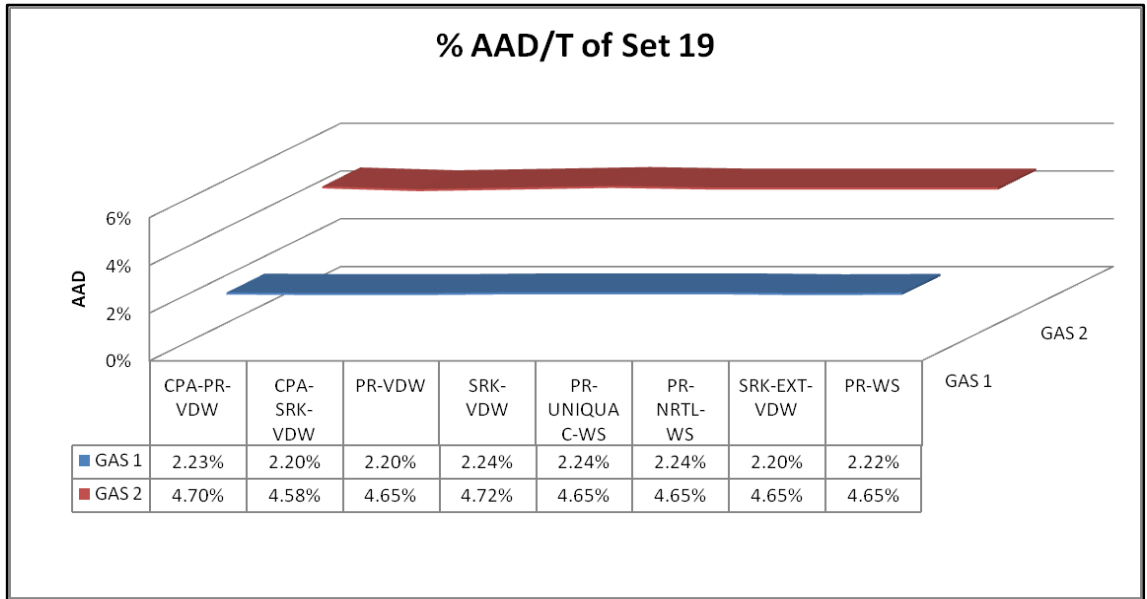Figure 4. 10: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-Gas 2

Figure 4. 11: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-Gas 3

Figure 4. 12: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-SNG 1

Figure 4. 13: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-SNG 2
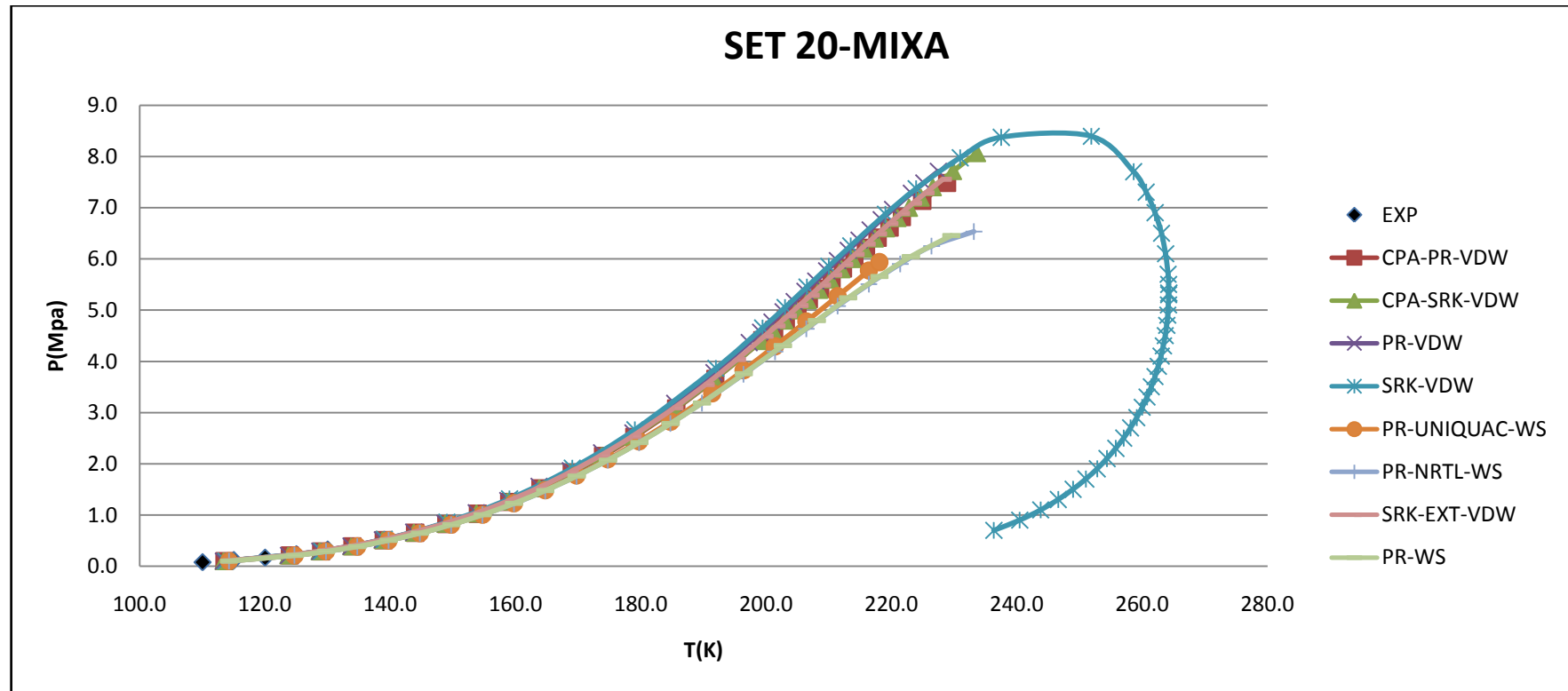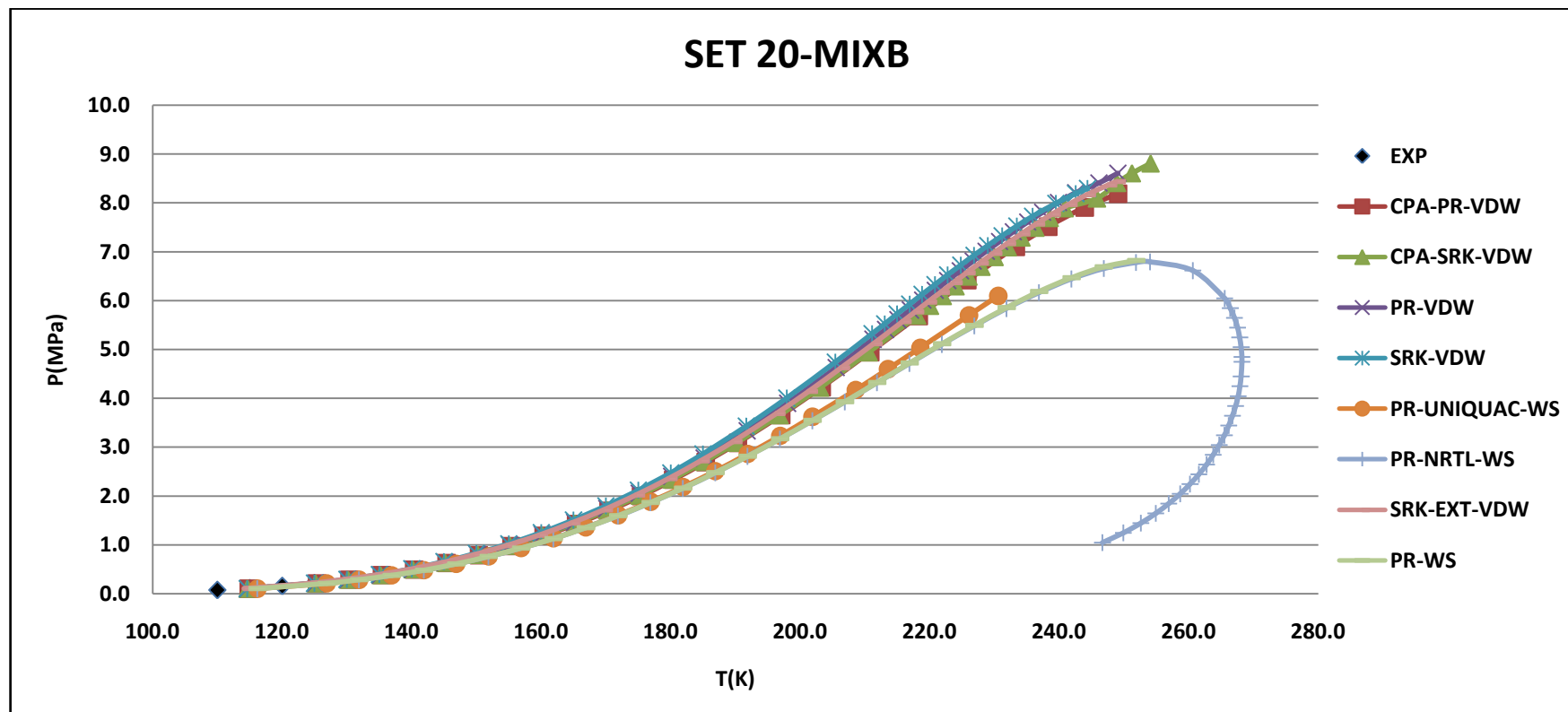
Figure 4. 14: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-SNG 3

Figure 4. 15: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-SNG 4

Figure 4. 16: Phase Envelope Generated from Different EOSs and Experimental Values for Set 15-SNG 5

% AAD/P of Set 15

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
GAS 1	0.94%	0.78%	0.73%	0.96%	10.20%	8.01%	0.76%	7.48%
GAS 2	7.17%	5.55%	6.14%	5.51%	19.52%	17.42%	5.57%	20.10%
GAS 3	58.80%	56.35%	58.47%	55.72%	86.80%	85.66%	55.30%	86.53%
SNG 1	2.90%	79.46%	2.04%	1.72%	7.69%	82.65%	1.89%	7.06%
SNG 2	4.17%	3.09%	3.81%	76.55%	7.29%	6.05%	3.17%	6.23%
SNG 3	2.47%	2.89%	2.64%	2.37%	5.05%	6.40%	2.93%	5.93%
SNG 4	3.09%	2.32%	2.54%	2.69%	10.08%	9.27%	2.32%	10.42%
SNG 5	3.37%	3.44%	3.51%	3.16%	8.83%	9.94%	4.10%	8.74%

Figure 4. 17: Percentage AAD/P Calculated from Different EOSs and Experimental
Values for Set 15

% AAD/T of Set 15

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
GAS 1	0.81%	0.03%	0.53%	0.15%	4.25%	5.08%	0.03%	5.01%
GAS 2	0.32%	0.35%	0.31%	0.30%	2.69%	3.07%	0.38%	4.87%
GAS 3	7.96%	4.94%	6.98%	6.96%	23.42%	7.89%	6.79%	15.13%
SNG 1	0.51%	8.44%	0.36%	0.08%	1.82%	10.06%	0.07%	2.99%
SNG 2	0.46%	0.18%	0.29%	9.52%	1.14%	1.90%	0.20%	1.65%
SNG 3	0.85%	0.11%	0.67%	0.47%	2.73%	5.66%	0.28%	4.26%
SNG 4	0.52%	0.20%	0.47%	0.24%	3.84%	4.56%	0.42%	4.50%
SNG 5	0.69%	0.15%	0.53%	0.43%	2.87%	5.43%	0.25%	3.88%

Figure 4. 18: Percentage AAD/T Calculated from Different EOSs and Experimental Values for Set 15

Set 15 contains 8 different mixtures of varieties chemical components and compositions. The individual phase envelope were modelled with eight EOS functions and presented in Appendix C. For Gas 1, VDW mixing rules shows good approximation of the phase envelope as the typical phase envelope but when it is purposely modelled by using WS mixing rules plus free Gibbs Energy as depicted in Appendices C5, C6 and C8, the modelled shows great deviations. The SNG's mixtures for set 15's phase envelope are also modelled and can be found in the Appendix C.

As expected, VDW mixing rules with equation of states gives better temperature predictions over WS mixing rule for gas 1 mixtures that have no carbon dioxide and nitrogen molar fractions. For gas 1 that have almost 90% mole of methane gaseous, SRK-EXT-VDW gives better result over SRK-VDW and surprisingly same percentage temperature deviations of about 0.03% when modelled with CPA-SRK-VDW. The ability of the SRK-EXT-VDW to predict gas mixtures without non hydrocarbon components is due to its simplicity and modifications on the temperature dependent function in the attractive term. SRK-EXT-VDW also gives less percentage AAD of temperature for all SNGs without carbon dioxide and nitrogen gases in the mixtures. For CPA-SRK-VDW, the predictions of the bubble point and dew point lines gives percentage AAD of temperature of less than 1 % for SNG 2, 3, 4 and 5 and any how yielded results of high percentage deviations of temperature when modelled for SNG 2 mixtures. For Gas 2, high percentage of nitrogen gases found in the mixture and the applicable EOS model for this gas mixture is SRK-VDW.

Nevertheless, all PR and SRK EOS associating with VDW mixing rules are capable of predicting phase envelope of the mixtures of SNG including CPA-PR-WS. Except that most of the PR and SRK with WS mixing rule where the deviations of the percentage AAD of temperature compared to experimental values for the synthetic natural gas mixtures used in this set of data is arbitrarily high due to the fact that the limitations of the WS mixing rule that unable to produce good results in predicting phase envelope of the SNG mixtures at low pressure (Velderama, 2003).

For the EOS model associating with the excess free Gibbs energy like PR-NRTL-WS and PR-UNIQUAC-WS, none of the gas mixtures in this set 15 gives a good

approximation result of the phase envelope calculations when modelled with these two type equation of states models. This is due to the fact that, the constituents gas mixtures in this study is not strongly polar-non polar mixtures and not strongly polar-polar mixtures. WS+ UNIQUAC gives good predictions of phase envelope calculations in strongly polar-polar mixtures and WS+ NRTL gives best results in strongly polar-nonpolar mixtures. This leads to the early conclusion that none of the WS plus free Gibbs energy EOS is capable of predicting hydrocarbon mixtures and this argument is so true with regards for set 6, set 9 and set 15.

The interesting phenomena was observed for Gas 3 mixture where the high experimental bubble point given is unable to depict and cross any point calculated by using all EOS models and resulted high percentage AAD for pressure and temperature and it comes to a conclusion that such deviation is due to the high content of carbon dioxide of about 3.92%. Where actually the modelled need to be verified in terms of the BIPs and certain parameters used in this software need to be verified and discussed. The individual phase envelope and for purpose of comparison, the plotted graph can be visualize in the Appendix C of C17 to C24.

For gas 3 of this set of data that have quite high mole percentage of carbon dioxide of about 3.92 %, none of the EOS models can accurately predicting phase envelope of the gas mixtures. Velderama suggested in his work that modelling carbon dioxide with hydrocarbon gas mixtures that can be classified as asymmetric mixtures is best modelled with EOS that used TWU temperature function with mixing rule of P&R and MWS-1P at low pressure and PTV EOS with Soave temperature function and associating VDW mixing rule with one or two parameters at moderate and high pressure of more than 10 atm (Velderama, 2003)

4.5: Resulted Calculation for SET 18
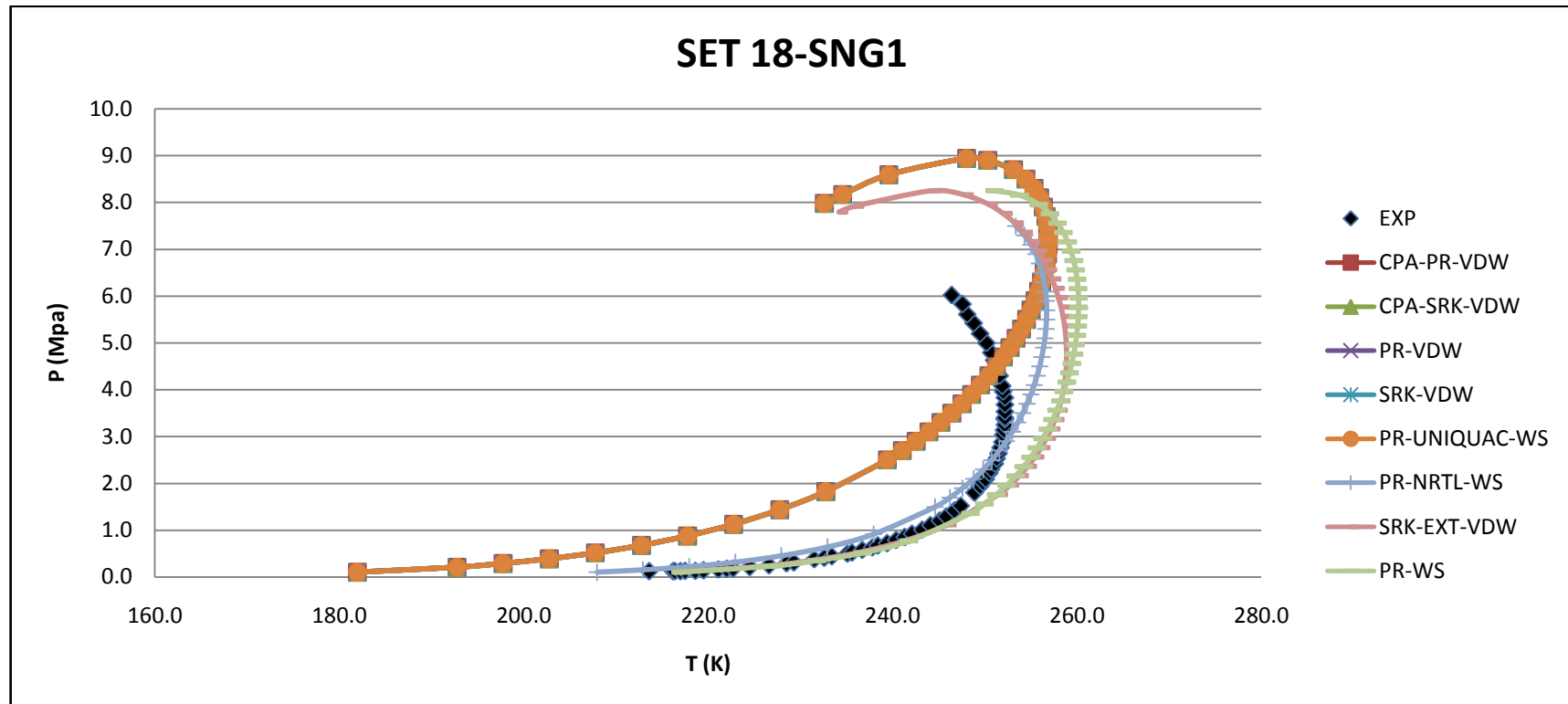
Figure 4. 19: Phase Envelope Generated from Different EOSs and Experimental Values for Set 18-SNG 1
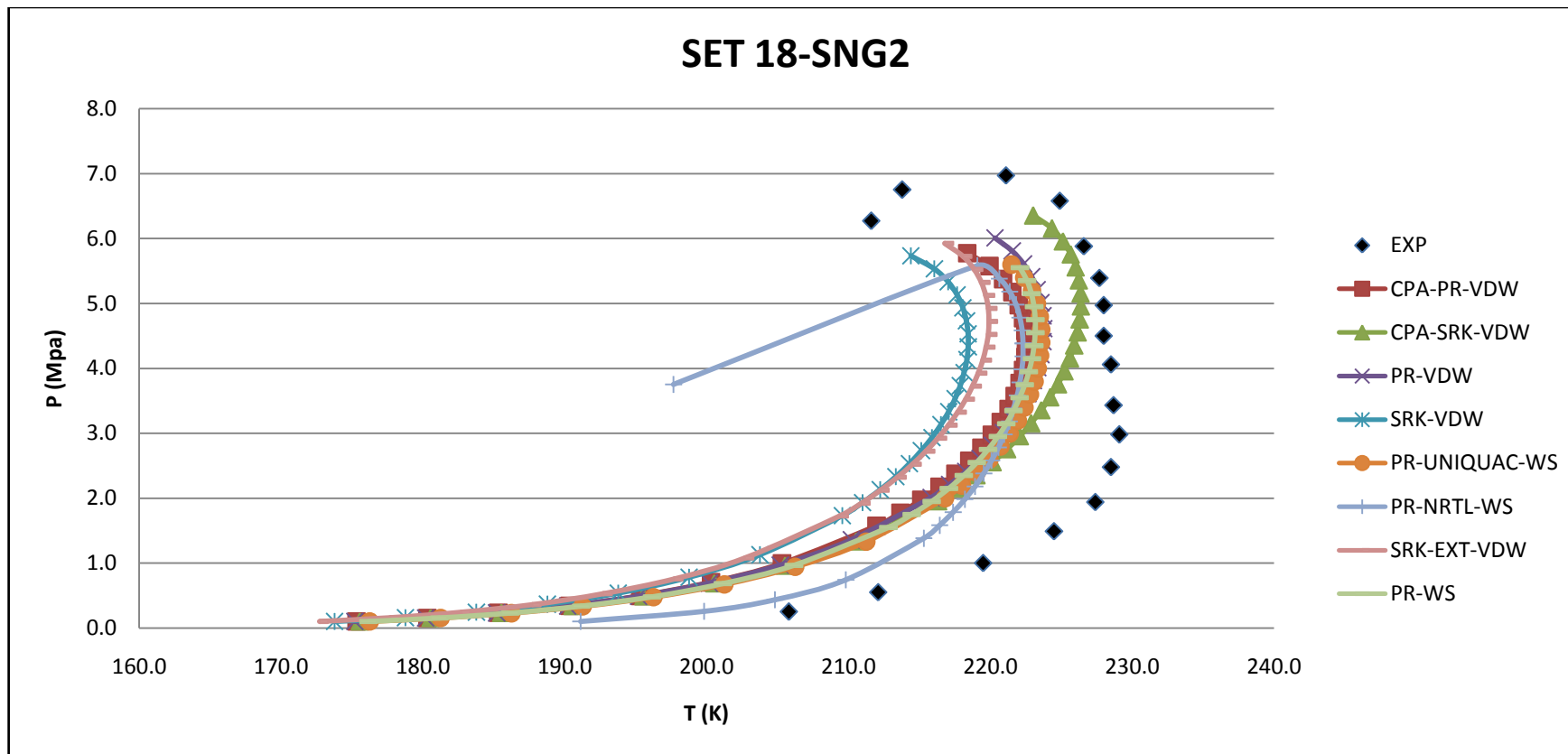
Figure 4. 20: Phase Envelope Generated from Different EOSs and Experimental Values for Set 18-SNG 2
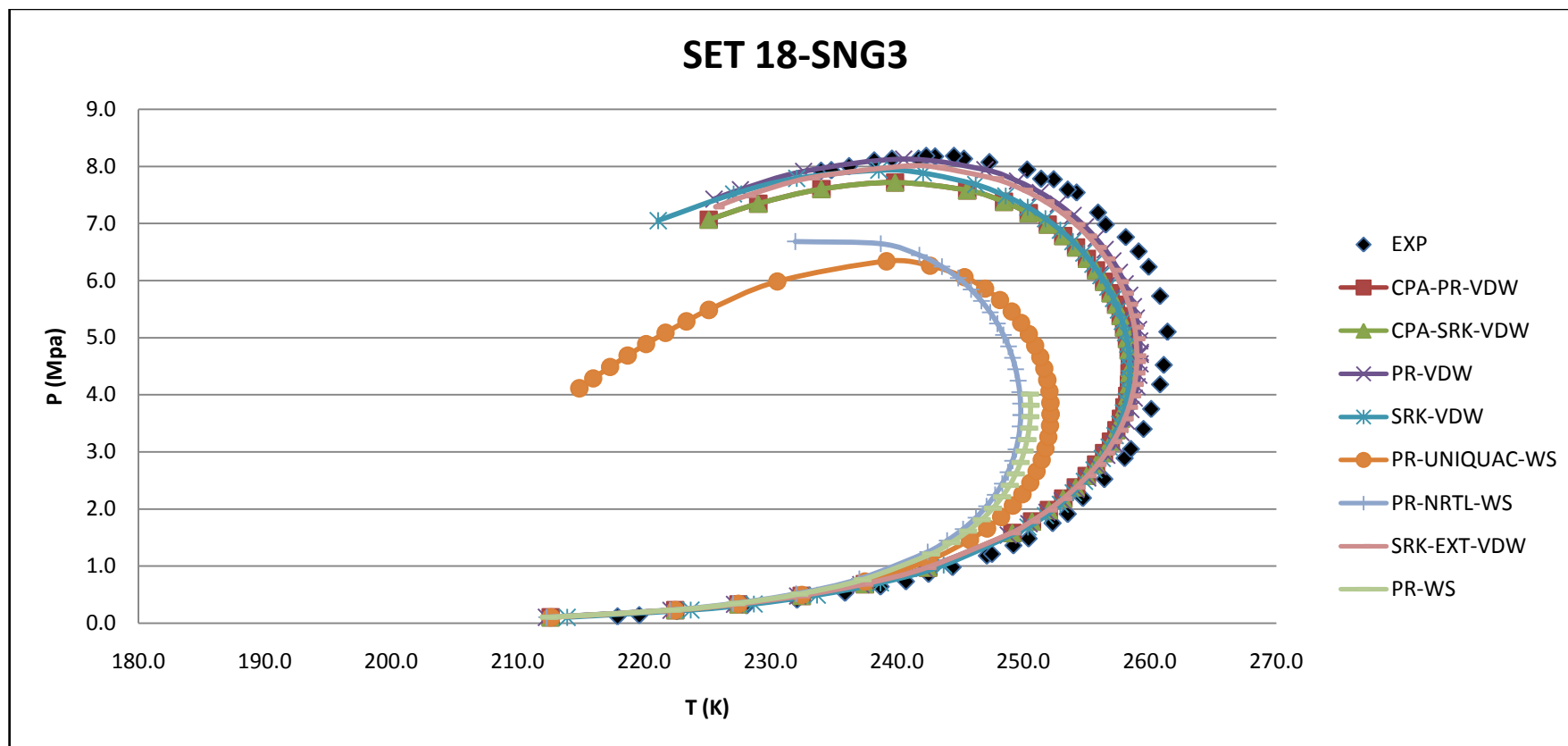
Figure 4. 21: Phase Envelope Generated from Different EOSs and Experimental Values for Set 18-SNG 3
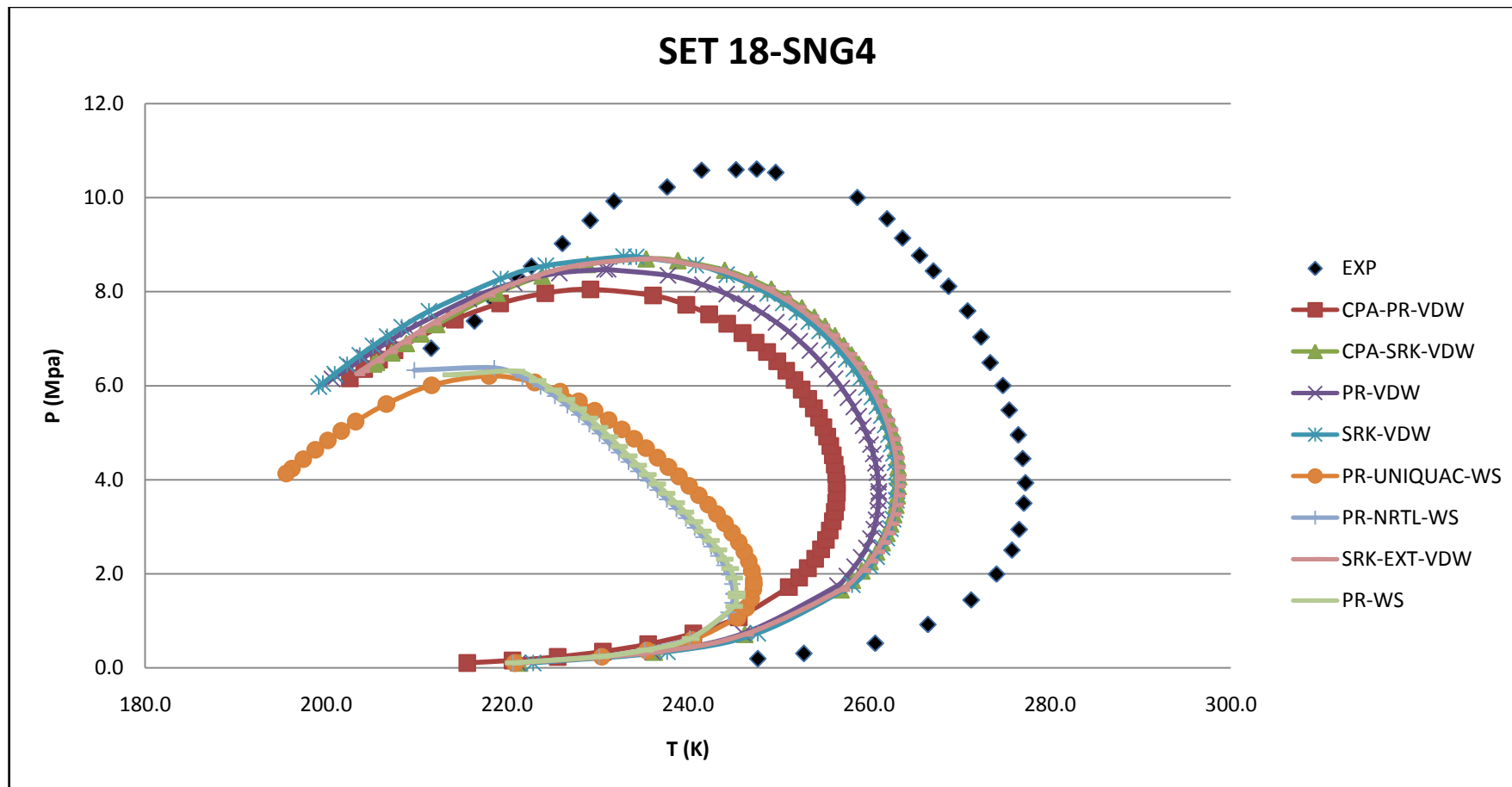
Figure 4. 22: Phase Envelope Generated from Different EOSs and Experimental Values for Set 18-SNG 4
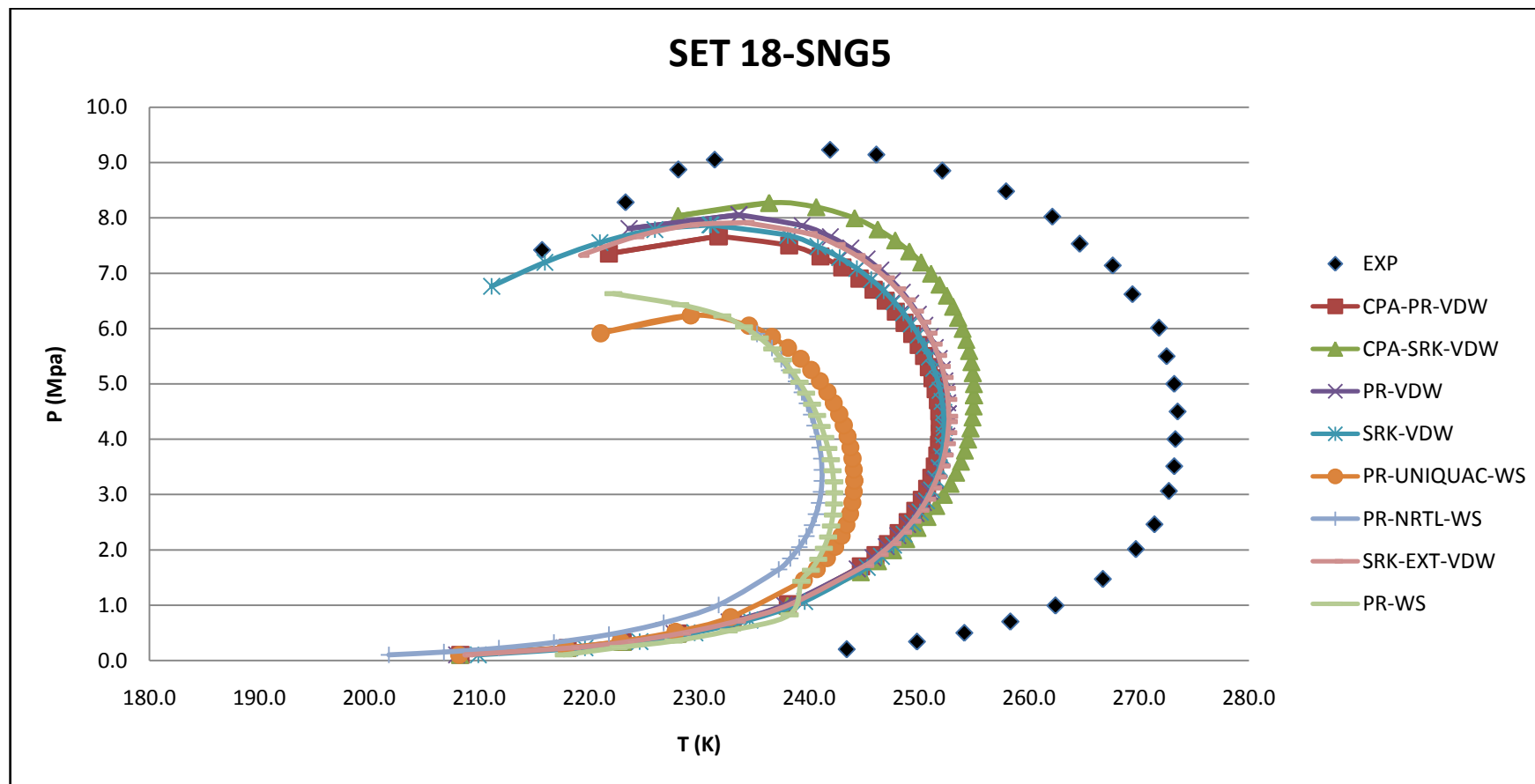
Figure 4. 23: Phase Envelope Generated from Different EOSs and Experimental Values for Set 18-SNG 5

% AAD/P of Set 18

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
SNG 1	6.74%	6.74%	6.74%	6.74%	6.74%	6.24%	8.39%	5.89%
SNG 2	5.17%	3.81%	4.78%	5.96%	6.96%	8.01%	5.06%	6.46%
SNG 3	5.25%	5.25%	4.04%	5.04%	11.31%	9.66%	4.42%	10.94%
SNG 4	8.85%	6.46%	8.81%	8.13%	19.79%	19.21%	8.05%	19.74%
SNG 5	5.57%	3.27%	3.95%	4.97%	12.72%	14.00%	5.40%	12.22%
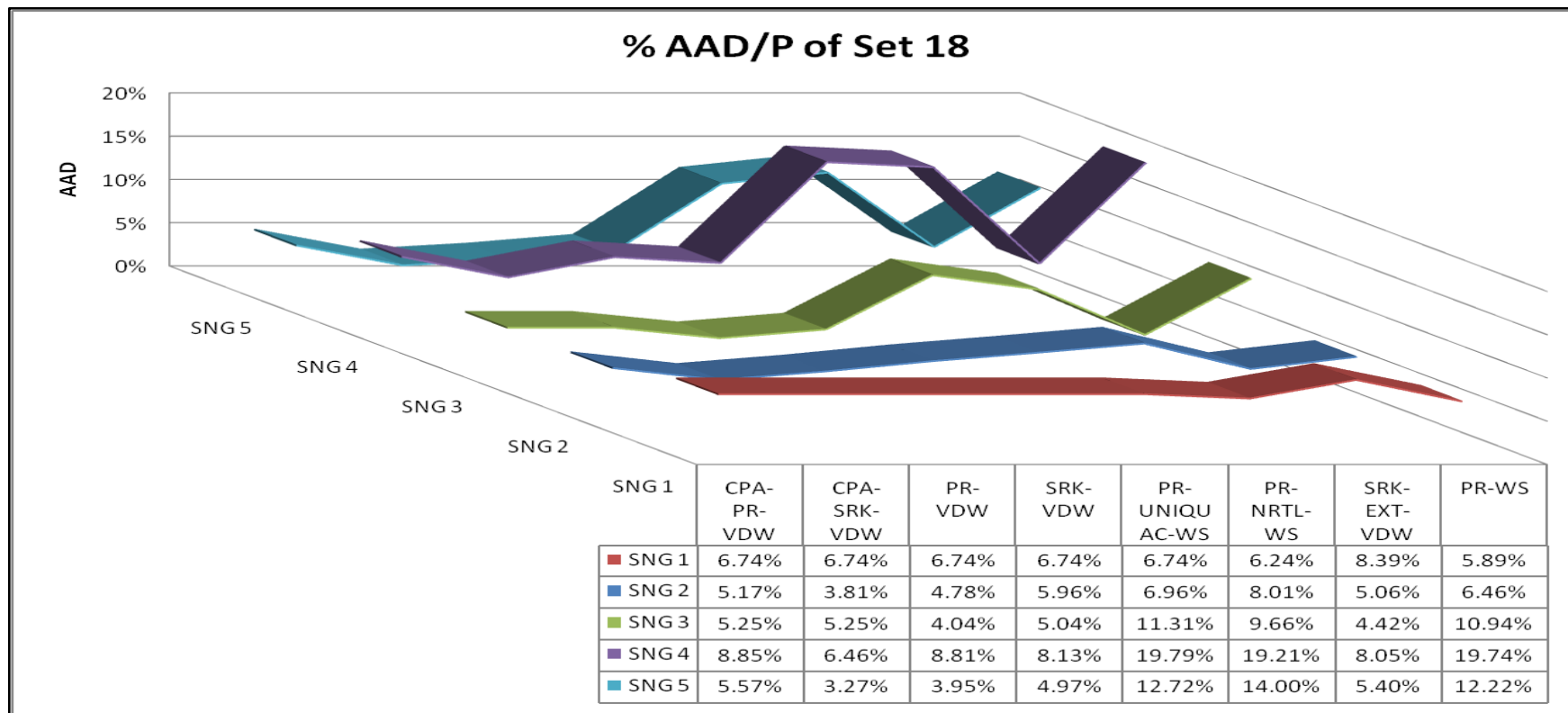
Figure 4. 24: Percentage AAD/P Calculated from Different EOSs and Experimental Values for Set 18

% AAD/T of Set 18

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
SNG 1	0.21%	0.21%	0.21%	0.21%	0.21%	0.29%	0.37%	0.40%
SNG 2	1.44%	0.56%	1.22%	2.75%	1.23%	1.64%	2.29%	1.30%
SNG 3	0.36%	0.36%	0.34%	0.36%	1.00%	1.44%	0.33%	1.40%
SNG 4	3.20%	2.70%	2.24%	1.90%	5.19%	5.81%	1.88%	5.74%
SNG 5	3.93%	3.20%	3.75%	3.84%	6.10%	7.01%	4.26%	6.83%
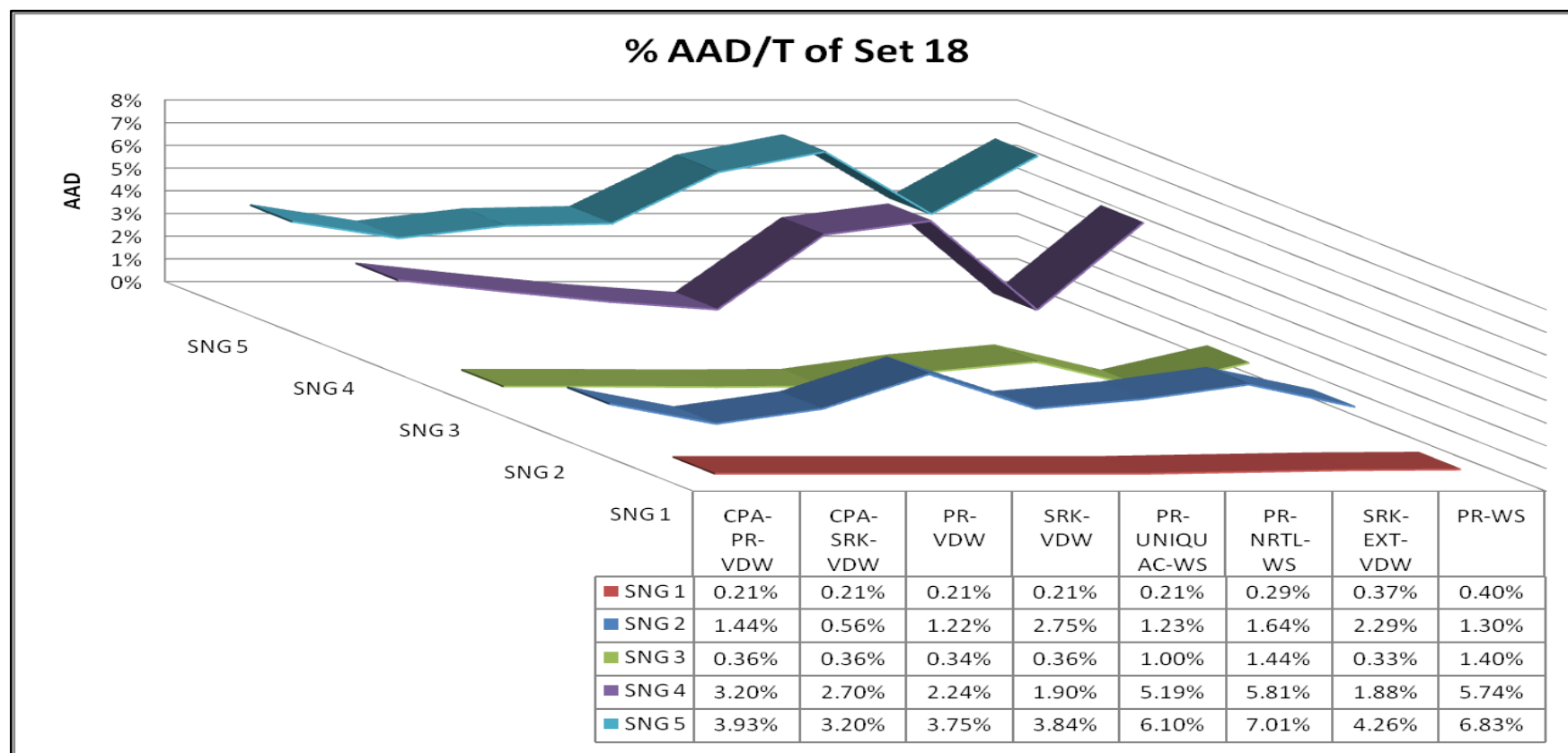
Figure 4. 25: Percentage AAD/T Calculated from Different EOSs and Experimental Values for Set 18

Set 18 comprise of five synthetic natural gas mixtures obtain from the literature and summaries of the chemical components are presented in Table 4.2. For predicting bubble point line for SNG1 that have high amount of carbon dioxide content of about 25.91 %, the applicable EOS models that gives less percentage temperature deviations to the experimental values is surprisingly all EOS models with both VDW mixing rule and WS mixing rules. All EOS models used in this study obtain less percentage temperature deviations of less than 1% and the lowest percentage pressure deviations obtain from the PR-WS models with 5.89%.

Thus, the significant high amount of carbon dioxide content of about 26% percent can be modelled with EOS plus free Gibbs energy with WS mixing rule and comes to the argument of previously discussed by Velderama where he suggested that EOS+ NRTL+WS mixing rule is only applicable for strongly polar and nonpolar systems and EOS+UNIQUAC+WS for the mixtures of strongly polar and polar mixtures is not true in this case (Velderama, 2003).

If we expand the argument by looking at the attached Appendix D, we found that all EOS models used in this study are only best modelled the dew point temperatures only and for pressure, it wasn't good at all where only one to four points are crossing and matching in this phase envelope modelling as can be seen in the Appendices D1 to 18. Thus, for SNG 1 mixture, none of the EOS modelled is applicable in modelling mixture of 26% carbon dioxide composition in terms of the pressure and temperature.

For SNG 2 with high percentage of methane gas compositions, the best EOS for predicting dew point lines for this mixture is CPA-SRK-VDW with less than 1 % percentage temperature deviations. But, the entire phase envelope generated is incomplete with high incompletes degree found in the modelled phase envelope by using PR-UNIQUAC-WS and PR-NRTL-WS as shown in Appendices D13 and D14.

For more than 80% of methane gaseous in the mixture as in SNG 3, 4 and 5, the applicability of the EOS in modelling phase envelope varies with the composition mixtures of nitrogen, carbon dioxide, ethane, propane, butane and pentane, hexane, heptanes and octane. For SNG 3, the best model of EOS in giving the less amount of temperature deviations compared to experimental temperature values is SRK-EXT-

VDW with 0.33% and PR-VDW with 0.34%. The explanation of such lower deviations is illustrated in Appendices D23 and D19.

For the increasing heavies components mixtures in SNG 4, the applicable EOS models in giving less percentage AAD/T is SRK-EXT-VDW and SRK-VDW as shown in Figure 4.24 and about 8% deviation in pressure observed for both models as in Figure 4.25. Another observation point is that, the combination of EOS+ free Gibbs Energy + WS like PR-UNIQUAC-WS and PR-NRTL-WS are unable to modelled mixture phase envelope above 6MPA as in Appendices D29 and D30 and same pressure range observed for the PR-WS that explains high deviation of temperature and pressure calculated for Appendix D34 and Table 4.6.

The reasons of such high percentage AAD found in SNG 4 when modelled with CPA-PR-VDW due to the introduction of CPA, when it was modelled with PR EOS and VDW mixing rule, the combination of the equation resulted in over prediction of bubble point line as in Appendix D25, which due to the increasing heavies components and for correction in this phase envelope modelling by using CPA-PR-VDW is by the introduction of splitting and lumping method that was suggested by Hartono where he states that CPA is unable for combining the physical effects from the classical models and a chemical contribution of PR and VDW mixing rules. (Hartono et al., 2003)

For SNG 5, the component mixtures is almost the same as in SNG 4 but the applicable EOS model for such a mixture coming from the RK EOS families and VDW mixing rule as previously explained from the Nasrifar et al in their measurement and modelling of hydrocarbon dew points from 15 EOSs (Nasrifar et al., 2005).

As in Appendices D39 and D40, for SNG 5, the incomplete phase envelope predictions and over prediction of bubble point line was observe and thus implies that the same conclusion as Nasrifar et al in his research is true for SNG 4 and however for SNG 5, SRK-EXT-VDW produced larger % AAD of temperature compared to other SRK families in this studies where such variation is due to the fact that this equation is not applicable to modelled SNG 5 that produces incomplete phase envelope as shown in Appendix D41 and yet the calculated percentage AAD of temperature for this modelled mixture is as less as 4.26% only. Thus, for SNG 5,

the applicable EOS for this mixture are SRK-VDW as it gives almost complete phase envelope modelling compared to CPA-SRK-VDW which unable to produce complete phase envelope and yet at an accurate % AAD/T of as less as 3.2% over 3.84% (Nasrifar et al., 2005).

This comes to a conclusion primarily that the increasing heavies components of about 0.01% per single carbon number constitutes to the high deviations of pressure and temperature and yet modelling phase envelope by calculation of the EOS models becomes surprisingly important.

4.6: Resulted Calculation for SET 19

Figure 4. 26: Phase Envelope Generated from Different EOSs and Experimental Values for Set 19-Gas 1

Figure 4. 27: Phase Envelope Generated from Different EOSs and Experimental Values for Set 19-Gas 2

% AAD/P of Set 19

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
■ GAS 1	3.22%	3.58%	3.25%	3.13%	3.13%	3.13%	3.51%	3.52%
■ GAS 2	4.75%	4.58%	4.75%	4.91%	4.76%	4.76%	4.76%	4.76%

Figure 4. 28: Percentage AAD/P Calculated from Different EOSs and Experimental Values for Set 19

% AAD/T of Set 19

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
■ GAS 1	2.23%	2.20%	2.20%	2.24%	2.24%	2.24%	2.20%	2.22%
■ GAS 2	4.70%	4.58%	4.65%	4.72%	4.65%	4.65%	4.65%	4.65%

Figure 4. 29: Percentage AAD/T Calculated from Different EOSs and Experimental Values for Set 19

For set 19 data that comprise of high content of carbon dioxide presented in the gas 1 and 2 mixtures of about 95% and 99%, all EOS models used in this study gives less percentage of AAD in terms of temperature and pressure of about less than 3% and 4 % as presented for Gas 1 in Figure 4.28 and Figure 4.29. The same trend observed for gas 2 mixtures that lead to the increasing of about 2% AAD for pressure deviations and temperature deviations.

Though the fact that % AAD of temperature and pressure for this two mixtures exhibit less than 10%, none of the EOS model use in this calculation of phase envelope is applicable for modelling dew points as expected in previous cases. This is true when the experimental dew point values were plotted on the same graphs as in Figures 4.26 and 4.27.Particular EOS modelling are best describe as in the Appendices E1 to E16 for both gases.

It comes to the conclusive event that for both mixtures, all the EOS model uses in this study are overestimate dew points line and the phase envelope calculate are incomplete and limited only to the dew points. For both gases which have quite high mole percentage of carbon dioxide of about more than 95% none of the EOS models can accurately predicting phase envelope of the gas mixtures. Velderama suggested in his work that modelling carbon dioxide with hydrocarbon gas mixtures that can be classified as asymmetric mixtures is best modelled with EOS that used TWU temperature function with mixing rule of P&R and MWS-1P at low pressure and PTV EOS with Soave temperature function and associating VDW mixing rule with one or two parameters at moderate and high pressure of more than 10 atm. (Velderama, 2003)

4.7: Resulted Calculation for SET 20

Figure 4. 30: Phase Envelope Generated from Different EOSs and Experimental Values for Set 20-MIX A

Figure 4. 31: Phase Envelope Generated from Different EOSs and Experimental Values for Set 20-MIX B
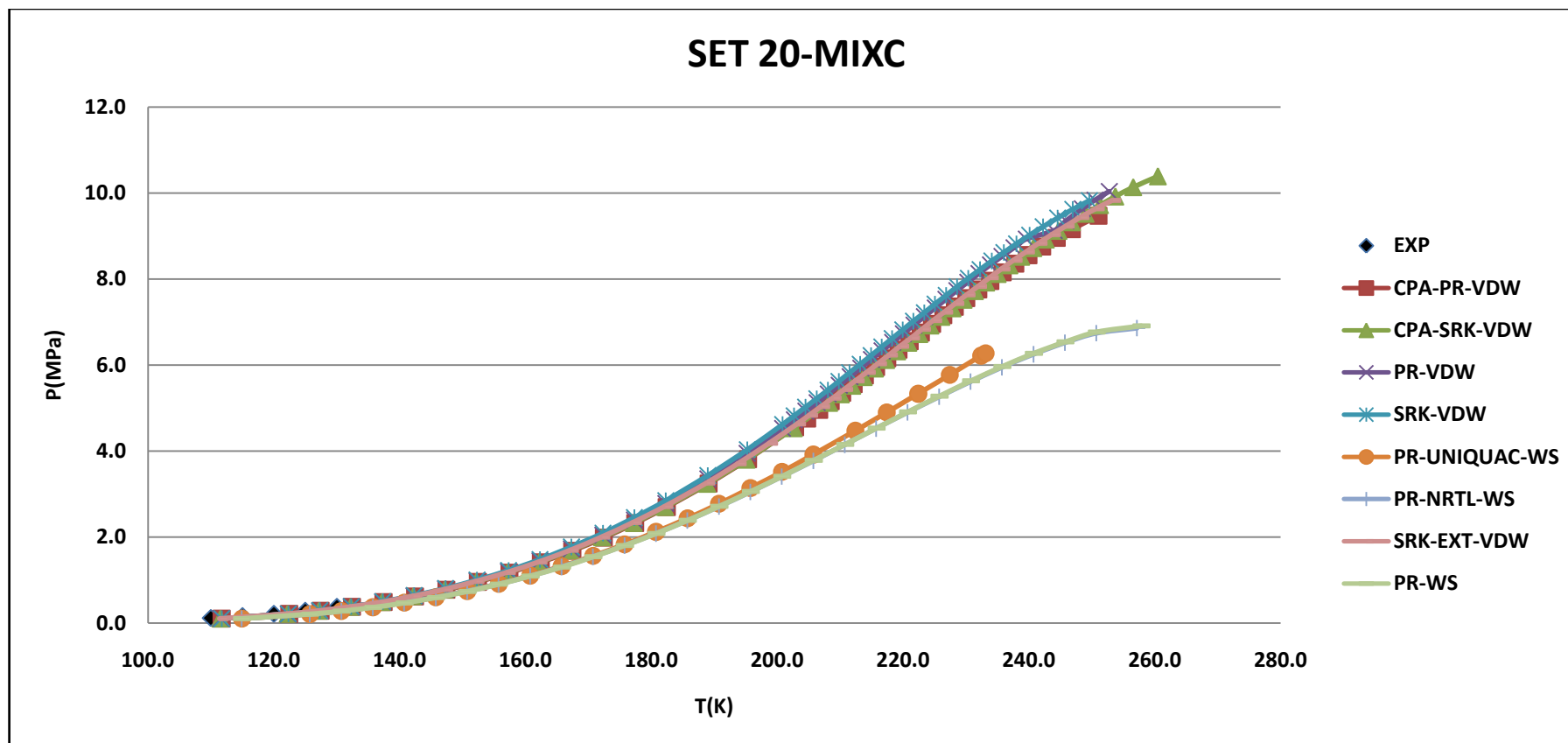
Figure 4.32: Phase Envelope Generated from Different EOSs and Experimental Values for Set 20-MIX C
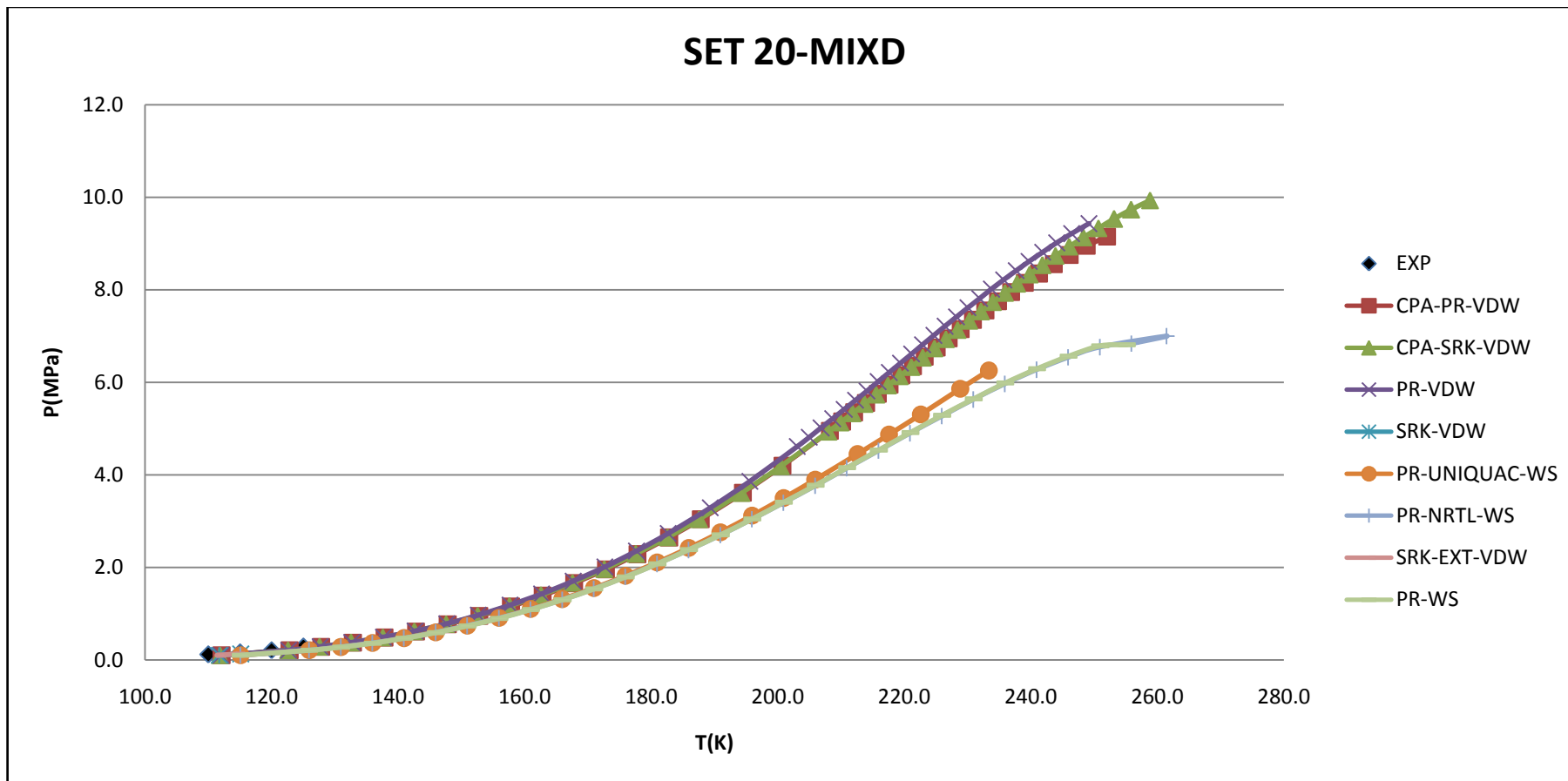
Figure 4.33: Phase Envelope Generated from Different EOSs and Experimental Values for Set 20-MIX D
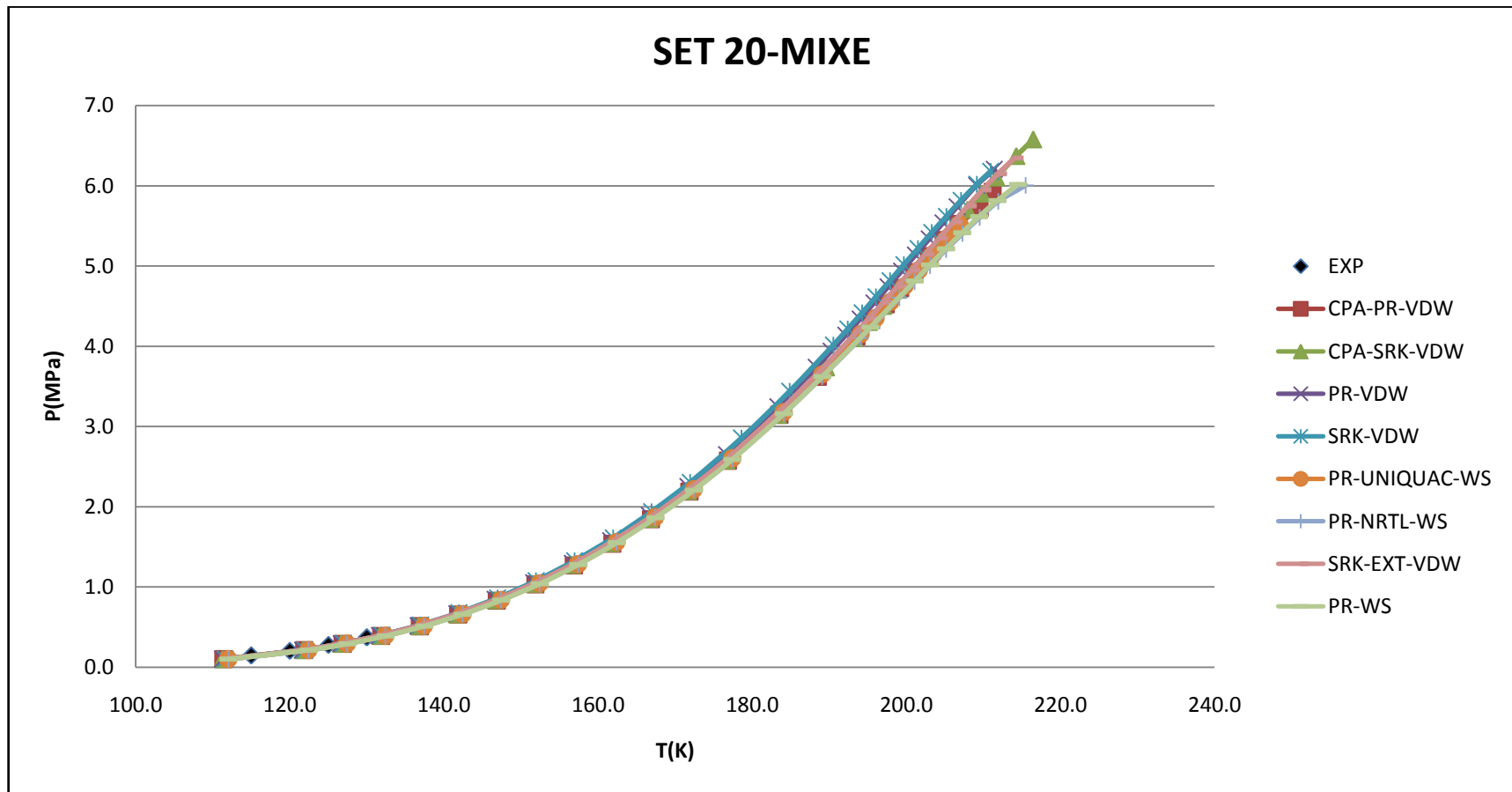
Figure 4.34: Phase Envelope Generated from Different EOSs and Experimental Values for Set 20-MIX E

% AAD/P of Set 20

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
MIXTURE A	17.41%	17.35%	17.30%	23.22%	17.49%	17.50%	17.35%	17.50%
MIXTURE B	20.67%	20.61%	20.57%	20.41%	20.83%	28.14%	20.59%	20.84%
MIXTURE C	9.57%	9.61%	9.67%	9.93%	10.13%	10.22%	9.63%	10.71%
MIXTURE D	11.53%	11.55%	11.57%	12.79%	11.62%	11.66%	11.98%	11.95%
MIXTURE E	11.76%	12.06%	12.34%	13.08%	12.29%	12.25%	12.13%	11.65%
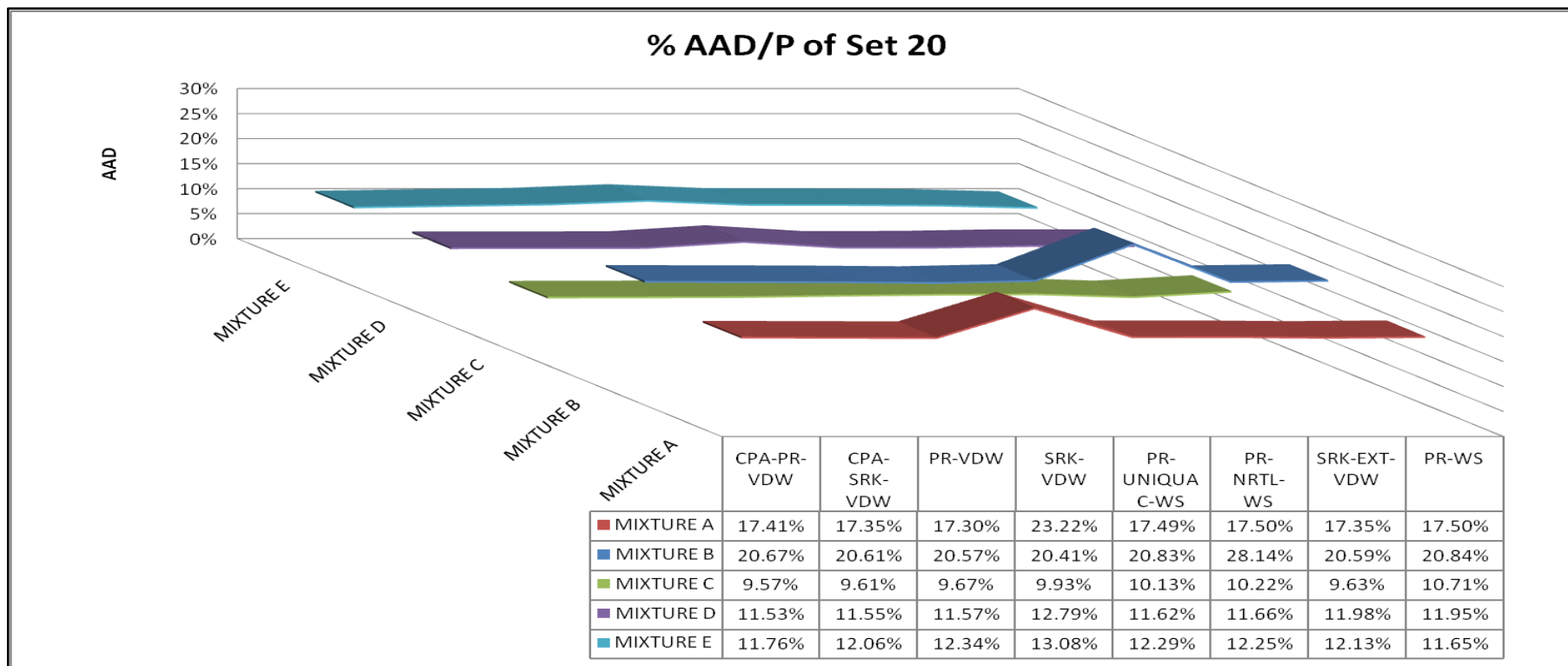
Figure 4. 35: Percentage AAD/P Calculated from Different EOSs and Experimental Values for Set 20

% AAD/T of Set 20

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
MIXTURE A	1.89%	1.91%	1.92%	2.74%	1.78%	1.78%	1.93%	1.78%
MIXTURE B	2.29%	2.24%	2.23%	2.18%	2.84%	3.83%	2.17%	2.85%
MIXTURE C	2.05%	1.93%	1.98%	1.99%	1.99%	1.99%	1.86%	2.00%
MIXTURE D	2.13%	2.13%	2.13%	1.29%	2.39%	2.37%	1.22%	2.40%
MIXTURE E	1.90%	1.82%	1.81%	1.90%	2.10%	2.10%	1.79%	2.11%
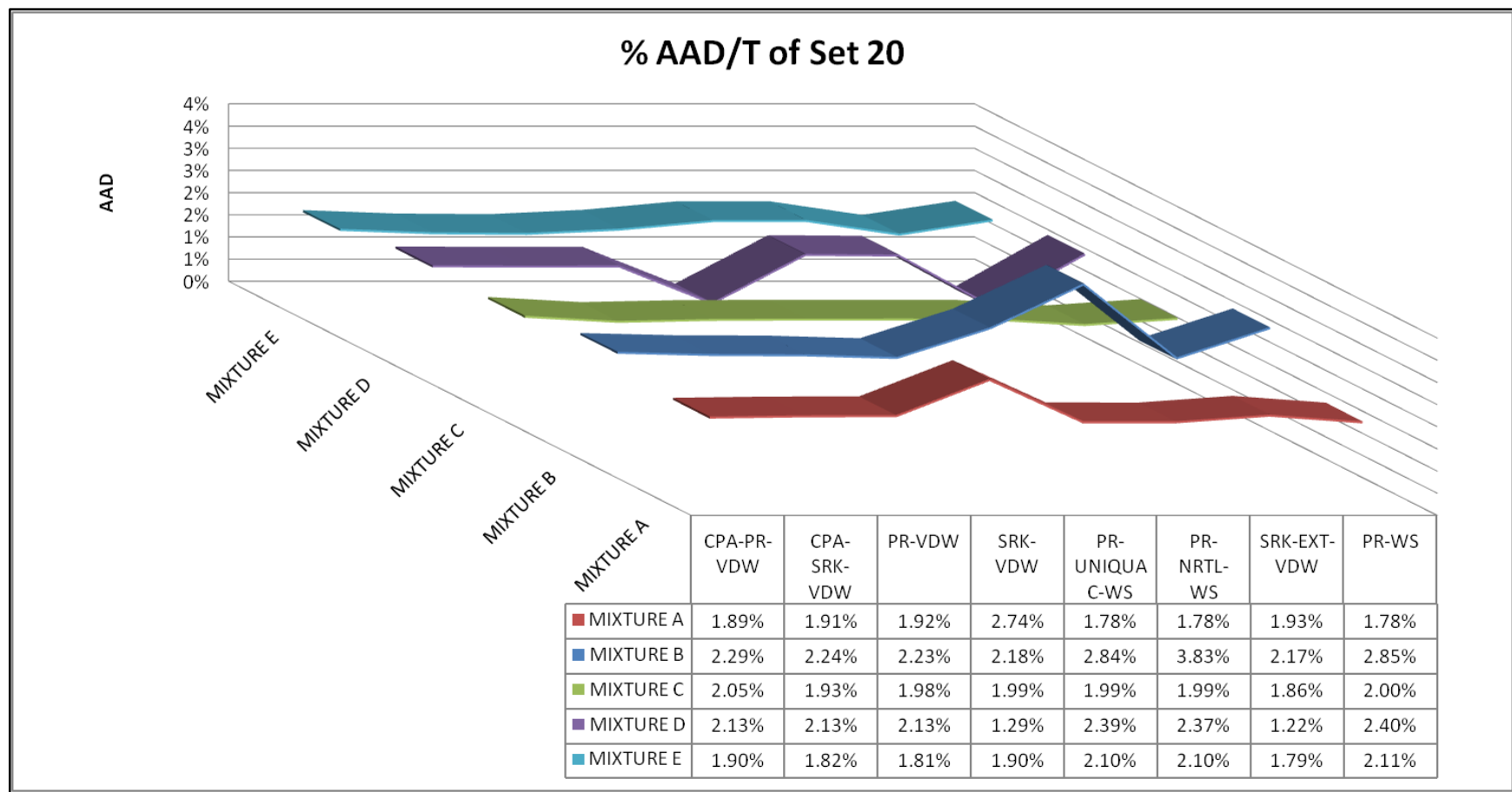
Figure 4. 36: Percentage AAD/T Calculated from Different EOSs and Experimental Values for Set 20

For set data 20, that contain about five gas mixtures of different chemical compositions and most of them contains no carbon dioxide gaseous as illustrated in Table 4.2. Mixture C to E contains nitrogen gases of less than 1 mol percent and all the mixtures have a pentane composition that varies from 0.01 % to 0.22 %.

For mixture A, most EOS models gives percentage AAD of temperature of less than 2% except for SRK-VDW EOS and large error observe for the mixture A for all type of EOS models. For all type of mixtures, in predicting their constituent bubble point pressure, most of the EOS models used in this study yield high percentage of AAD for pressures as in Figure 4.35 and less than 3% of percentage AAD observed for temperature deviations from the experimental values as illustrated in Figure 4.36 except that for PR-NRTL-WS at 3.83% with incomplete phase envelope modelled observed as in Appendix F6.

For the ease of comparison due to the limited bubble point data obtain from the literature, not all EOS model using WS mixing rule exhibits high percentage deviations in temperature, pressure and high degree of incompleteness of phase envelope. For example in Appendix F4, the excessive and over estimation of the bubble point line was generated when modelled with SRK-VDW. Thus gives highest percentage AAD for pressure at 23.22% and 2.74% for temperature which are the highest of its class interval.

The most applicable EOS functions that best modelling phase envelope for mixture A that have lowest % AAD for pressure and temperature with complete phase envelope predictions is PR-VDW. Even though WS mixing rule gives lowest % AAD for mixture A, the phase envelope predictions is incomplete thus unable to predict phase envelope accurately. This gives a conclusive event that WS+ EOS models+ Gibbs energy is able to predict bubble points with reasonable percentage error as other EOS models but with a limitation. As previously cases, WS+EOS+ free Gibbs energy shows great percentage deviation in temperature and pressure for predicting dew points but for bubble points, it is at its capabilities as shows for mixture A.

With no non hydrocarbon components for mixture B, great percentage deviations observed for all EOS models and temperature deviations is around 3% and the highest observed when modelled with PR-NRTL-WS is at 3.83%. This is due to the

overestimation of bubble point line and under estimation of dew point line that was plotted as illustrated in Appendix F14. For mixture B, the superior EOS models for predicting bubble points is CPA-PR-VDW, but actually the EOS models that gives lowest percentage AAD of temperature is SRK-EXT-VDW but the incomplete phase envelope was predicted as in Appendix F15.

From here, all the mixtures composition have no heavies fraction and yet with high methane gas and less than 1 % of nitrogen composition as in mixture C, D and E. In set 6, and set 15 as previously discussed, the constituent gas mixtures have high percentage of methane too and yet predicting dew point pressure by using eight EOS models obtain a reasonable percentage AAD but for this set 20, predicting bubble point by using eight EOS models yield quite high amount of percentage AAD in terms of temperature with less than 3%.

The same mixtures C, D and E were modelled previously by Nasrifar et al. In his studies that conducted to test the applicability of the PR-VDW and NM-VDW in predicting bubble points, and comes to a conclusion that mixtures C and D are best modelled with NM-VDW and mixtures E with PR-VDW. They only tested PR-EOS and NM-EOS with zero binary interaction parameters and thus in testing eight EOS tools for predicting mixtures data C, D and E, the conclusive applicability of the EOS models to that particular mixtures may varies. (Nasrifar et al., 2002)

For mixture C, D and E, predicting bubble point by using PR-EOS gives percentage AAD of temperature at about 2% which almost no difference with other EOS models and for average deviation in pressure, PR-EOS gives almost 10% for mixture C, 11% for mixture D and 12% for mixture E. The variations of average deviations of pressure are no difference between PR-EOS and other EOS models use in this study.

By knowing previously that WS mixing rule is unable to predict a complete phase envelope for all mixtures, the same trends was observed for mixture C, D and E thus implies that using WS mixing rule is poor at predicting a complete phase diagrams and yet it is superior and comparable to the other EOS in predicting bubble point pressure and temperature as in mixture C and E. But for mixture D, a complete phase envelope as in Appendix F30 was plotted for PR-NRTL-WS with percentage AAD of temperature and pressure at about 2.10% and 12.25%.

The most applicable EOS that gives lowest percentage AAD for pressure and temperature with complete phase diagram plotted for mixture C and D is SRK-EXT-VDW. What reported by previous work done by the great Nasrifar et al., is that they observe the same trend of high deviations in terms of pressure in mixtures C, D and E due to the fact that the mixtures tested contain nitrogen gases that produce a large error due to large kij for nitrogen + hydrocarbon binaries. (Nasrifar et al., 2002, 2006)

4.8: Summary of the Resulted Calculation for All Mixtures Used in This Study

If comparing %AAD of T and P alone, it is hard to derive a conclusion on which EOS are applicable for constituent mixtures of natural gas because some of the EOS gives same % AAD of T as seen previously. An added step in determining the applicability of the EOS for a natural gas mixtures is by taking mean average of both % AAD/T and %AAD/P. The lowest percentage mean gives an indication of the applicability of the EOS model and its mixing rule in predicting bubble point line or dew point line of the mixtures. The resulted values of these findings are said to have the same discussion as previously discussed earlier in this chapter.

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/P	0.13%	0.33%	0.19%	0.27%	0.64%	1.49%	0.17%	1.08%
%AAD/T	2.84%	2.37%	2.94%	3.04%	8.28%	7.44%	2.33%	6.90%
MEAN %	1.48%	1.35%	1.56%	1.66%	4.46%	4.46%	1.25%	3.99%
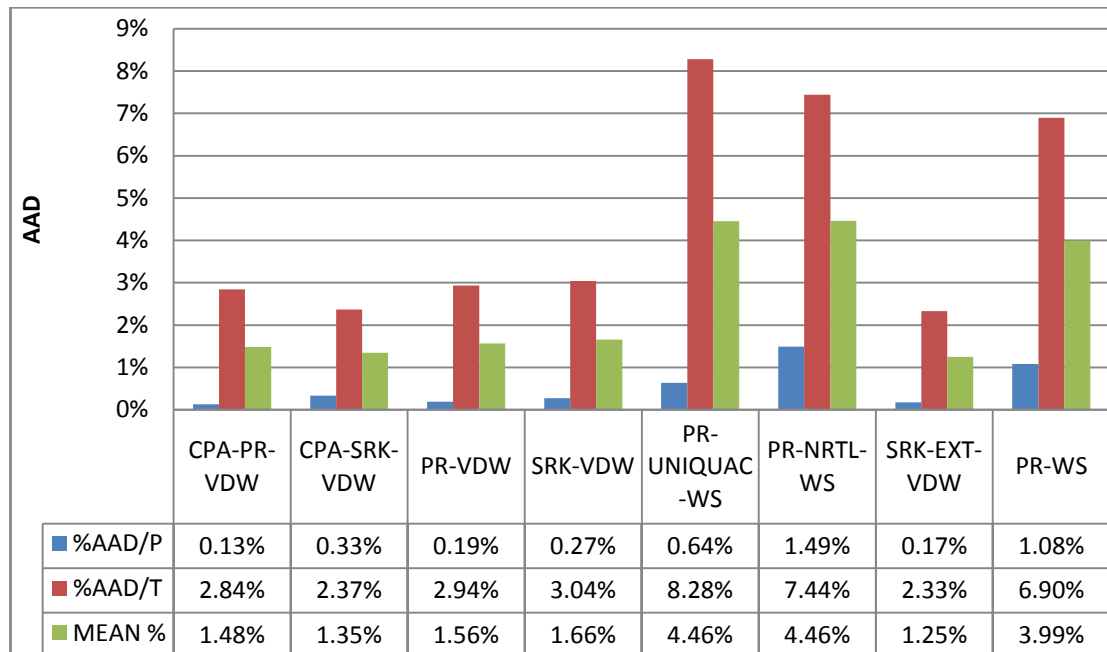
Figure 4. 37: Summary of % Mean of SET 6: SNG 2

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For SNG 2 of set 6, the lowest percentage mean is best modelled from SRK-EXT-VDW as in Figure 4.37, while CPA-SRK-VDW is recommended and applicable for modelling SNG 3 and 4 as depicted in Figures 4.38 and 4.39. Hence, for Gas 1 of set 9 is best modelled with SRK-VDW with lowest percentage mean of 0.42% as shown in Figure 4.40.

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.91%	0.18%	0.70%	0.32%	2.53%	3.62%	0.19%	3.21%
%AAD/P	5.40%	1.78%	3.47%	2.29%	19.66%	17.28%	2.03%	22.05%
MEAN %	3.16%	0.98%	2.08%	1.30%	11.09%	10.45%	1.11%	12.63%

Figure 4. 38: Summary of % Mean of SET 6: SNG 3

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	12.84%	0.68%	1.63%	0.98%	4.41%	6.19%	0.80%	5.46%
%AAD/P	89.12%	6.15%	7.41%	6.74%	21.47%	21.05%	6.40%	18.05%
MEAN %	50.98%	3.42%	4.52%	3.86%	12.94%	13.62%	3.60%	11.76%
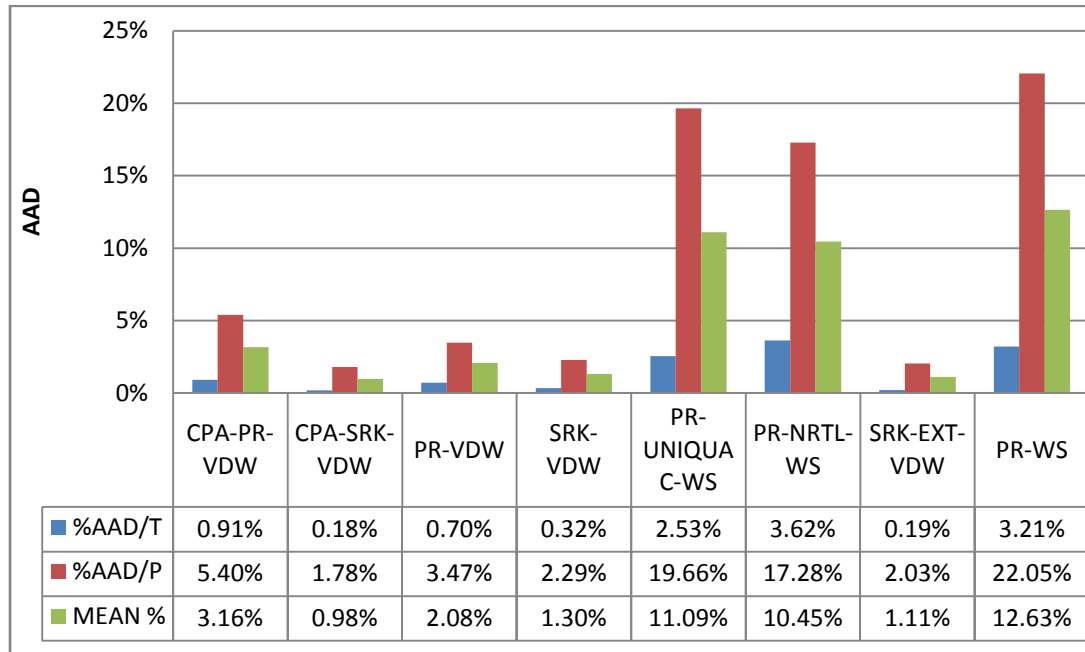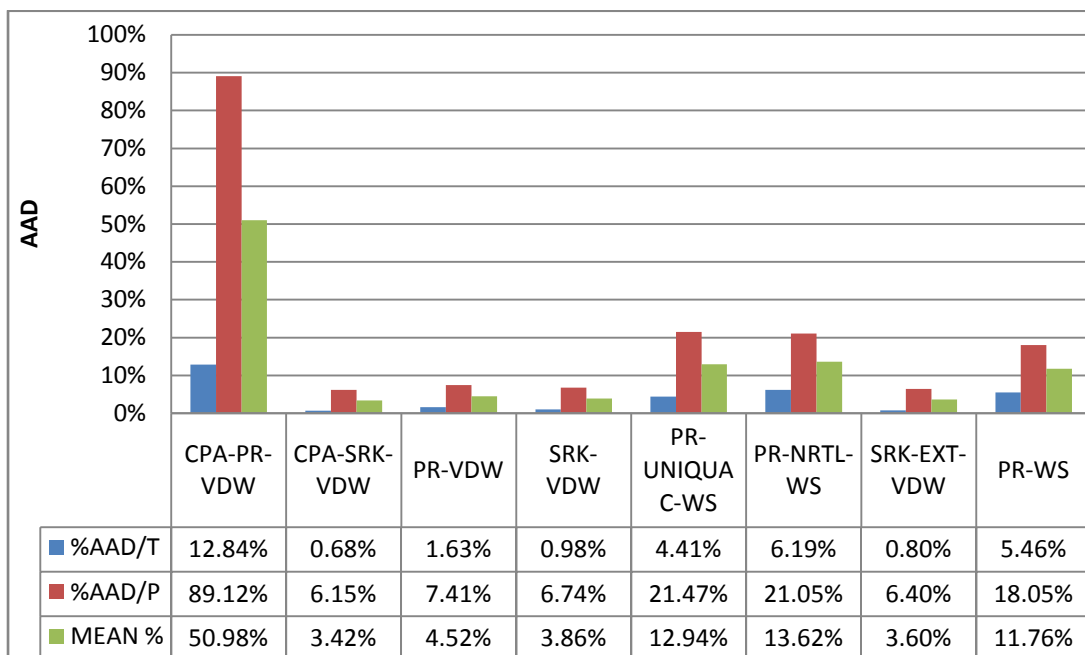
Figure 4. 39: Summary of % Mean of SET 6: SNG 4

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.43%	0.21%	0.38%	0.15%	1.79%	3.19%	0.27%	2.71%
%AAD/P	3.43%	0.66%	1.95%	0.68%	15.11%	18.51%	1.13%	16.53%
%MEAN	1.93%	0.43%	1.16%	0.42%	8.45%	10.85%	0.70%	9.62%
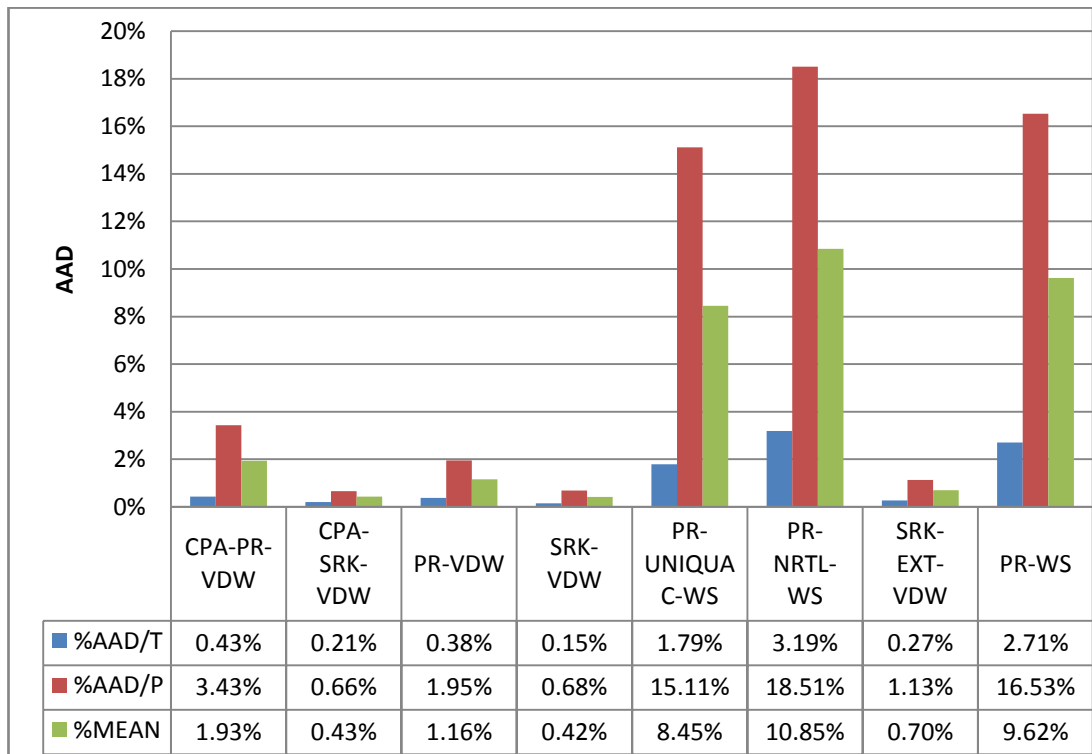
Figure 4. 40: Summary of % Mean of SET 9: GAS 1

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	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.81%	0.03%	0.53%	0.15%	4.25%	5.08%	0.03%	5.01%
%AAD/P	0.94%	0.78%	0.73%	0.96%	10.20%	8.01%	0.76%	7.48%
%MEAN	0.87%	0.40%	0.63%	0.56%	7.22%	6.54%	0.40%	6.25%
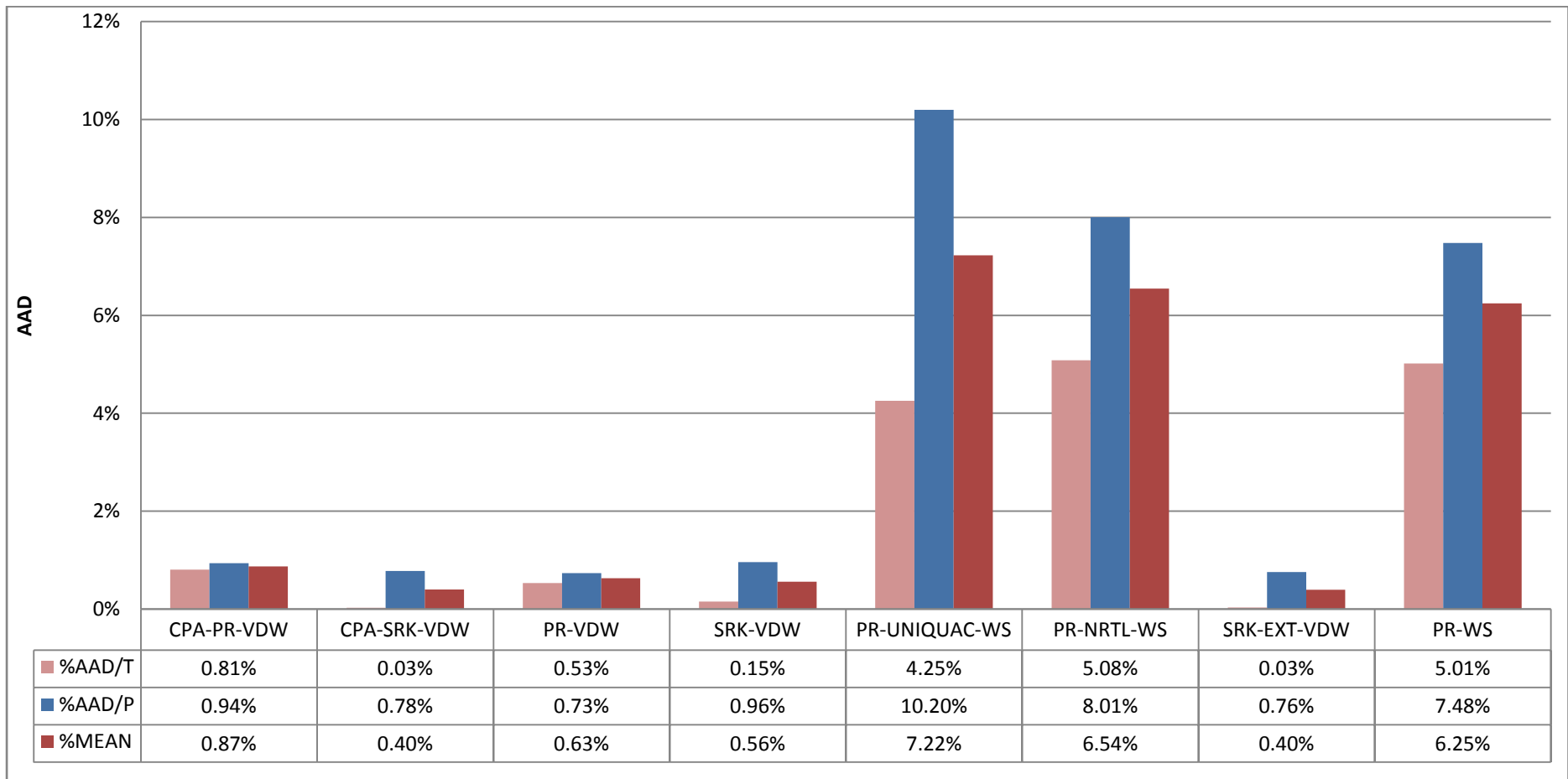
Figure 4. 41: Summary of % Mean of SET 15: GAS 1

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.32%	0.35%	0.31%	0.30%	2.69%	3.07%	0.38%	4.87%
%AAD/P	7.17%	5.55%	6.14%	5.51%	19.52%	17.42%	5.57%	20.10%
%MEAN	3.75%	2.95%	3.23%	2.90%	11.11%	10.24%	2.97%	12.49%
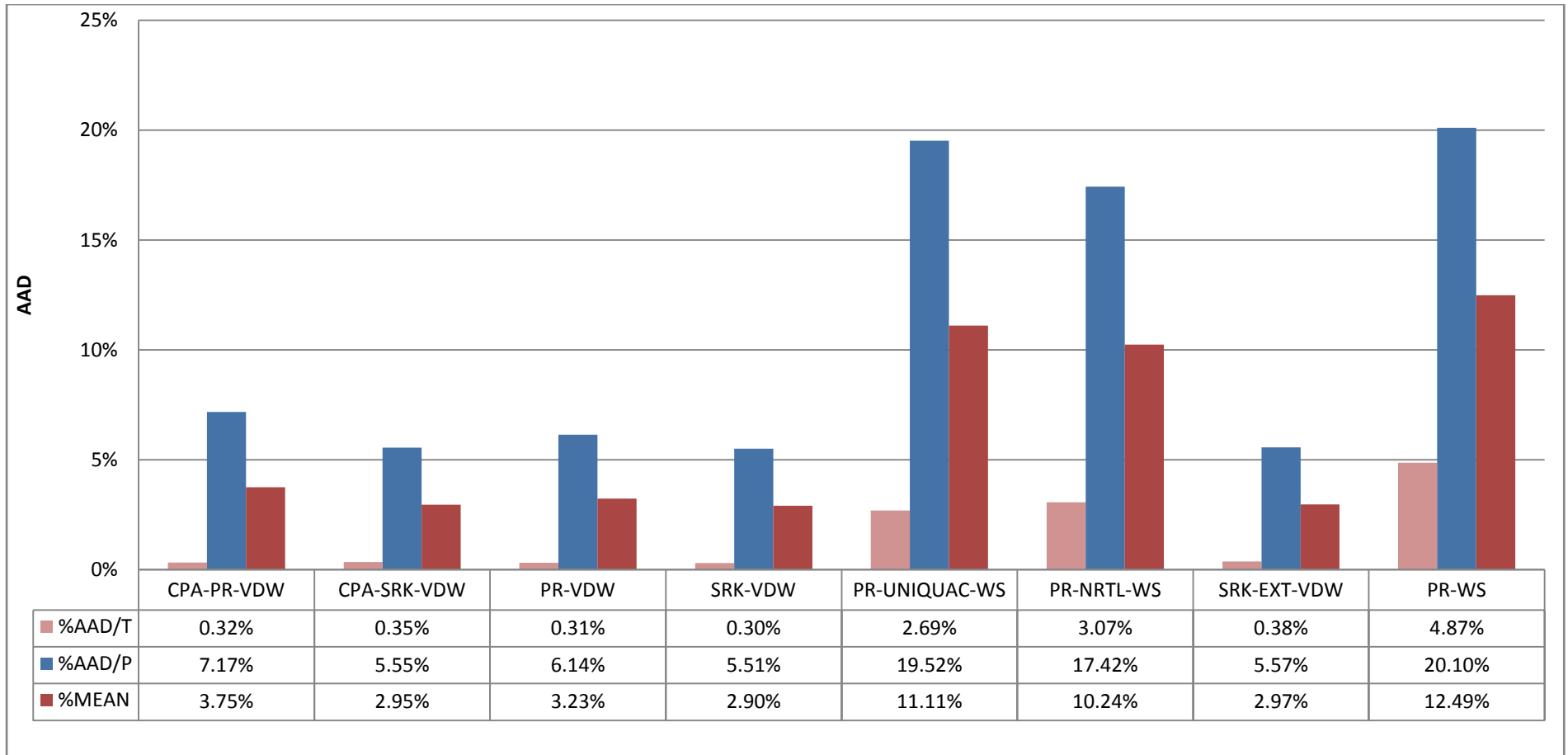
Figure 4. 42: Summary of % Mean of SET 15: GAS 2

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
■ %AAD/T	7.96%	4.94%	6.98%	6.96%	23.42%	7.89%	6.79%	15.13%
■ %AAD/P	58.80%	56.35%	58.47%	55.72%	86.80%	85.66%	55.30%	86.53%
■ %MEAN	33.38%	30.64%	32.72%	31.34%	55.11%	46.77%	31.04%	50.83%
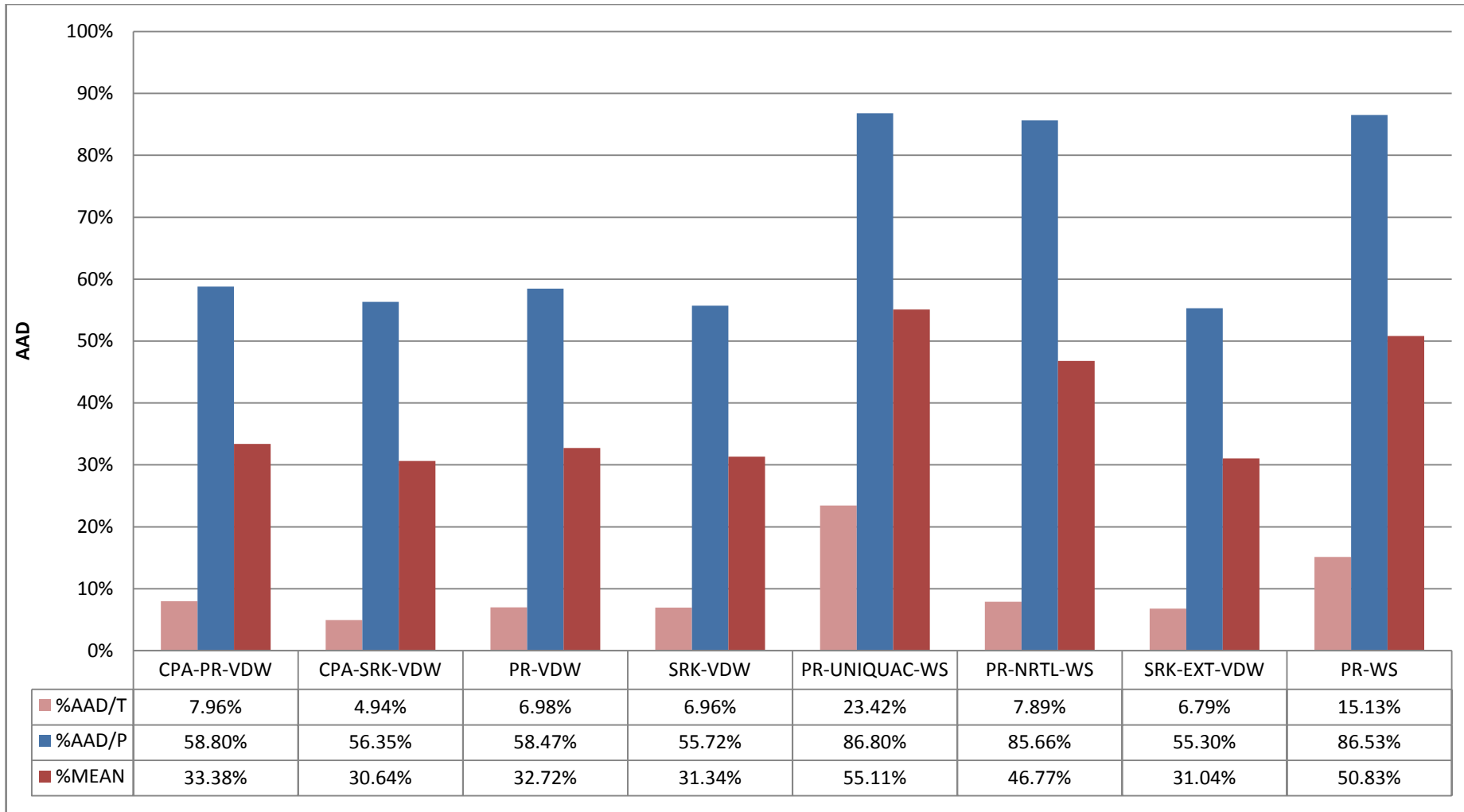
Figure 4. 43: Summary of % Mean of SET 15: GAS 3

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.51%	8.44%	0.36%	0.08%	1.82%	10.06%	0.07%	2.99%
%AAD/P	2.90%	79.46%	2.04%	1.72%	7.69%	82.65%	1.89%	7.06%
%MEAN	1.70%	43.95%	1.20%	0.90%	4.76%	46.35%	0.98%	5.03%
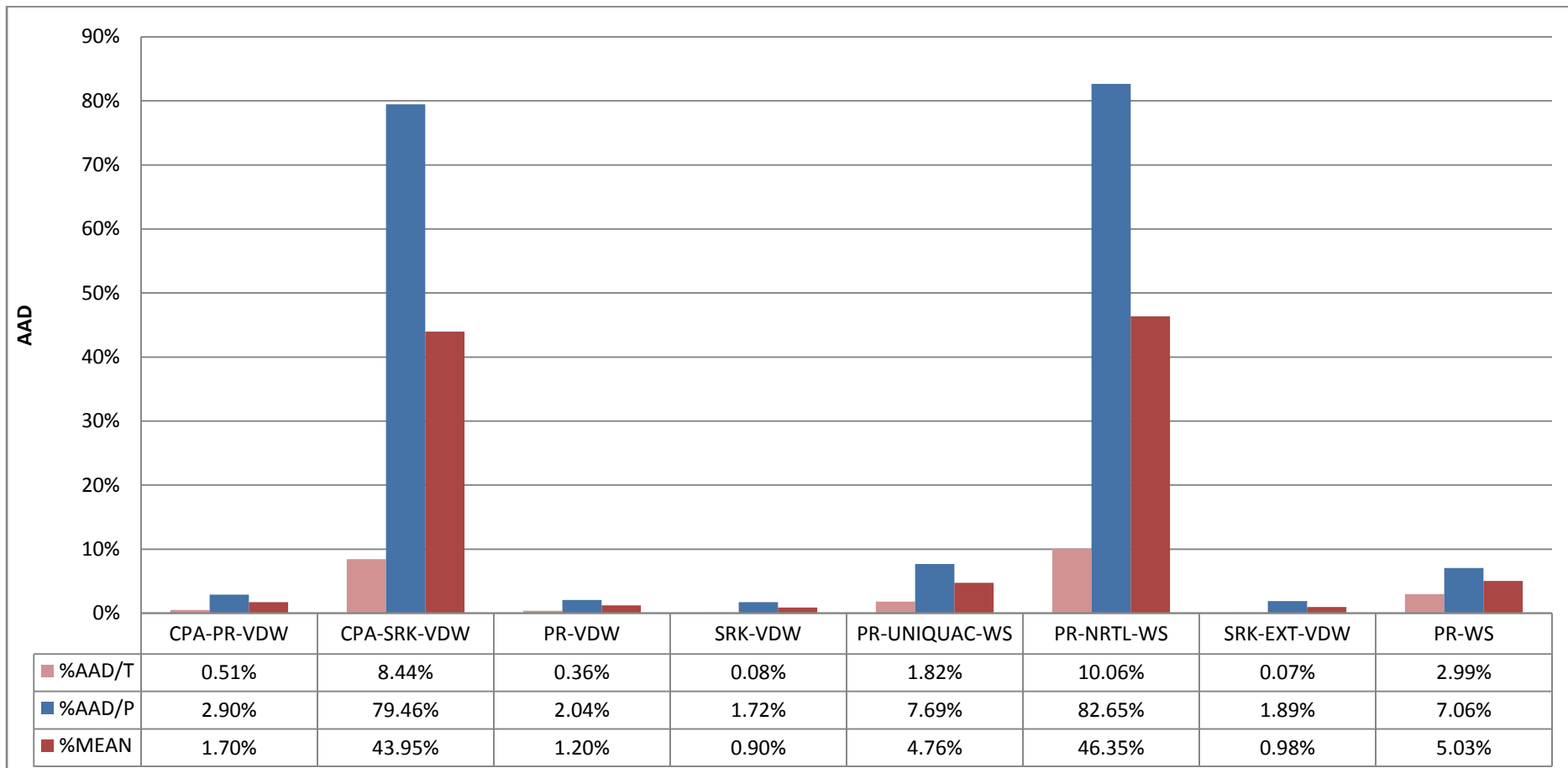
Figure 4. 44: Summary of % Mean of SET 15: SNG 1

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.46%	0.18%	0.29%	9.52%	1.14%	1.90%	0.20%	1.65%
%AAD/P	4.17%	3.09%	3.81%	76.55%	7.29%	6.05%	3.17%	6.23%
%MEAN	2.31%	1.64%	2.05%	43.04%	4.21%	3.97%	1.68%	3.94%
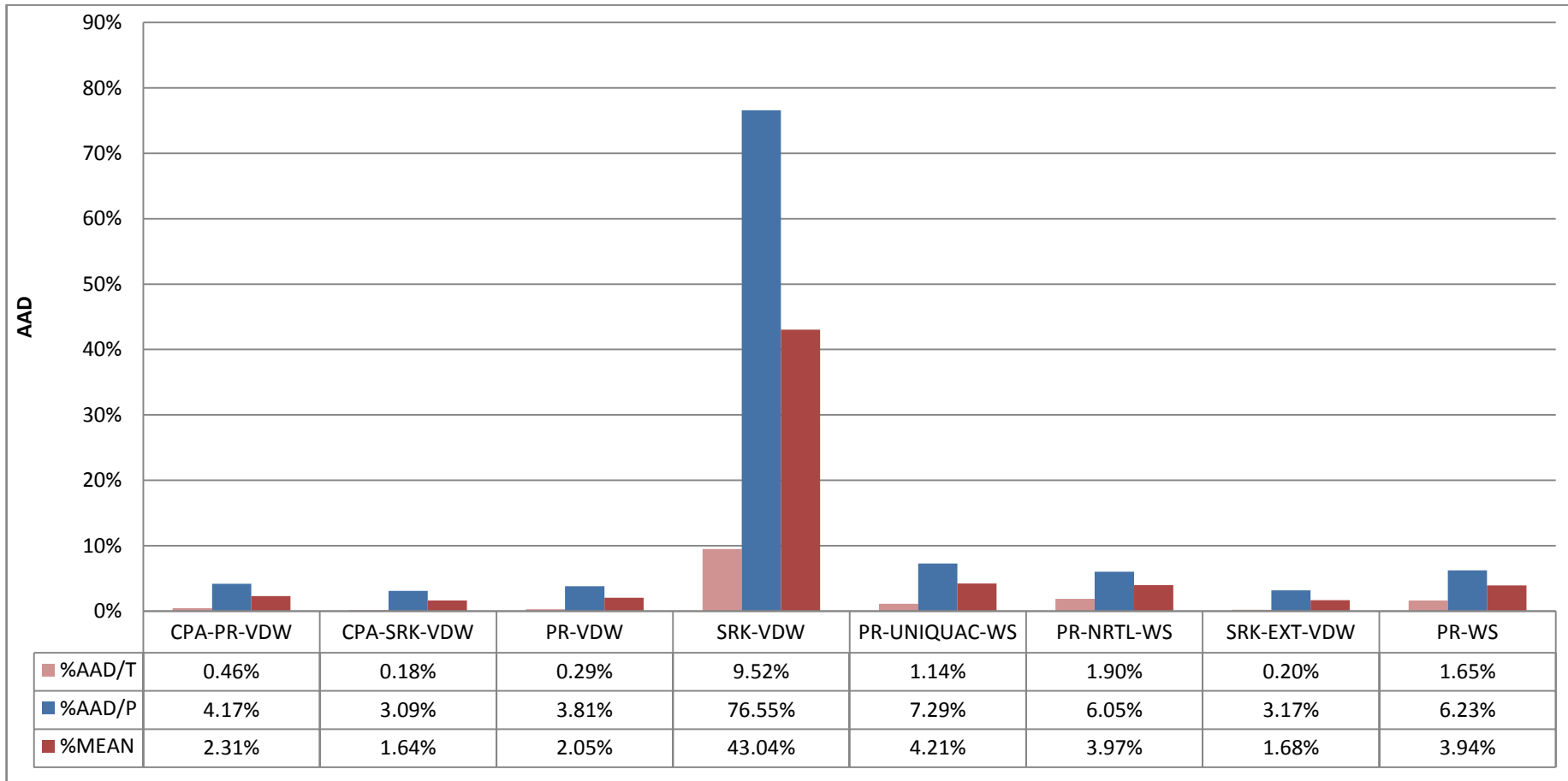
Figure 4. 45: Summary of % Mean of SET 15: SNG 2

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.85%	0.11%	0.67%	0.47%	2.73%	5.66%	0.28%	4.26%
%AAD/P	2.47%	2.89%	2.64%	2.37%	5.05%	6.40%	2.93%	5.93%
%MEAN	1.66%	1.50%	1.66%	1.42%	3.89%	6.03%	1.61%	5.10%
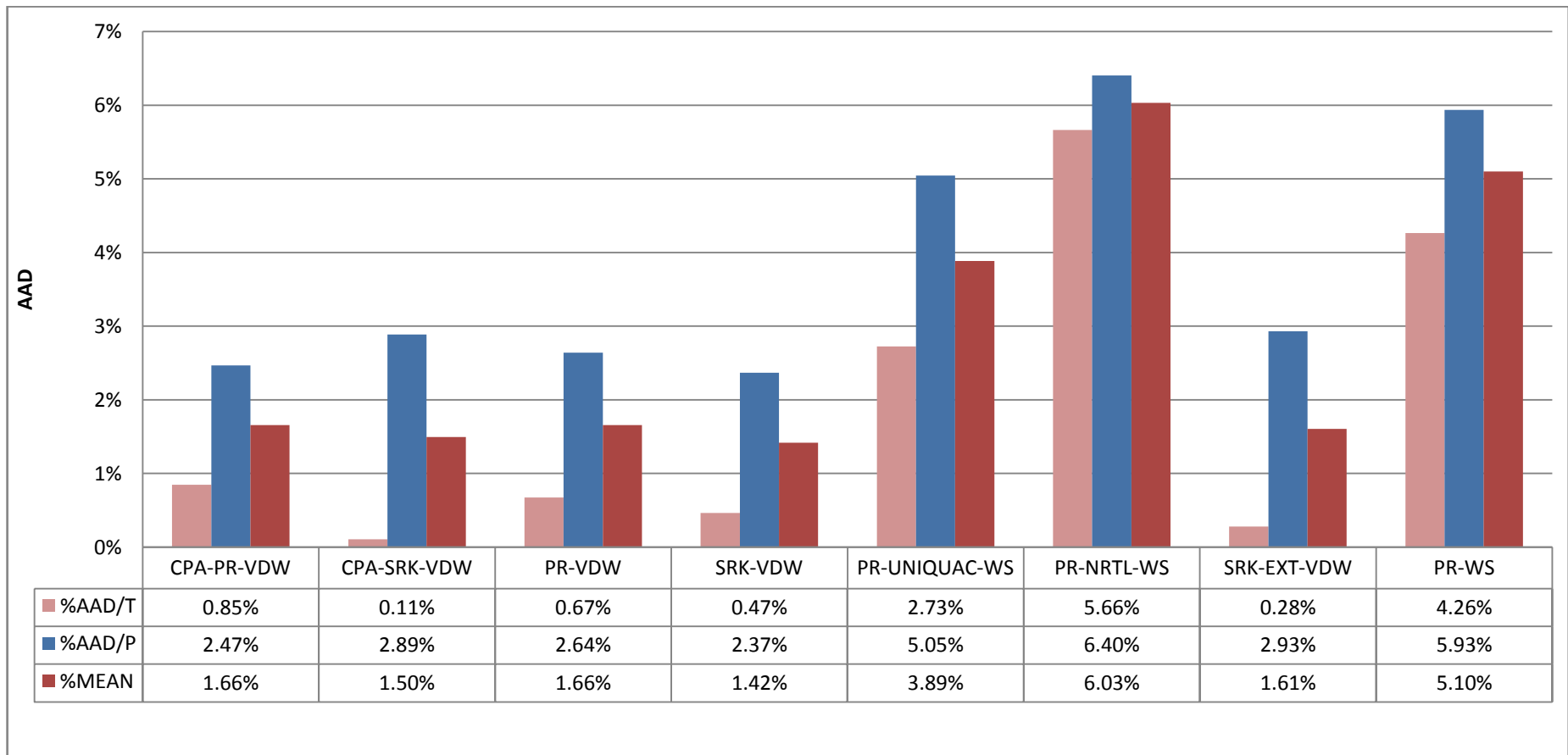
Figure 4. 46: Summary of % Mean of SET 15: SNG 3

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.52%	0.20%	0.47%	0.24%	3.84%	4.56%	0.42%	4.50%
%AAD/P	3.09%	2.32%	2.54%	2.69%	10.08%	9.27%	2.32%	10.42%
%MEAN	1.81%	1.26%	1.51%	1.47%	6.96%	6.92%	1.37%	7.46%
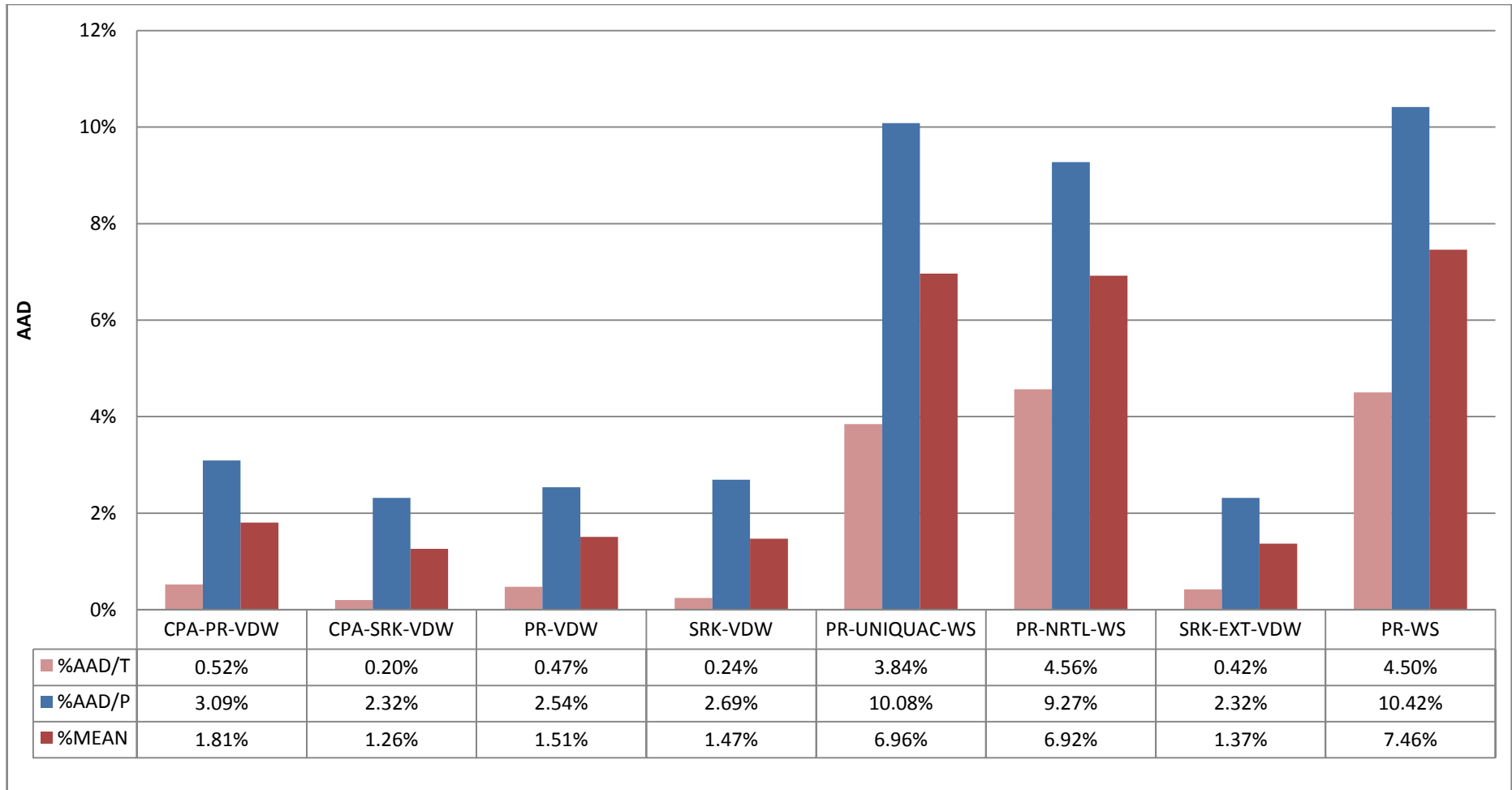
Figure 4. 47: Summary of % Mean of SET 15: SNG 4

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.69%	0.15%	0.53%	0.43%	2.87%	5.43%	0.25%	3.88%
%AAD/P	3.37%	3.44%	3.51%	3.16%	8.83%	9.94%	4.10%	8.74%
%MEAN	2.03%	1.79%	2.02%	1.79%	5.85%	7.69%	2.17%	6.31%
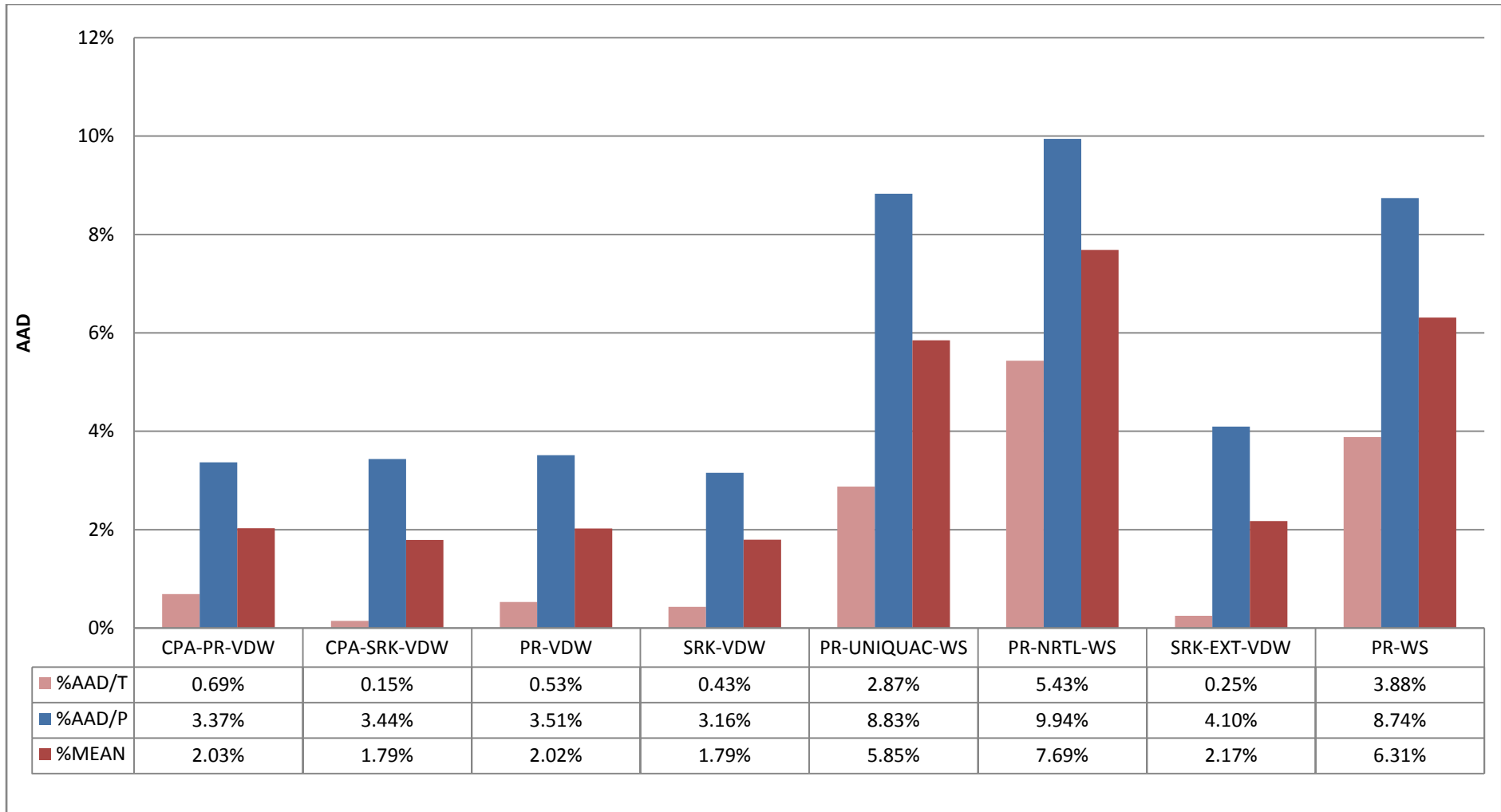
Figure 4. 48: Summary of % Mean of SET 15: SNG 5

Set 15 have eight mixtures and CPA-SRK-VDW is applicable in predicting phase behaviours of GAS 3, SNG 2 and SNG 4 as summarized in Figures 4.43, 4.45 and 4.47. For SNG 5, it is found that two EOS models give lowest percentage mean of 1.79%; which are CPA-SRK-VDW and SRK-VDW. It is presented in Figure 4.48. The same trend observed for GAS 1 and SNG 5 where the applicable EOS models are CPA-SRK-VDW and SRK-EXT-VDW, as presented in Figures 4.41 and 4.48. GAS 2, SNG 1 and SNG 3 of set 15 shared the same EOS model for describing phase behaviours of the constituent mixtures which is SRK-VDW and illustrated in Figures 4.42, 4.44 and 4.46.

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
■%AAD/T	0.21%	0.21%	0.21%	0.21%	0.21%	0.29%	0.37%	0.40%
■%AAD/P	6.74%	6.74%	6.74%	6.74%	6.74%	6.24%	8.39%	5.89%
■%MEAN	3.48%	3.48%	3.48%	3.48%	3.48%	3.27%	4.38%	3.15%
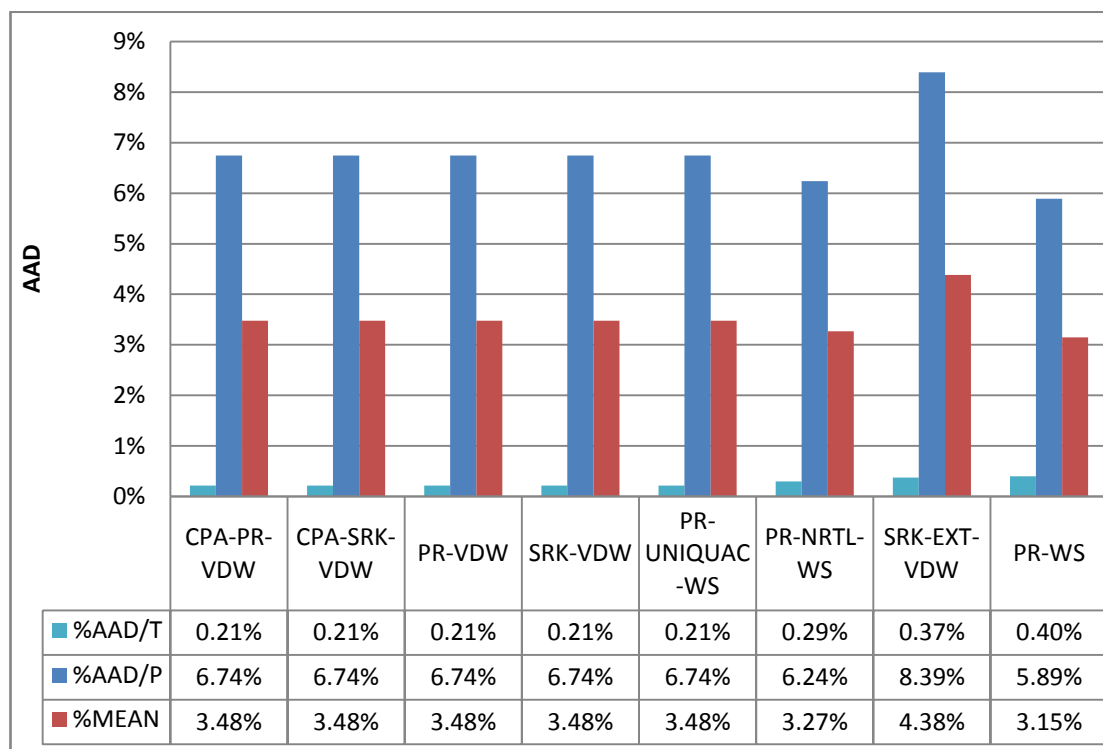
Figure 4. 49: Summary of % Mean of SET 18: SNG 1

SNG 1 of set 18 is best model with PR-WS as shown above. WS mixing rule with PR EOS is also capable of predicting dew point of the mixtures with 25.91% of carbon dioxide compared to VDW mixing rule and other EOS use in this study. CPA-SRK-VDW is applicable for predicting phase behaviour of SNG 2, 4 and 5, where SNG 3 is best modelled with PR-VDW. The resulted mean values for set 18 are presented from Figures 4.49 to 4.53.

Set 19 have more than 90% molar composition of carbon dioxide and comparing to SNG 1 of set 18 with 25.91 % of carbon dioxide content, the applicable EOS models

for GAS 1 and GAS 2 is SRK-VDW and CPA-SRK-VDW as depicted in Figures 4.54 and 4.55. Hence, it is found that PR-WS is unable to predict phase behaviour of natural gas mixtures with more than 25.91% carbon dioxide.

Figure 4. 50: Summary of % Mean of SET 18: SNG 2

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	1.44%	0.56%	1.22%	2.75%	1.23%	1.64%	2.29%	1.30%
%AAD/P	5.17%	3.81%	4.78%	5.96%	6.96%	8.01%	5.06%	6.46%
%MEAN	3.31%	2.19%	3.00%	4.36%	4.09%	4.82%	3.68%	3.88%

Figure 4. 51: Summary of % Mean of SET 18: SNG 3

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	0.36%	0.36%	0.34%	0.36%	1.00%	1.44%	0.33%	1.40%
%AAD/P	5.25%	5.25%	4.04%	5.04%	11.31%	9.66%	4.42%	10.94%
%MEAN	2.80%	2.80%	2.19%	2.70%	6.15%	5.55%	2.38%	6.17%

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	3.20%	2.70%	2.24%	1.90%	5.19%	5.81%	1.88%	5.74%
%AAD/P	8.85%	6.46%	8.81%	8.13%	19.79%	19.21%	8.05%	19.74%
%MEAN	6.02%	4.58%	5.52%	5.02%	12.49%	12.51%	4.97%	12.74%
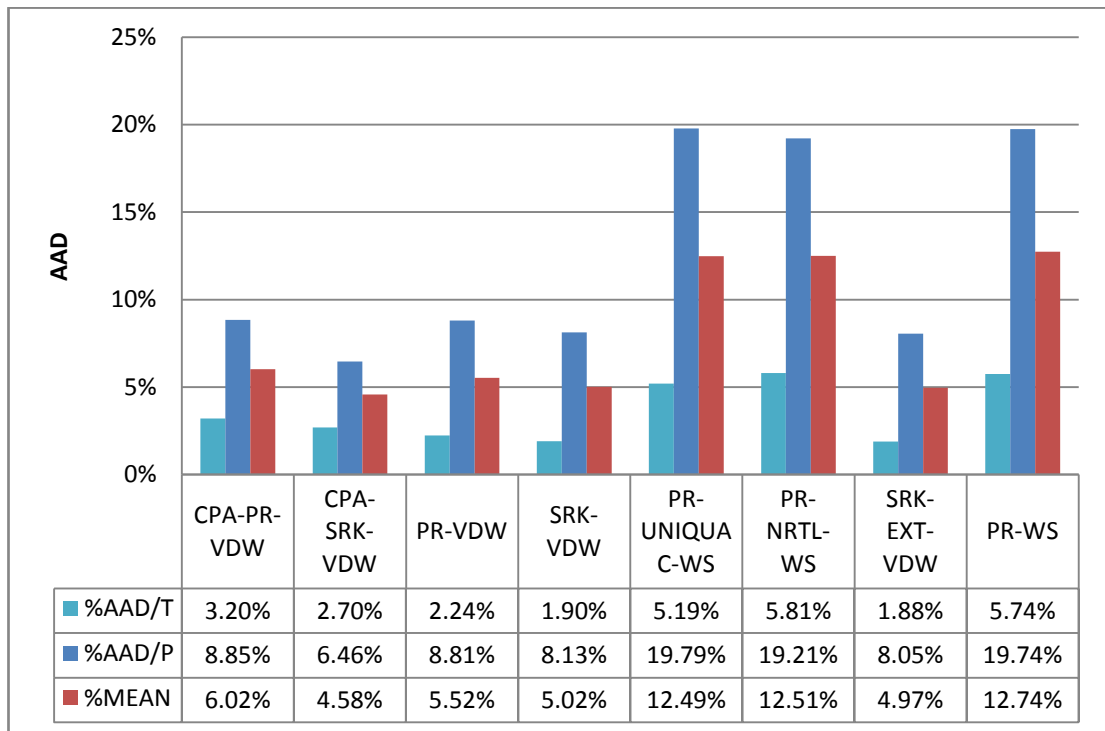
Figure 4. 52: Summary of % Mean of SET 18: SNG 4

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	3.93%	3.20%	3.75%	3.84%	6.10%	7.01%	4.26%	6.83%
%AAD/P	5.57%	3.27%	3.95%	4.97%	12.72%	14.00%	5.40%	12.22%
%MEAN	4.75%	3.23%	3.85%	4.40%	9.41%	10.50%	4.83%	9.53%
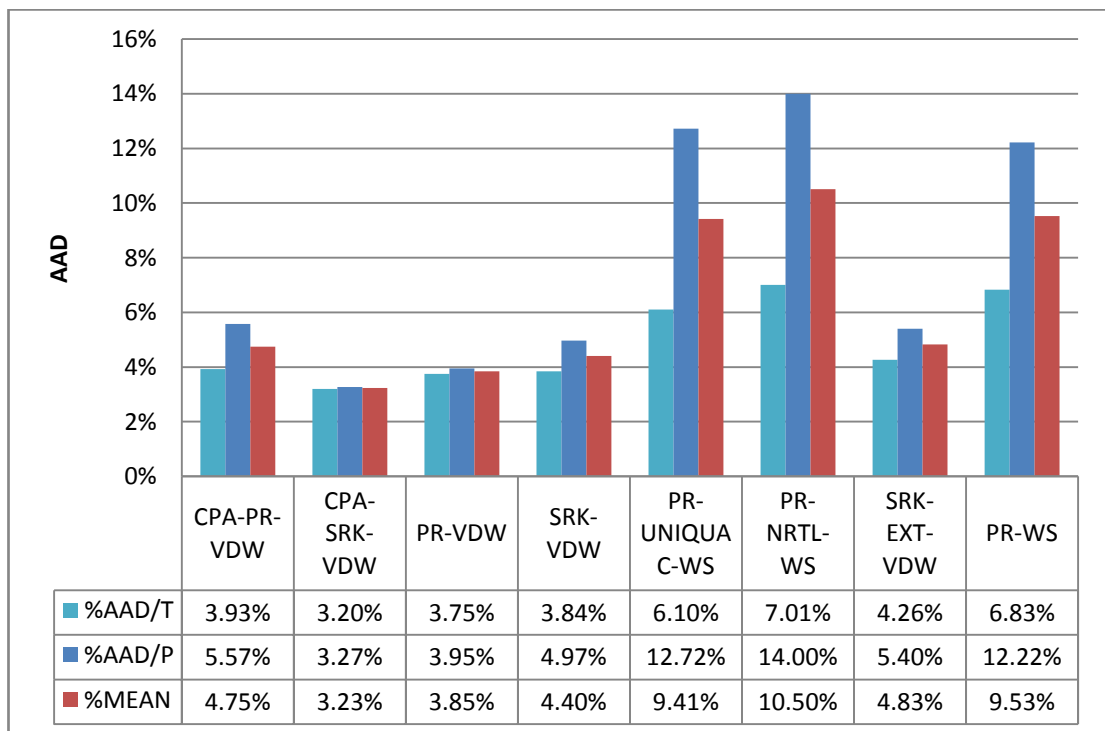
Figure 4. 53: Summary of % Mean of SET 18: SNG 5

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	2.23%	2.20%	2.20%	2.24%	2.24%	2.24%	2.20%	2.22%
%AAD/P	3.22%	3.58%	3.25%	3.13%	3.13%	3.13%	3.51%	3.52%
%MEAN	2.73%	2.89%	2.72%	2.68%	2.69%	2.69%	2.86%	2.87%
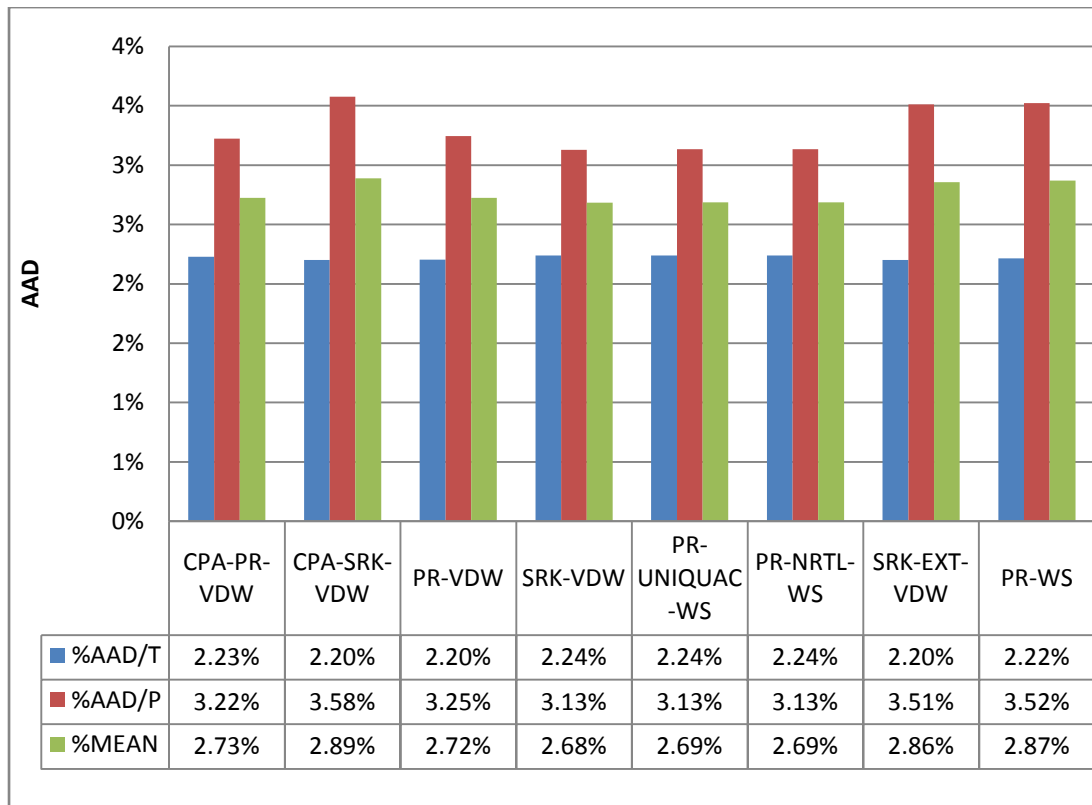
Figure 4. 54: Summary of % Mean of SET 19: GAS 1

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	4.70%	4.58%	4.65%	4.72%	4.65%	4.65%	4.65%	4.65%
%AAD/P	4.75%	4.58%	4.75%	4.91%	4.76%	4.76%	4.76%	4.76%
%MEAN	4.72%	4.58%	4.70%	4.81%	4.70%	4.70%	4.70%	4.70%
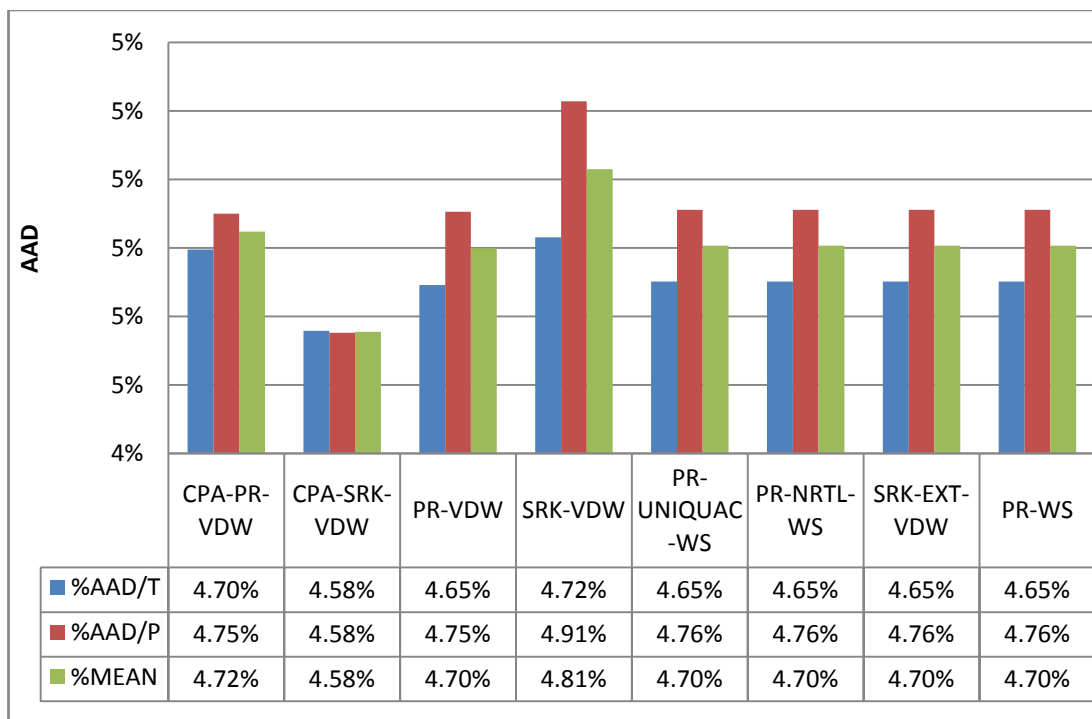
Figure 4. 55: Summary of % Mean of SET 19: GAS 2

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	1.89%	1.91%	1.92%	2.74%	1.78%	1.78%	1.93%	1.78%
%AAD/P	17.41%	17.35%	17.30%	23.22%	17.49%	17.50%	17.35%	17.50%
%MEAN	9.65%	9.63%	9.61%	12.98%	9.63%	9.64%	9.64%	9.64%
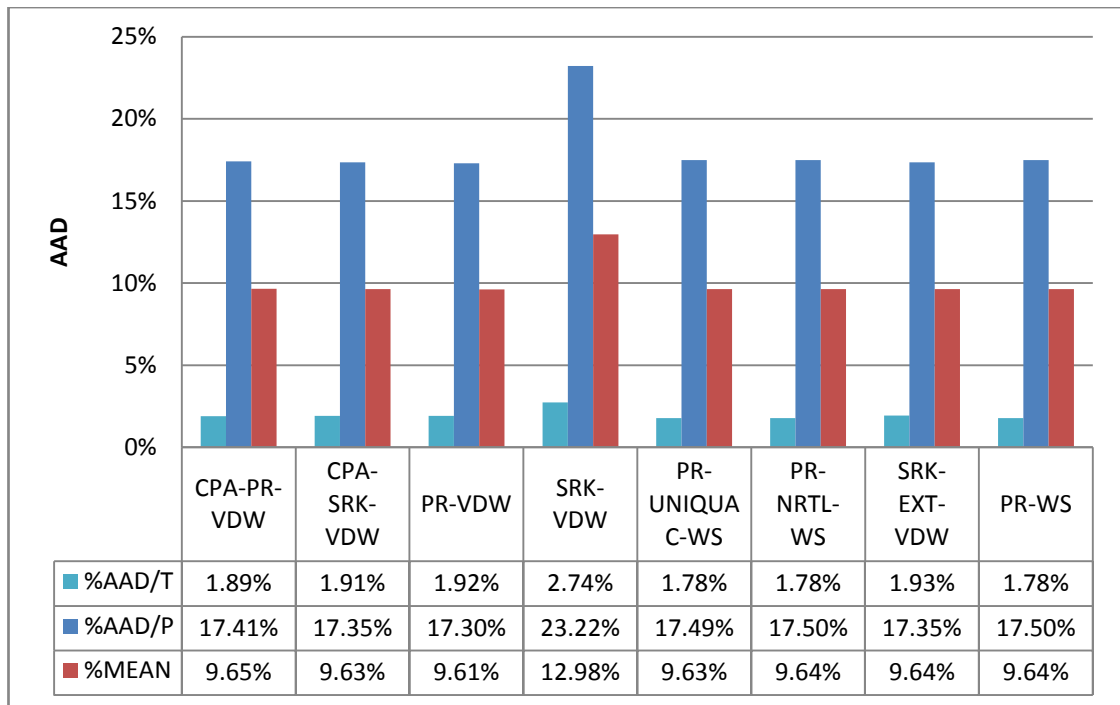
Figure 4. 56: Summary of % Mean of SET 20: MIX A

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	2.29%	2.24%	2.23%	2.18%	2.84%	3.83%	2.17%	2.85%
%AAD/P	20.67%	20.61%	20.57%	20.41%	20.83%	28.14%	20.59%	20.84%
%MEAN	11.48%	11.42%	11.40%	11.29%	11.84%	15.98%	11.38%	11.84%
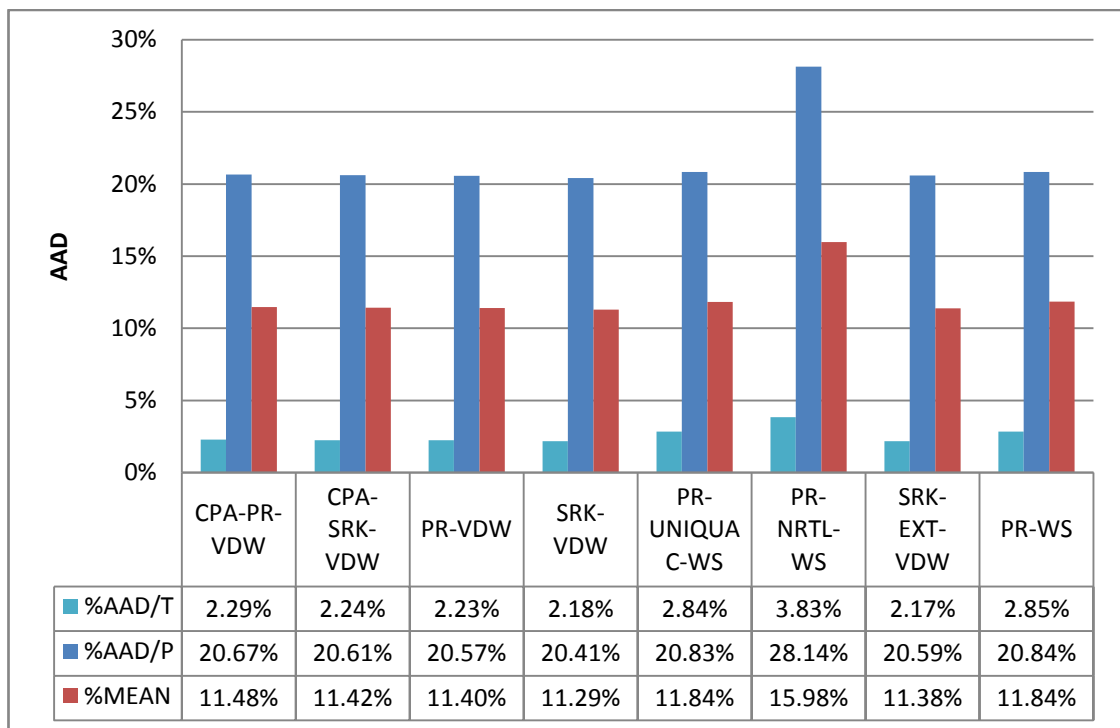
Figure 4. 57: Summary of % Mean of SET 20: MIX B

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	2.05%	1.93%	1.98%	1.99%	1.99%	1.99%	1.86%	2.00%
%AAD/P	9.57%	9.61%	9.67%	9.93%	10.13%	10.22%	9.63%	10.71%
%MEAN	5.81%	5.77%	5.82%	5.96%	6.06%	6.10%	5.74%	6.36%
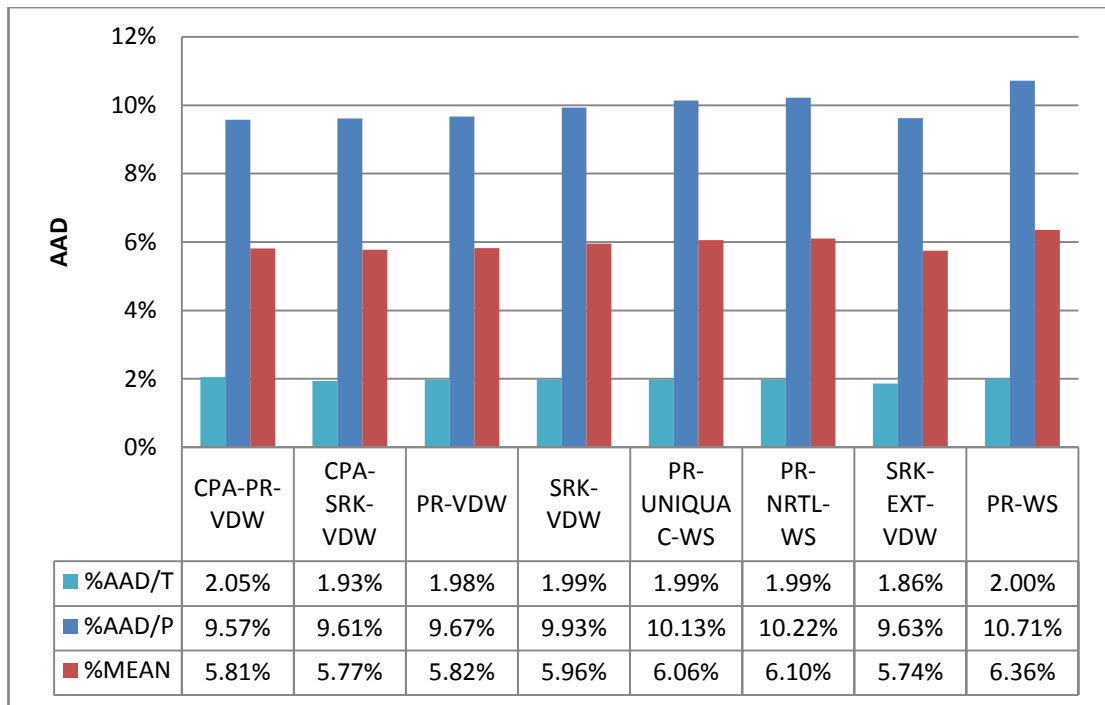
Figure 4. 58: Summary of % Mean of SET 20: MIX C

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	2.13%	2.13%	2.13%	1.29%	2.39%	2.37%	1.22%	2.40%
%AAD/P	11.53%	11.55%	11.57%	12.79%	11.62%	11.66%	11.98%	11.95%
%MEAN	6.83%	6.84%	6.85%	7.04%	7.01%	7.01%	6.60%	7.17%
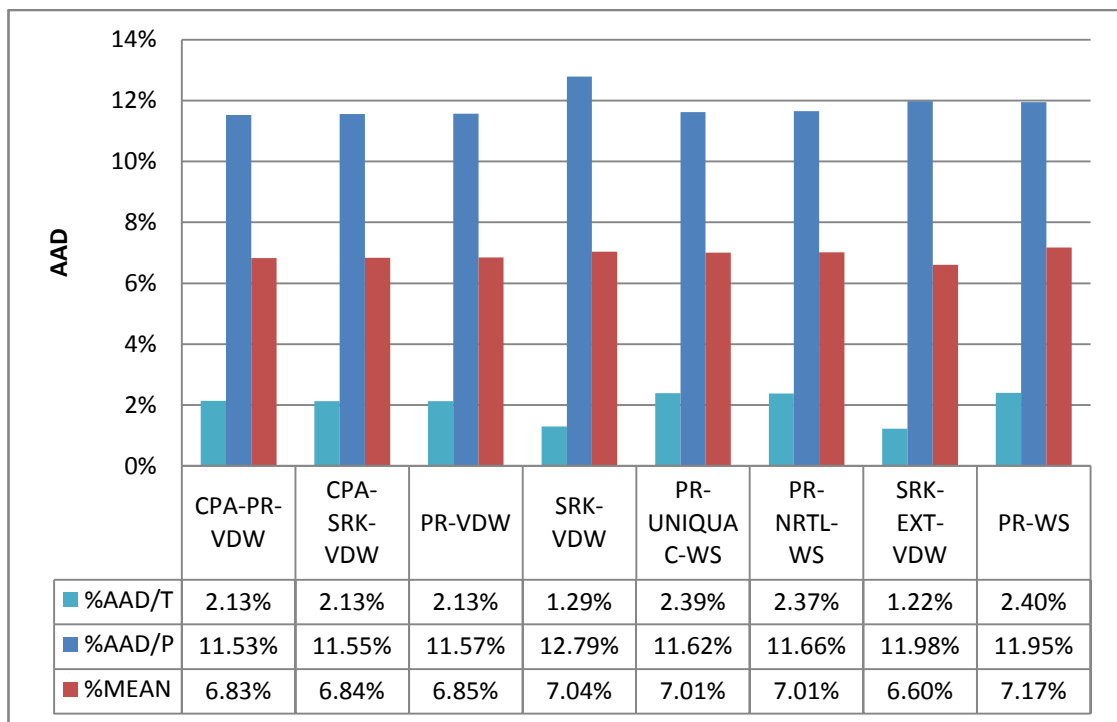
Figure 4. 59: Summary of % Mean of SET 20: MIX D

100

	CPA-PR-VDW	CPA-SRK-VDW	PR-VDW	SRK-VDW	PR-UNIQUAC-WS	PR-NRTL-WS	SRK-EXT-VDW	PR-WS
%AAD/T	1.90%	1.82%	1.81%	1.90%	2.10%	2.10%	1.79%	2.11%
%AAD/P	11.76%	12.06%	12.34%	13.08%	12.29%	12.25%	12.13%	11.65%
%MEAN	6.83%	6.94%	7.08%	7.49%	7.19%	7.17%	6.96%	6.88%
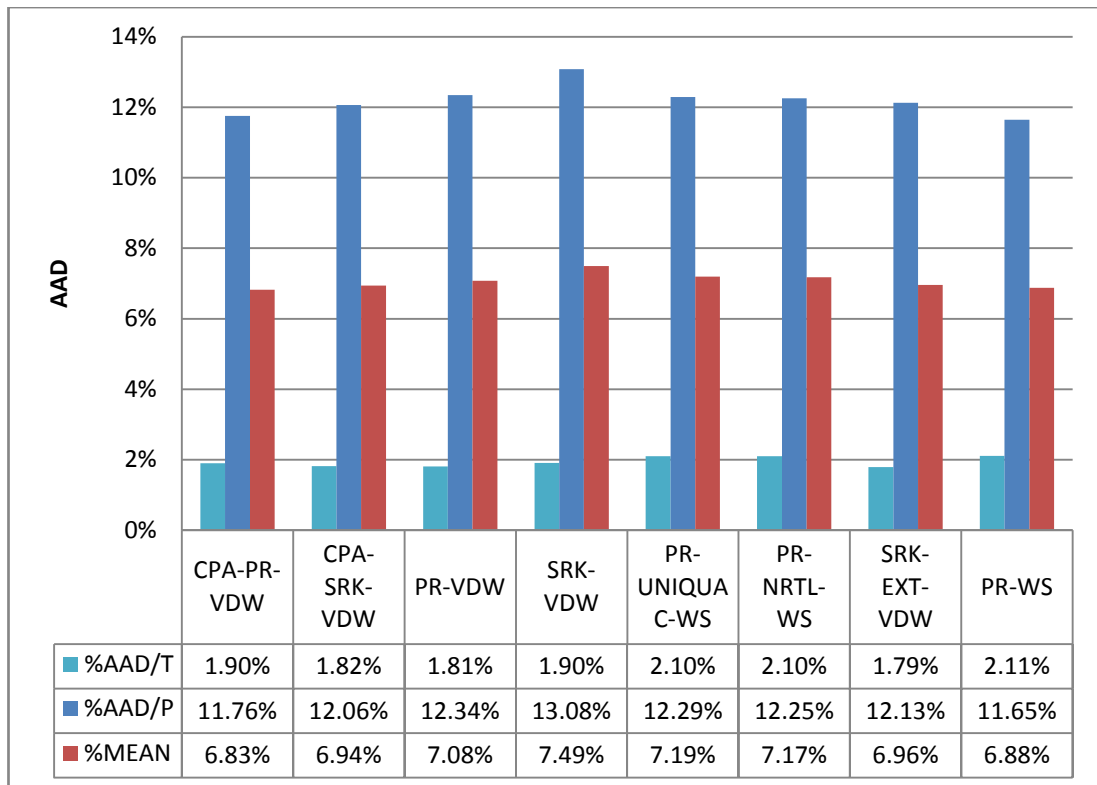
Figure 4. 60: Summary of % Mean of SET 20: MIX E

For MIX A of set 20, the mixture is best modelled with PR-VDW while SRK-VDW is applicable for predicting phase behaviour of MIX B as illustrated in Figures 4.56 and 4.57 It is found that SRK-EXT-VDW is superior in modelling phase envelope of MIX C and D. For MIX E with 90% molar composition of methane gas, it is best modelled with CPA-PR-VDW. These outcomes result are presented in Figures 4.58 to 4.60.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1: Conclusions

We had analysed that different sets of natural gas mixtures will have different EOS models that are applicable and capable in predicting natural gas mixtures phase behaviours. And even slightly changes in chemical compositions had governed the percentages AAD of temperature and pressure to be varies depending on type of mixtures and the present of non-hydrocarbon components in the mixtures.

Hence, it is found that SRK families with VDW mixing rules have wide applications and superb in predicting phase behaviours of different mixtures with 83% dominant level compared to PR families with WS mixing rules when tested for 24 set of natural gas mixtures data. PR-WS is superb at predicting phase behaviours of natural gas mixtures with 25.91% carbon dioxide content, 1.56% of nitrogen and 0.11% of n-hexane. Hence, PR-VDW is superior at predicting synthetic natural gas mixture with 0.77% nitrogen, 1.75 of carbon dioxide, 84.45% of methane and 0.05% of n-hexane. Thus, the application of PR families is limited for several mixtures only and requires some modification of the EOS parameters.

For the effect of different mixing rules used in this study, VDW mixing rules is best described phase envelopes of natural gas mixtures with different heavies content as heavy as n-octane and its dominated 24 set of mixtures as high as 95% over WS mixing rule.

The introduction of CPA-EOS models are a great success with the introduction of the "pseudo-association", which had treated quadrupolar molecules like CO_2 that is being able to act as an associating compounds. The use of this concept provides satisfactory results for natural gas mixtures and SNGs. "EOS+Gibbs free Energy" models used in this study provides reasonable results but not superior enough like other EOS models cause it seems to be the most appropriate for modelling mixtures with highly asymmetric components. The combination of WS + NRTL gives the best

result only for strongly nonpolar + strongly polar mixtures and WS + UNIQUAC is best in modelling strongly polar + strongly polar mixtures. For natural gas, the polarity degree of the constituent components presented in the mixtures used in this study are said to have a very minimum values and that explained the applicability of those models.

Therefore, it is conclusive that no single EOS provides reliable predictions of bubble point line and dew point line of all 24 set of natural gas mixtures used in this study and application of VDW mixing rules is reasonable over WS mixing rules and it is found that RK families with Soave temperature functions have wider applications over PR families for this 24 set of natural gas mixtures.

5.2: Recommendations

For many mixtures used in this study and millions of papers had presented in the academia world that related to the fluid phase equlibria, there is so little research that discussed about the polarity values of the natural gas mixtures. This should be investigated to get the exact polarity of the constituent natural gas mixtures to the applicability of the EOS models in predicting natural gas behaviours, because there is a breakthrough in science world if EOS/G^E models can be used in describing phase behaviours of natural gas at satisfactory deviations of temperature and pressure.

However, all EOS models used in this study shows great percentage deviation error of both T and P as seen in SNG 4 (Set 6), GAS 3 (Set 15), and all types of mixtures as in Set 20. It is recommended that if the deviations are so high, the tested EOS models should used different temperature function like Soave-polar, Mathias and TWU in order to get lowest percentage AAD of T and P. Another recommendation is that the tested EOS models should be modified by associating with different mixing rule other than VDW and WS, such as P&R, ZM, HV or SWP. Thus, the models need to be optimized and requires tuning before chosen as the only model for other thermodynamics calculation. That is what needs to be done further.

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APPENDIXES

APPENDIX A

In conjunction with the results calculated in chapter 4 for the set 6, most of the figures ranging from 4.1 to 4.5 are derived from the individual phase behaviour calculated as shown in the Appendix A.
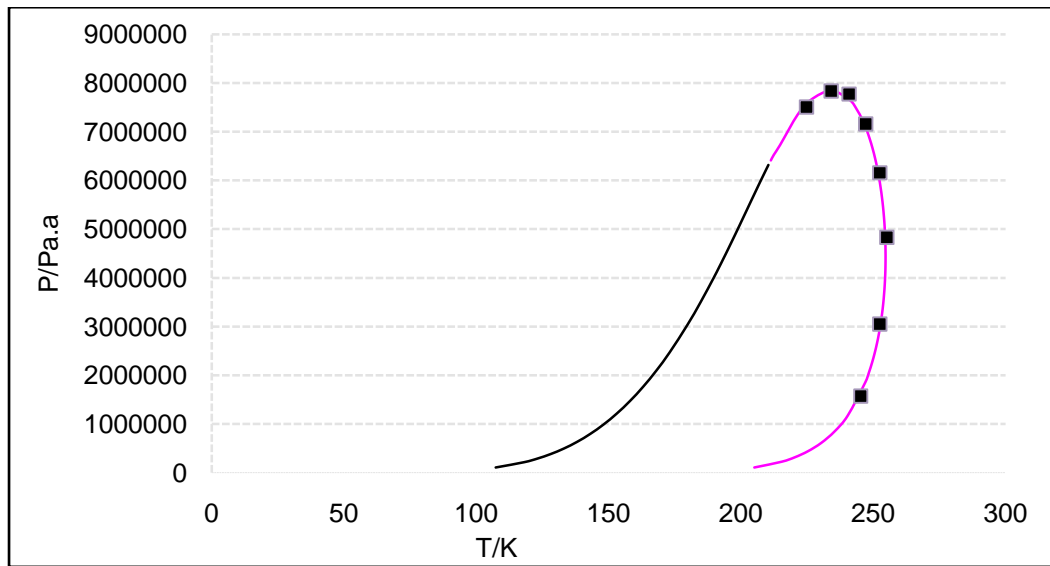
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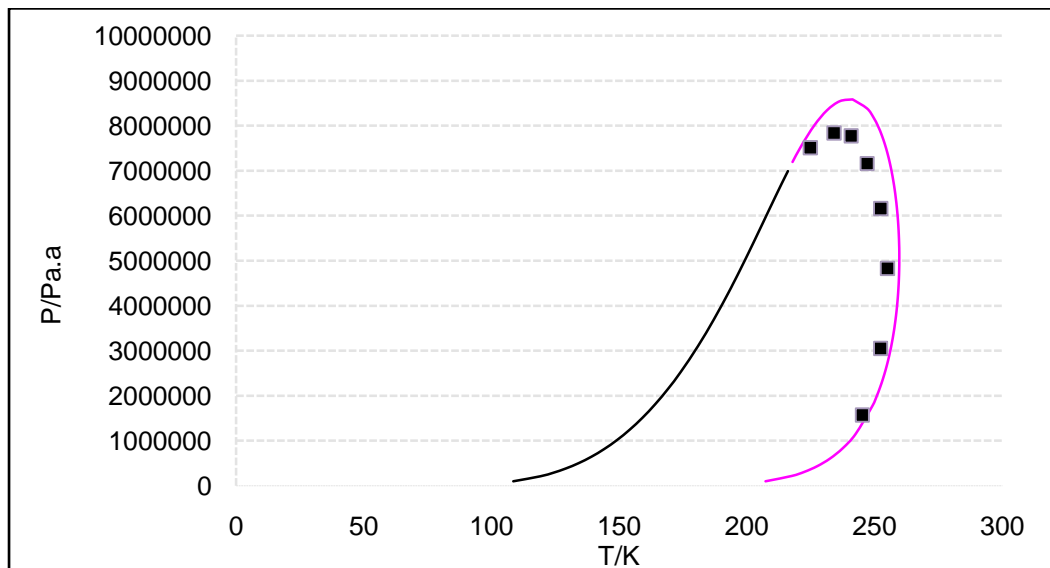

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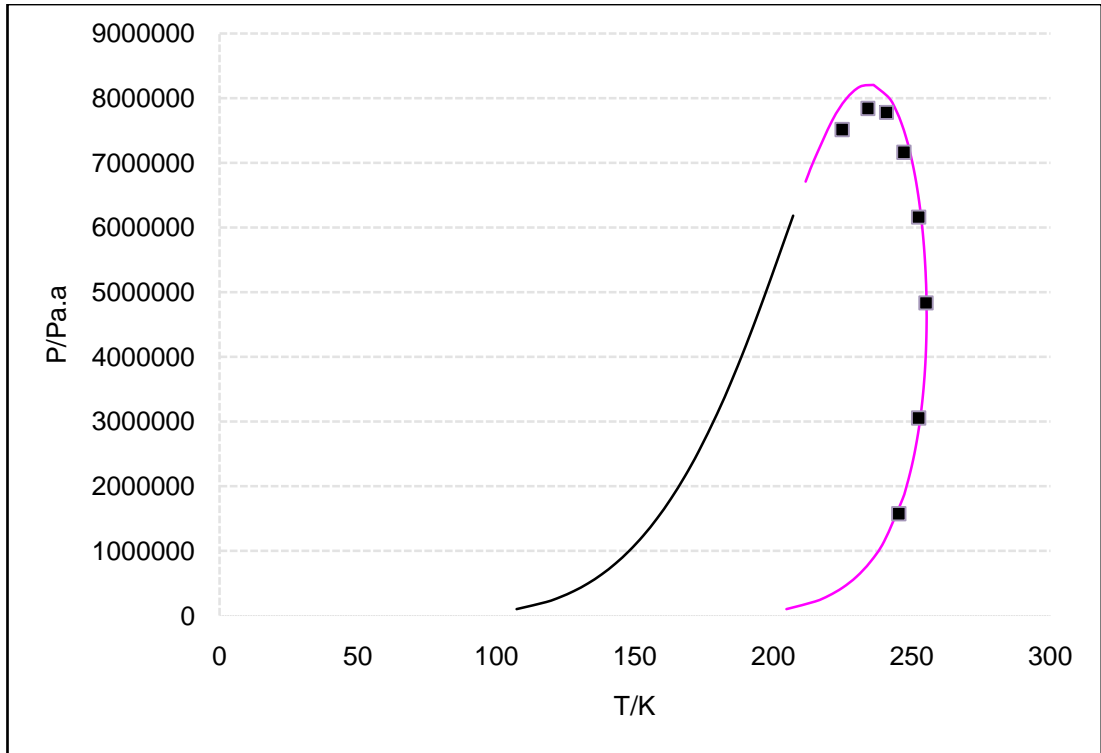
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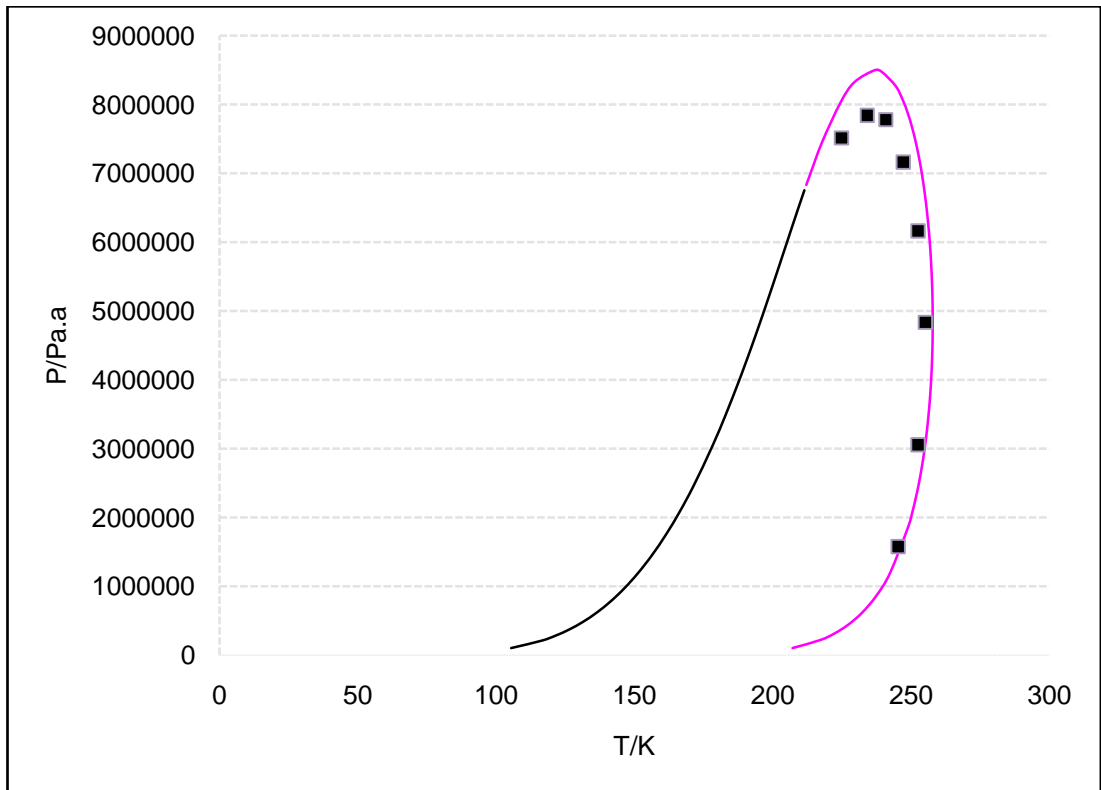
A 4: SET 6-SNG 2; SRK-VDW
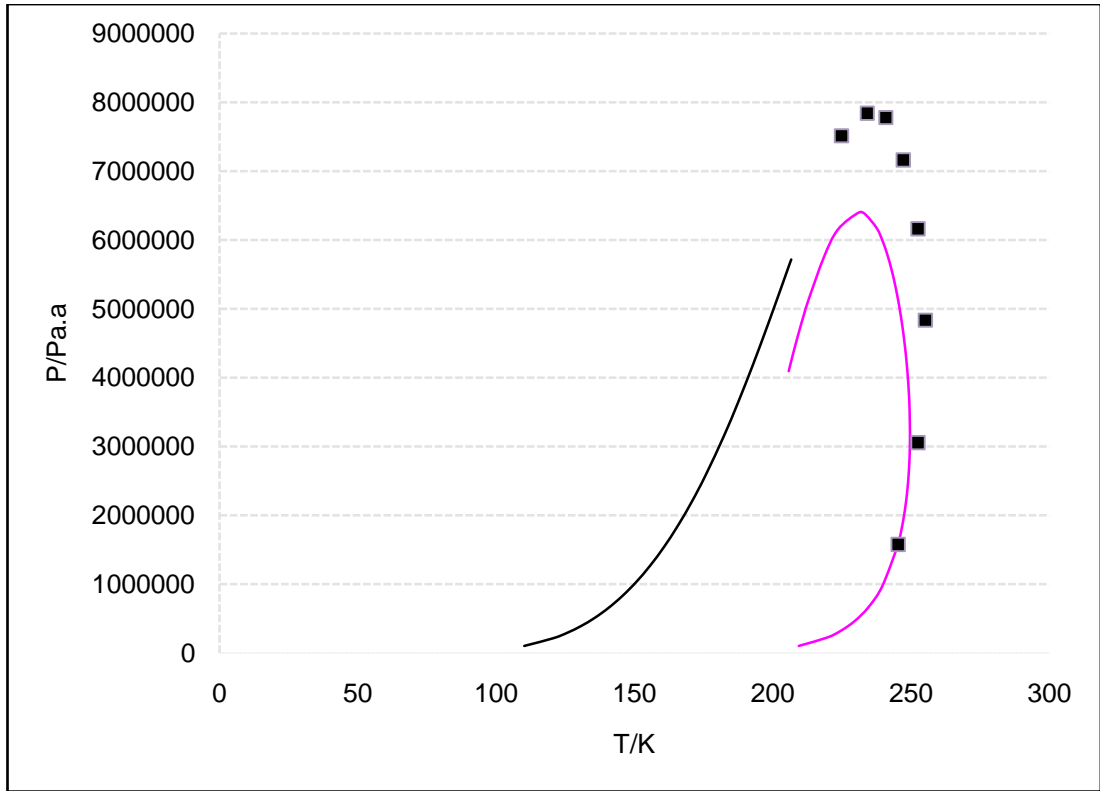
A 5: SET 6-SNG 2; PR-UNIQUAC-WS
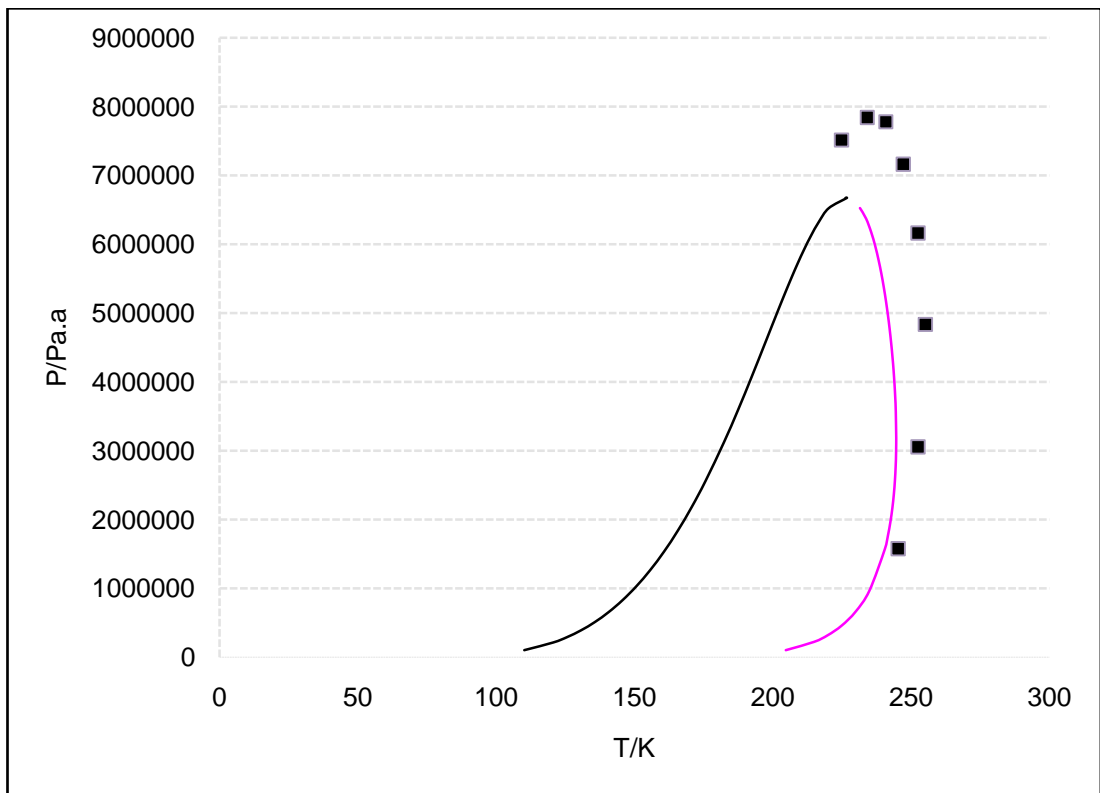
A 6: SET 6-SNG 2; PR-NRTL-WS
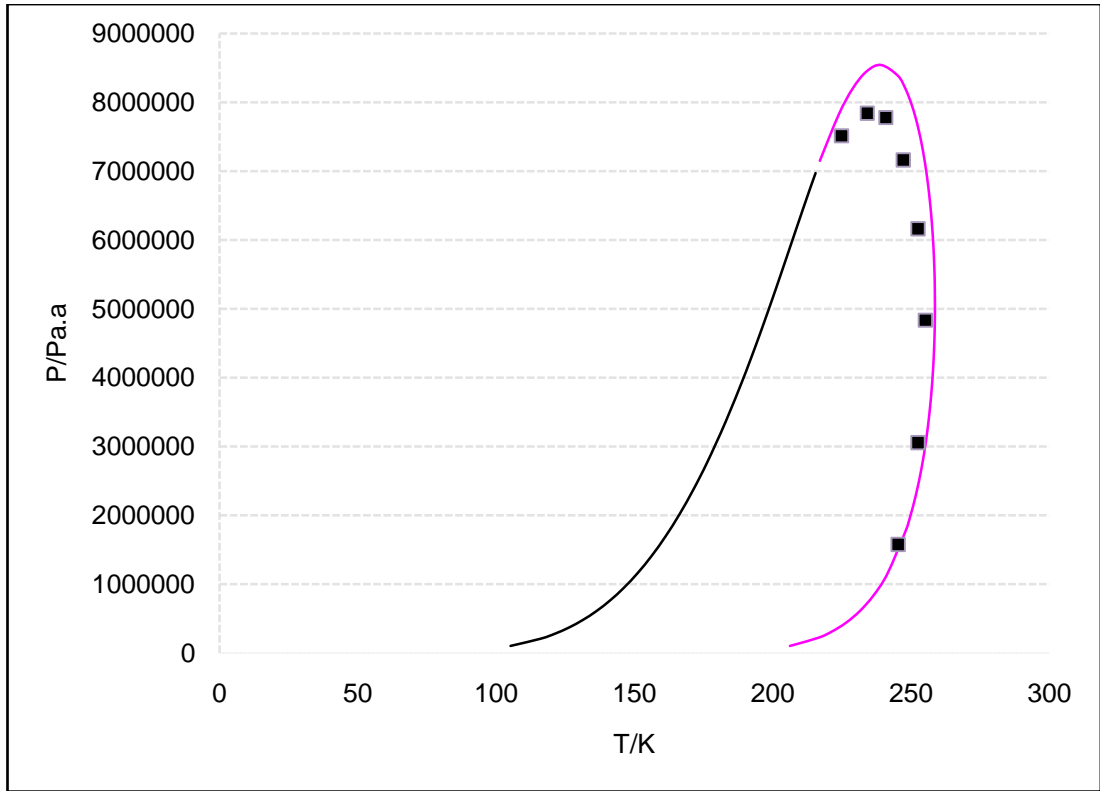
A 7: SET 6-SNG 2; SRK-EXT-VDW
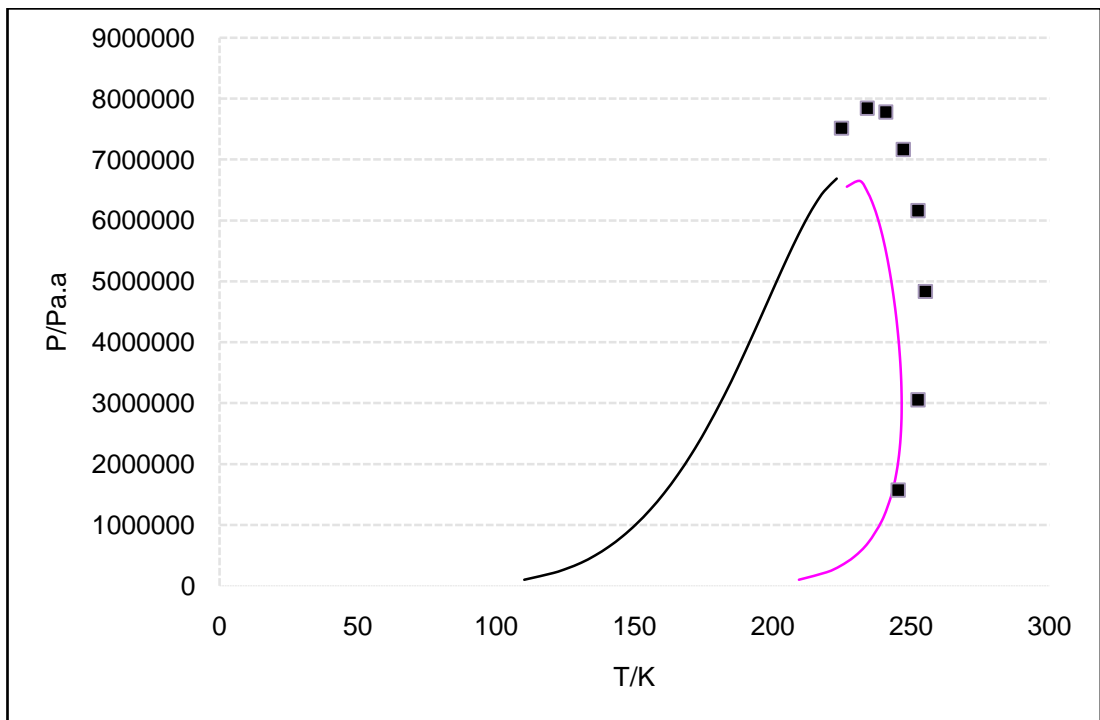
A 8: SET 6-SNG 2; PR-WS
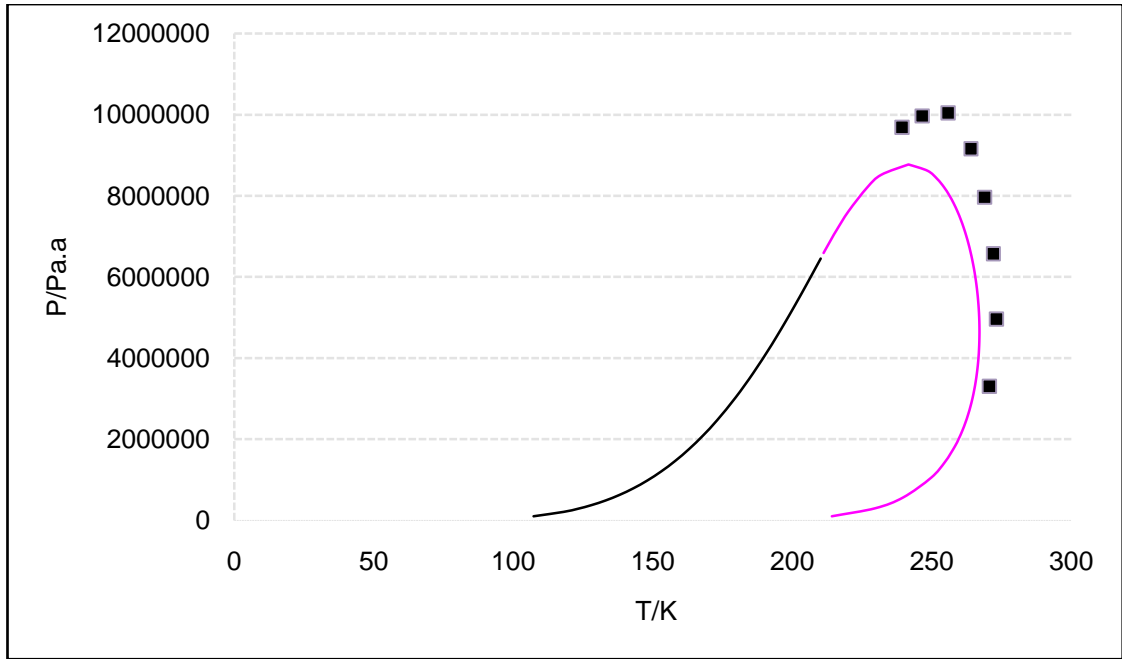
A 9: SET 6-SNG 3; CPA-PR-VDW
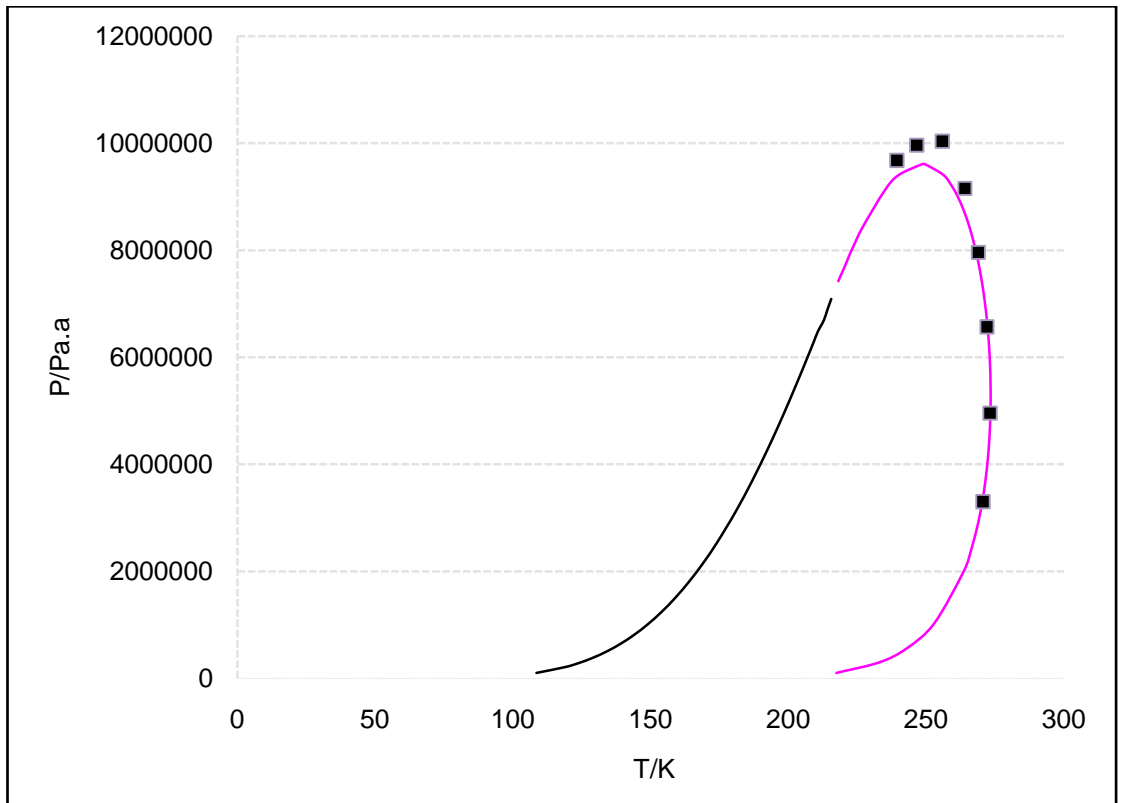
A 10: SET 6-SNG 3; CPA-SRK-VDW
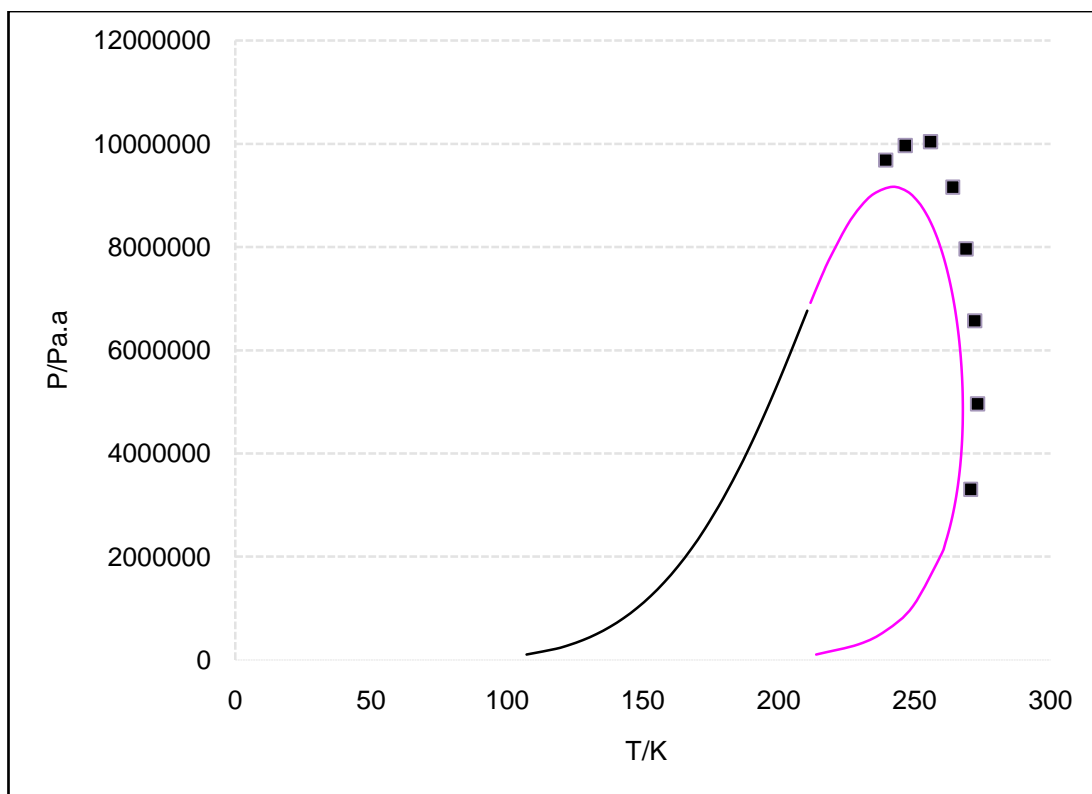
A 11: SET 6-SNG 3; PR-VDW
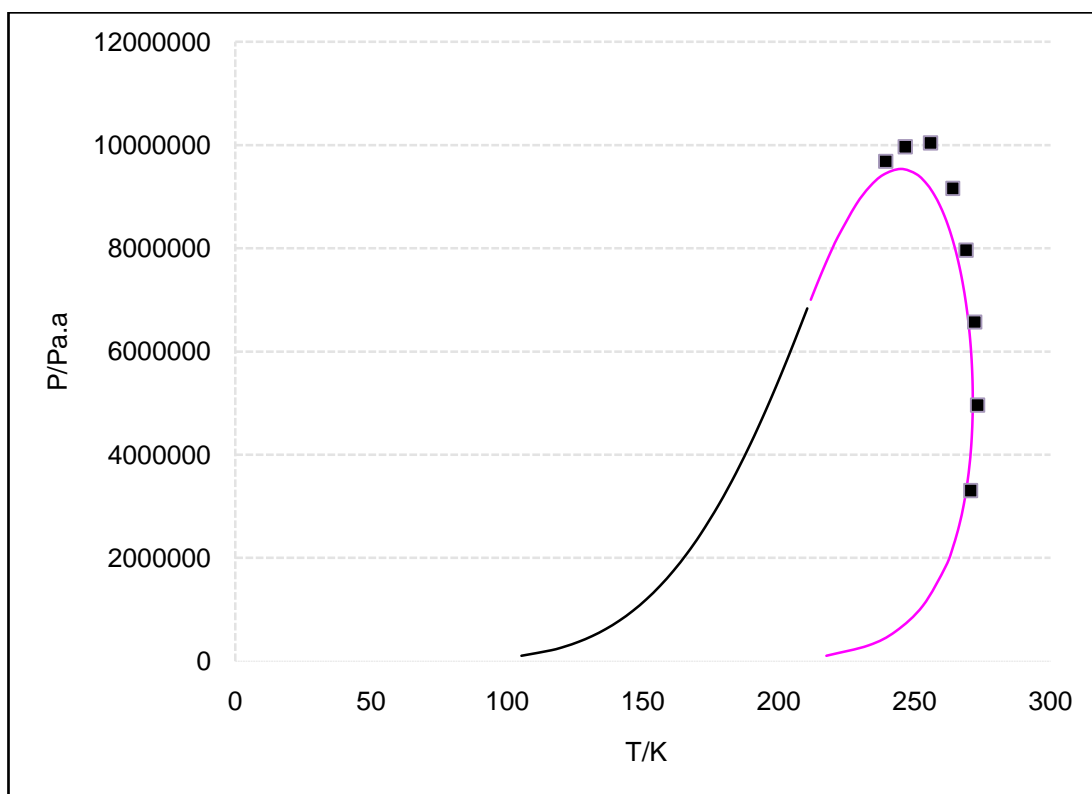
A 12: SET 6-SNG 3; SRK-VDW
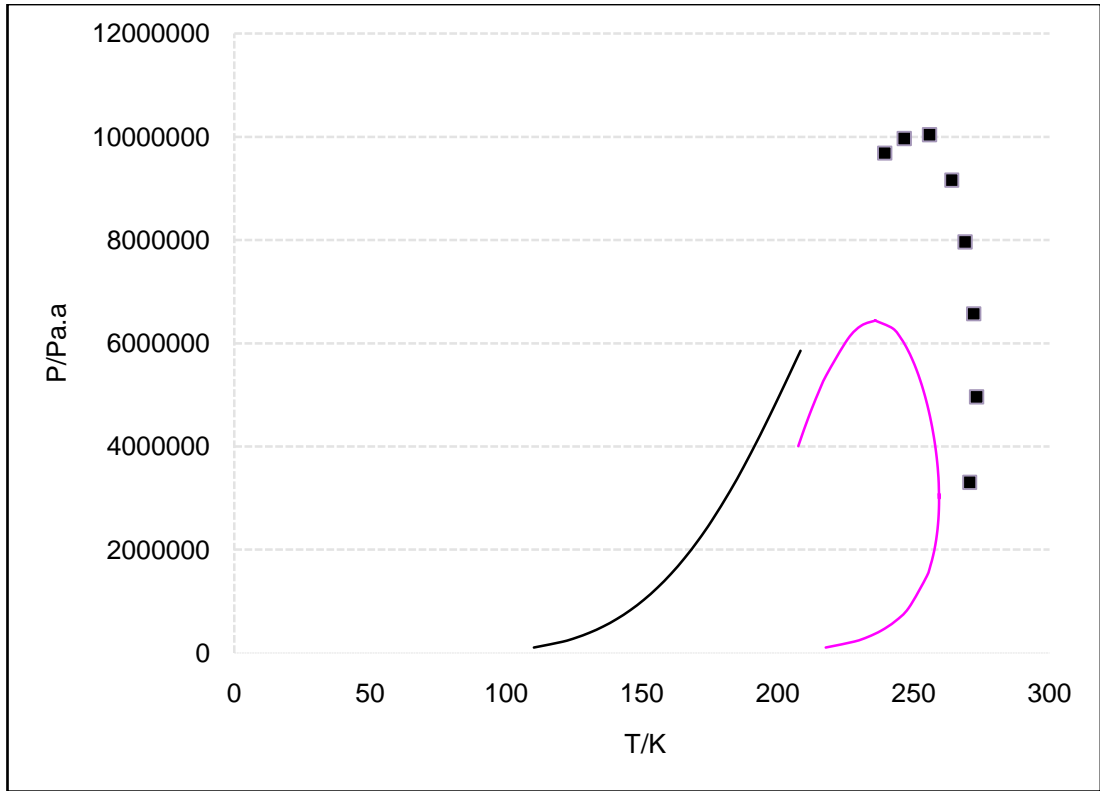
A 13: SET 6-SNG 3; PR-UNIQUAC-WS
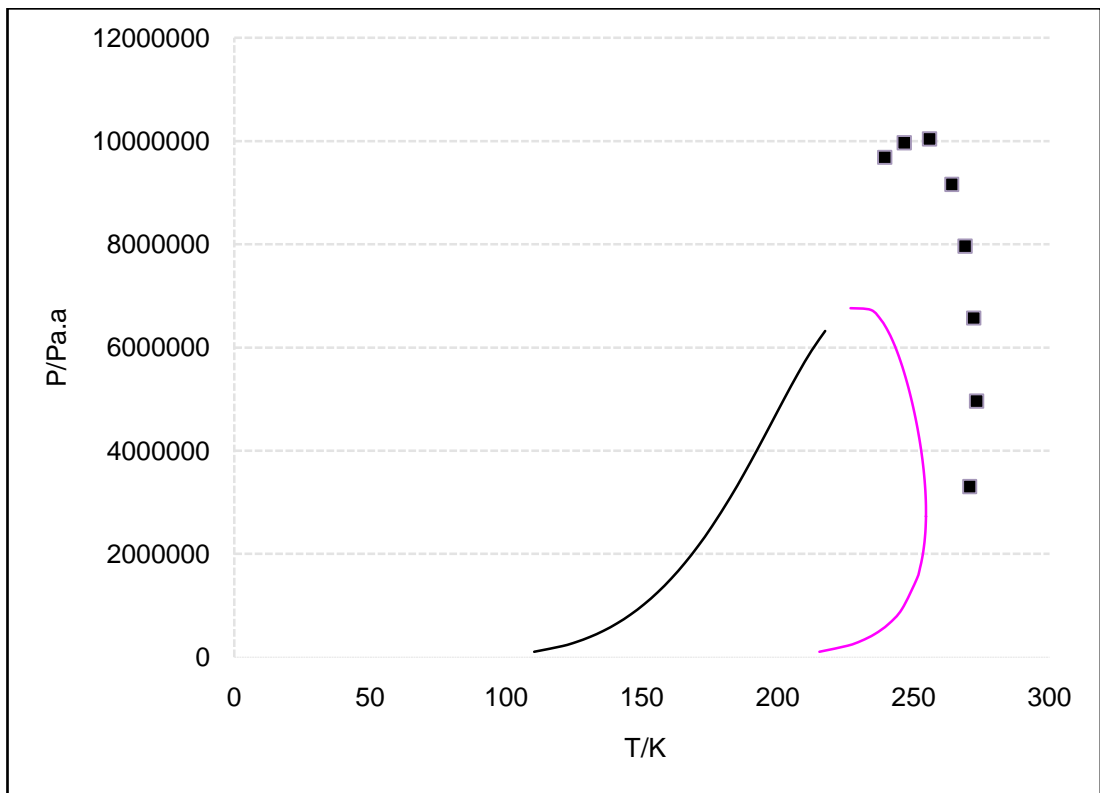
A 14: SET 6-SNG 3; PR-NRTL-WS
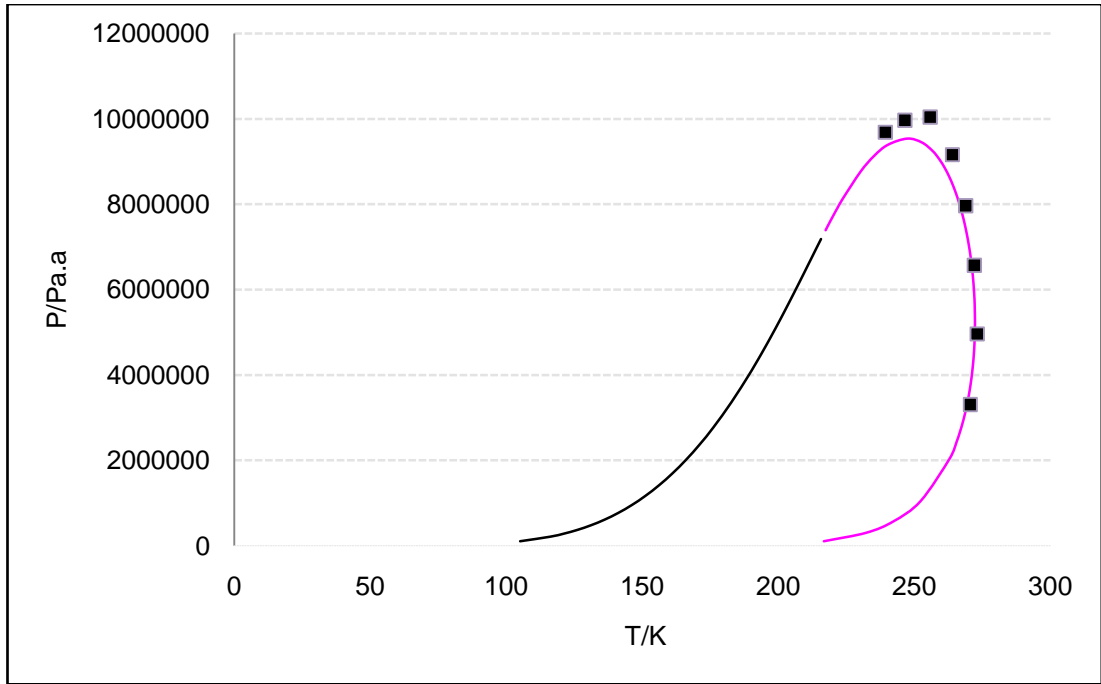
A 15: SET 6-SNG 3; SRK-EXT VDW

A 16: SET 6-SNG 3; PR-WS

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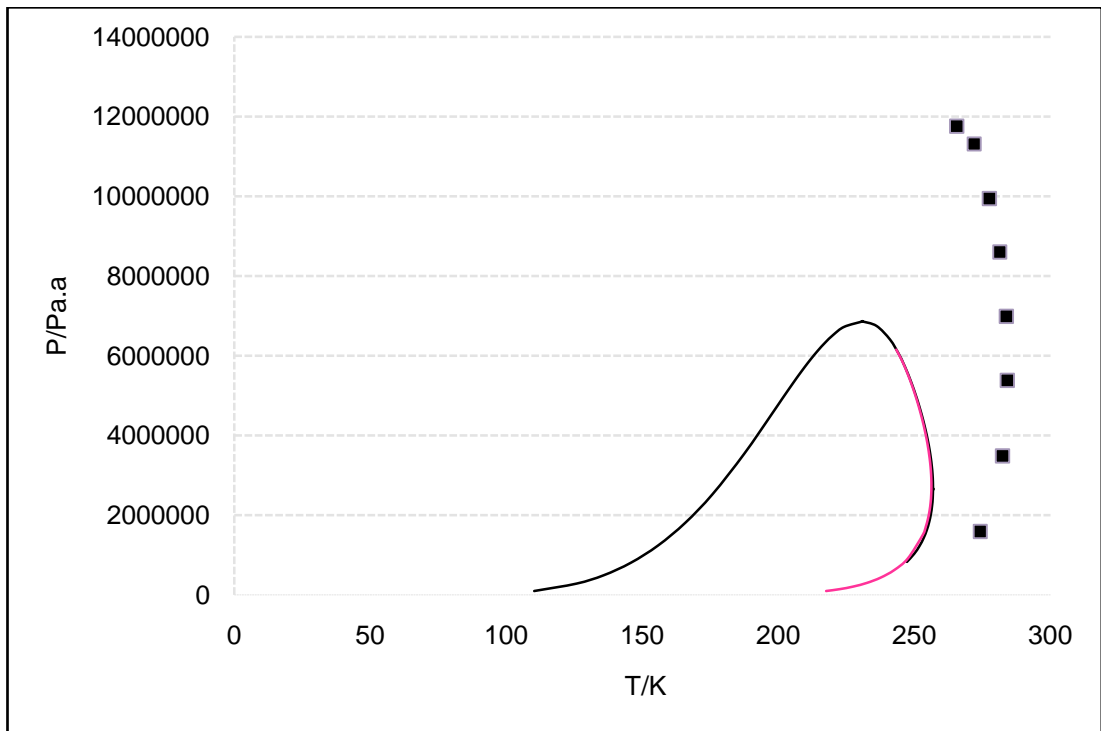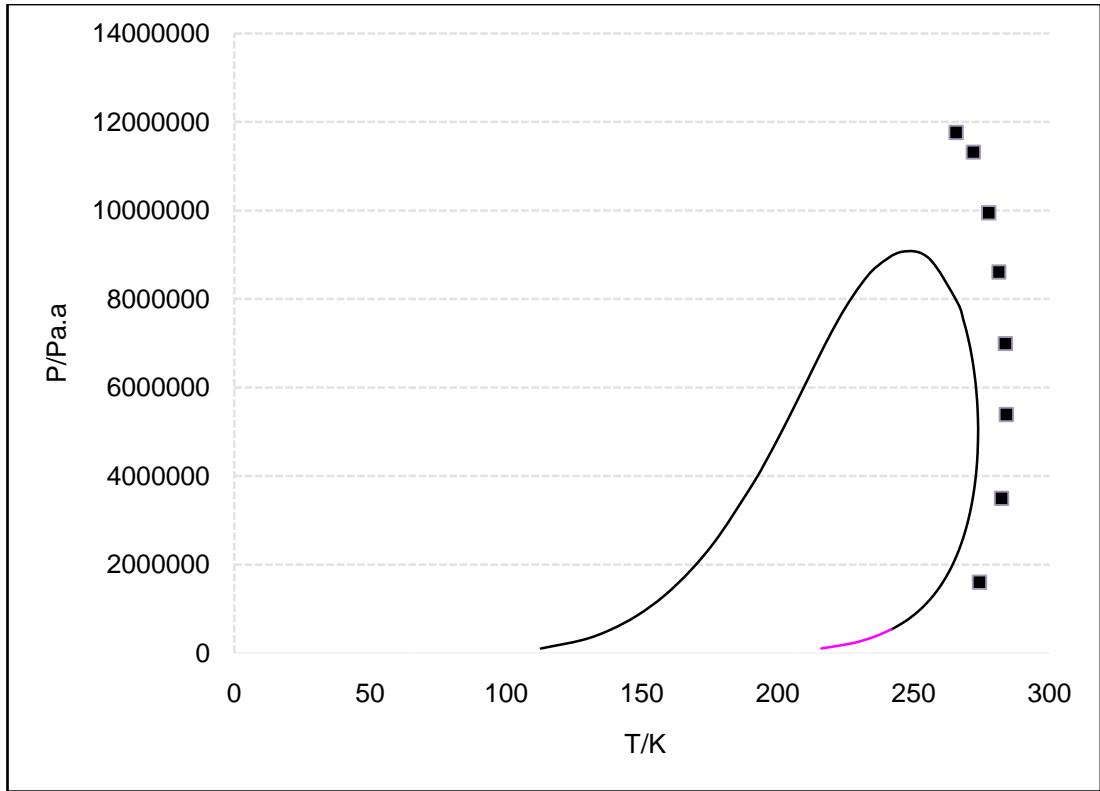
A 17: SET 6-SNG 4; CPA-PR-VDW
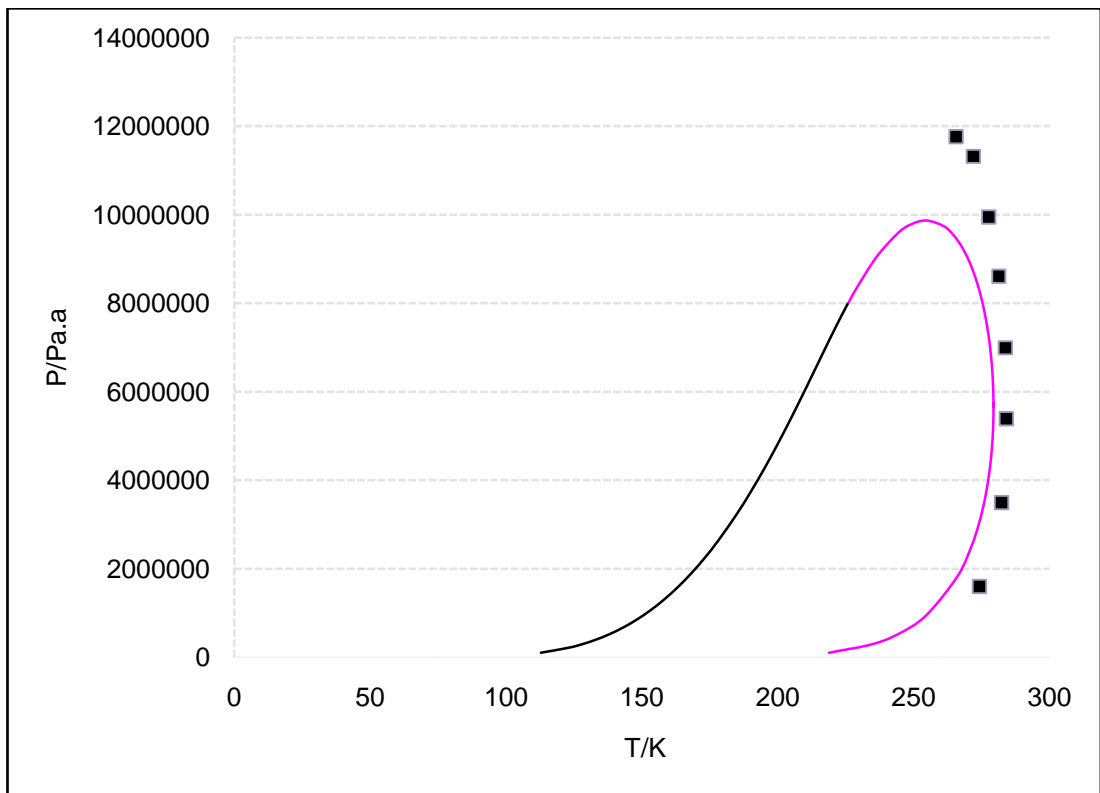
A 18**:** SET 6-SNG 4; CPA-SRK-VDW
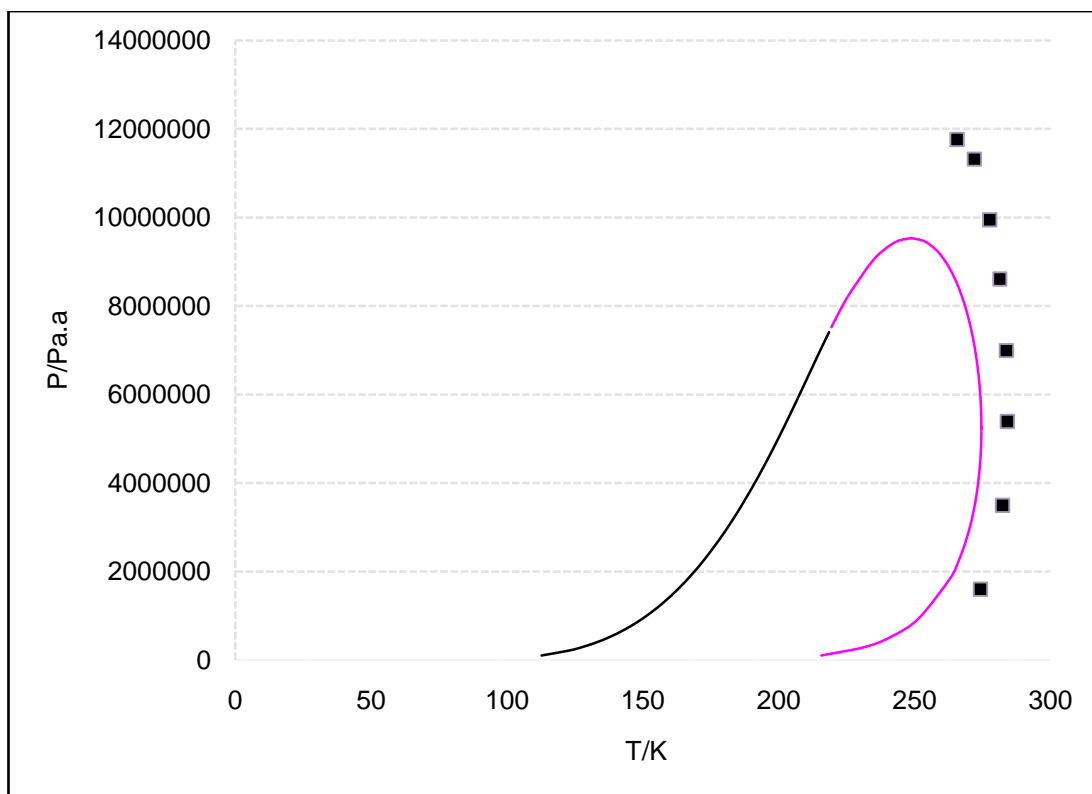
A 19**:** SET 6-SNG 4; PR-VDW
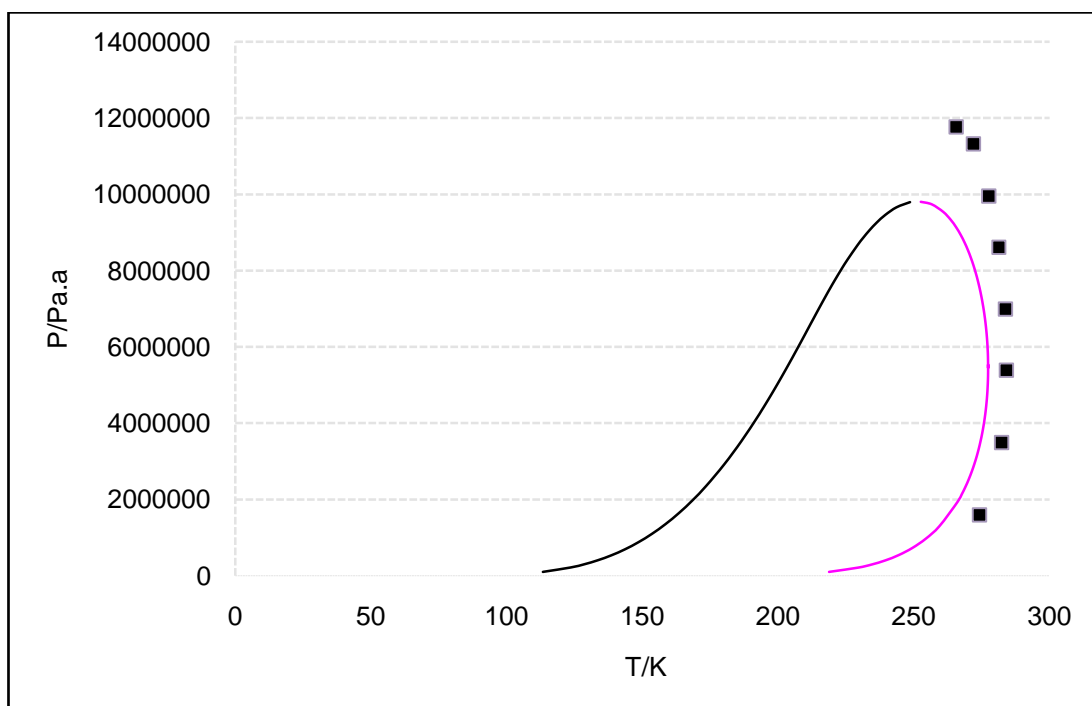
A 20: SET 6-SNG 4; SRK-VDW
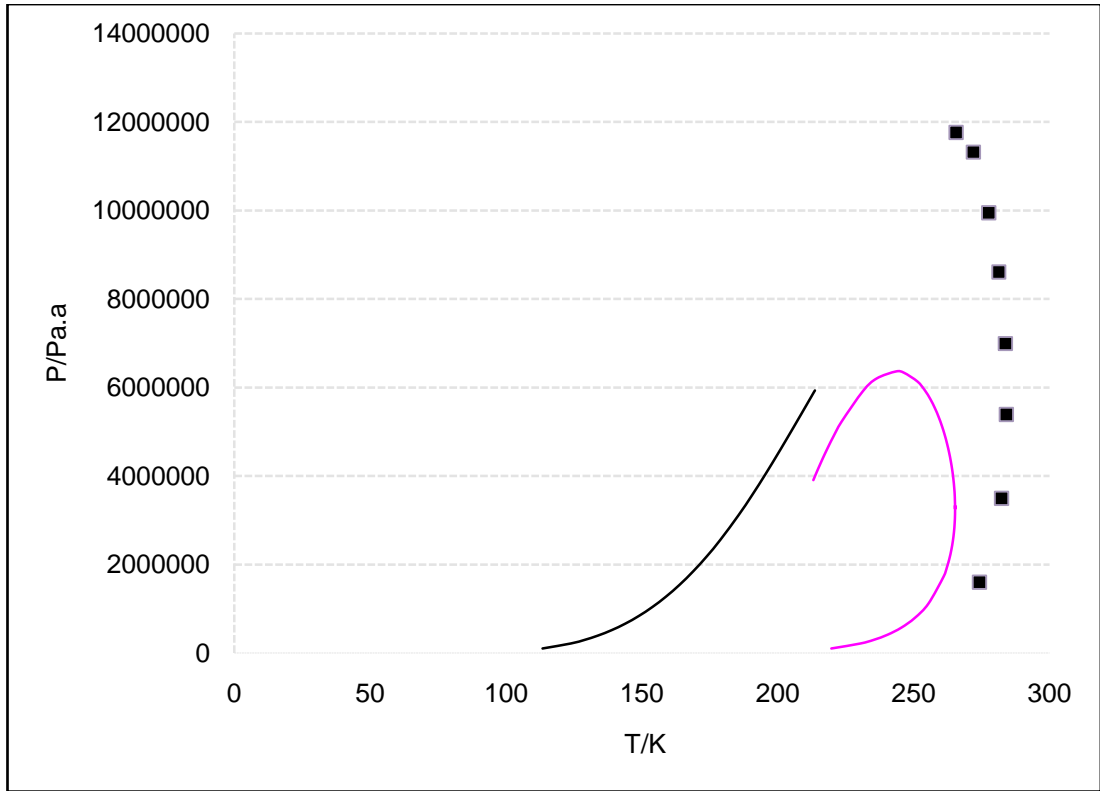
A 21: SET 6-SNG 4; PR-UNIQUAC-WS
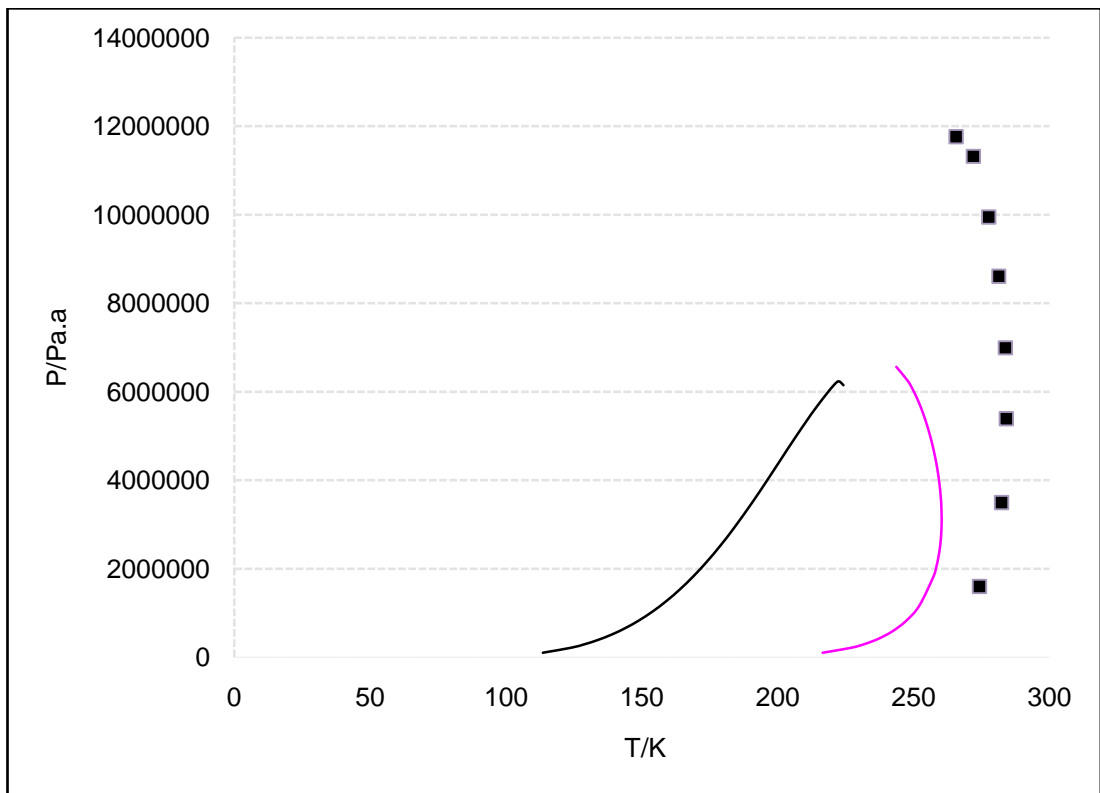
A 22: SET 6-SNG 4; PR-NRTLC-WS
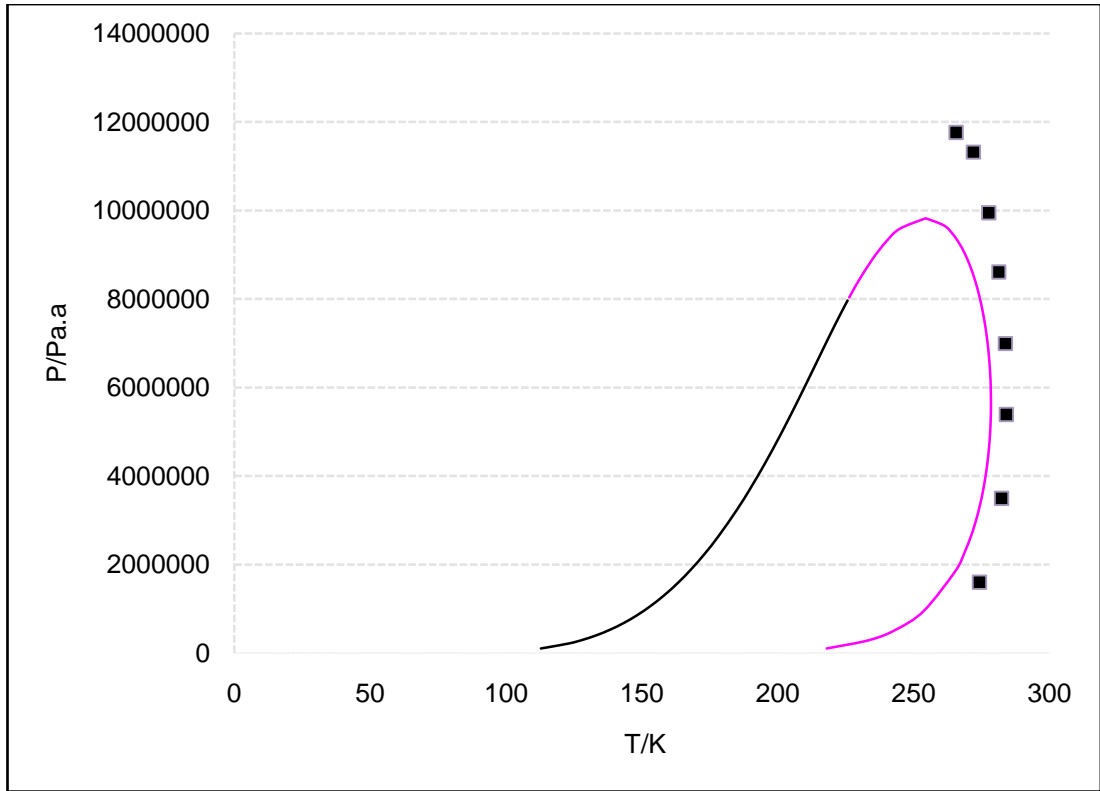
A 23: SET 6-SNG 4; SRK-EXT-WS
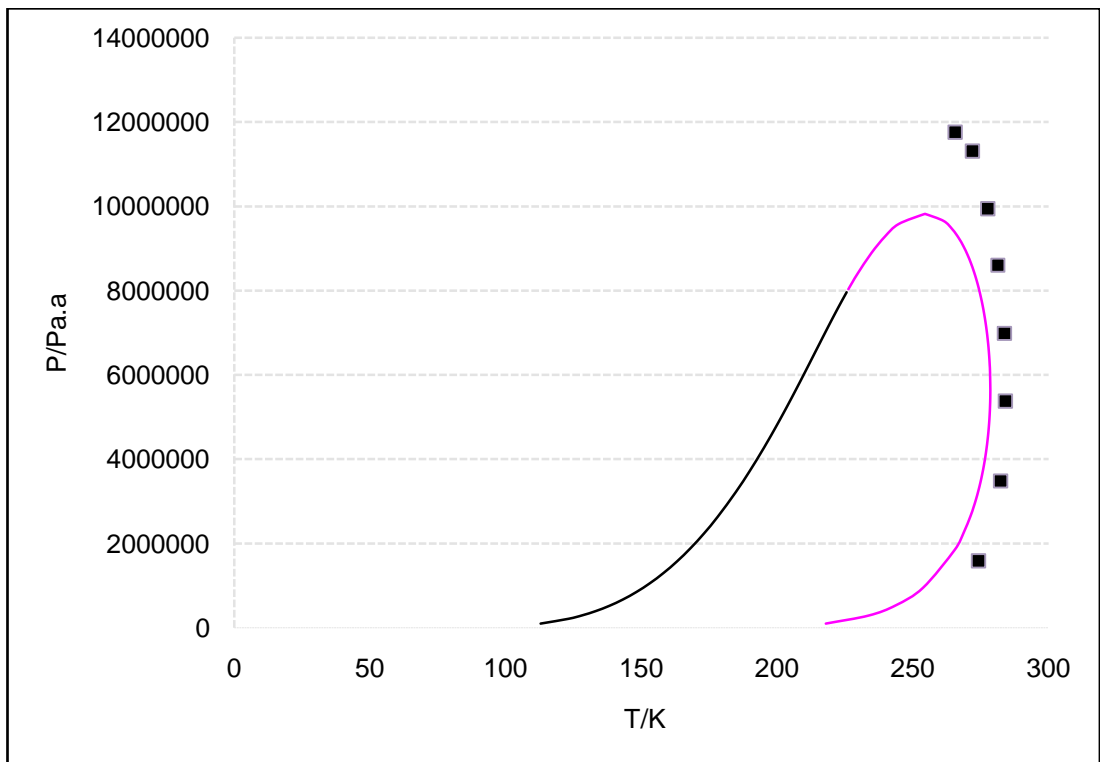
A 24: SET 6-SNG 4; PR-WS

APPENDIX B

In conjunction with the results calculated in chapter 4 for the set 9, most of the figures ranging from 4.6 to 4.8 are derived from the individual phase behaviour calculated as shown in the Appendix B.
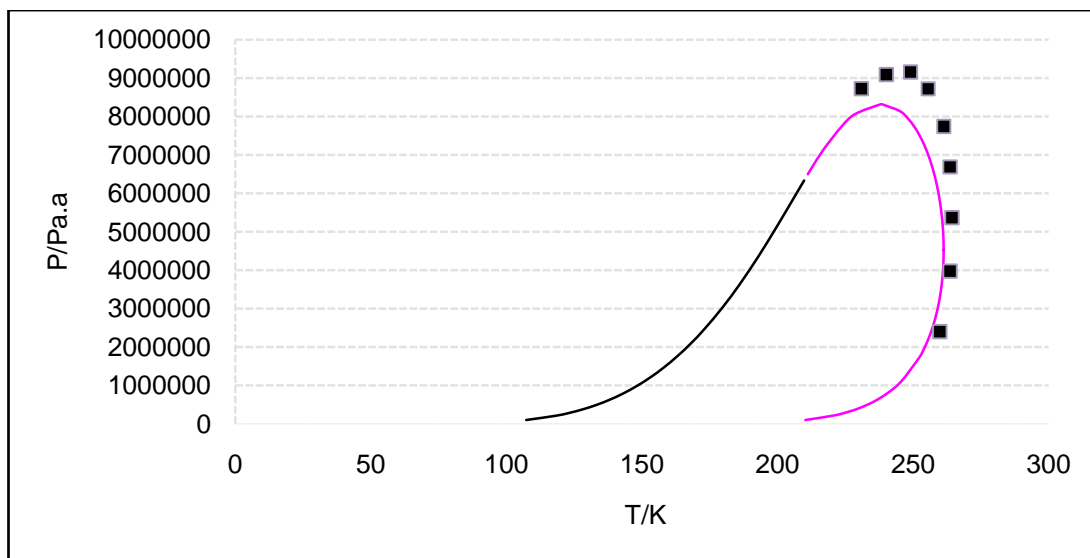
B 1: SET 9-GAS 1; CPA-PR-VDW
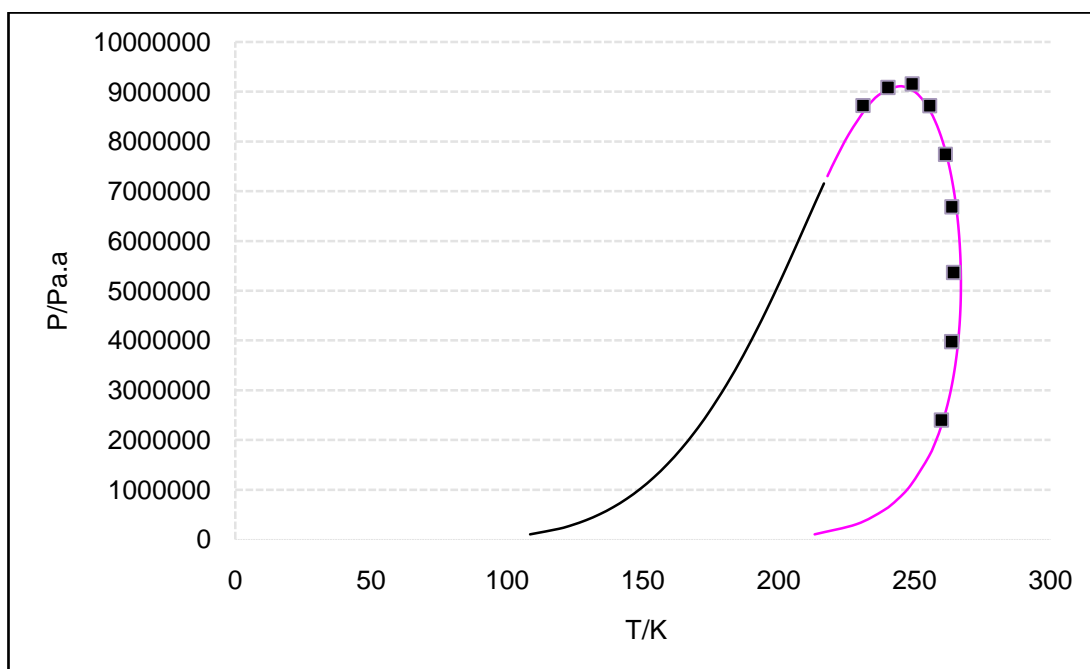
B 2: SET 9-GAS 1; CPA-SRK-VDW
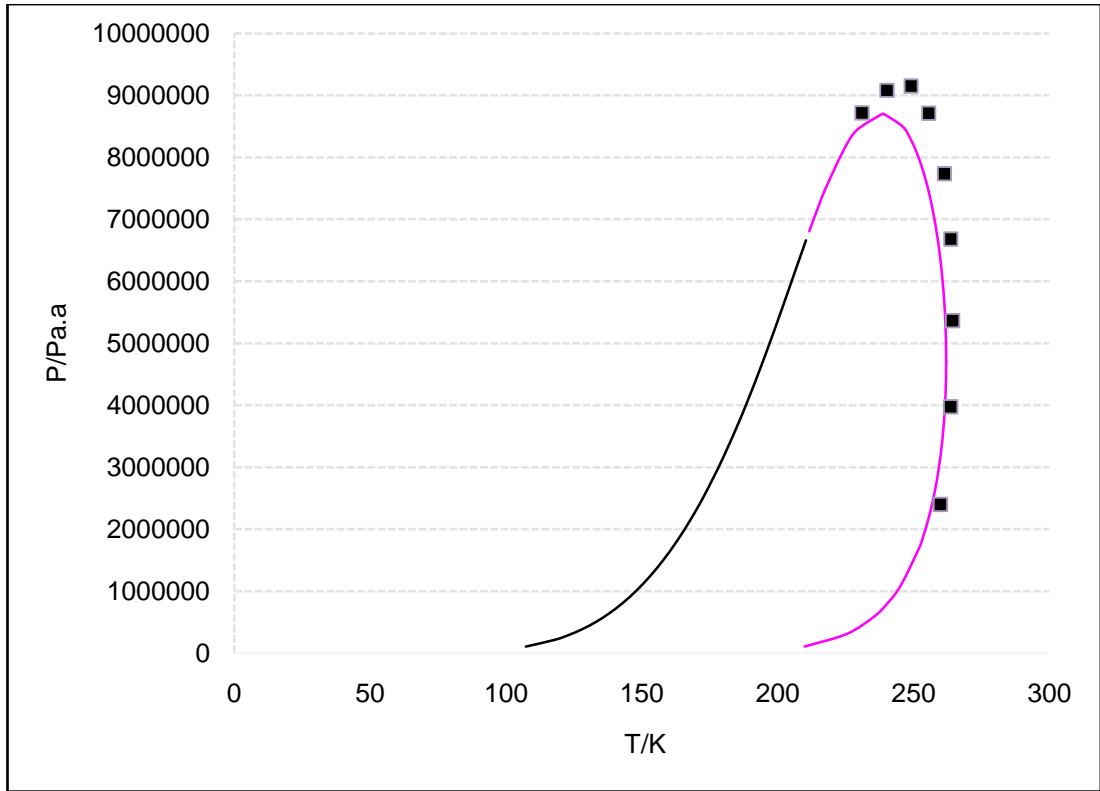
B 3: SET 9-GAS 1; PR-VDW
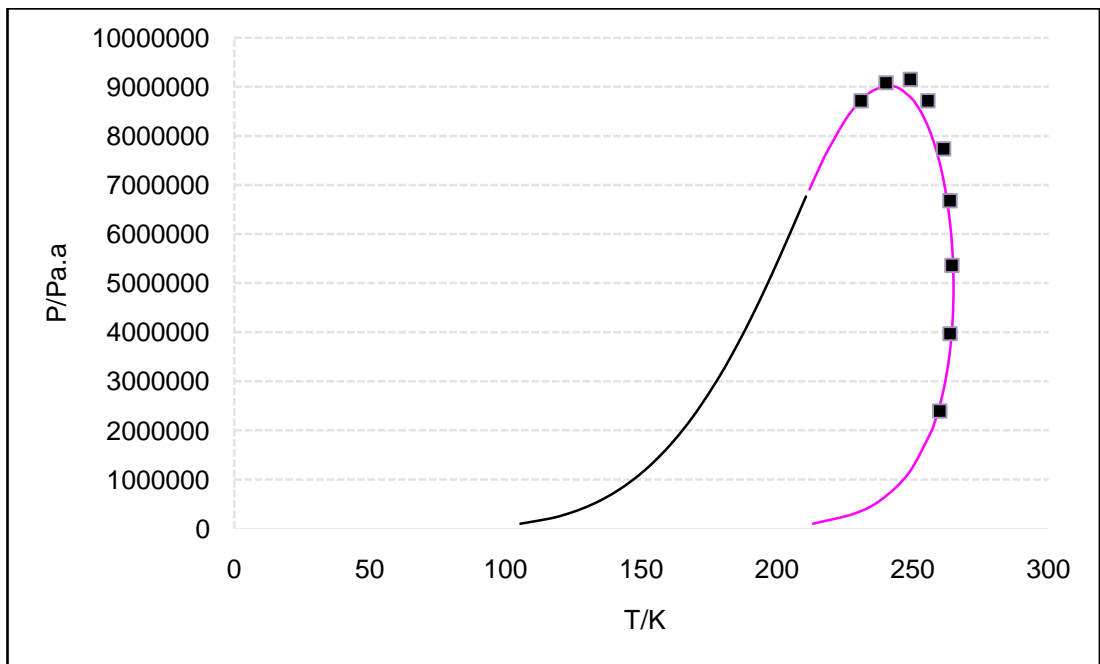
B 4: SET 9-GAS 1; SRK-VDW
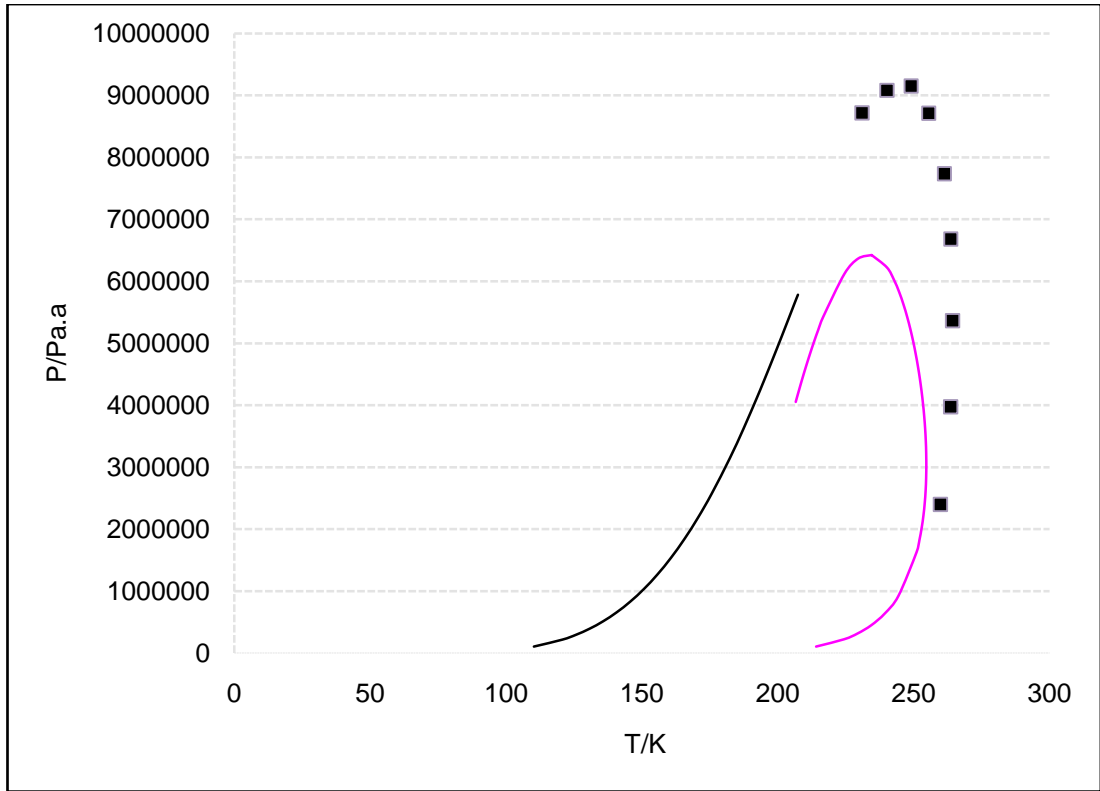
B 5: SET 9-GAS 1; PR-UNIQUAC-WS
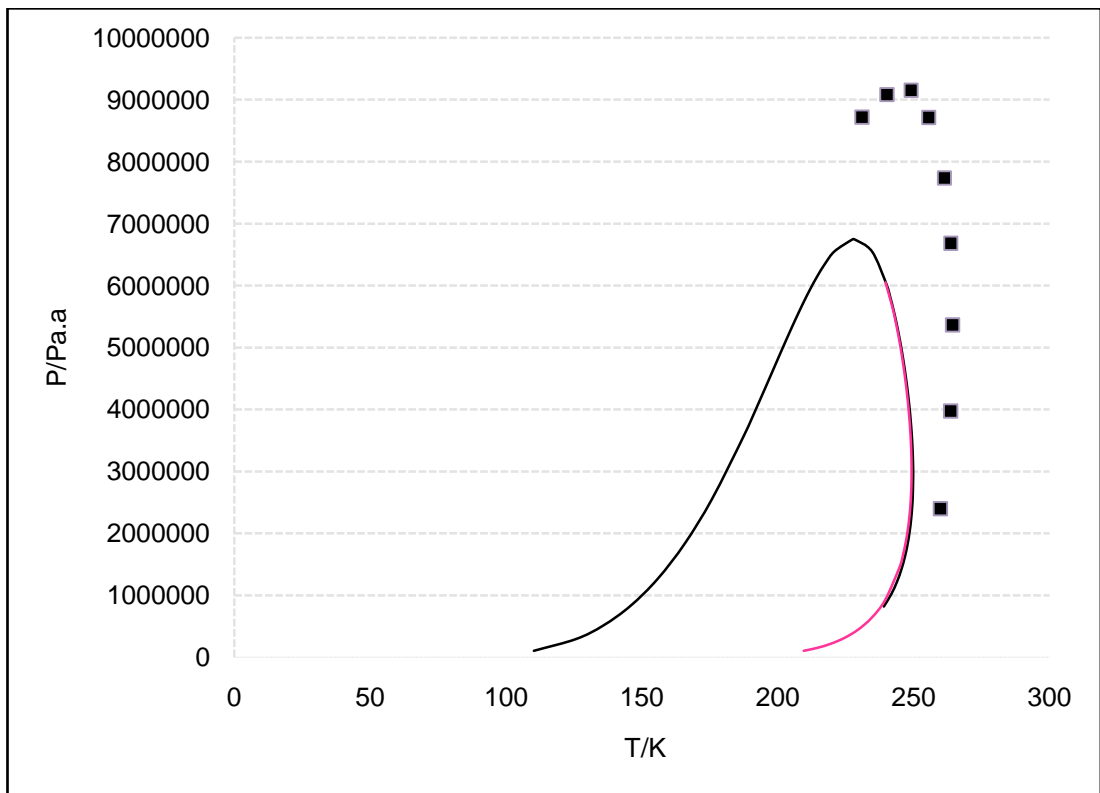
B 6: SET 9-GAS 1; PR-NRTL-WS

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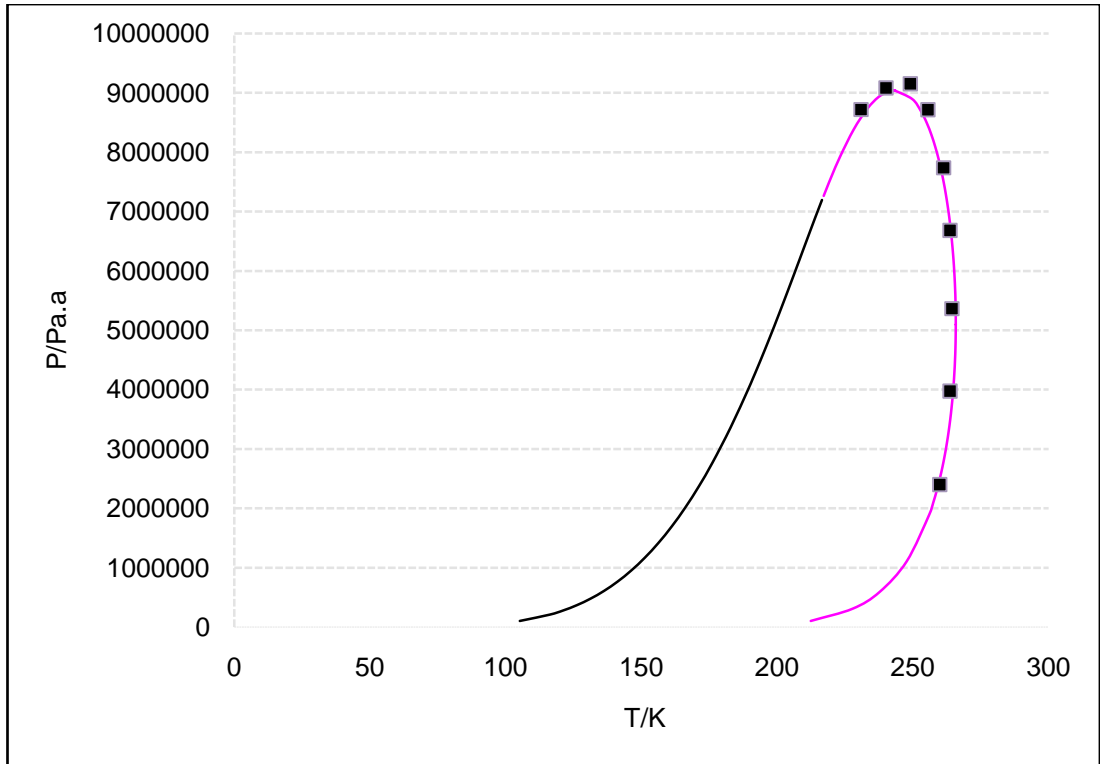
B 7**:** SET 9-GAS 1; SRK-EXT-VDW
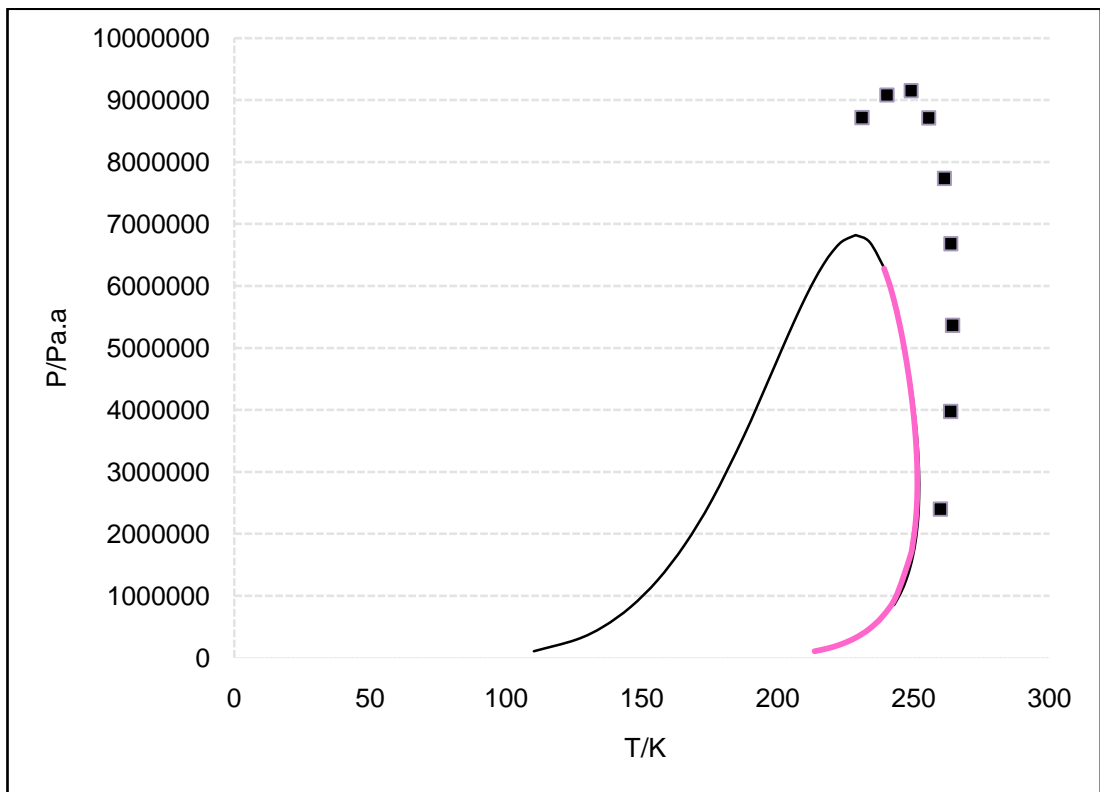
B 8: SET 9-GAS 1; PR-WS

APPENDIX C

In conjunction with the results calculated in chapter 4 for the set 15, most of the figures ranging from 4.9 to 4.18 are derived from the individual phase behaviour calculated as shown in the Appendix C.
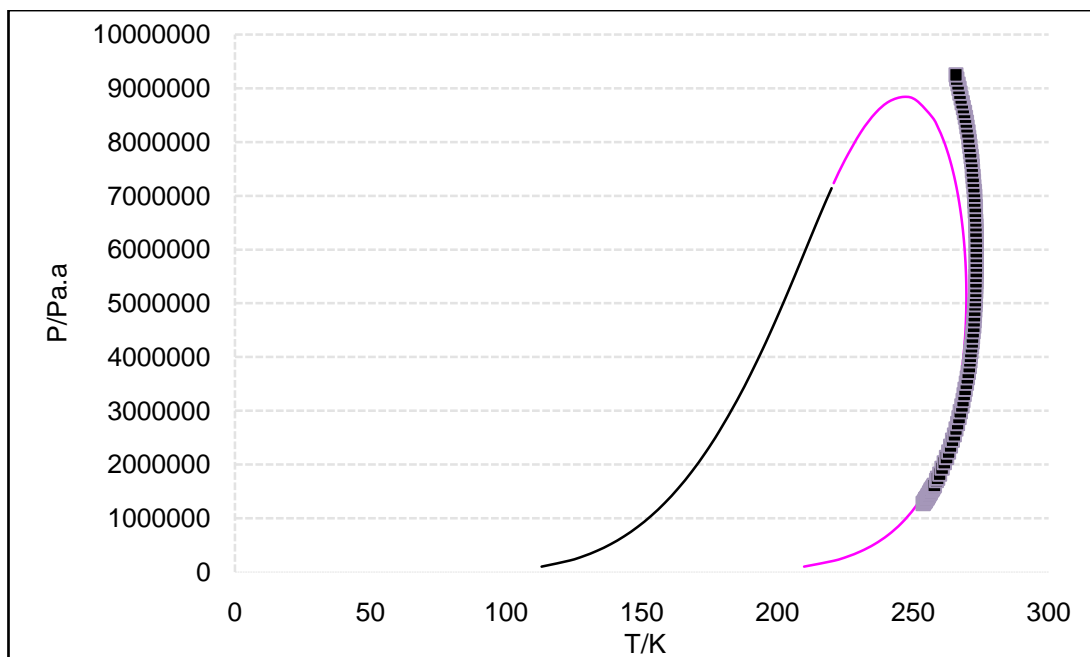

C 1: SET 15-GAS 1; CPA-PR-VDW
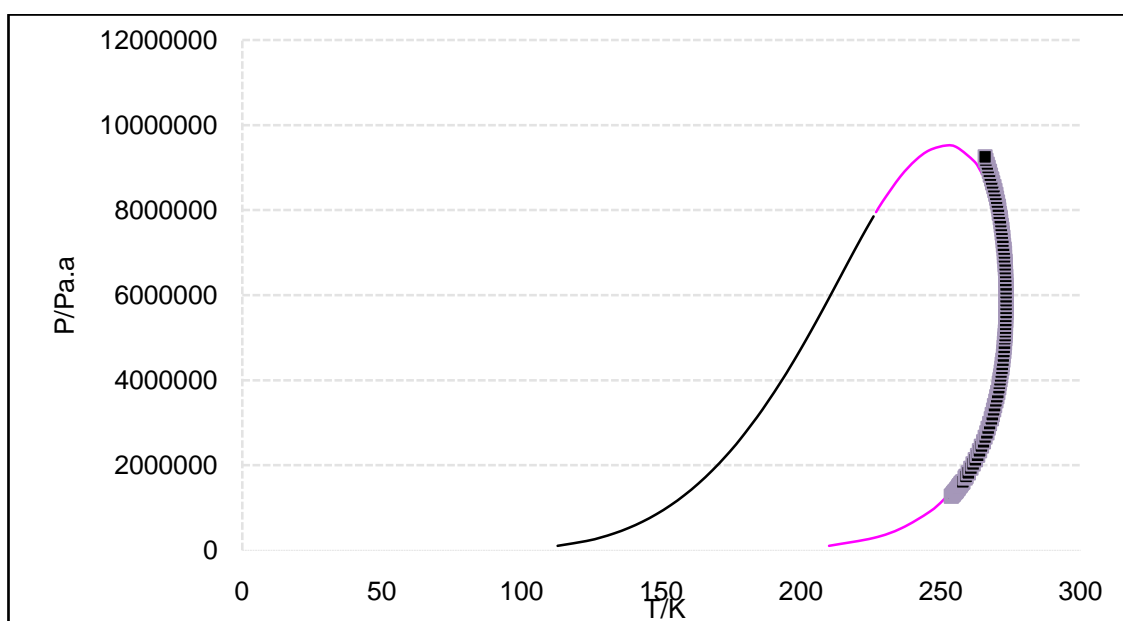
C 2: SET 15-GAS 1; CPA-SRK-VDW
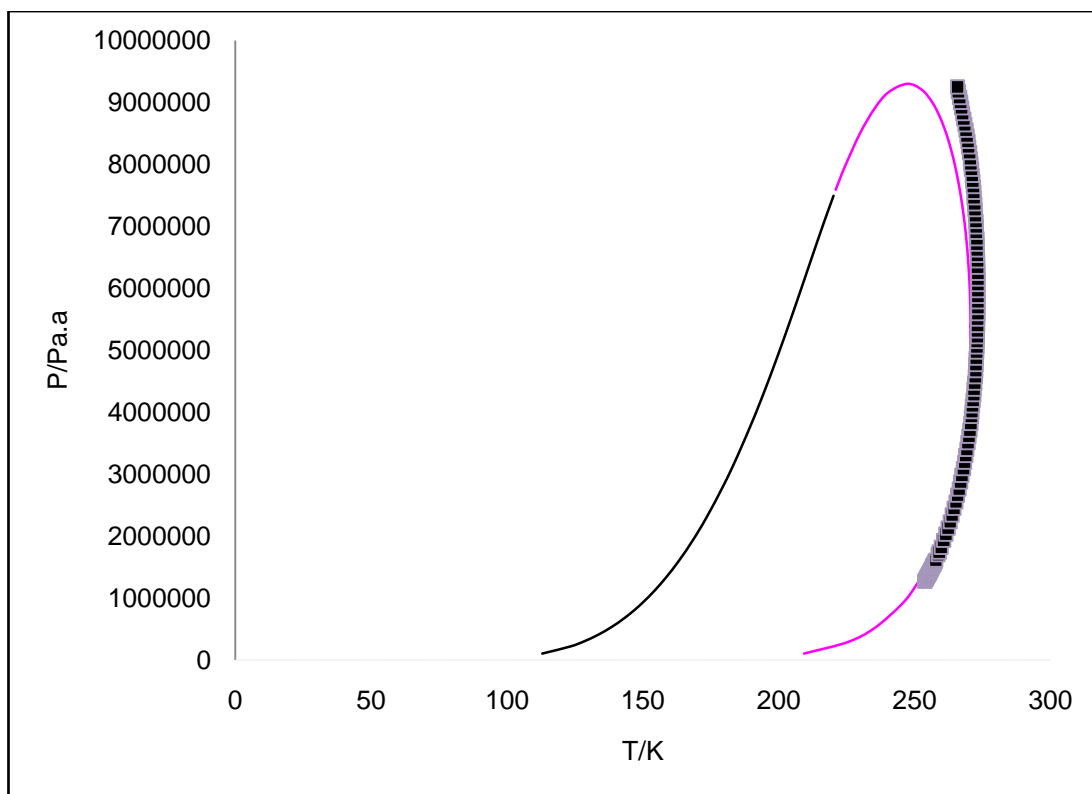
C 3: SET 15-GAS 1; PR-VDW
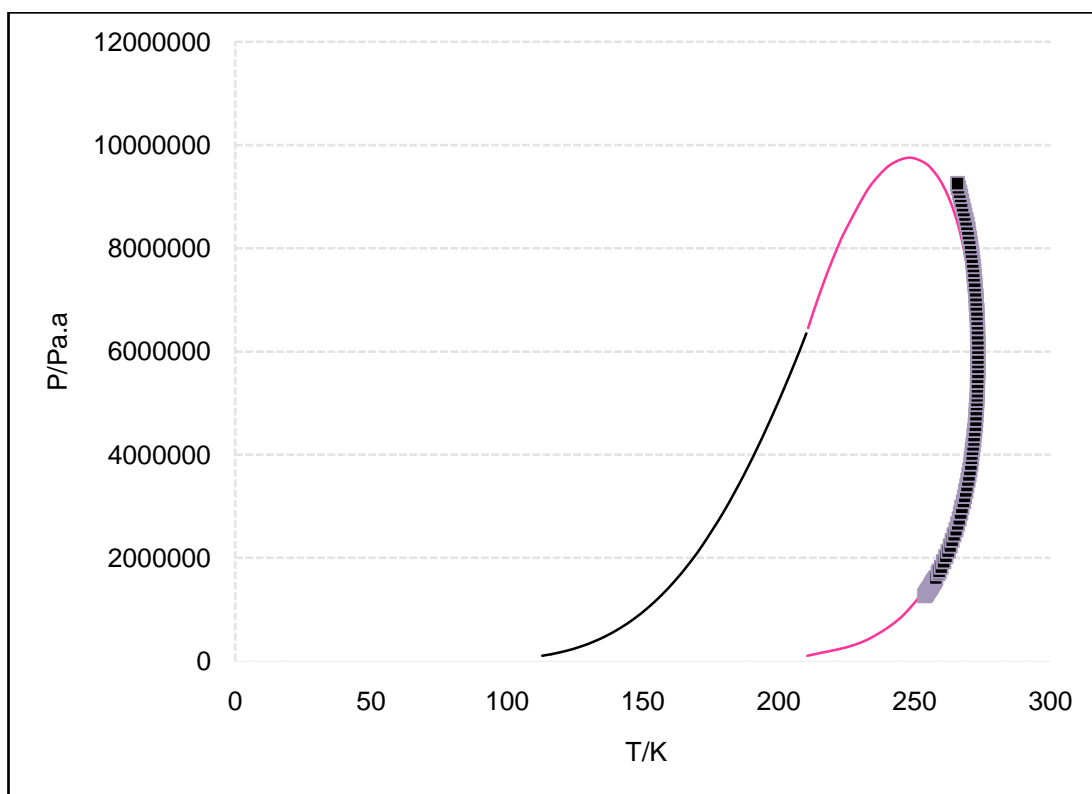
C 4: SET 15-GAS 1; SRK-VDW
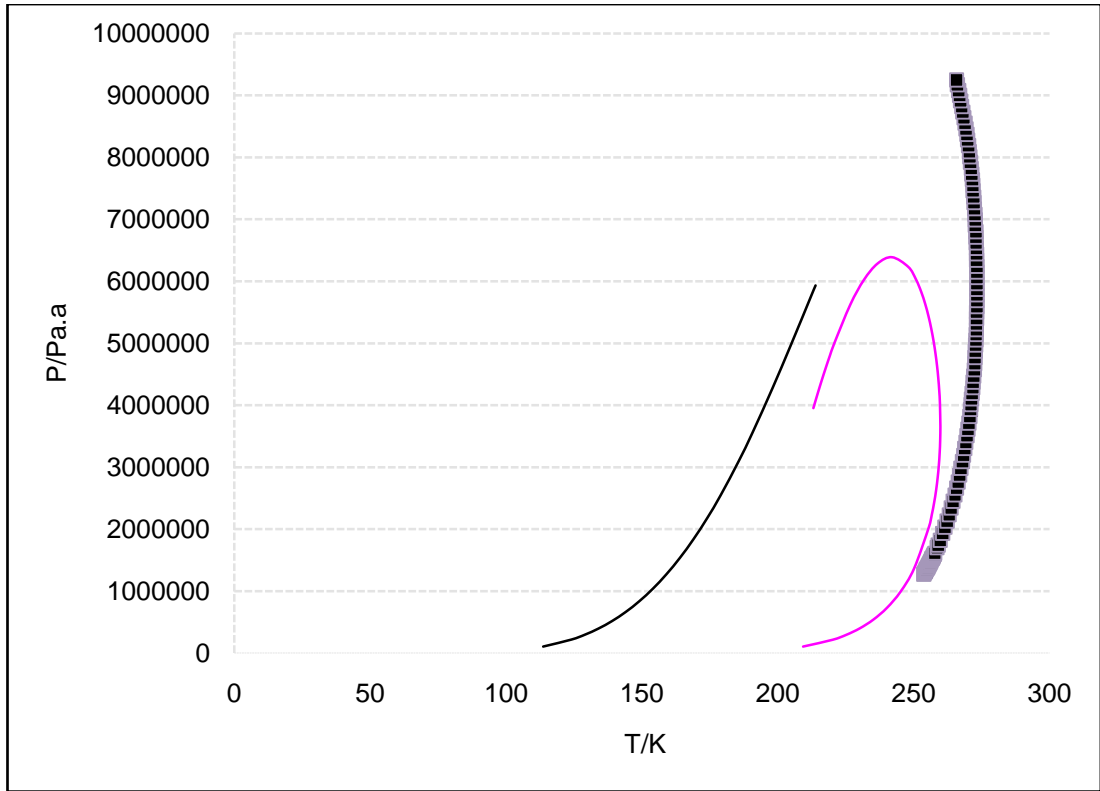
C 5: SET 15-GAS 1; PR-UNIQUAC-WS
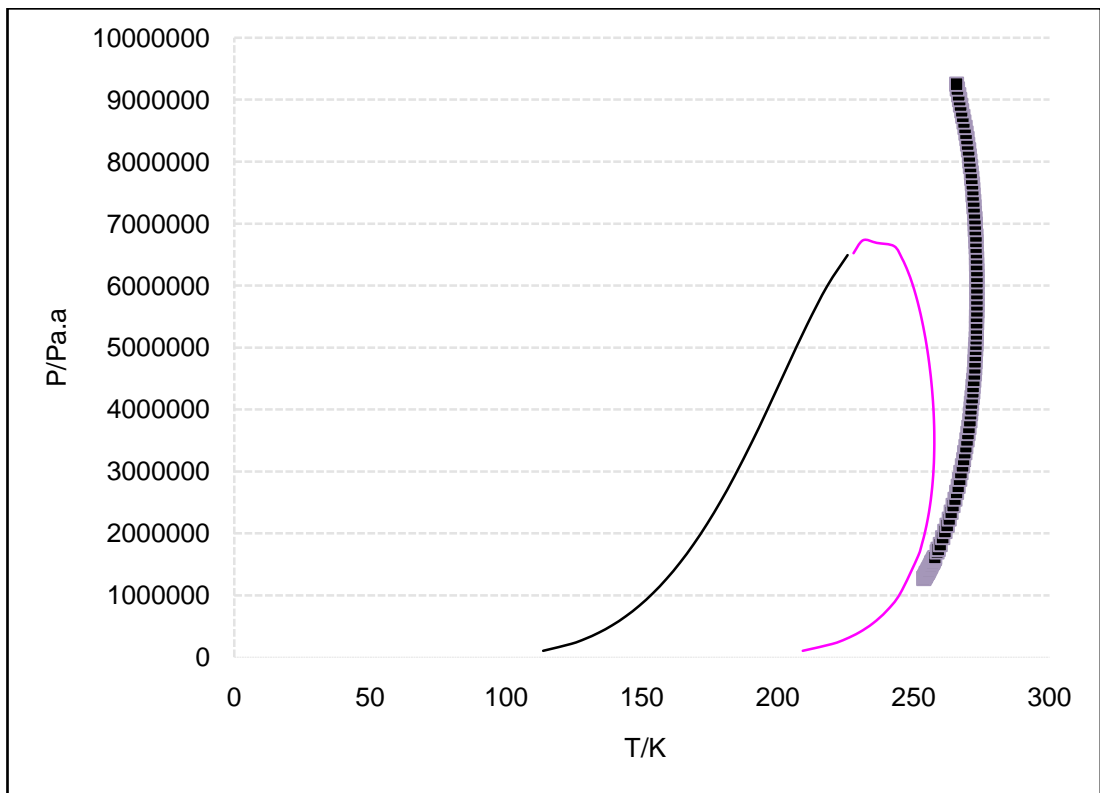
C 6: SET 15-GAS 1; PR-NRTL-WS
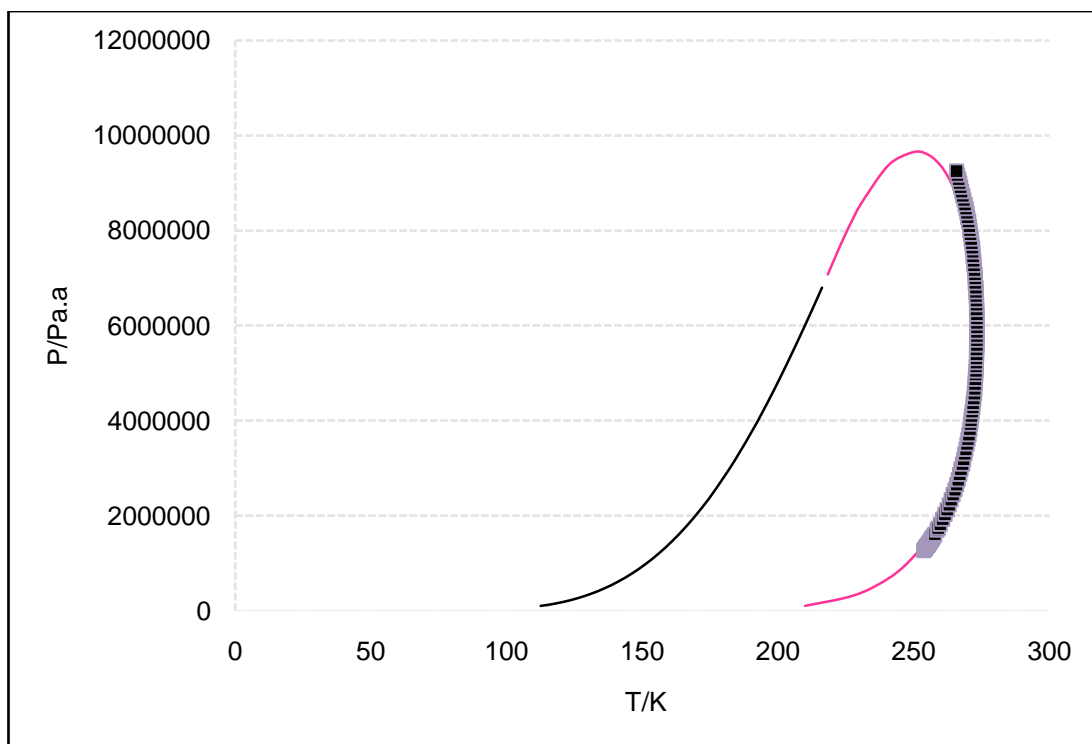
C 7: SET 15-GAS 1; SRK-EXT-VDW
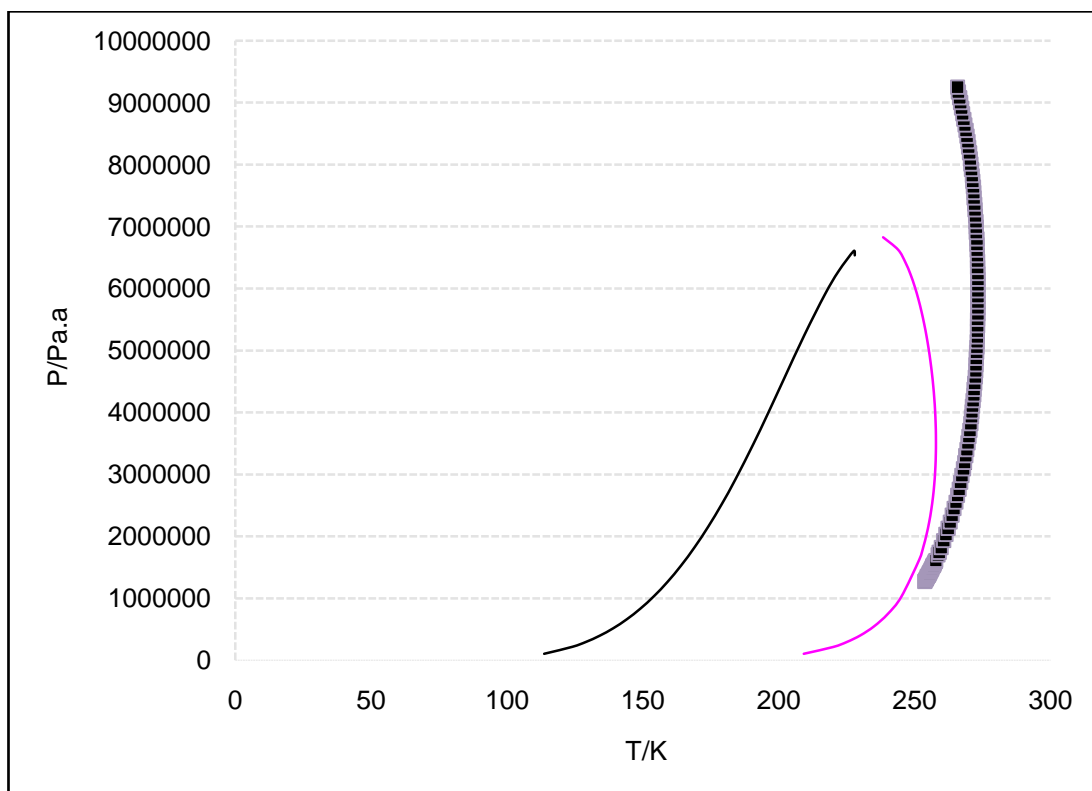
C 8: SET 15-GAS 1; PR-WS
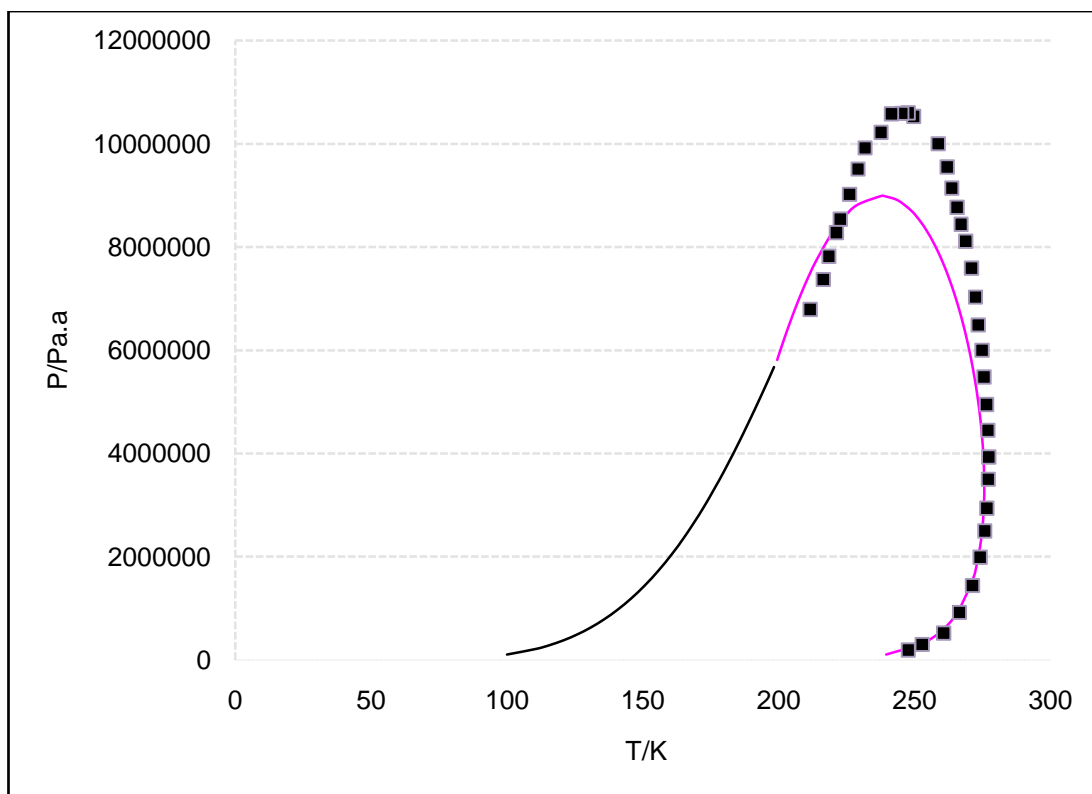
C 9: SET 15-GAS 2; CPA-PR-VDW
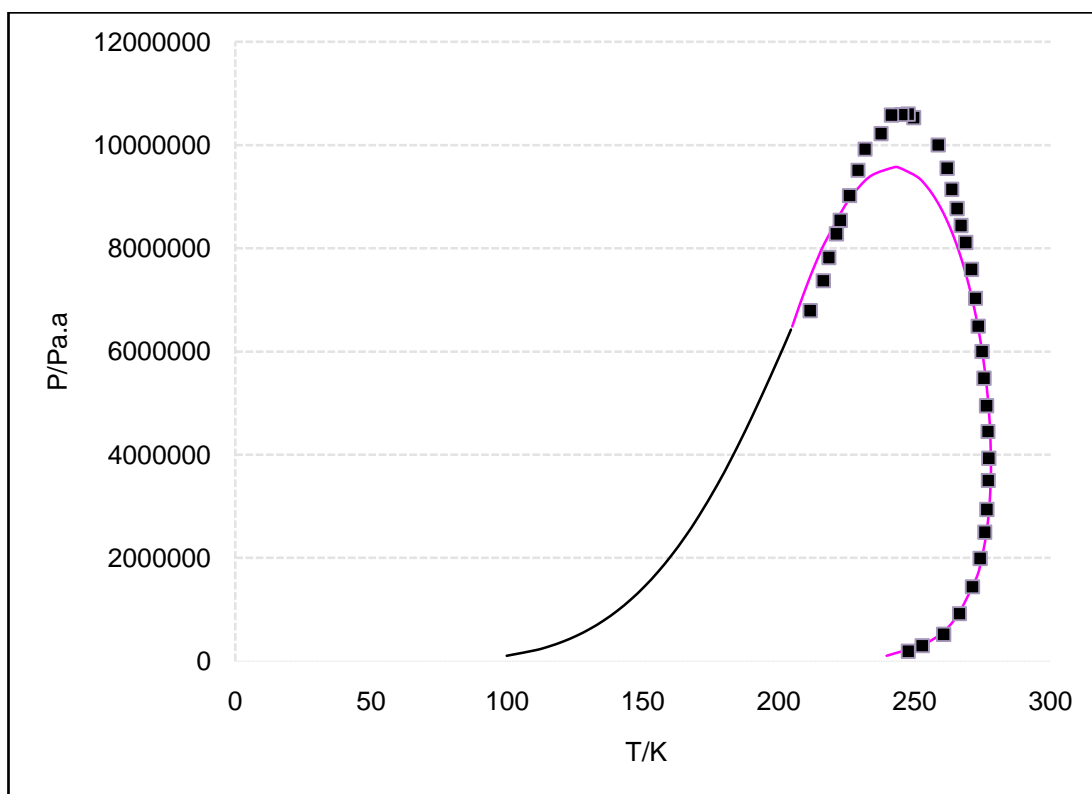
C 10: SET 15-GAS 2; CPA-SRK-VDW
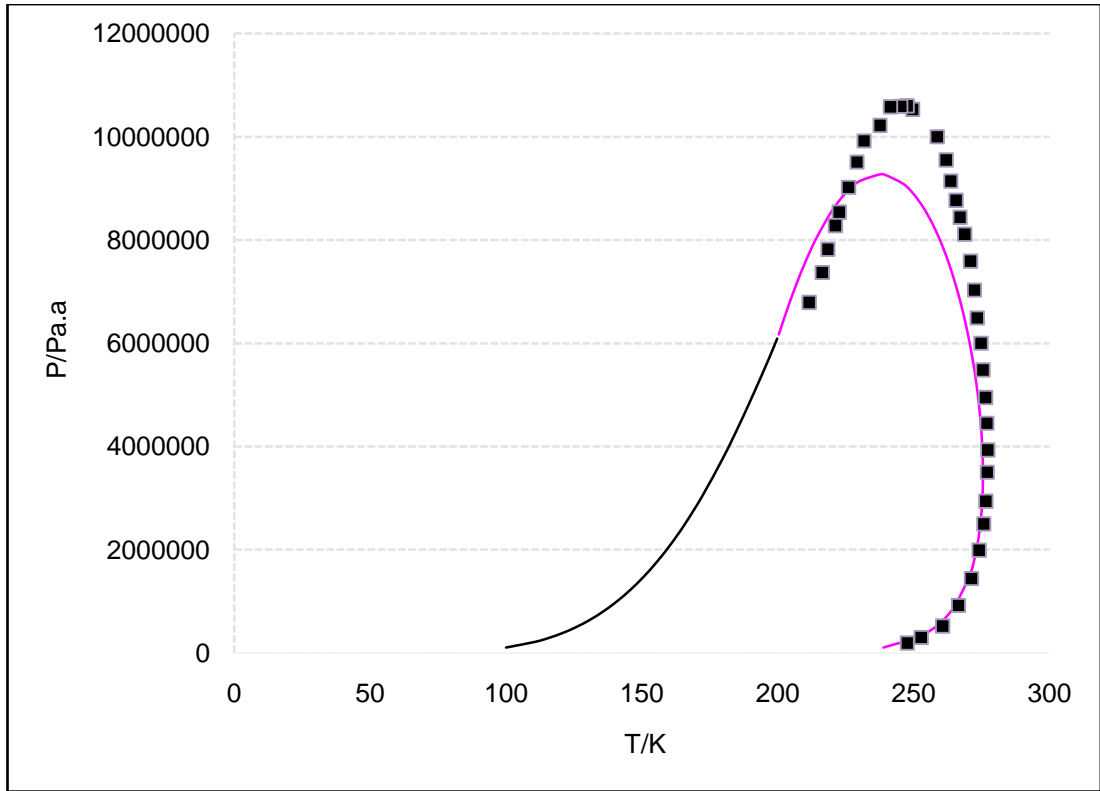
C 11: SET 15-GAS 2; PR-VDW
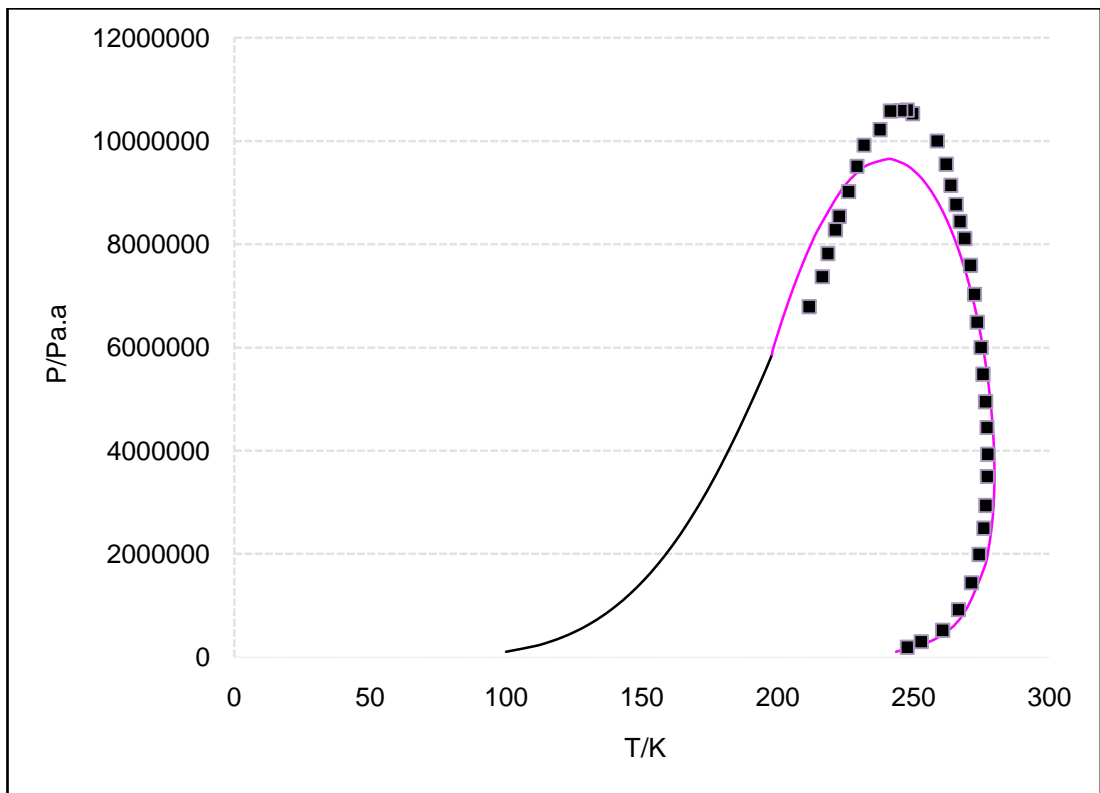
C 12: SET 15-GAS 2; SRK-VDW
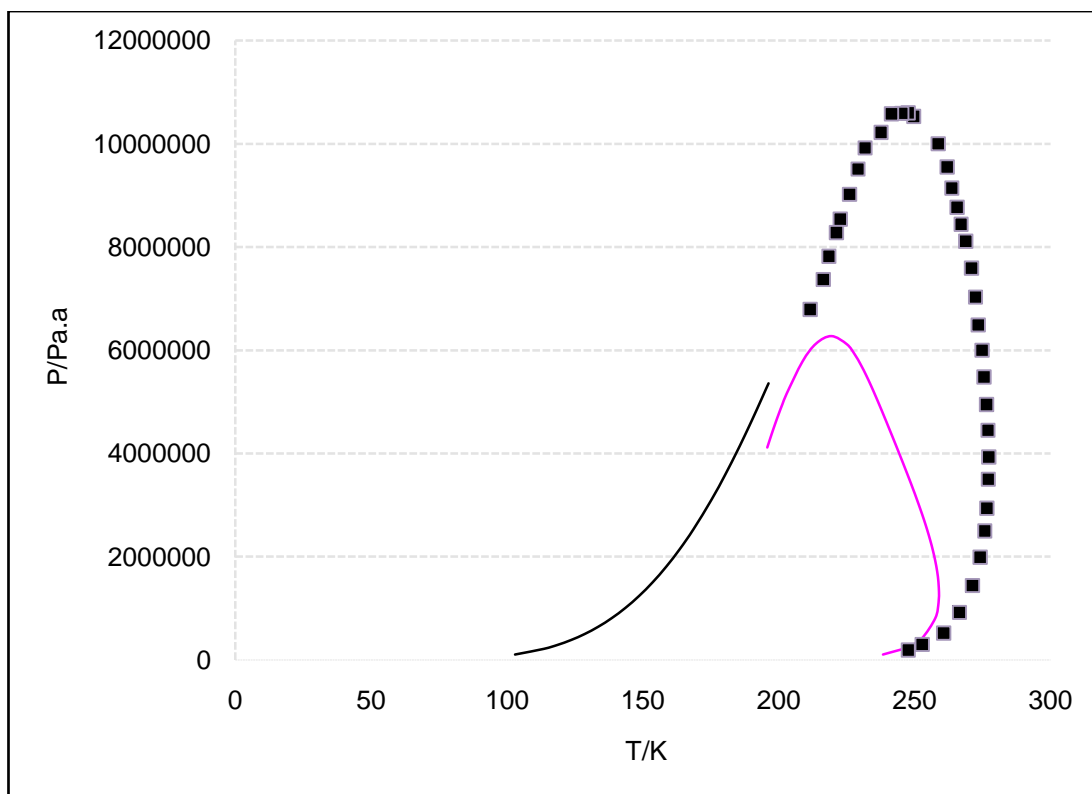
C 13**:** SET 15-GAS 2; PR-UNIQUAC-WS
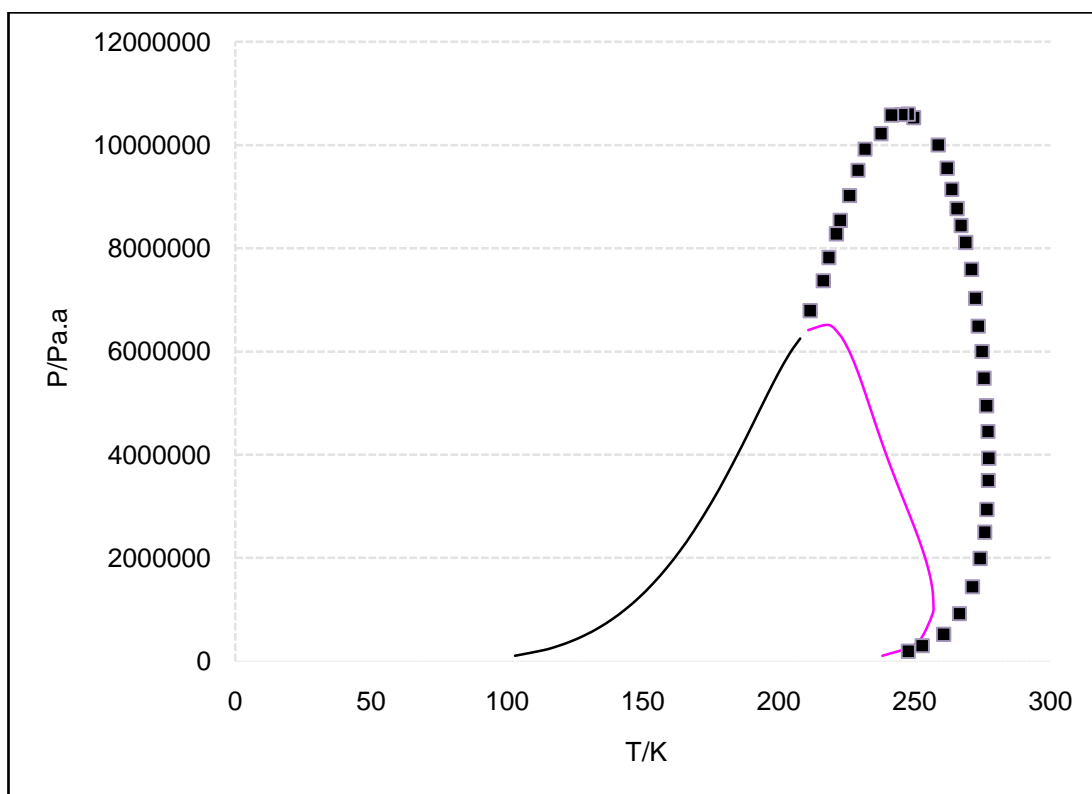
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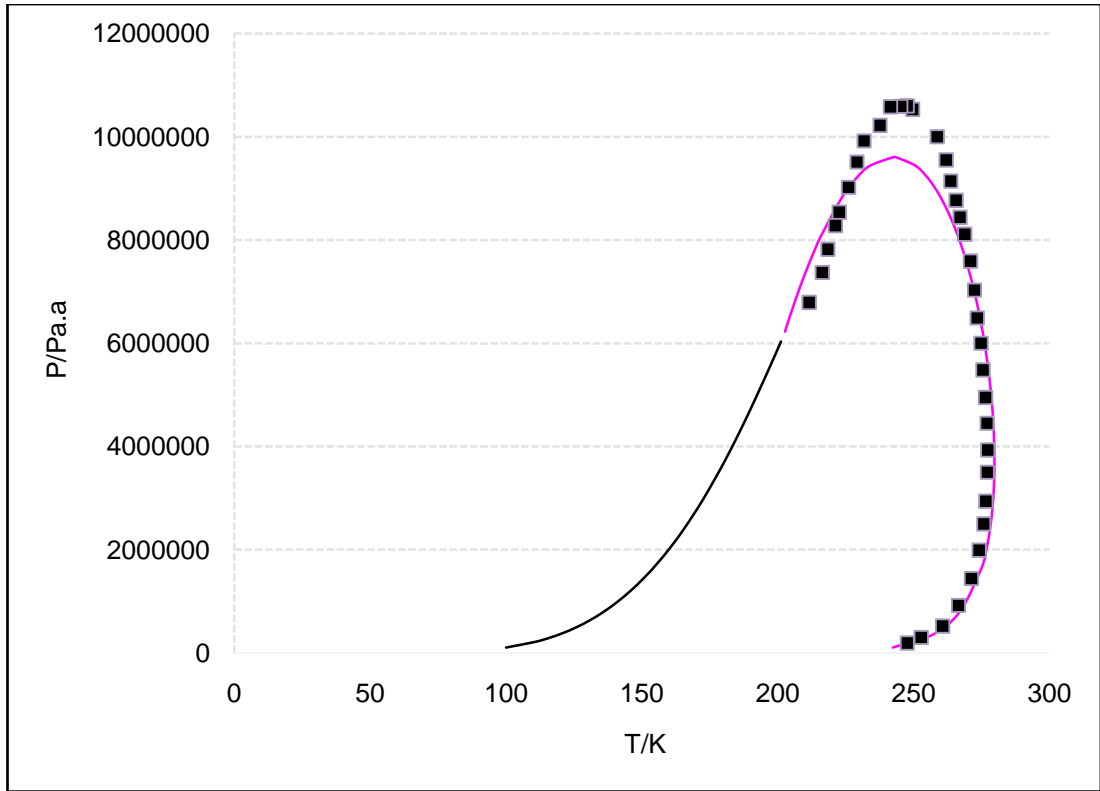
C 15: SET 15-GAS 2; SRK-EXT-VDW
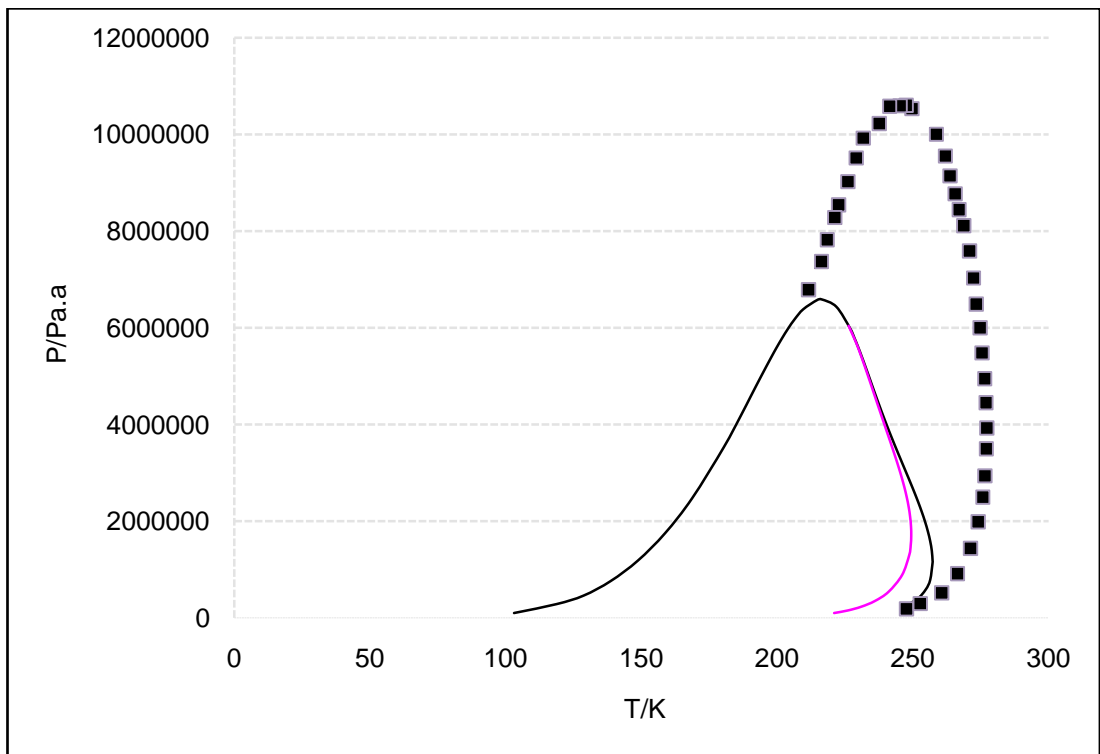
C 16: SET 15-GAS 2; PR-WS

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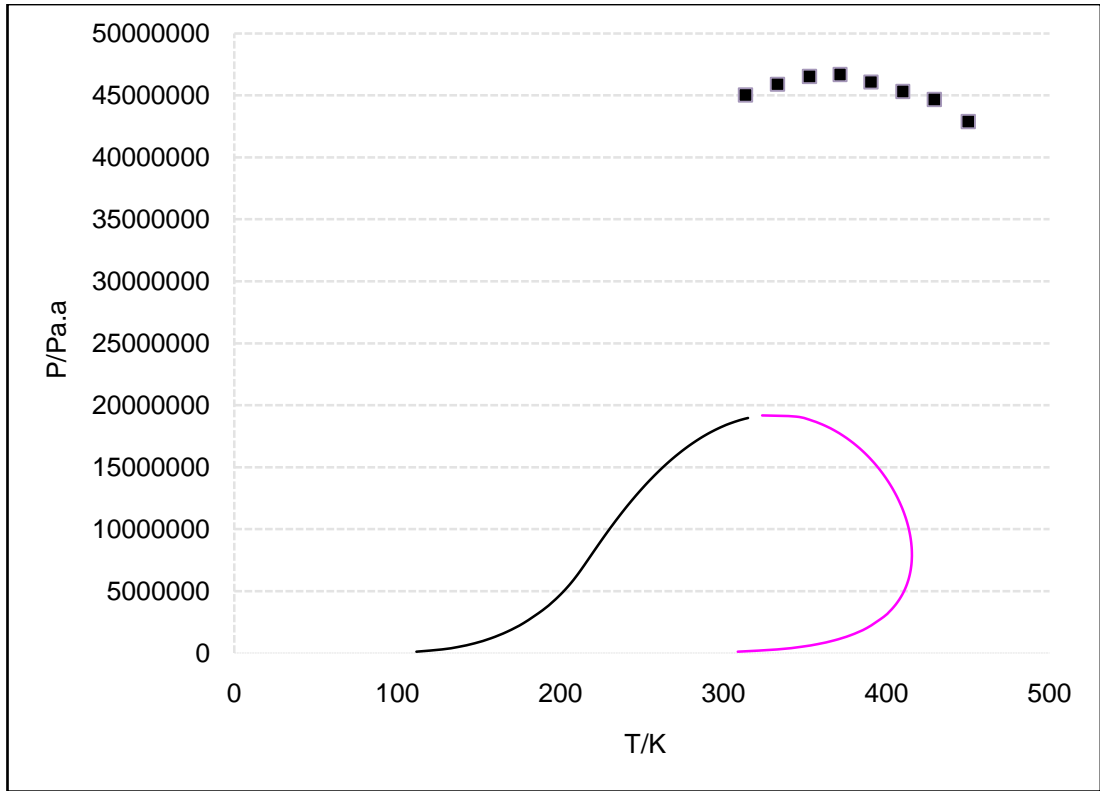
C 17**:** SET 15-GAS 3; CPA-PR-VDW
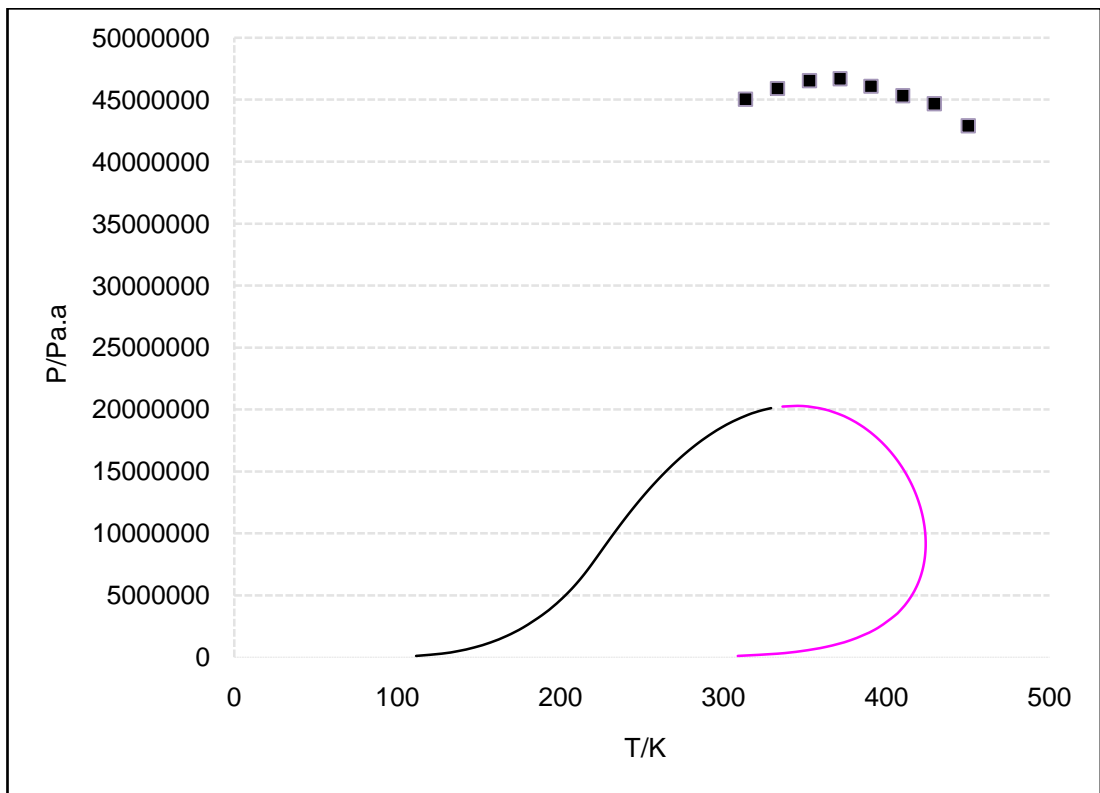
C 18: SET 15-GAS 3; CPA-SRK-VDW
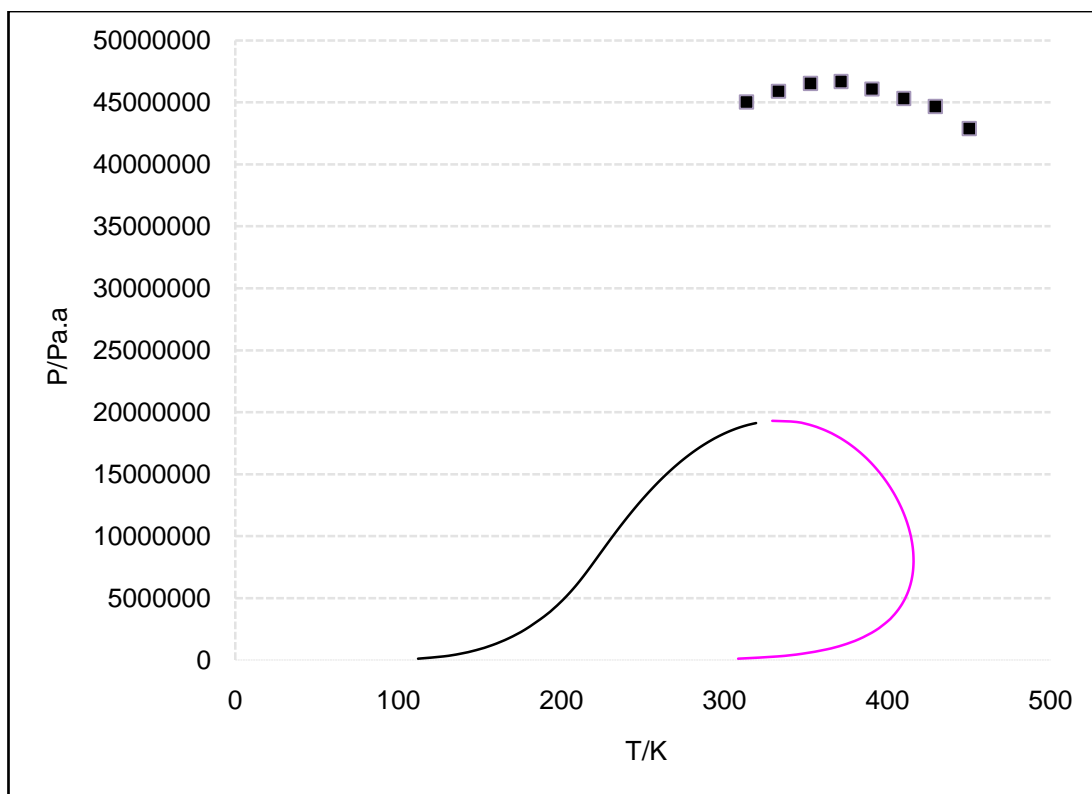
C 19**:** SET 15-GAS 3; PR-VDW
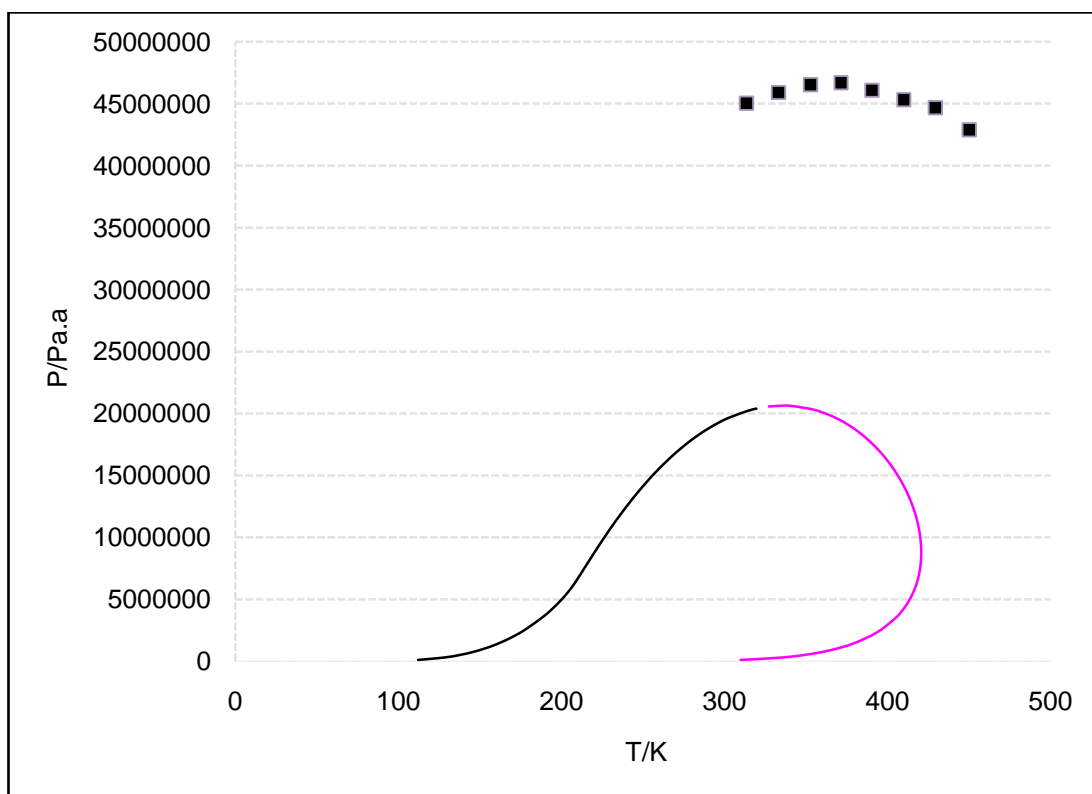
C 20: SET 15-GAS 3; SRK-VDW
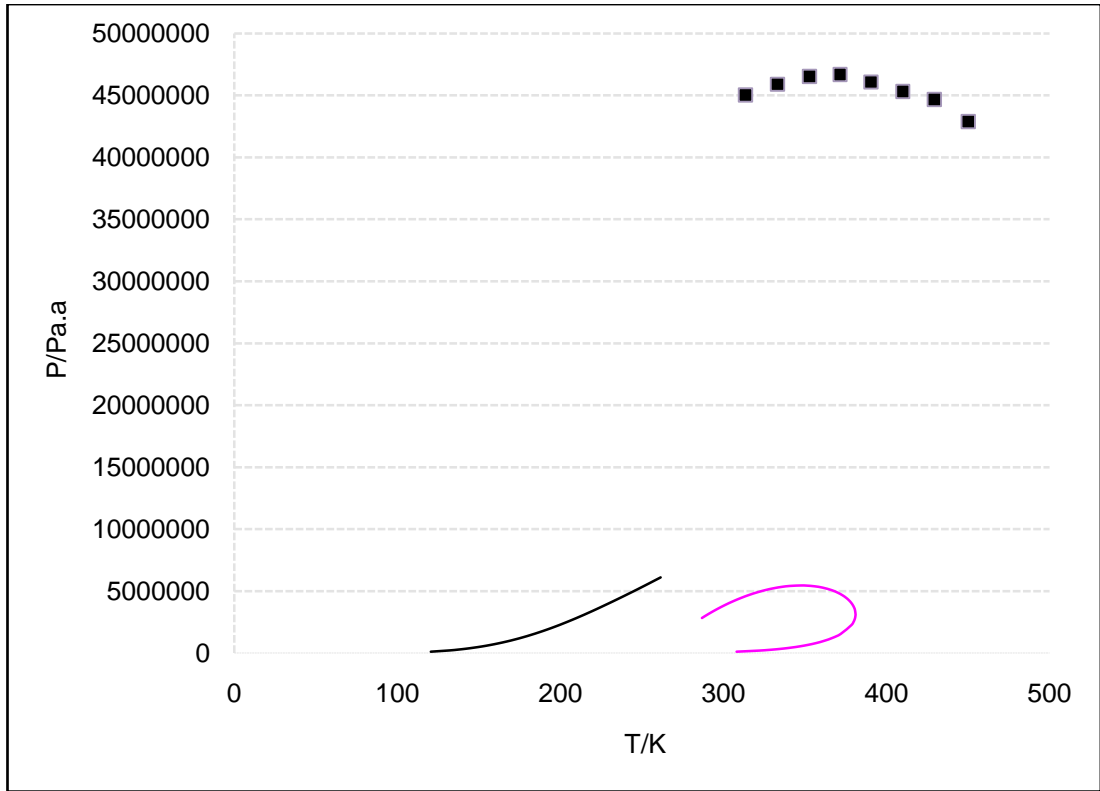
C 21: SET 15-GAS 3; PR-UNIQUAC-WS
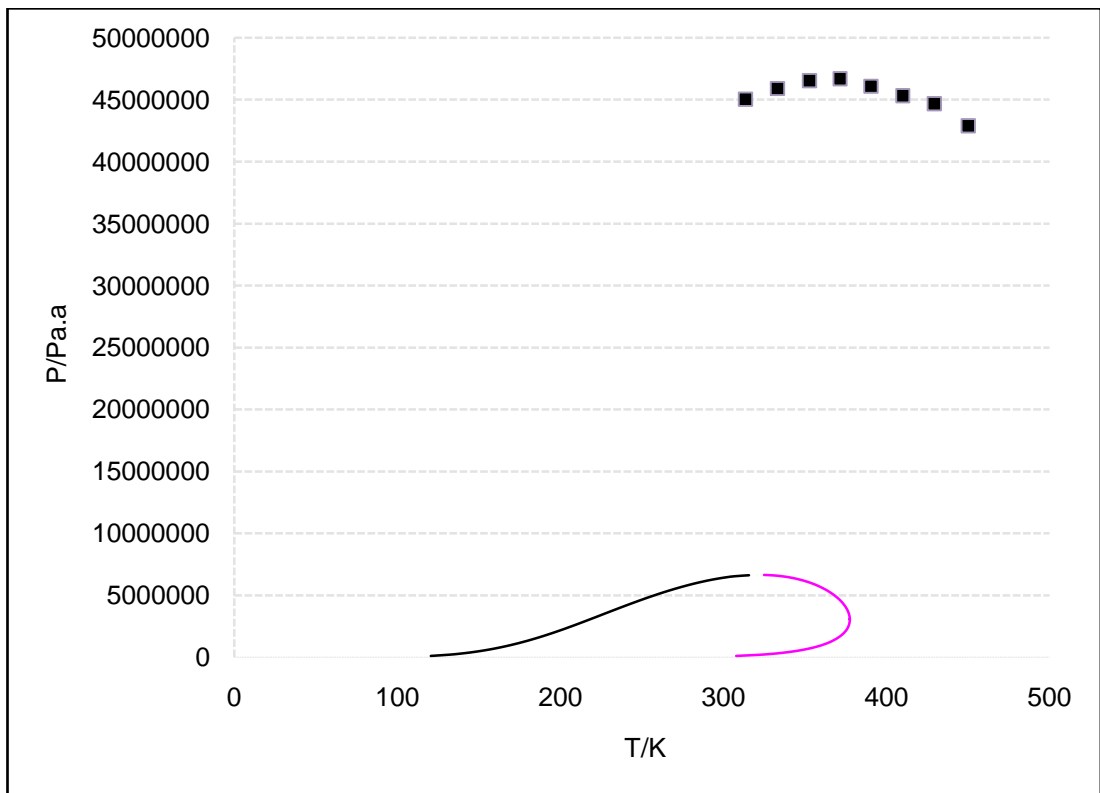
C 22**:** SET 15-GAS 3; PR-NRTL-WS

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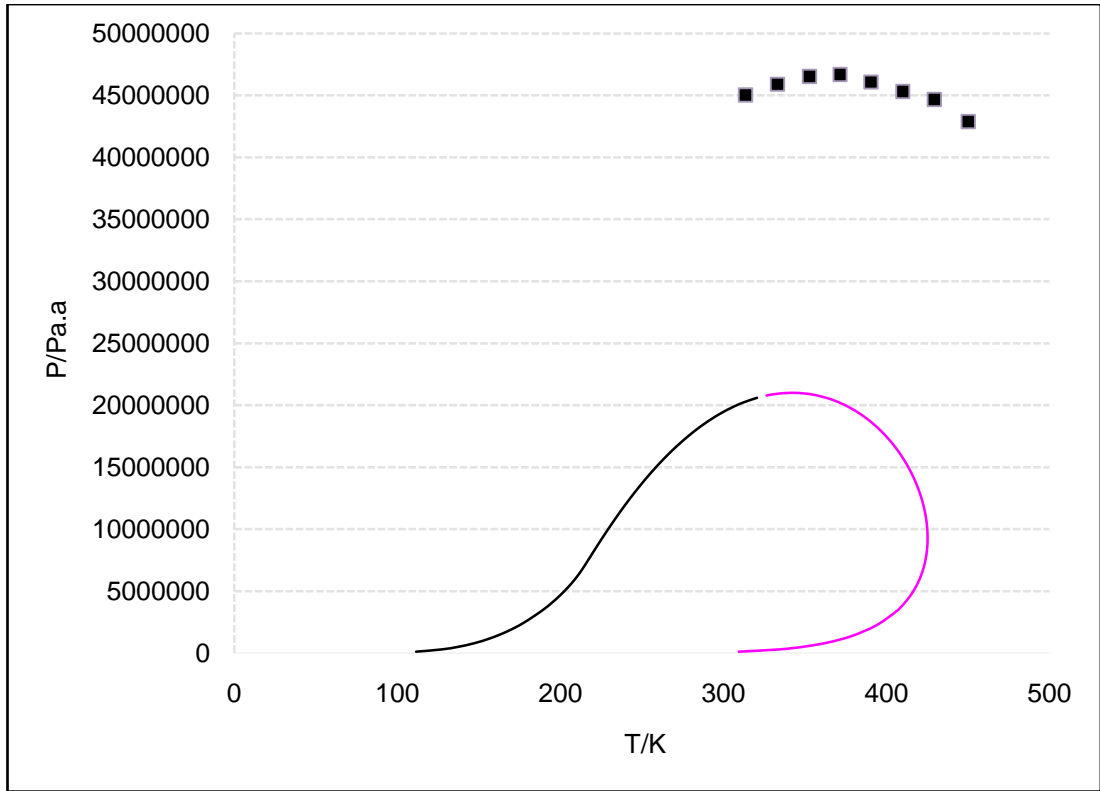
C 23: SET 15-GAS 3; SRK-EXT-VDW
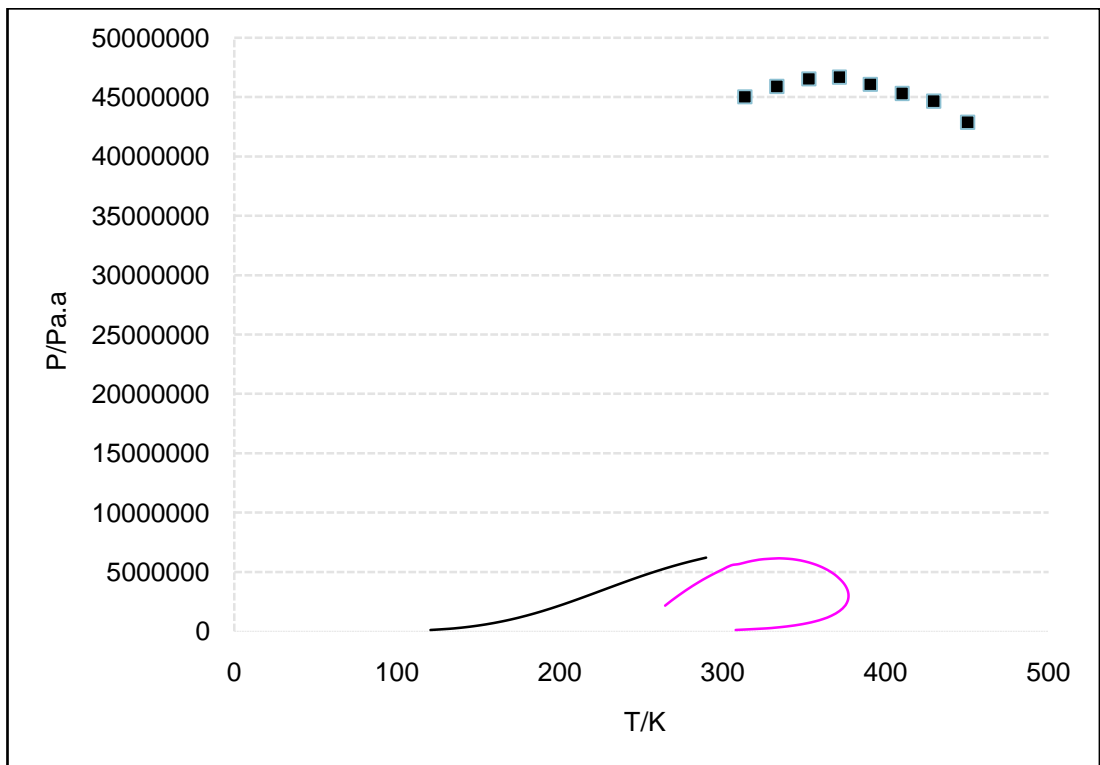
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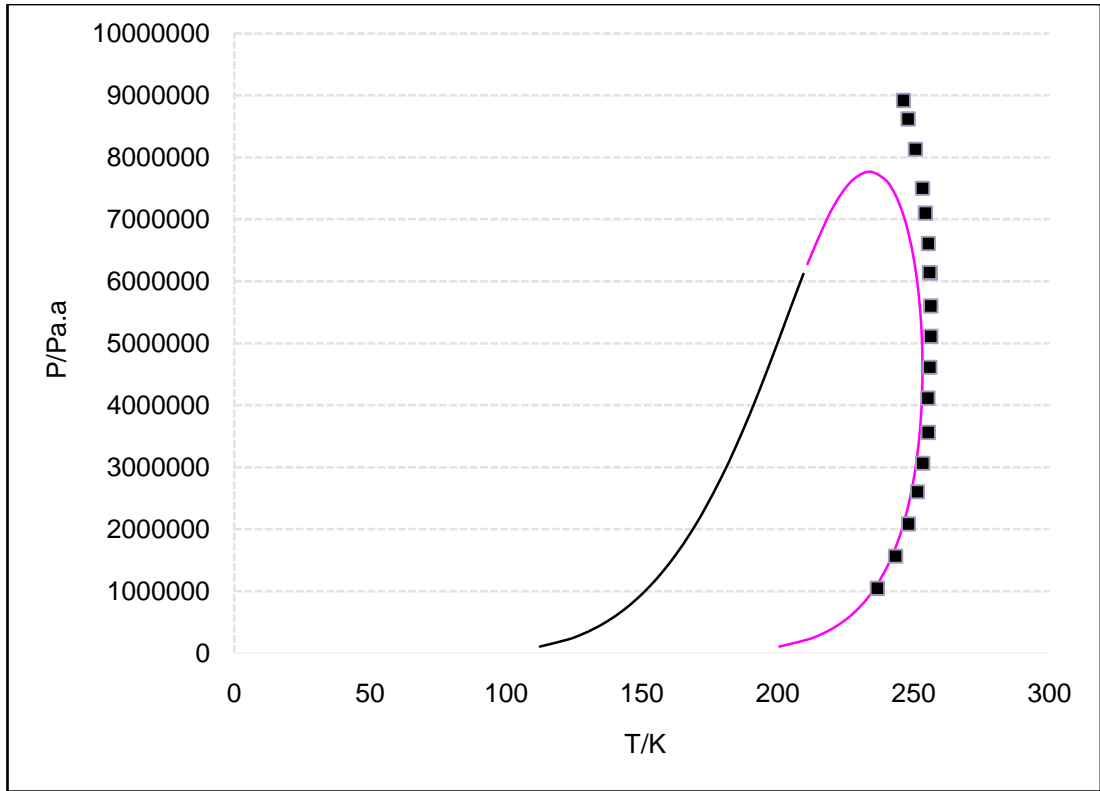
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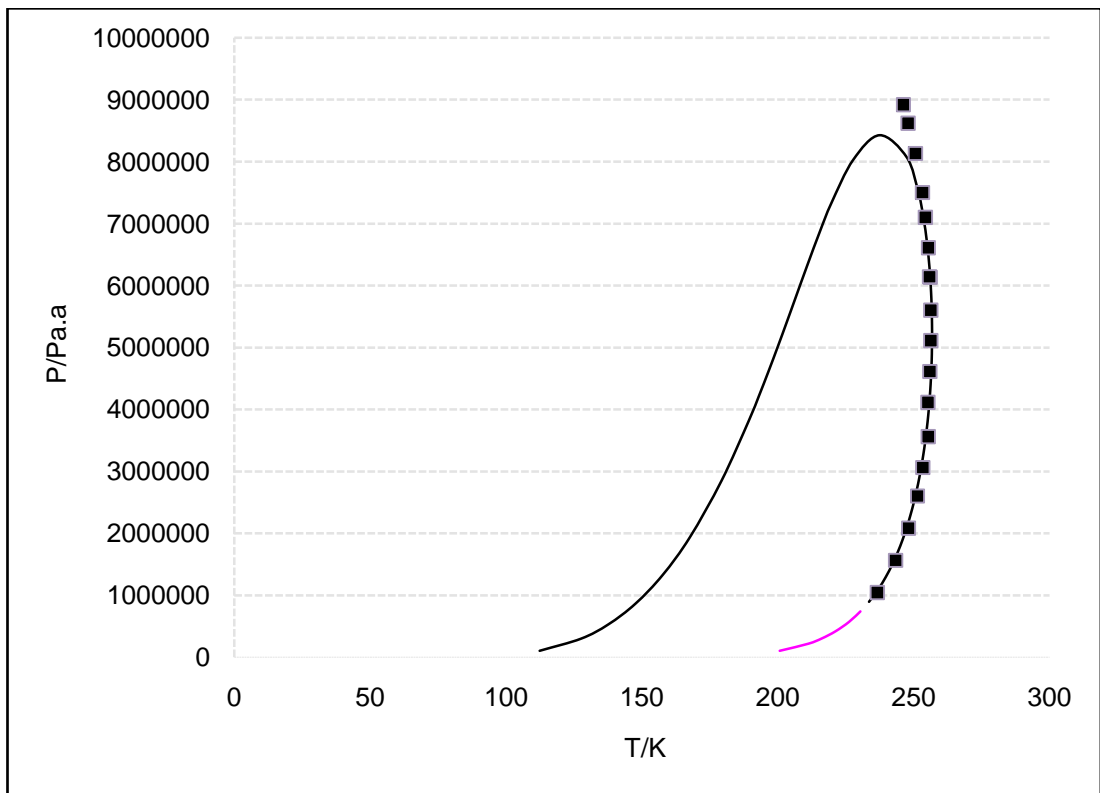
C 26: SET 15-SNG 1; CPA-SRK-VDW

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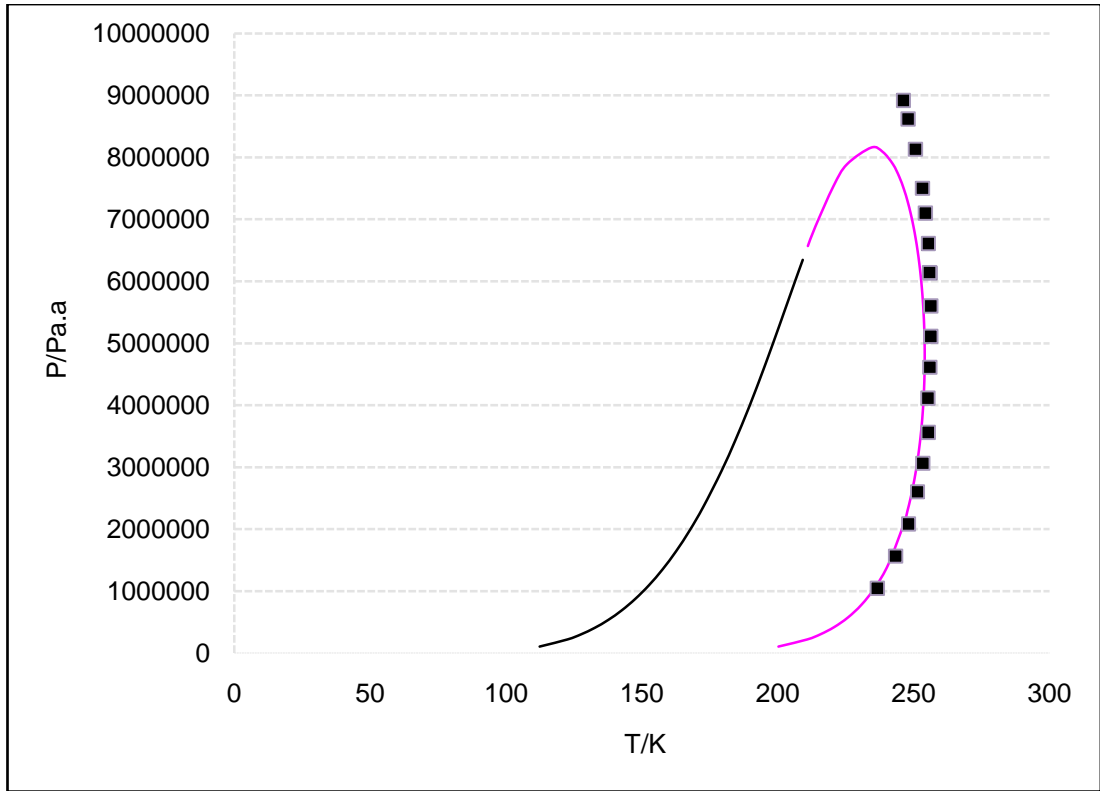
C 27: SET 15-SNG 1; PR-VDW
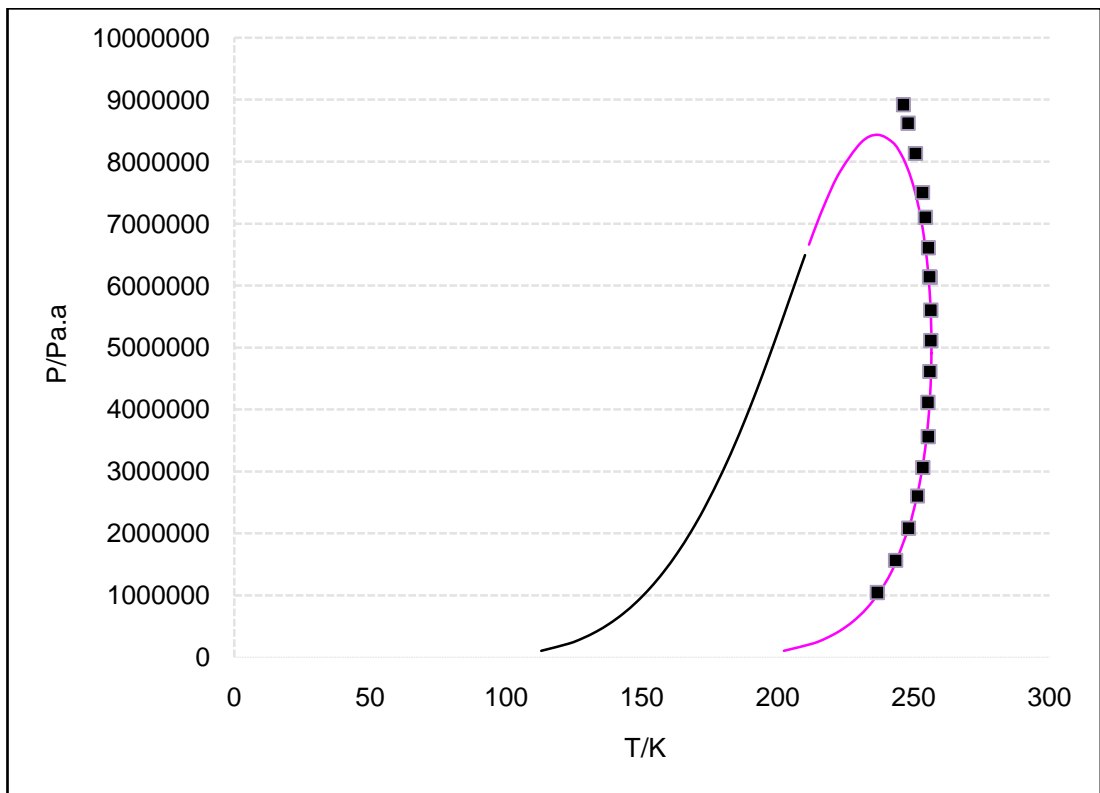
C 28: SET 15-SNG 1; SRK-VDW
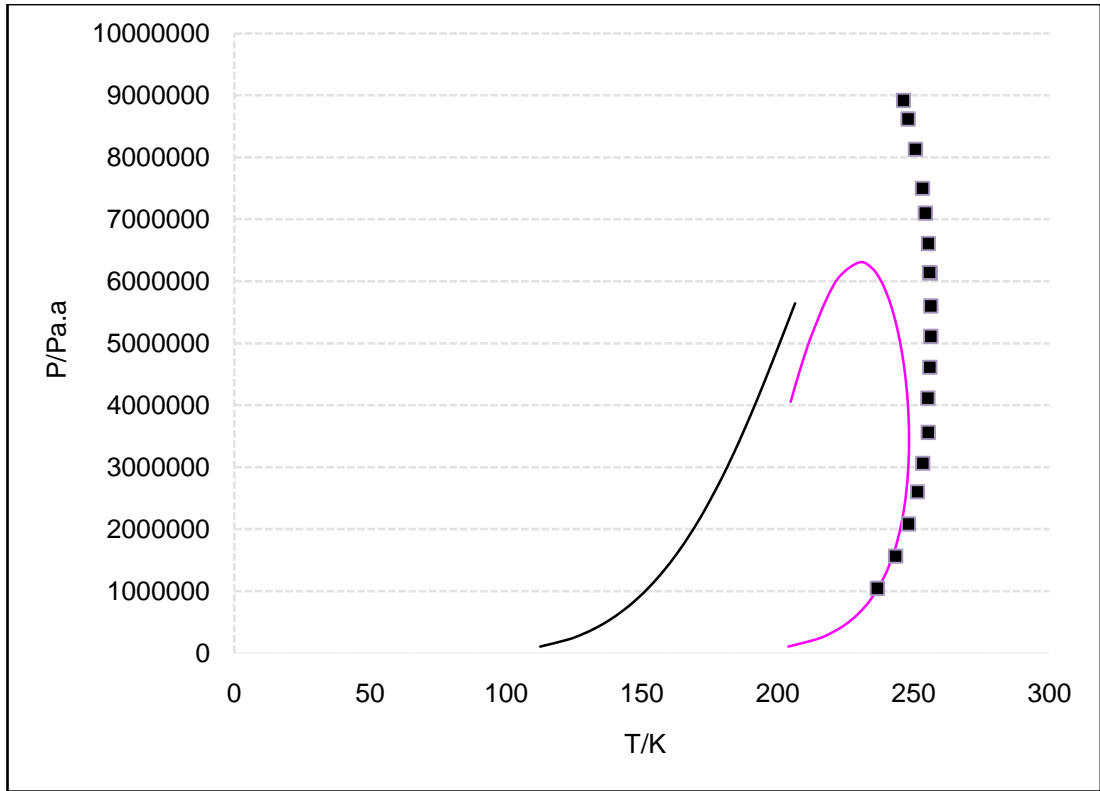
C 29: SET 15-SNG 1; PR-UNIQUAC-WS
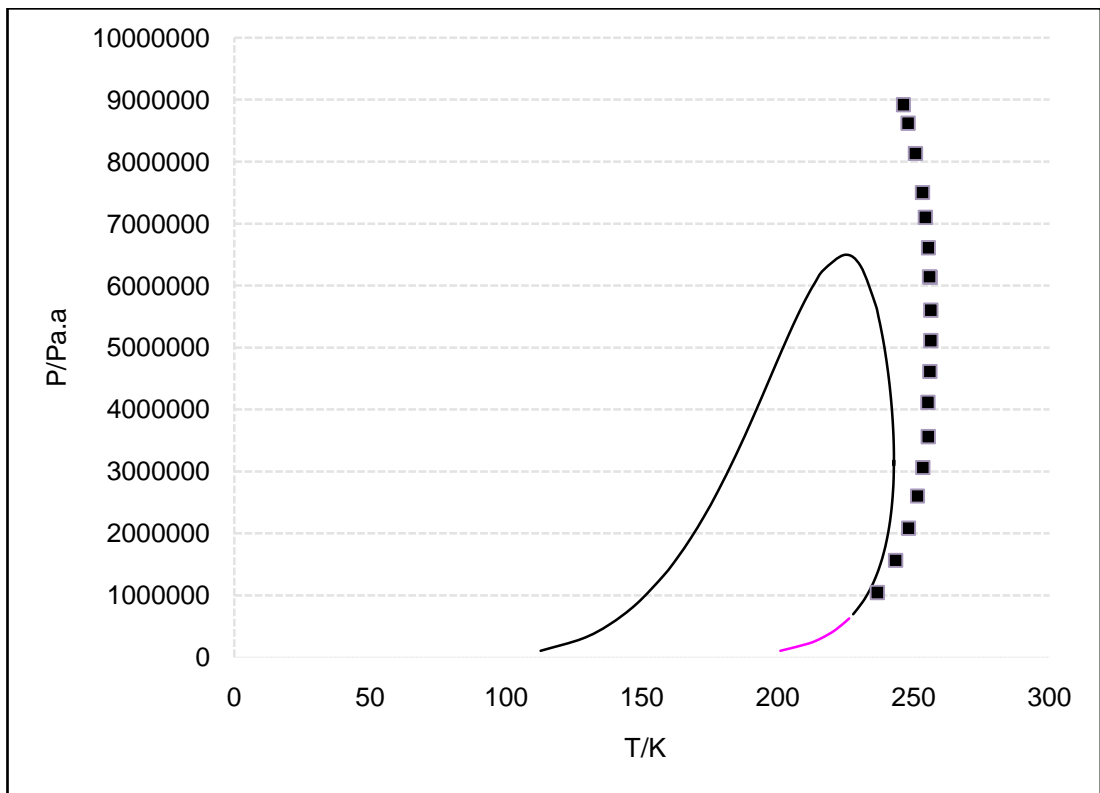
C 30: SET 15-SNG 1; PR-NRTL-WS
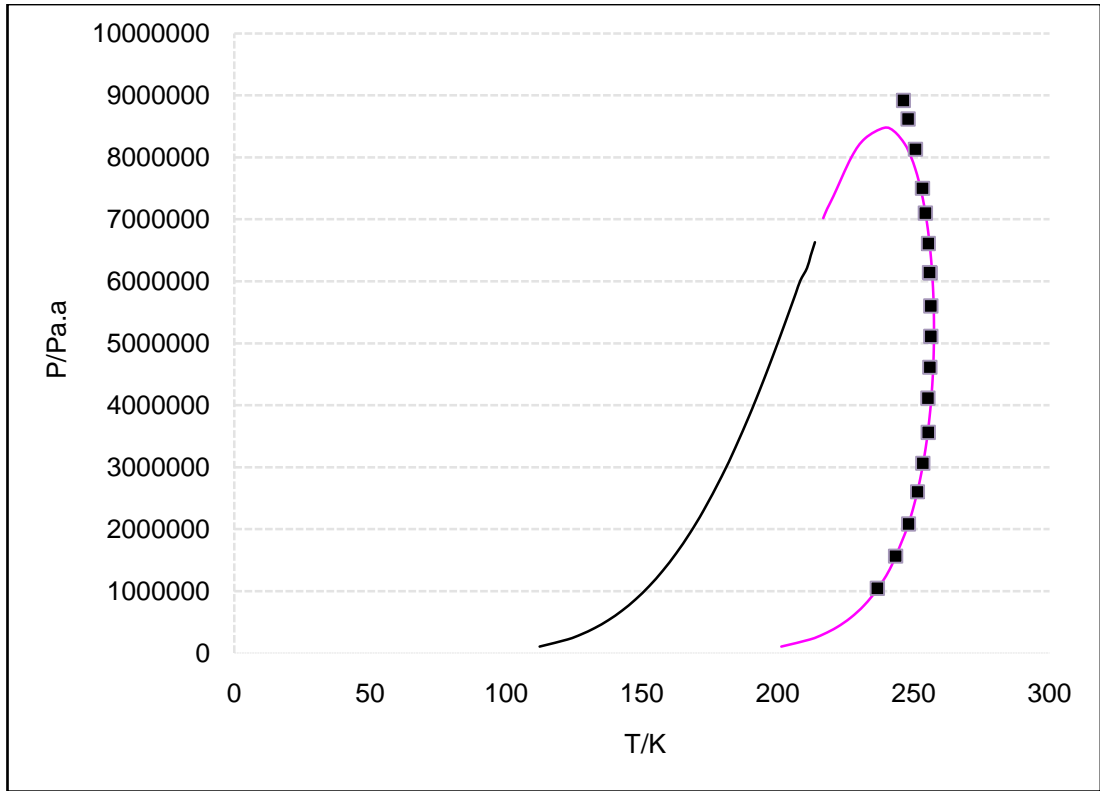
C 31: SET 15-SNG 1; SRK-EXT-VDW
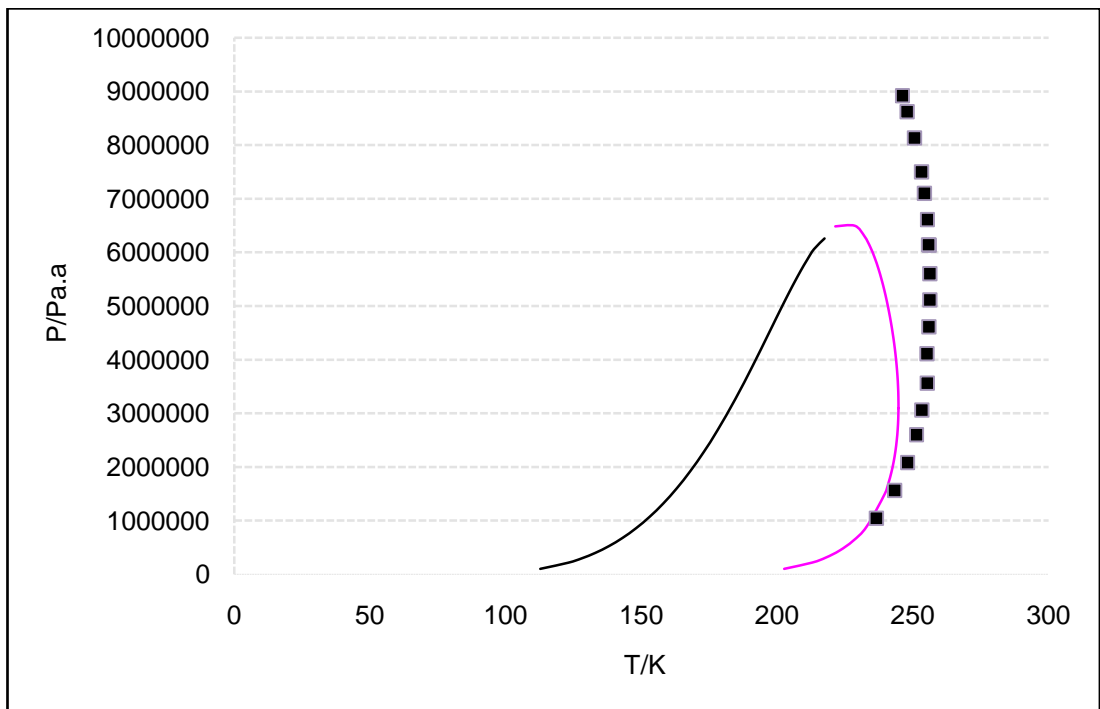
C 32: SET 15-SNG 1; PR-WS
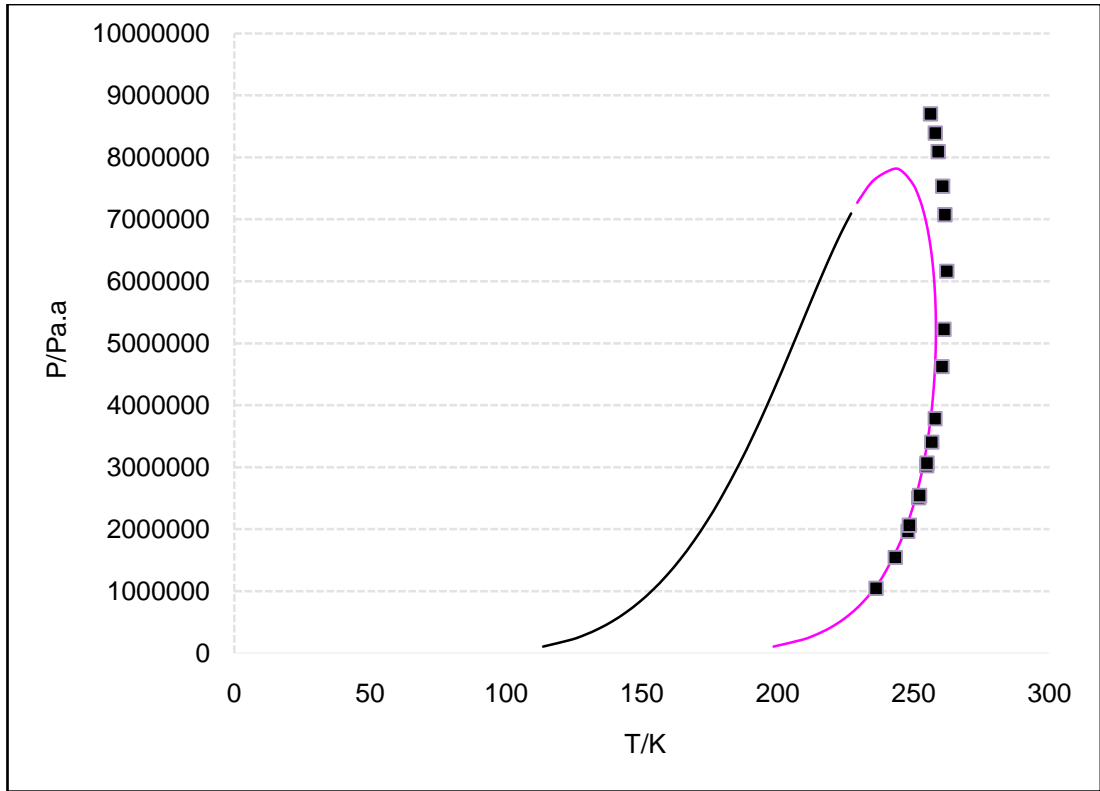
C 33**:** SET 15-SNG 2; CPA-PR-VDW
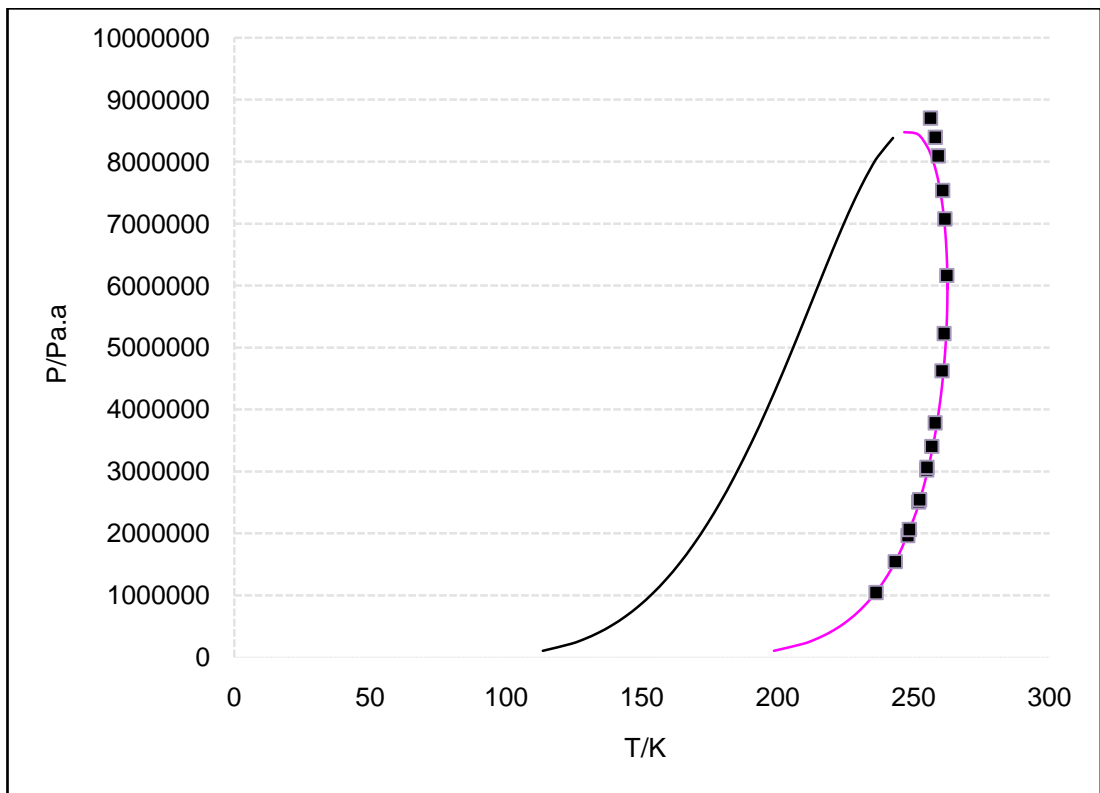
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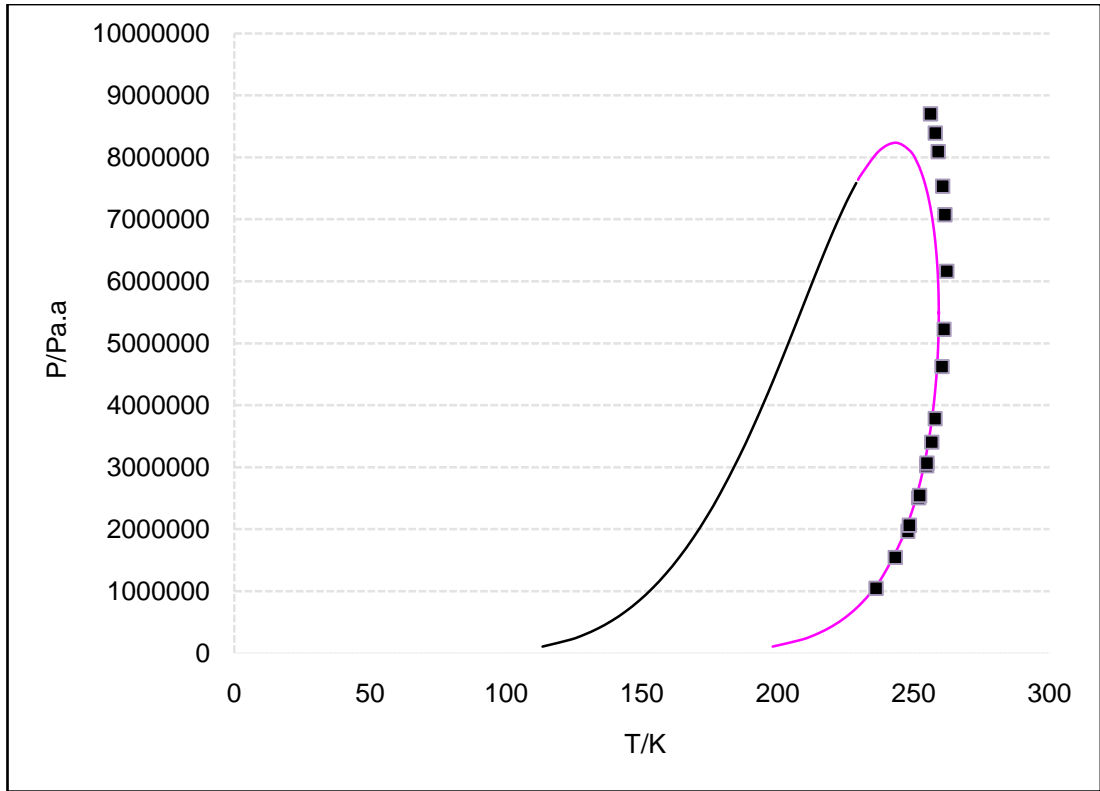
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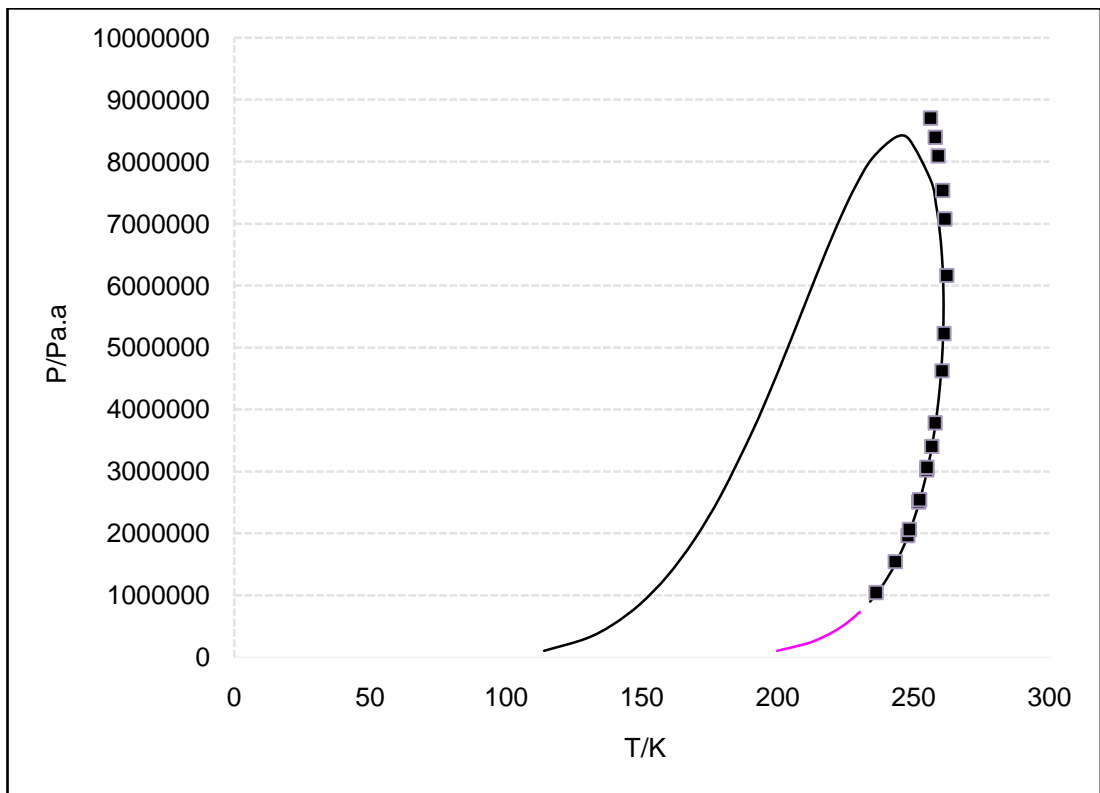
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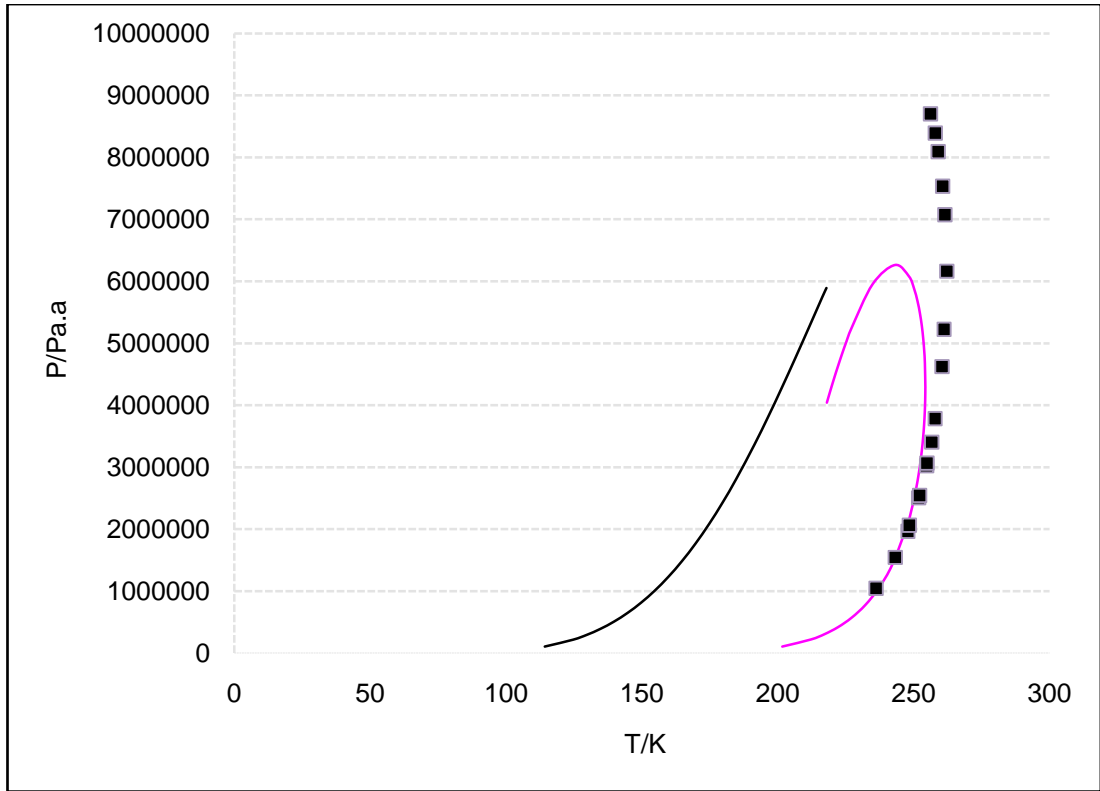
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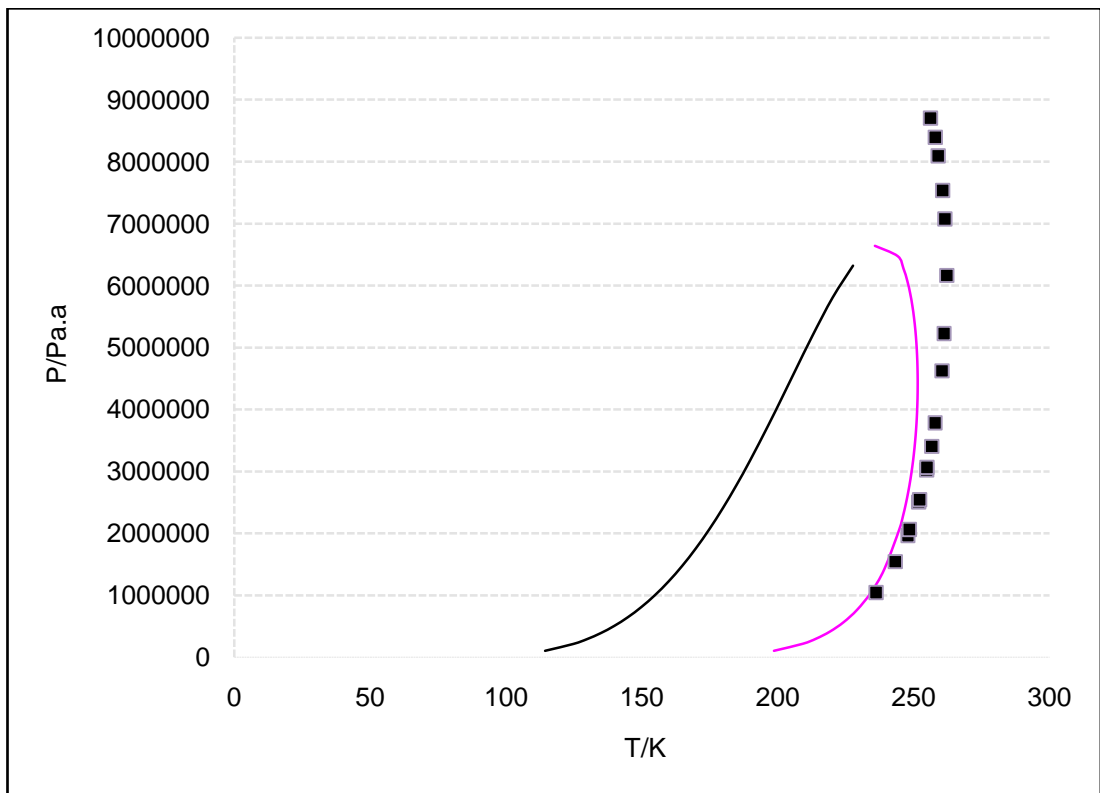
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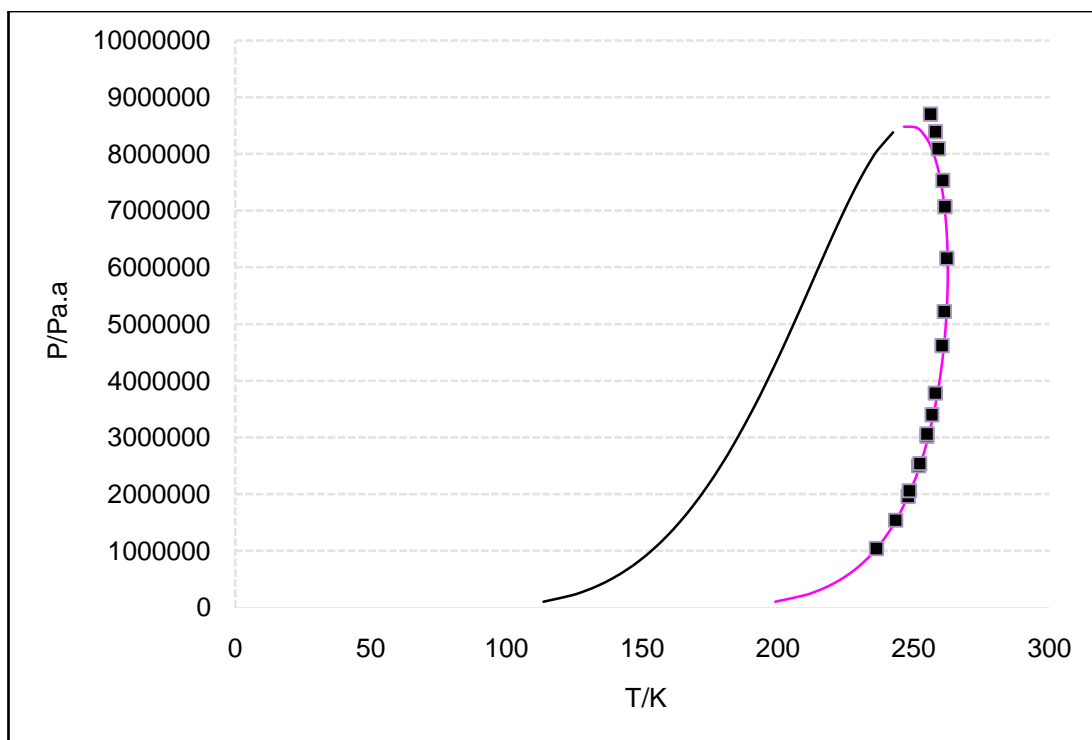
C 39**:** SET 15-SNG 2; SRK-EXT-VDW
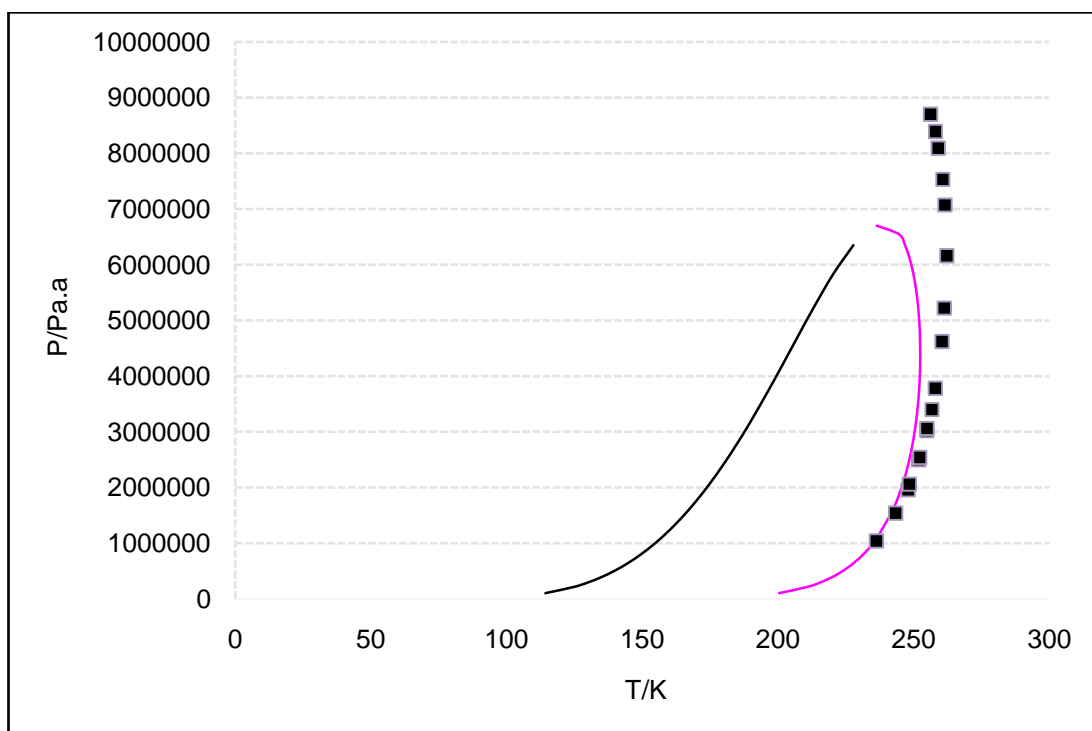
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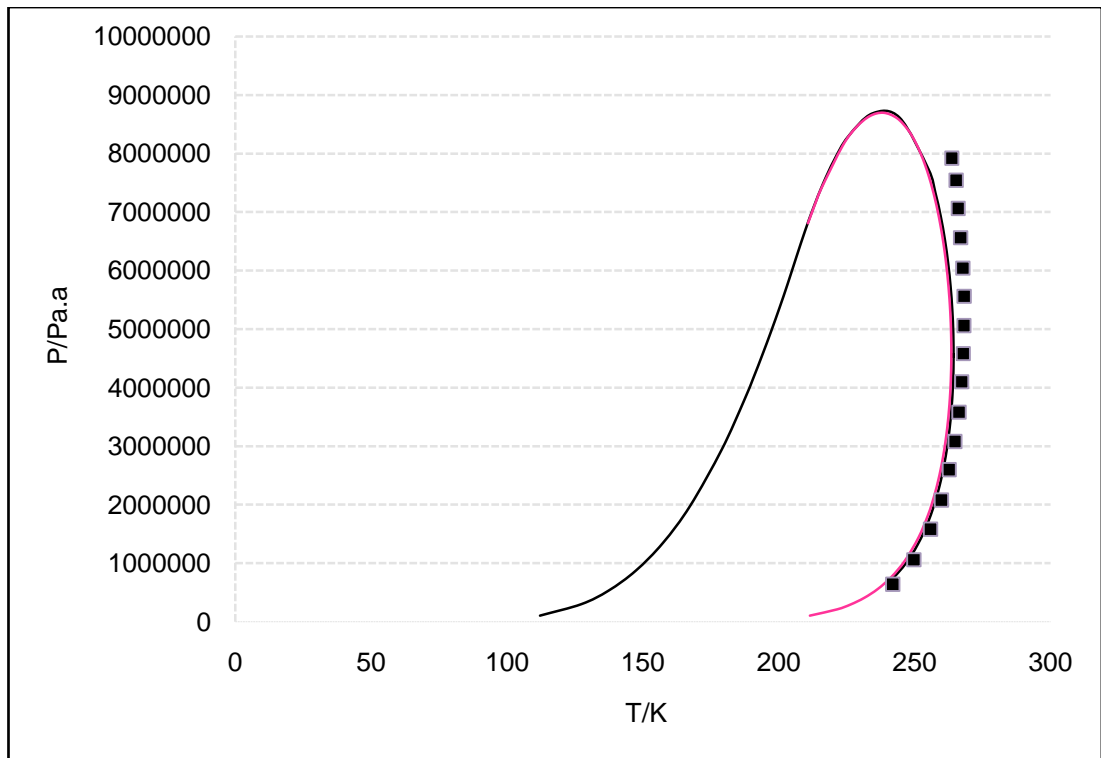
C 41: SET 15-SNG 3; CPA-PR-VDW
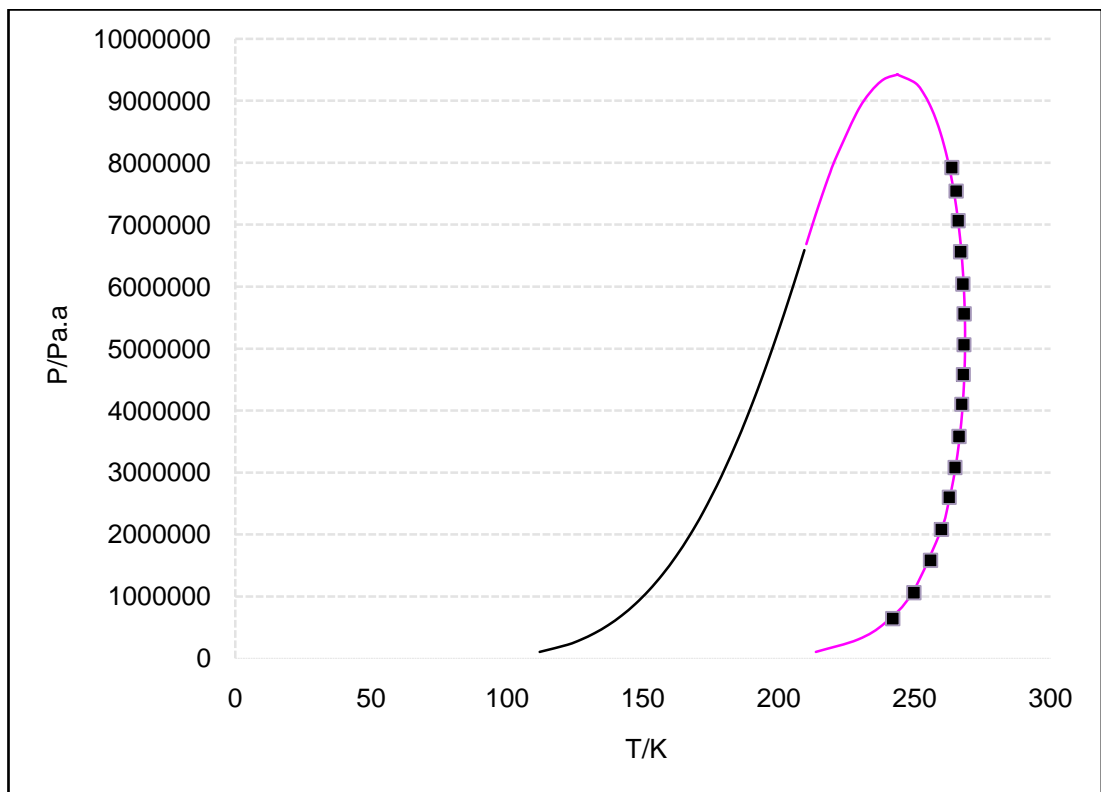
C 42: SET 15-SNG 3; CPA-SRK-VDW

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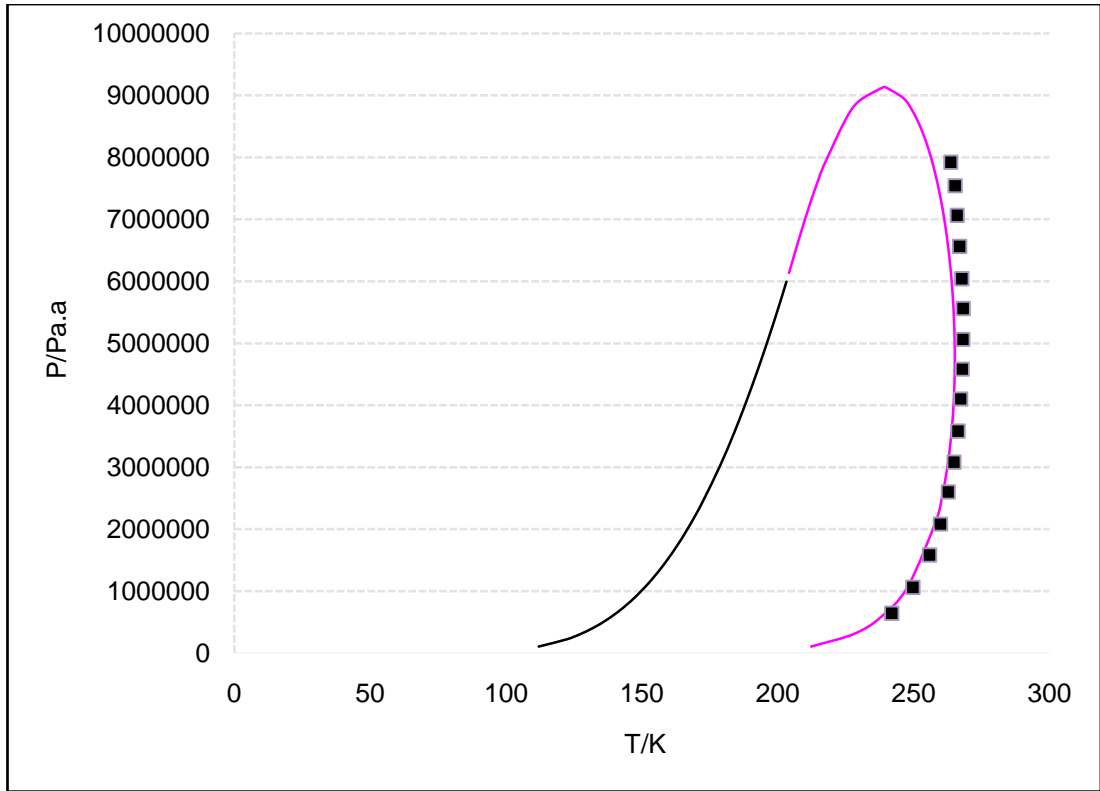
C 43: SET 15-SNG 3; PR-VDW
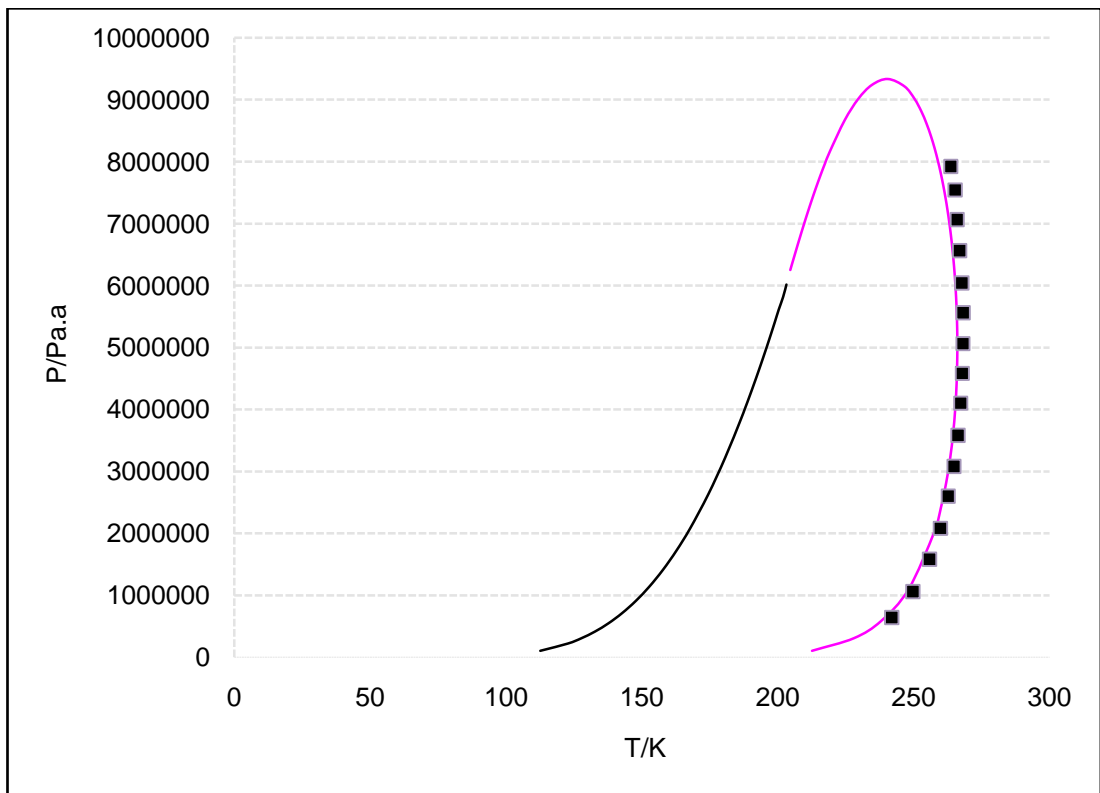
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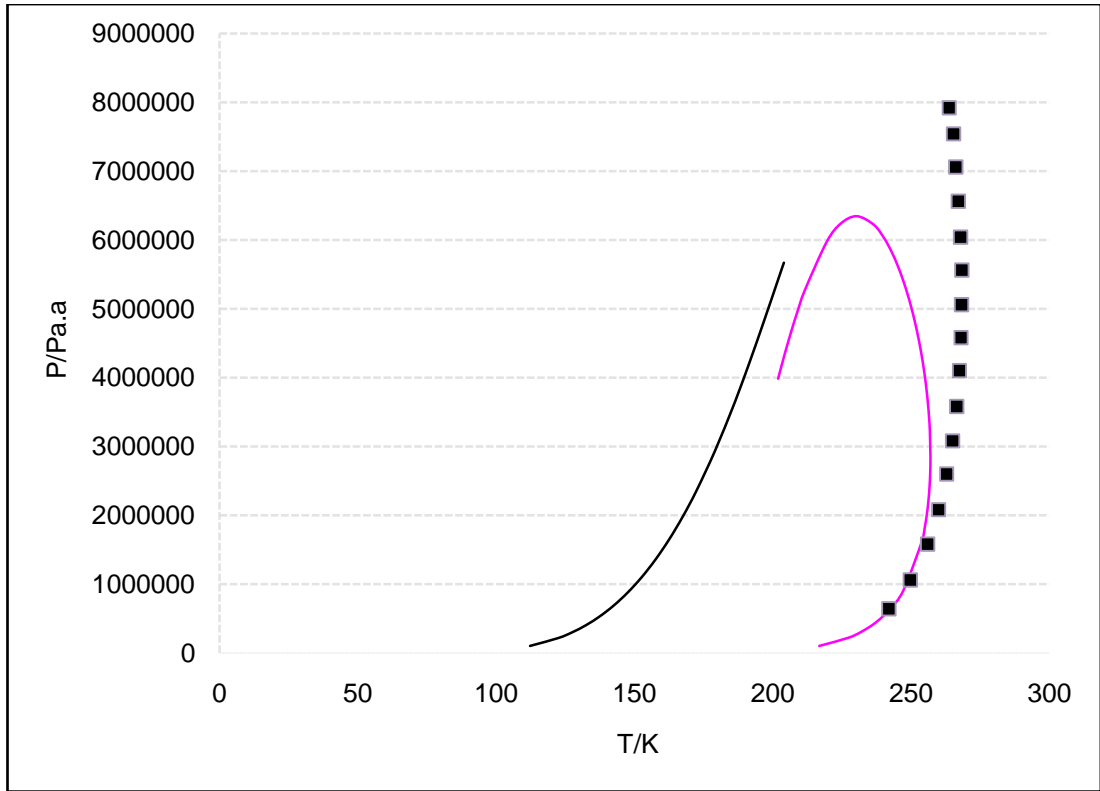
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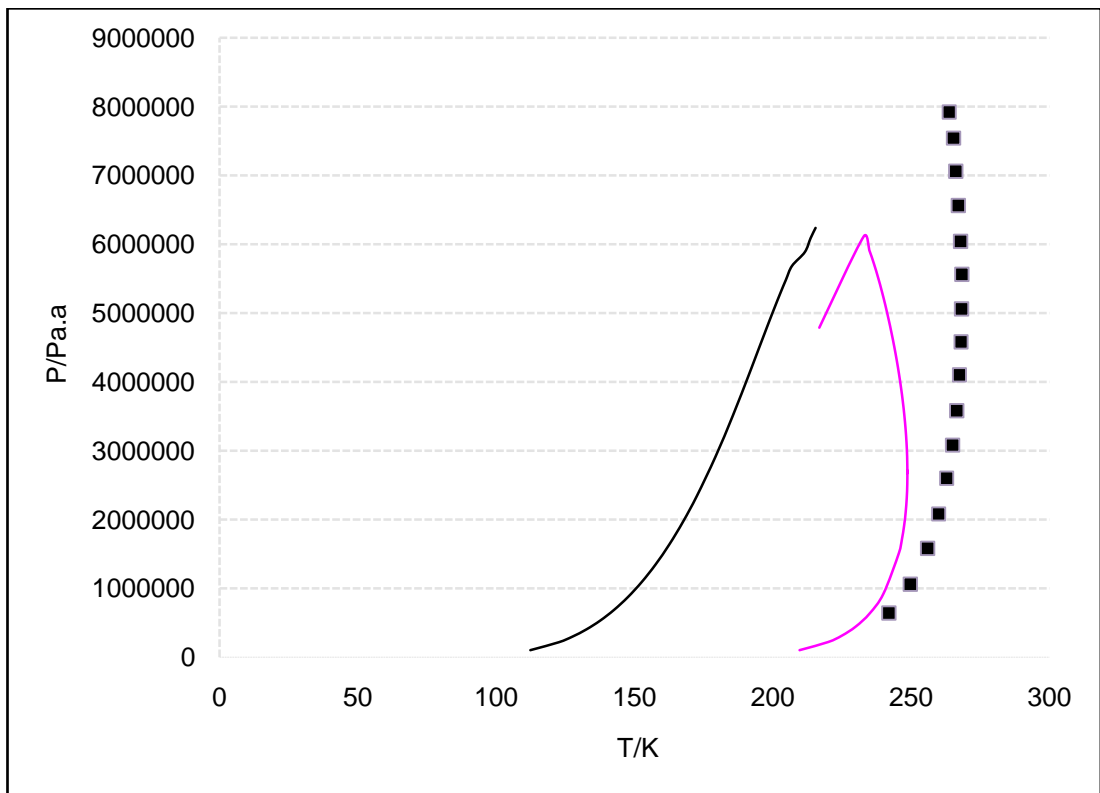
C 46: SET 15-SNG 3; PR-NRTL-WS
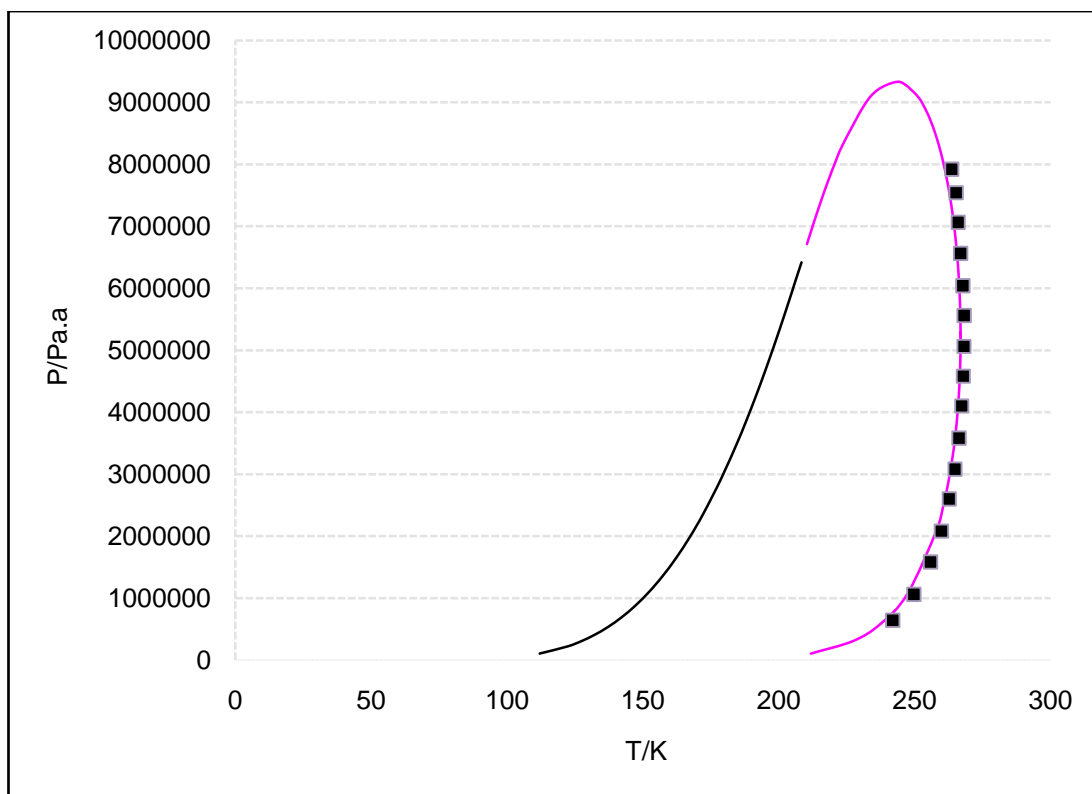
C 47: SET 15-SNG 3; SRK-EXT-VDW
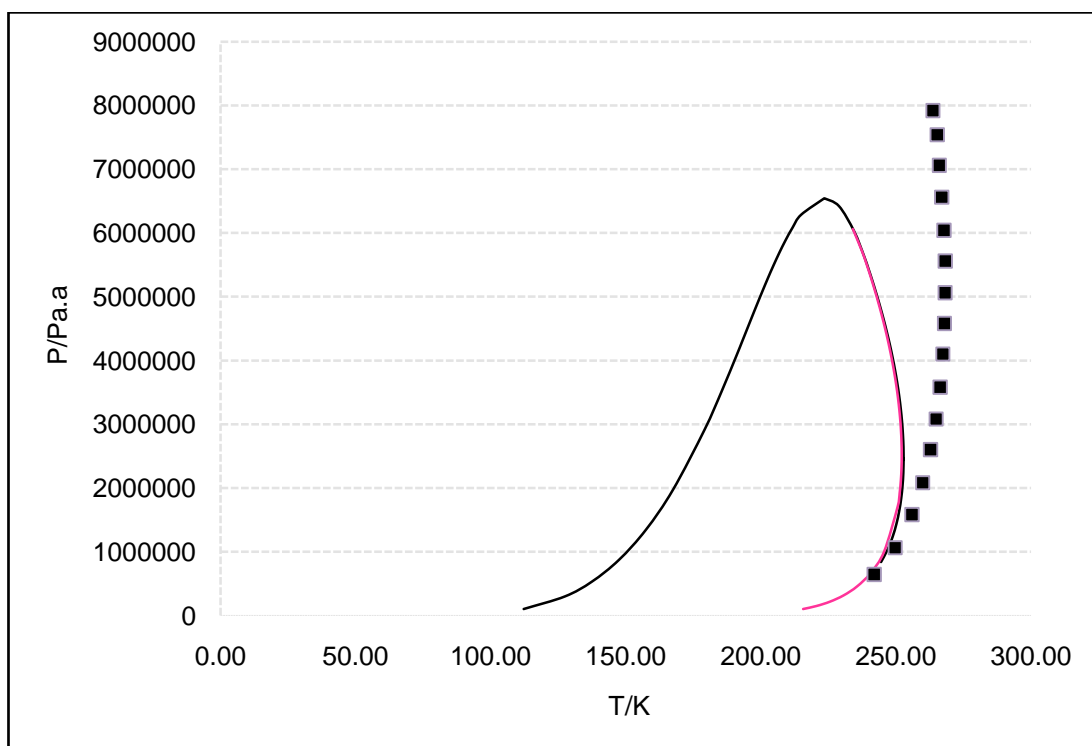
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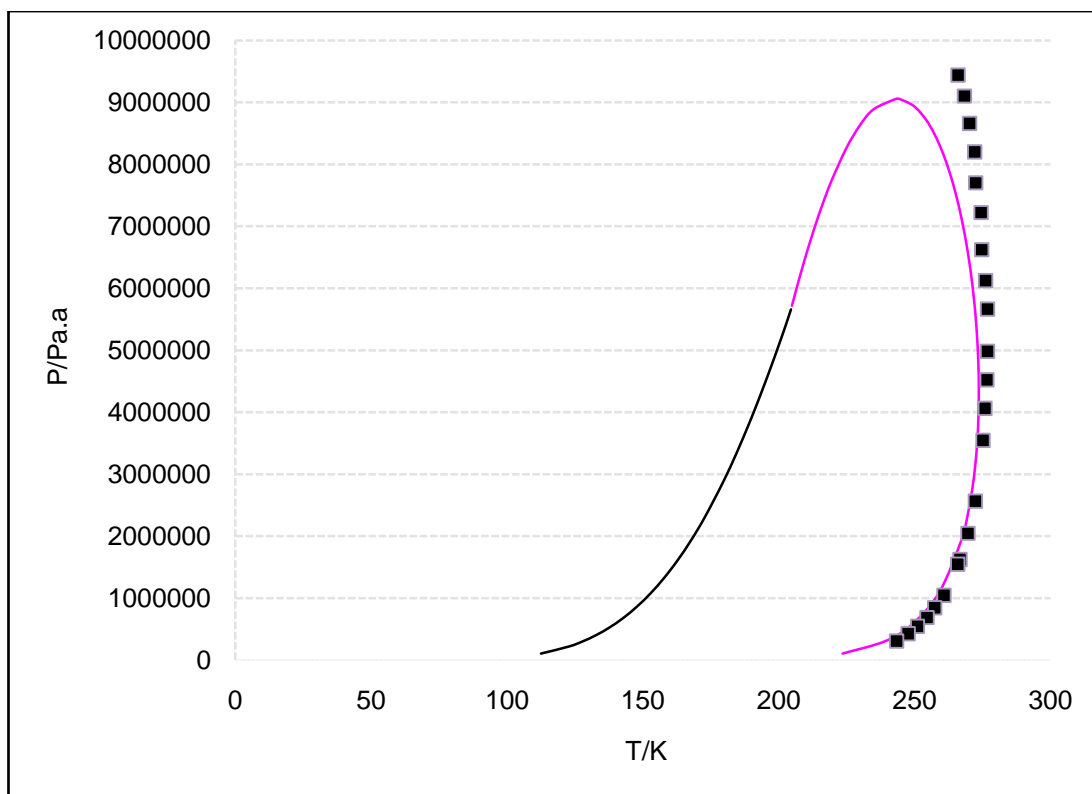
C 49: SET 15-SNG 4; CPA-PR-VDW
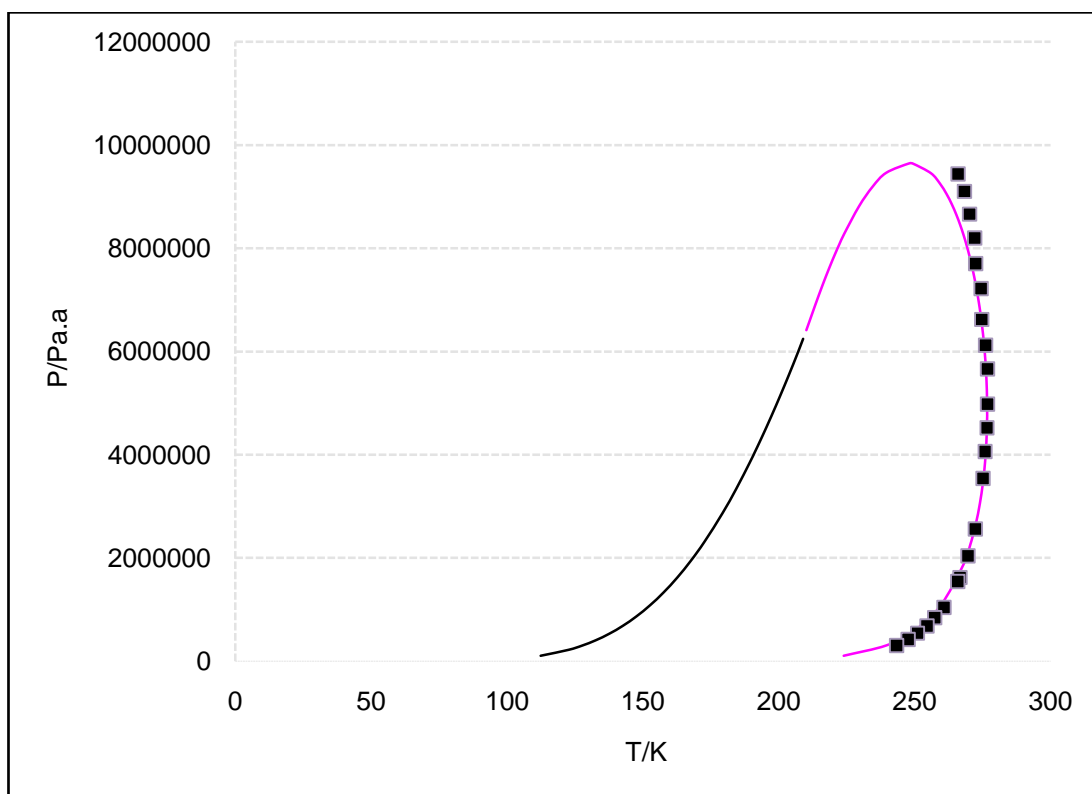
C 50: SET 15-SNG 4; CPA-SRK-VDW

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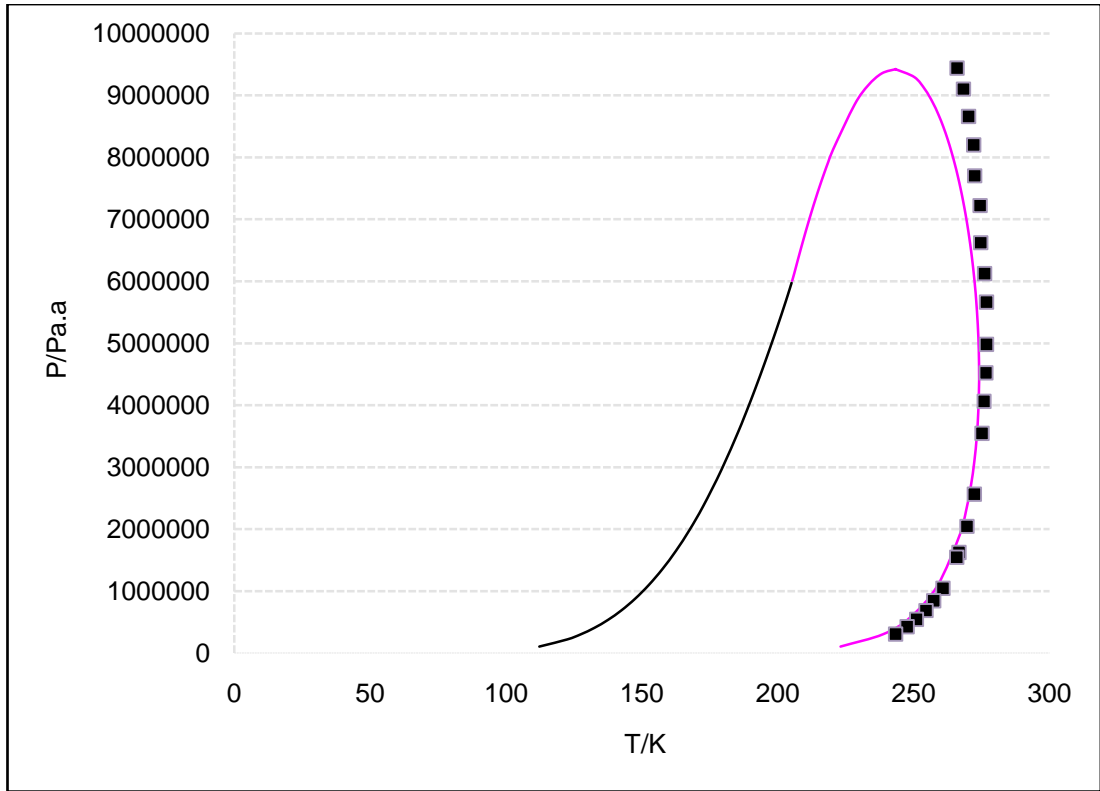
C 51: SET 15-SNG 4; PR-VDW
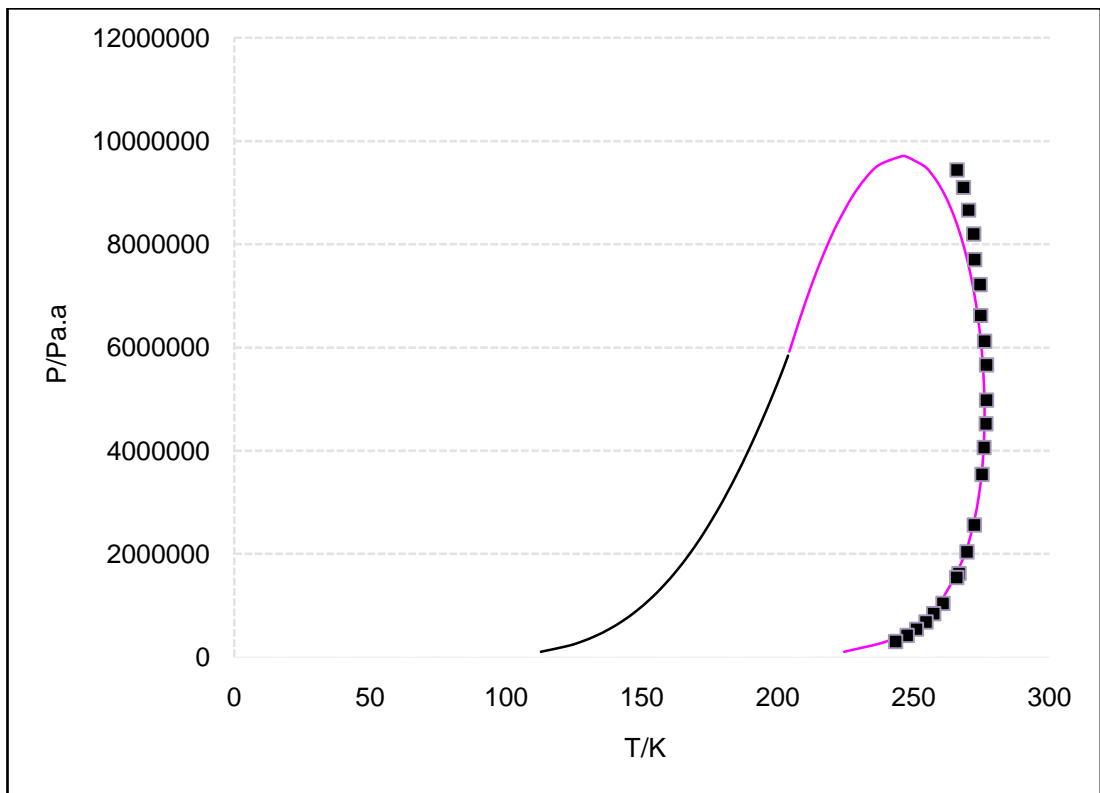
C 52: SET 15-SNG 4; SRK-VDW
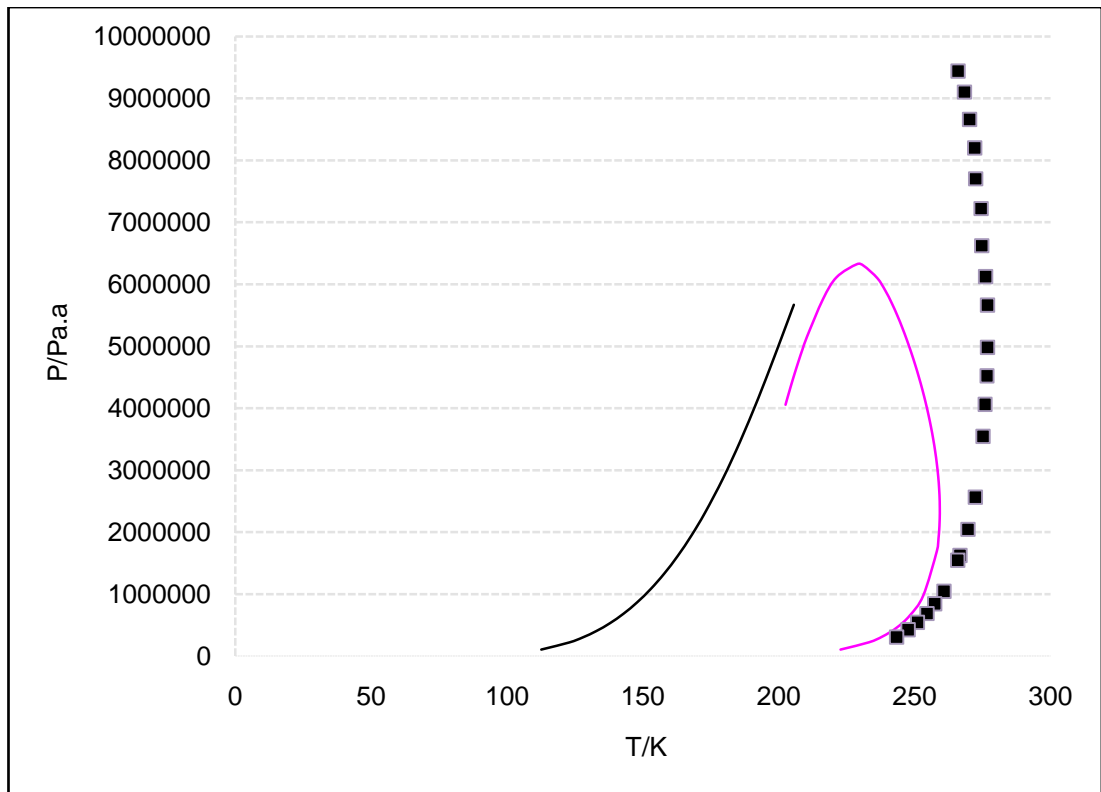
C 53: SET 15-SNG 4; PR-UNIQUAC-WS
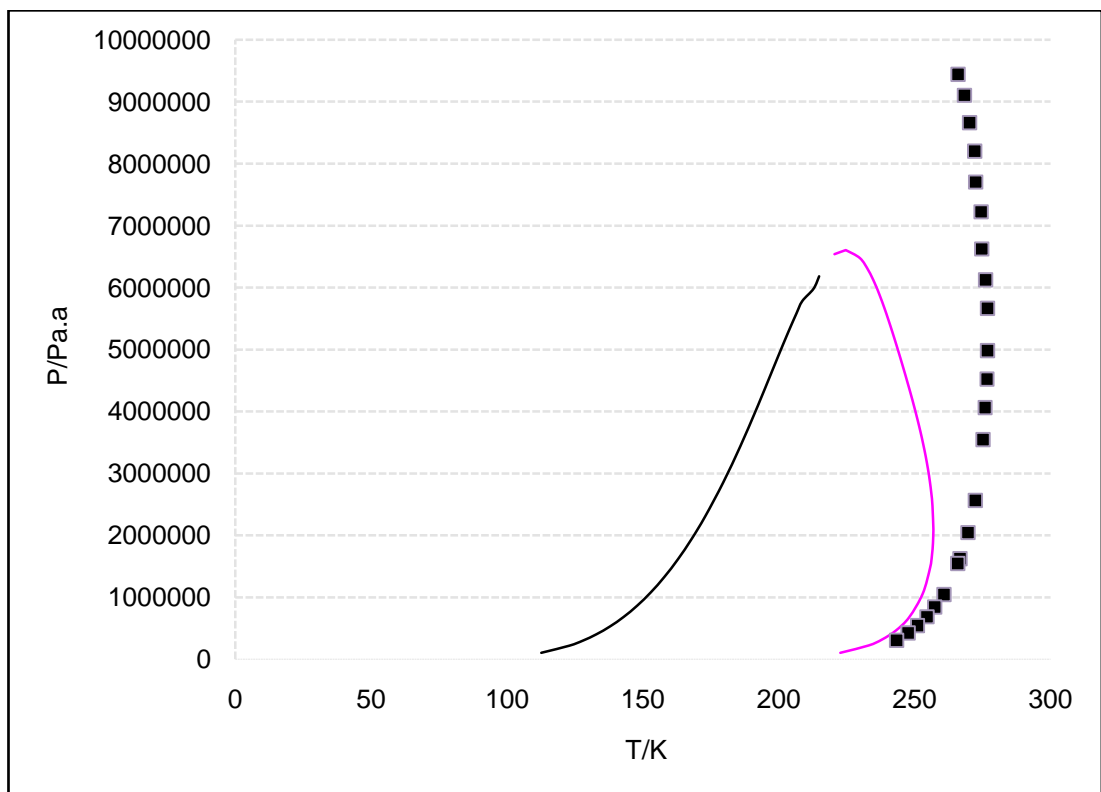
C 54: SET 15-SNG 4; PR-NRTL-WS
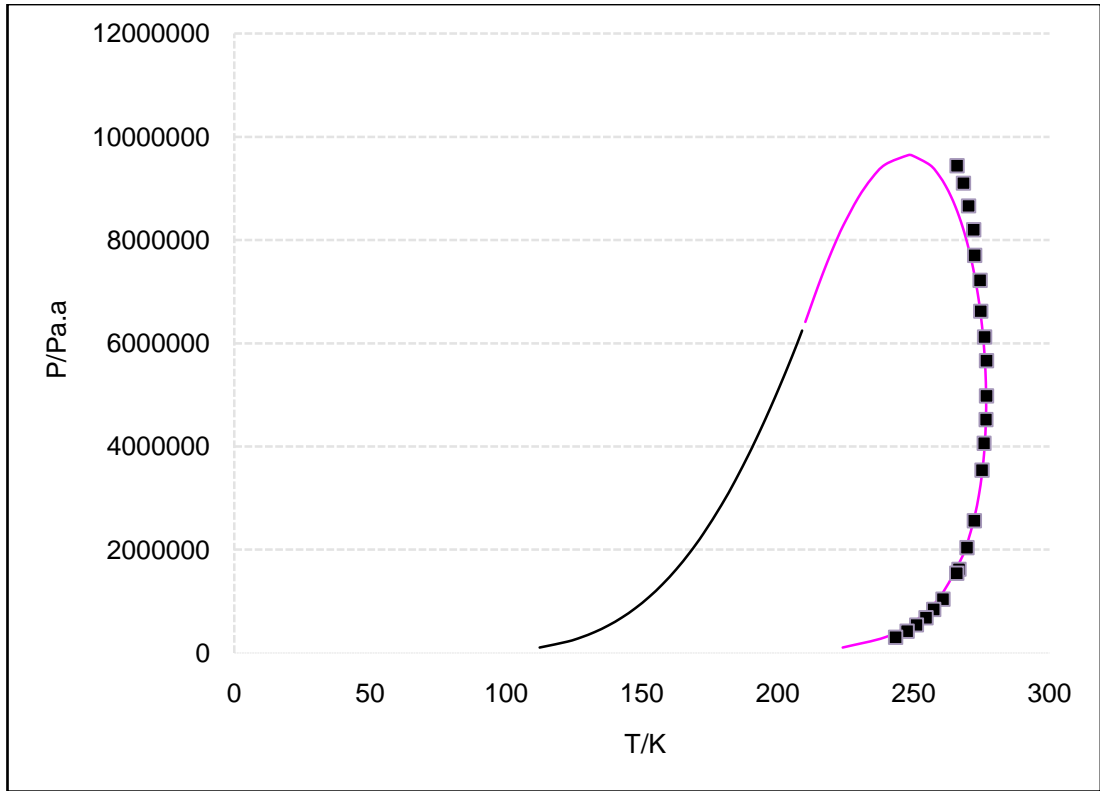
C 55: SET 15-SNG 4; SRK-EXT-VDW
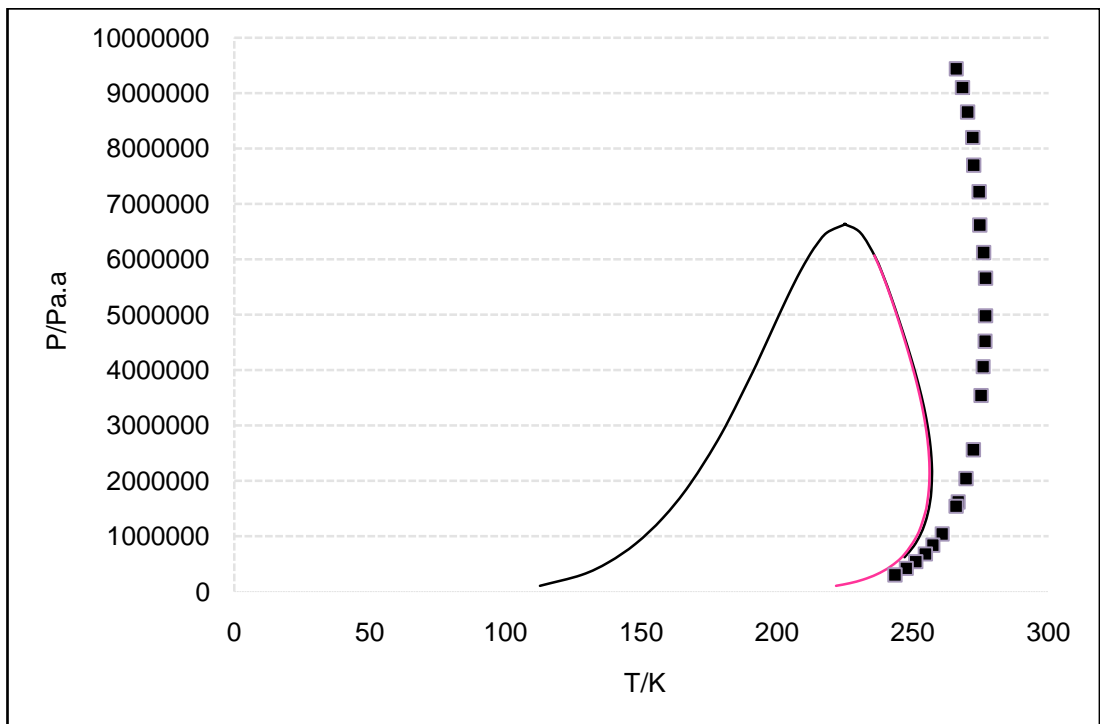
C 56: SET 15-SNG 4; PR-WS

150
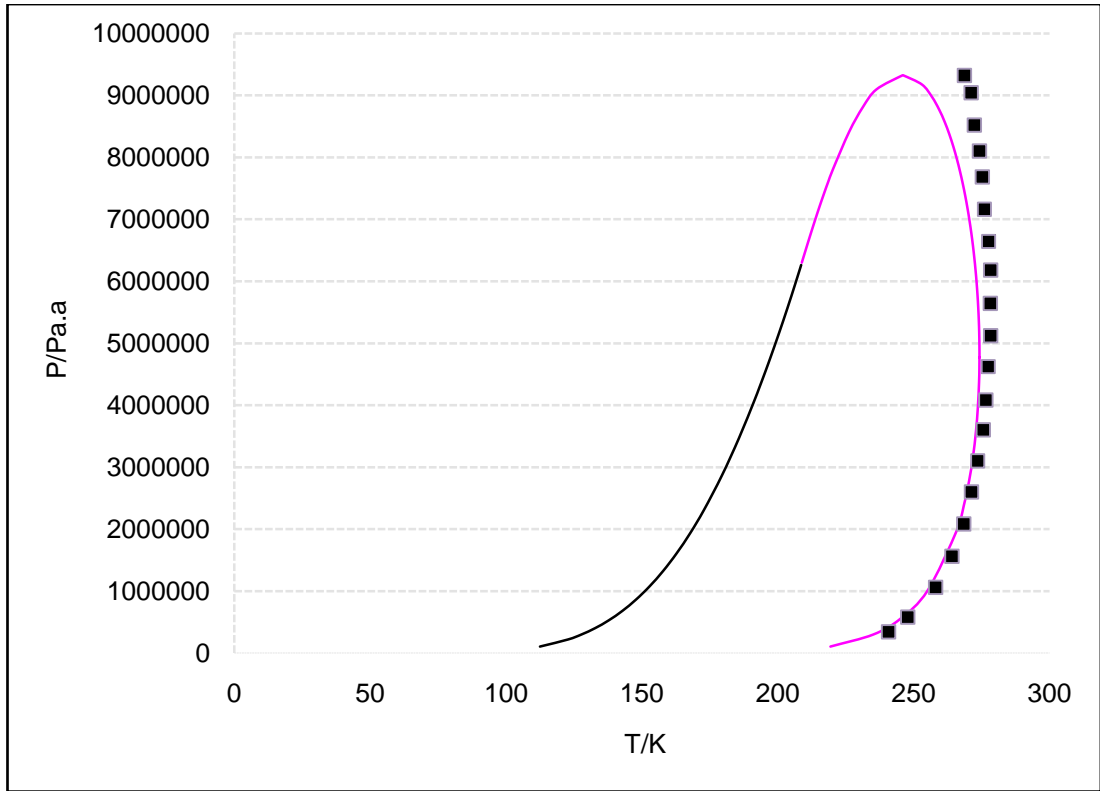
C 57: SET 15-SNG 5; CPA-PR-VDW
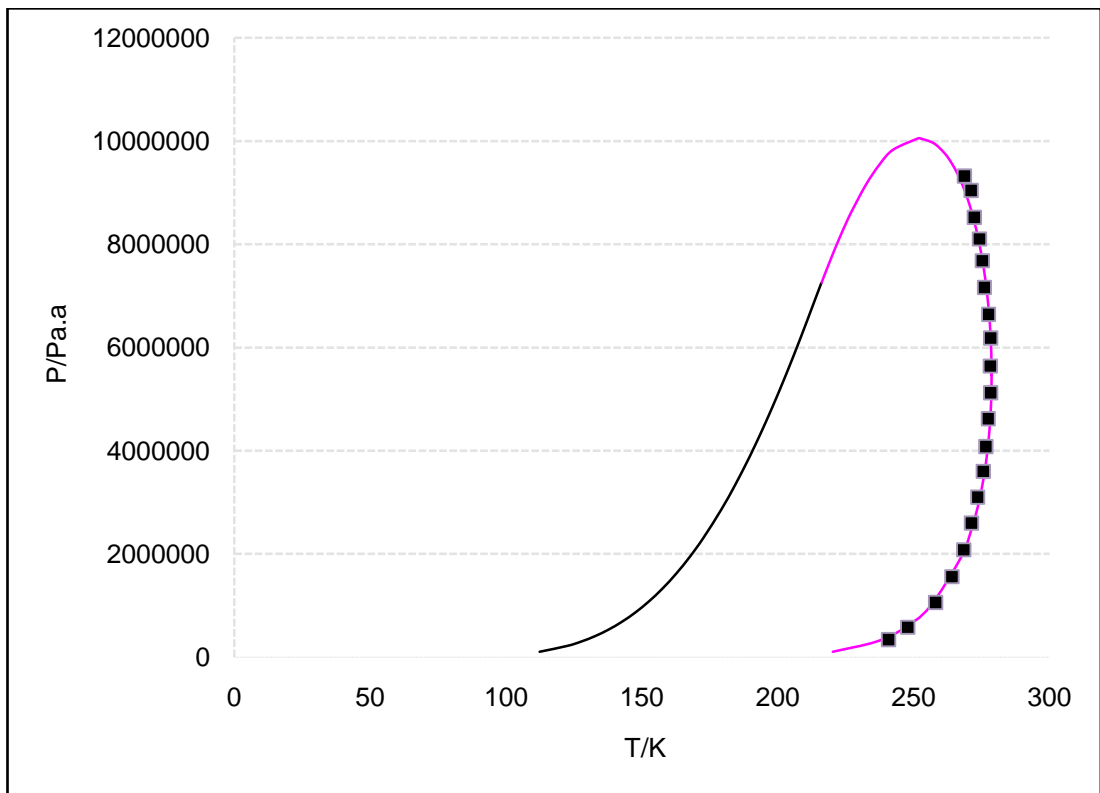
C 58: SET 15-SNG 5; CPA-SRK-VDW

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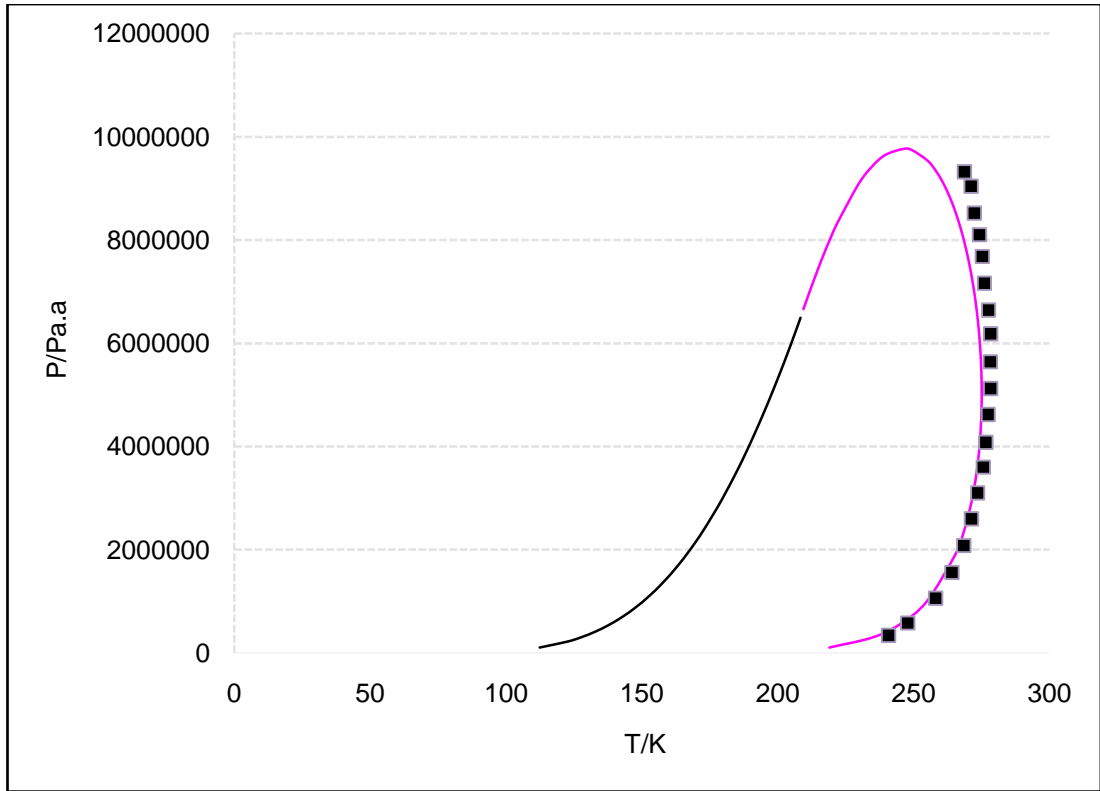
C 59: SET 15-SNG 5; PR-VDW
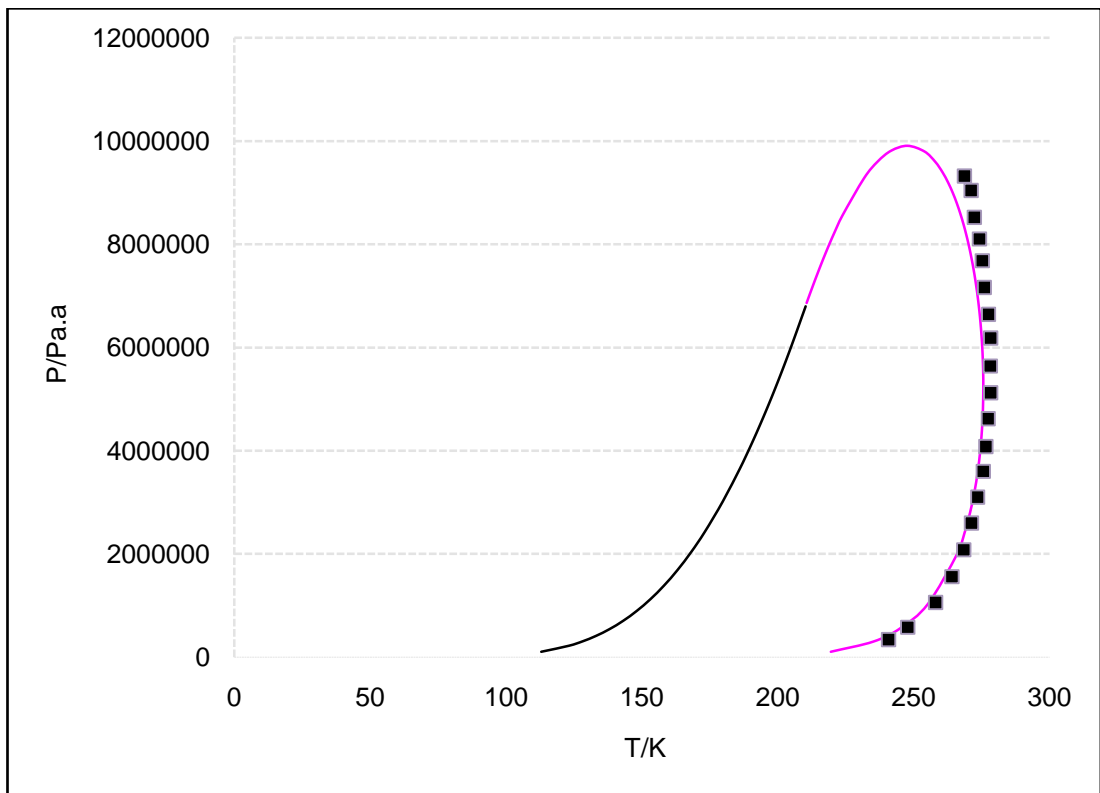
C 60: SET 15-SNG 5; SRK-VDW
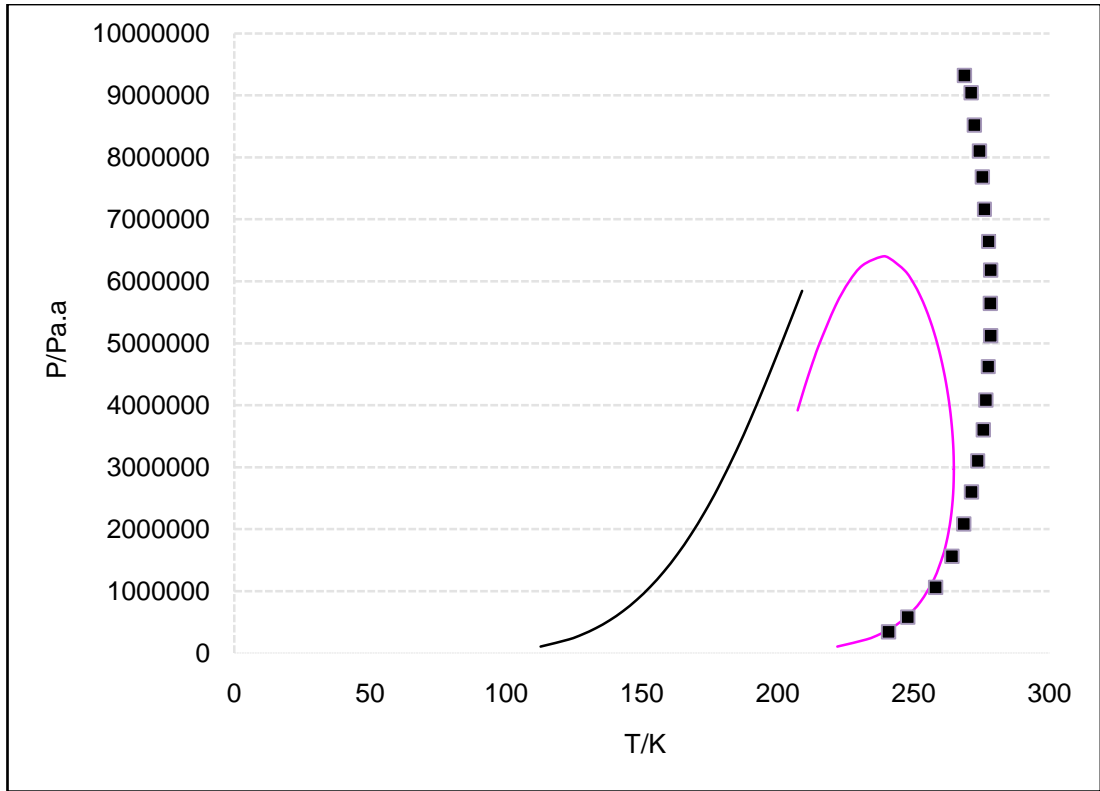
C 61: SET 15-SNG 5; PR-UNIQUAC-WS
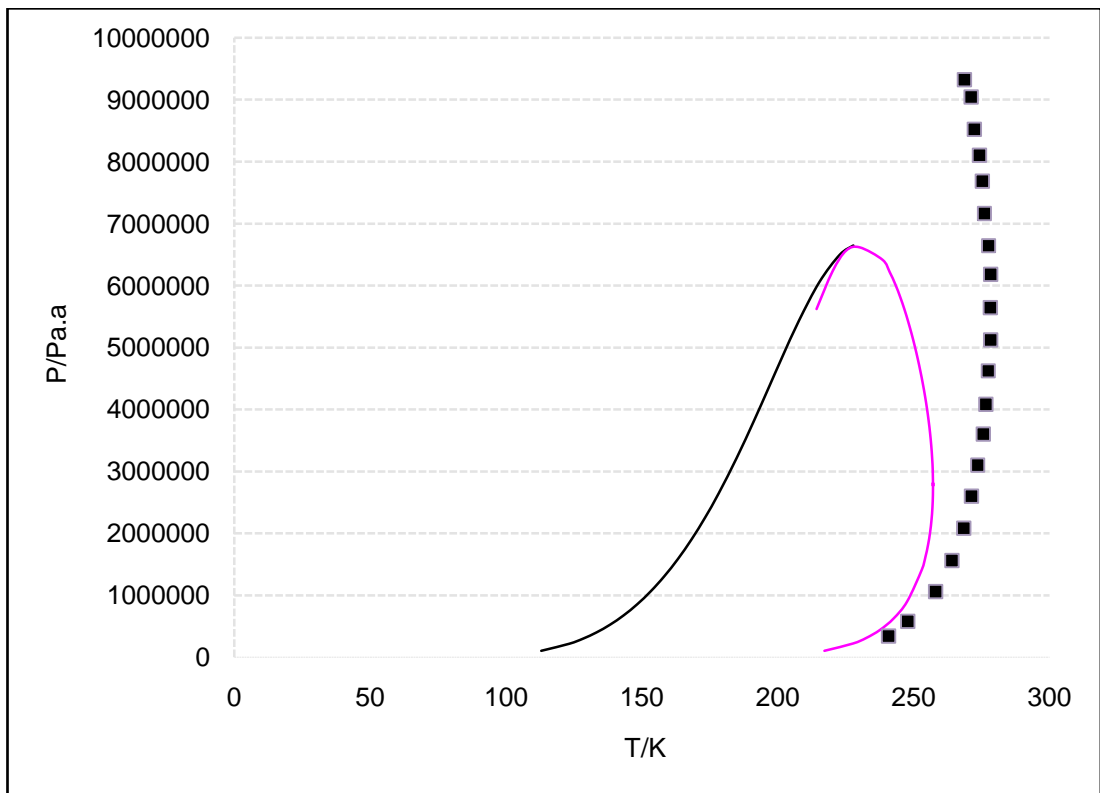
C 62**:** SET 15-SNG 5; PR-NRTL-WS
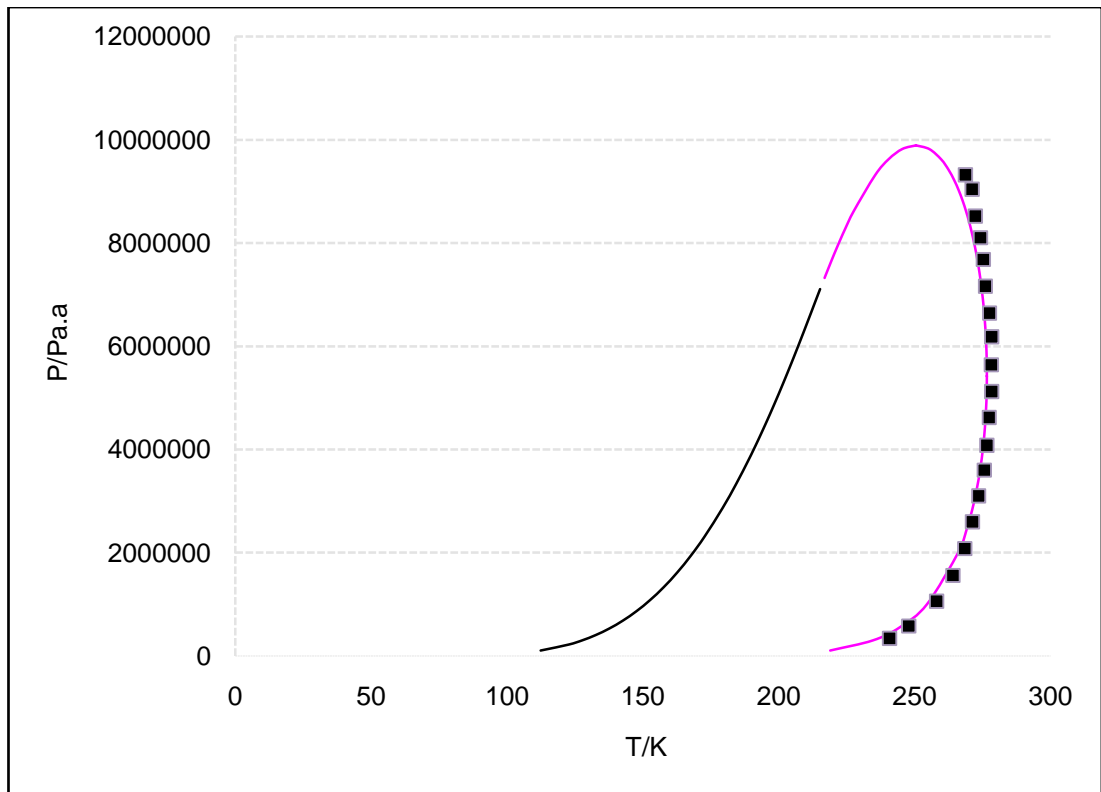
C 63: SET 15-SNG 5; SRK-EXT-VDW
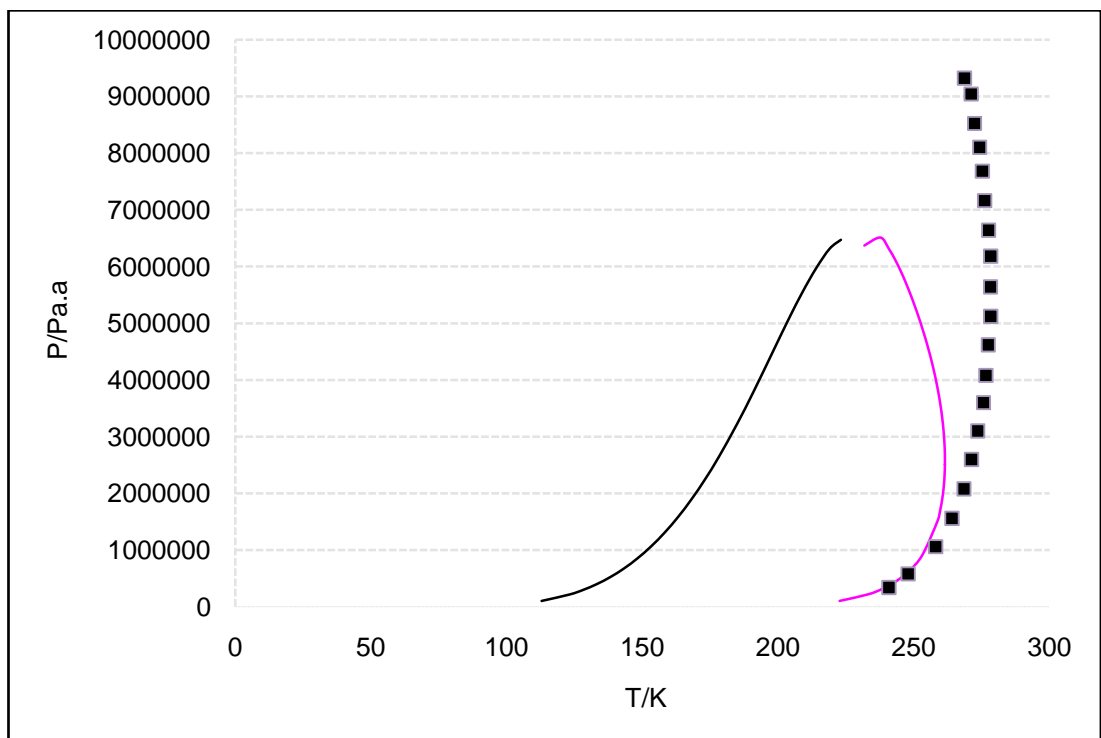
C 64: SET 15-SNG 5; PR-WS

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In conjunction with the results calculated in chapter 4 for the set 18, most of the figures ranging from 4.19 to 4.25 are derived from the individual phase behaviour calculated as shown in the Appendix D.
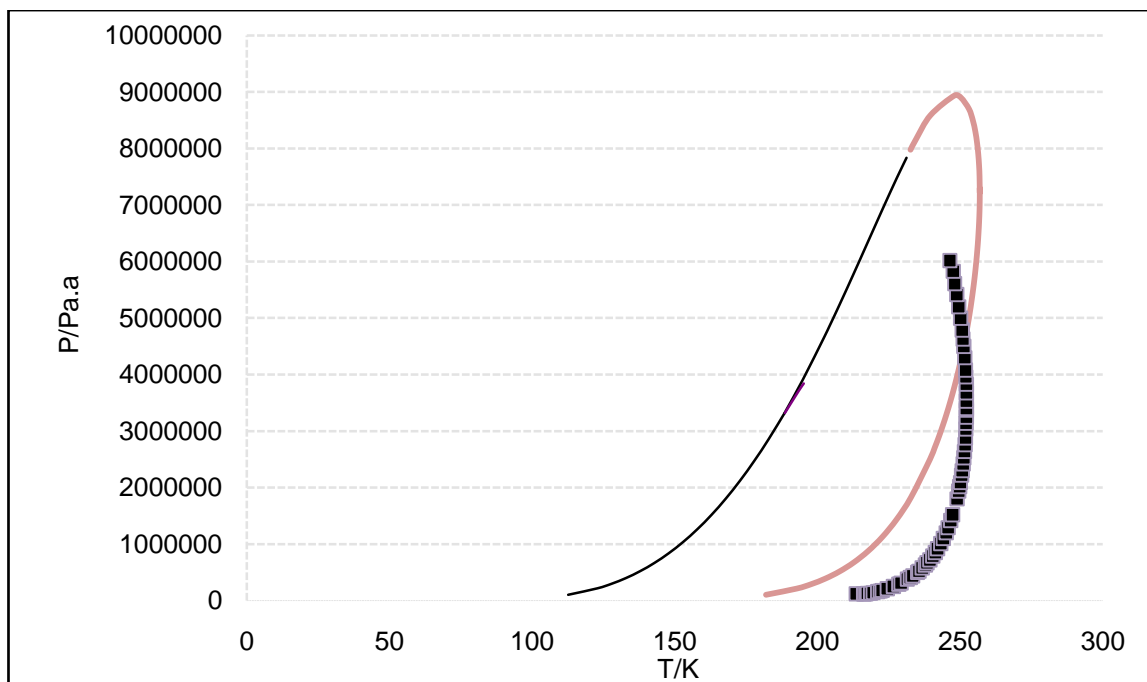
D 1: SET 18-SNG 1; CPA-PR-VDW
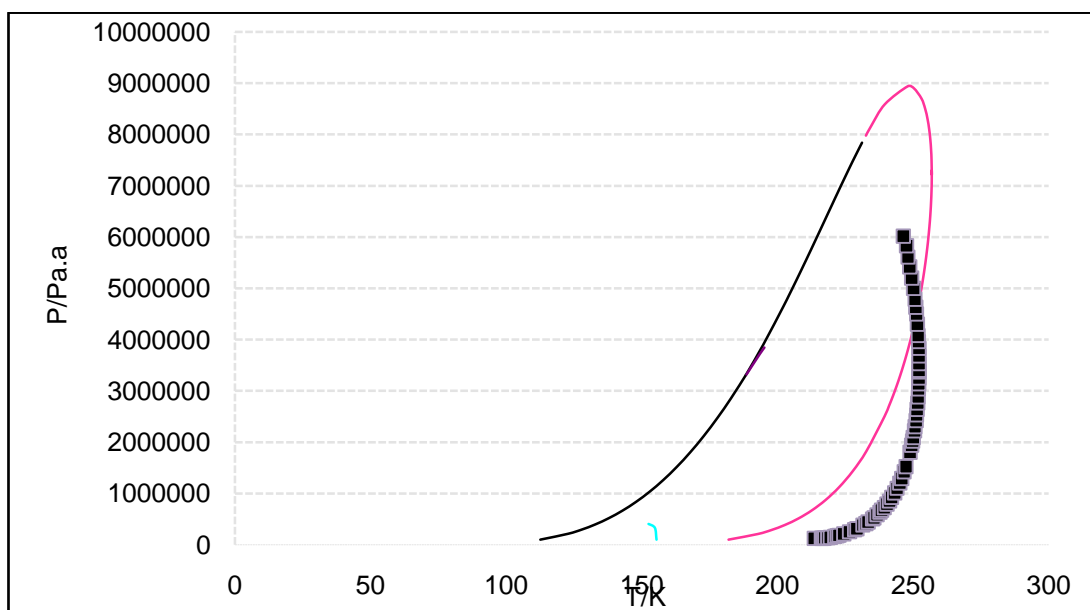
D 2**:** SET 18-SNG 1; CPA-SRK-VDW
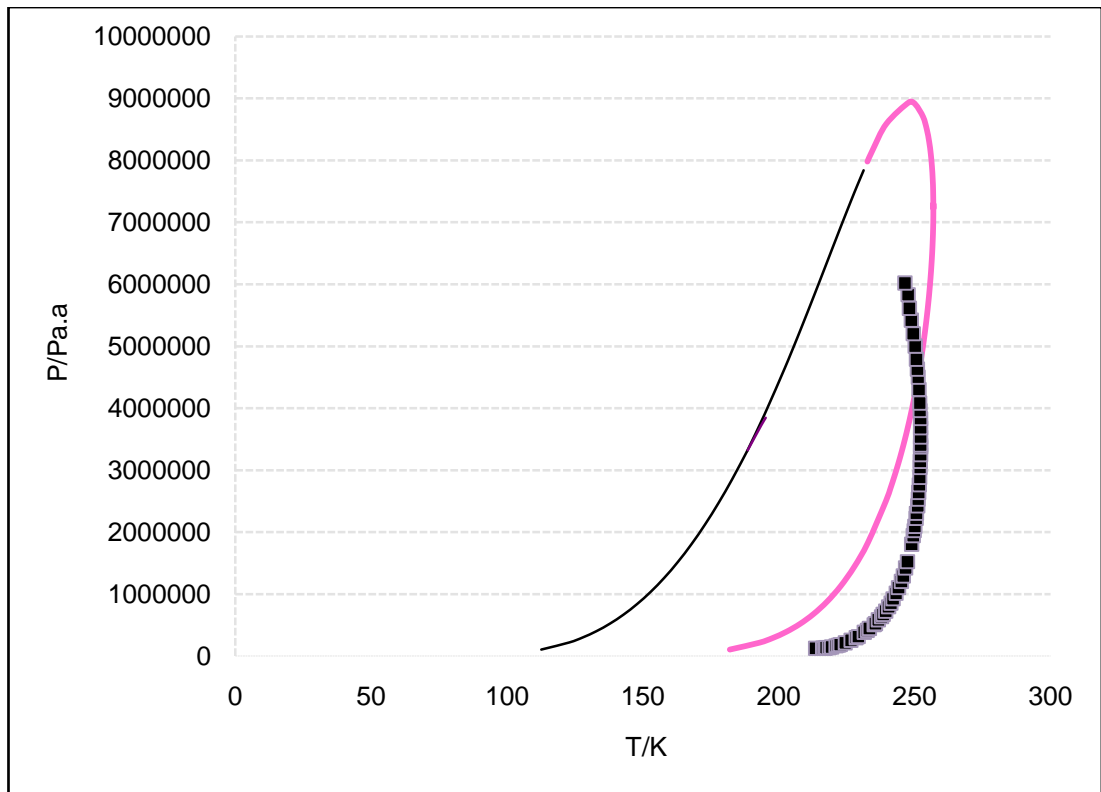
D 3: SET 18-SNG 1; PR-VDW
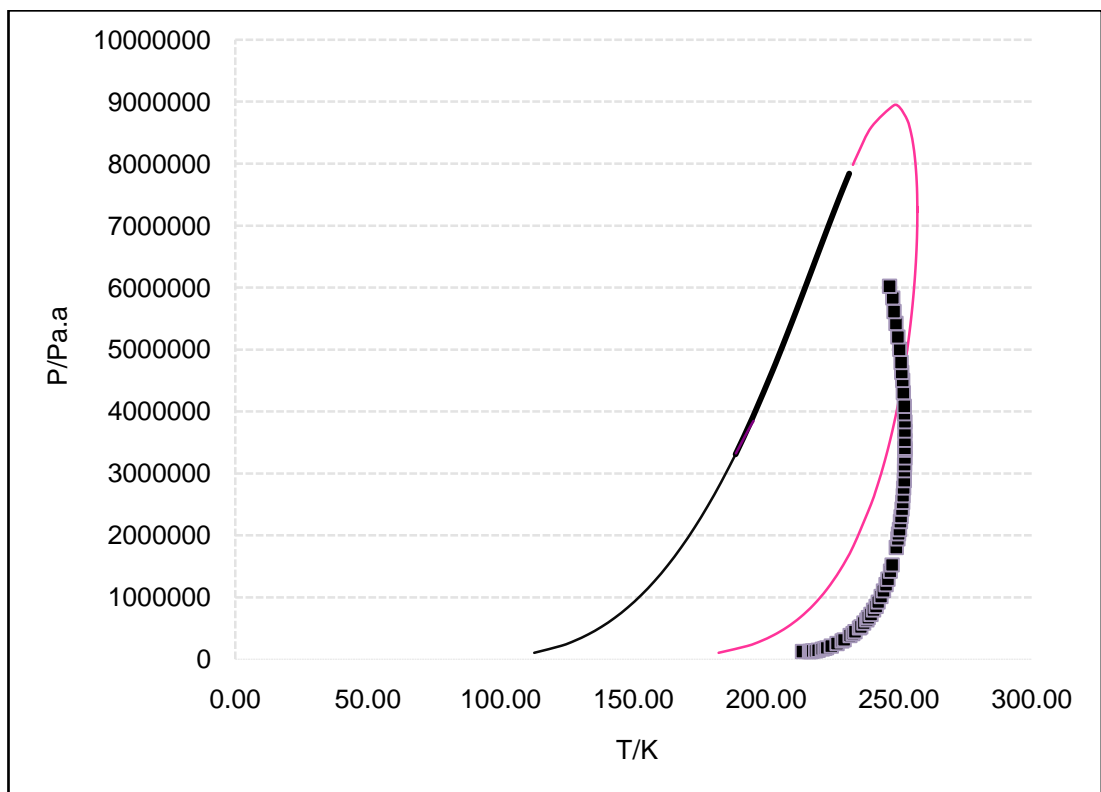
D 4: SET 18-SNG 1; SRK-VDW

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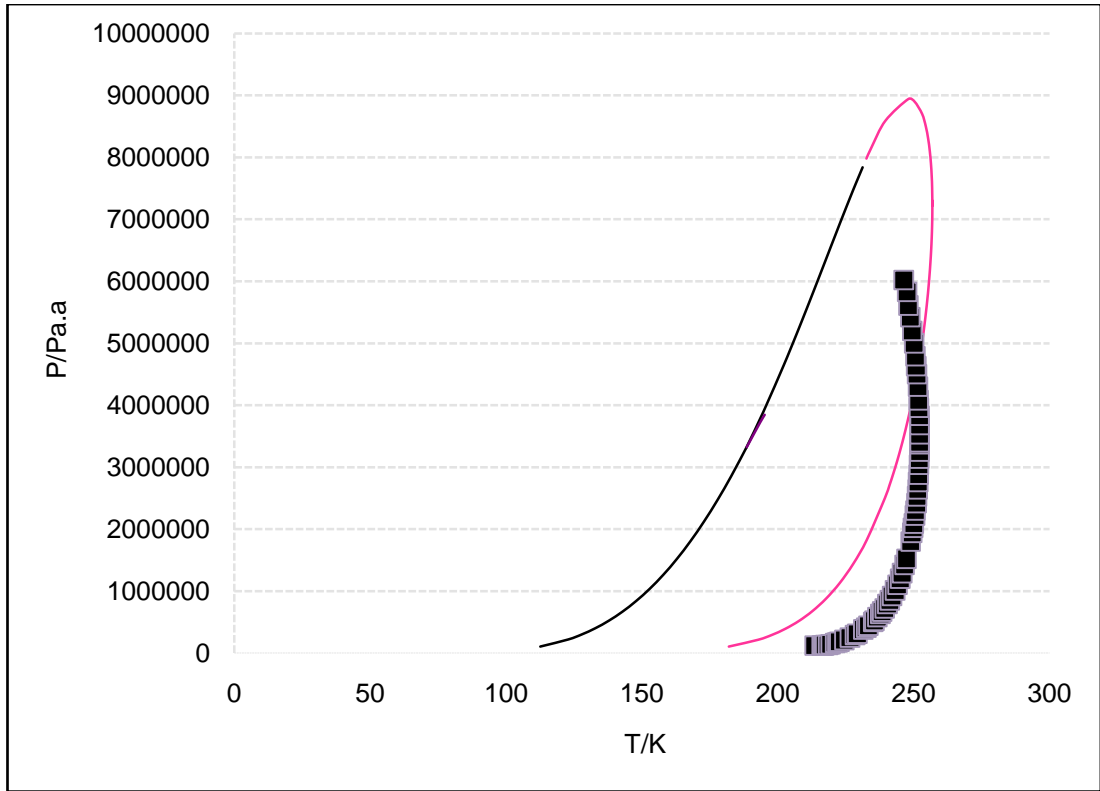
D 5: SET 18-SNG 1; PR-UNIQUAC-WS
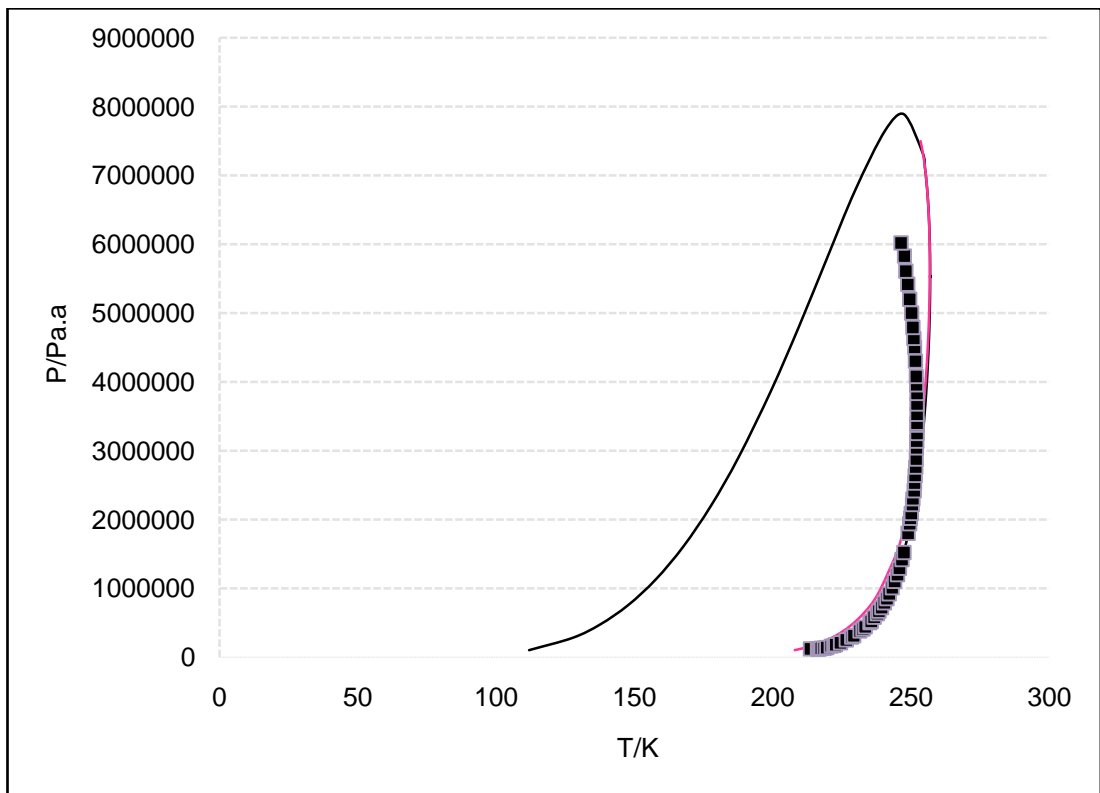
D 6: SET 18-SNG 1; PR-NRTL-WS
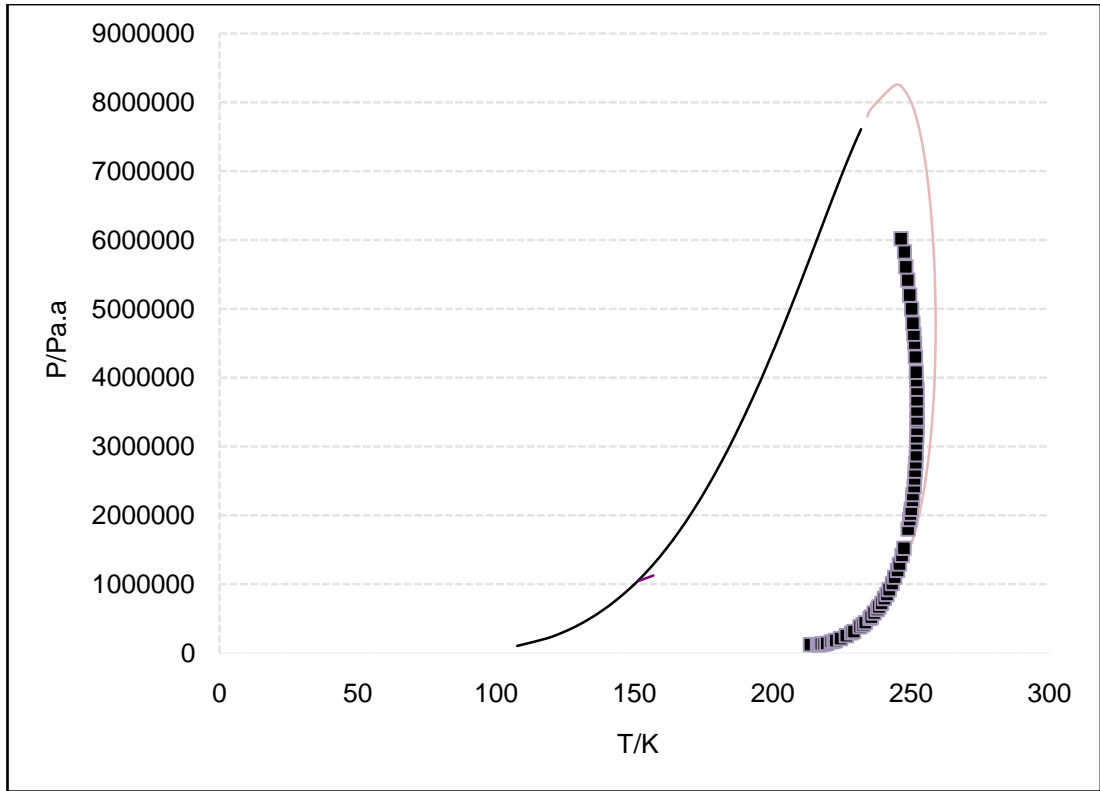
D 7: SET 18-SNG 1; SRK-EXT-VDW
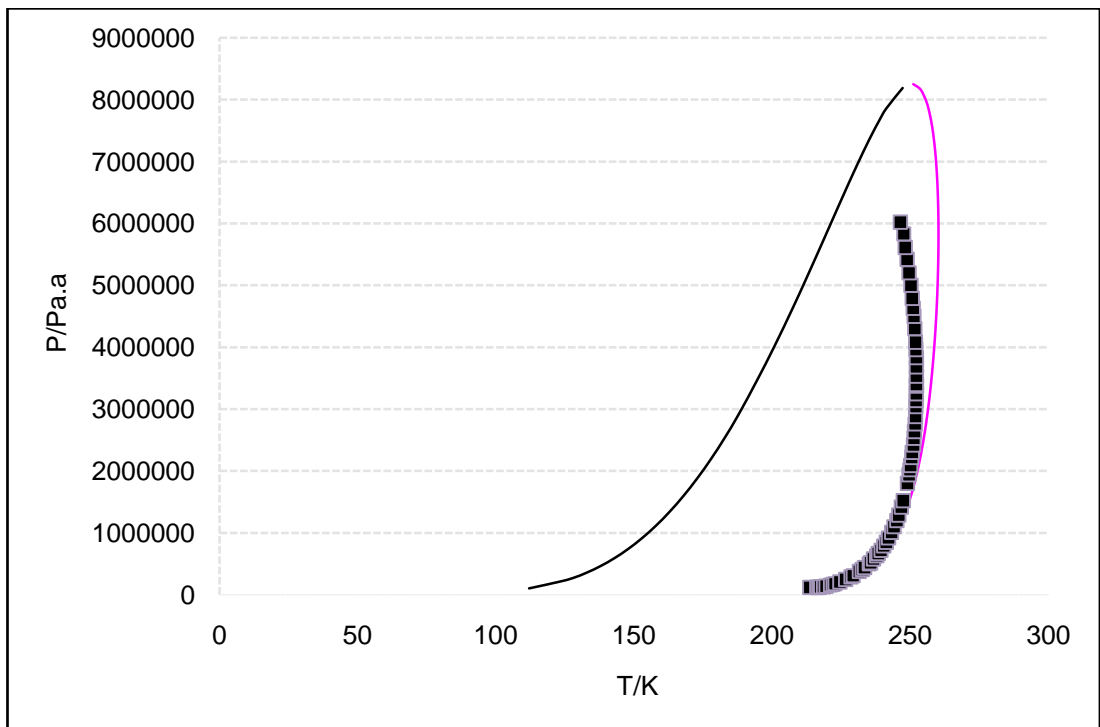
D 8: SET 18-SNG 1; PR-WS
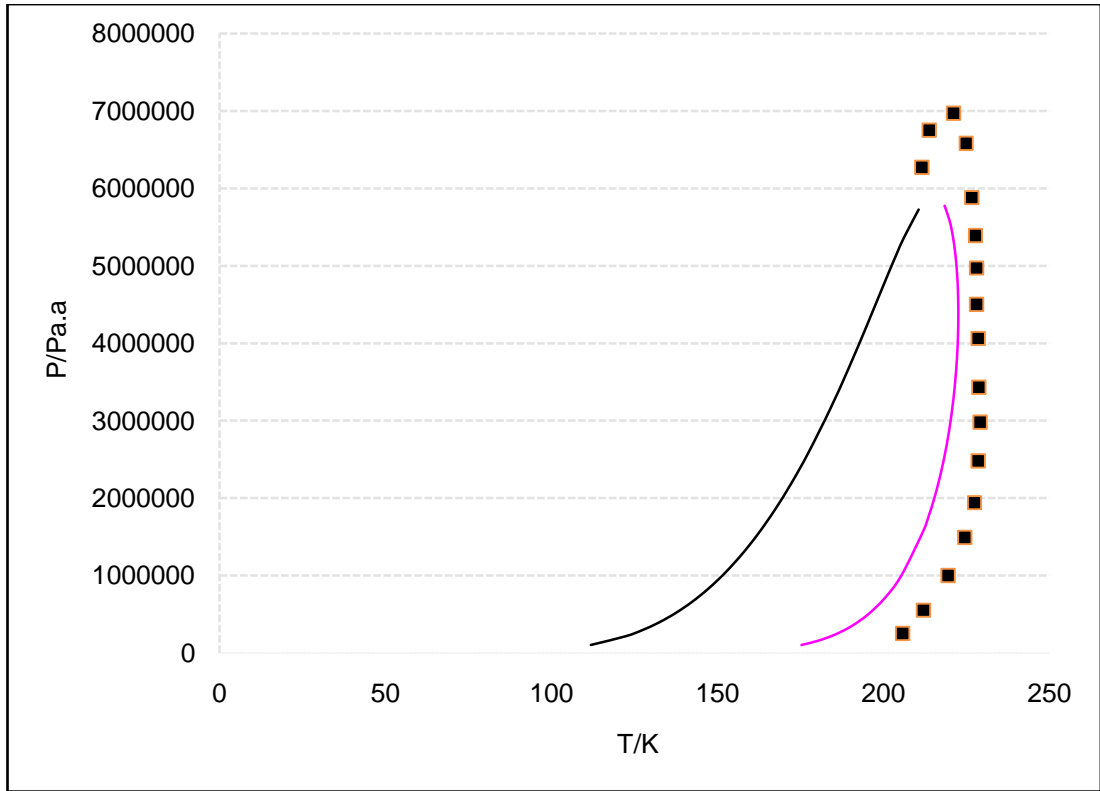
D 9: SET 18-SNG 2; CPA-PR-VDW
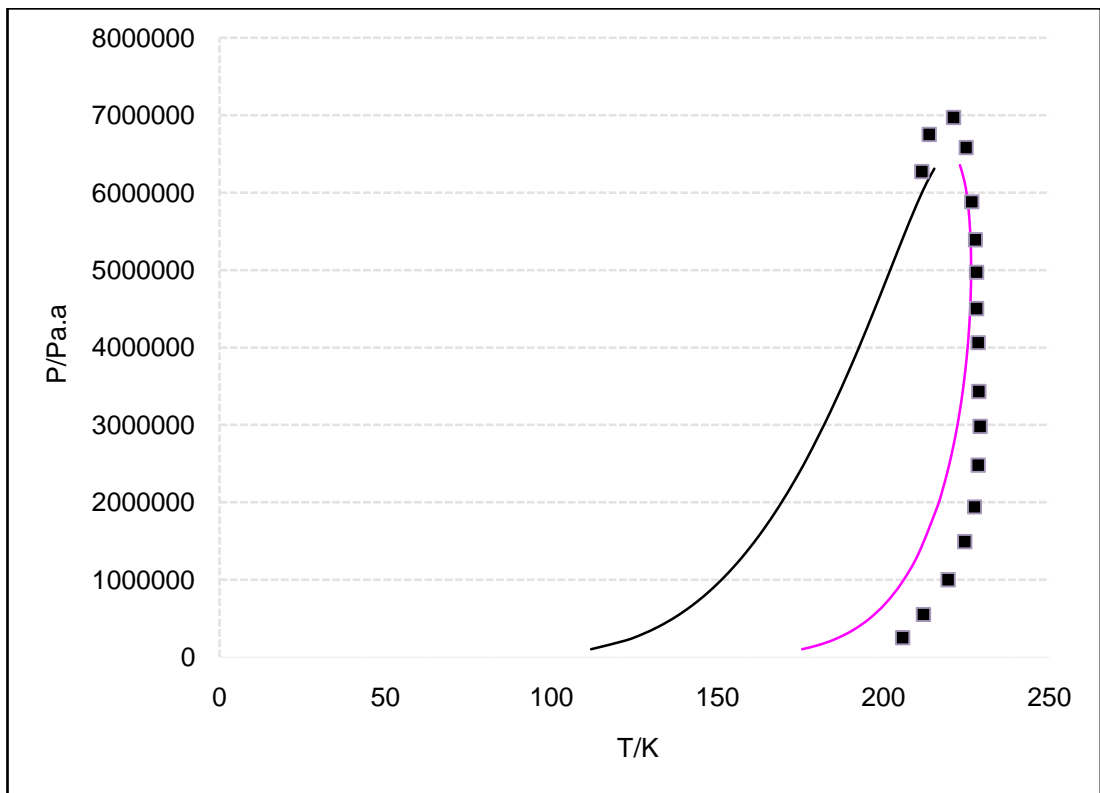
D 10: SET 18-SNG 2; CPA-SRK-VDW
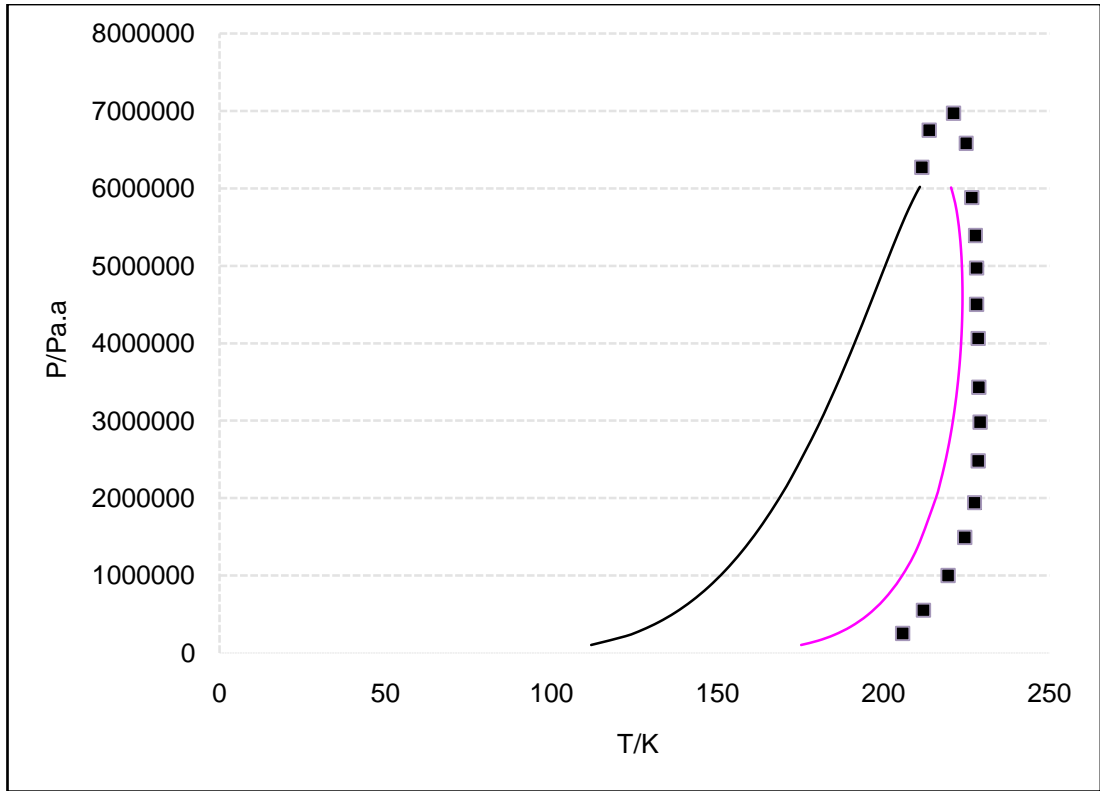
D 11: SET 18-SNG 2; PR-VDW
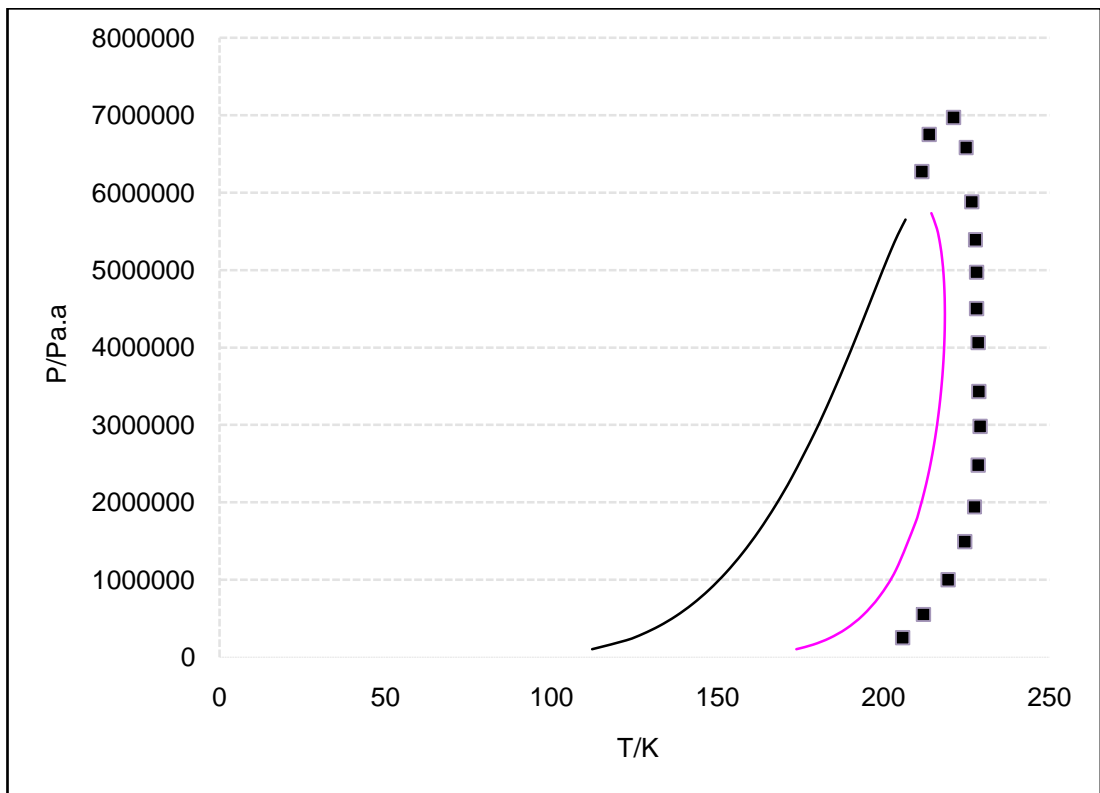
D 12: SET 18-SNG 2; SRK-VDW
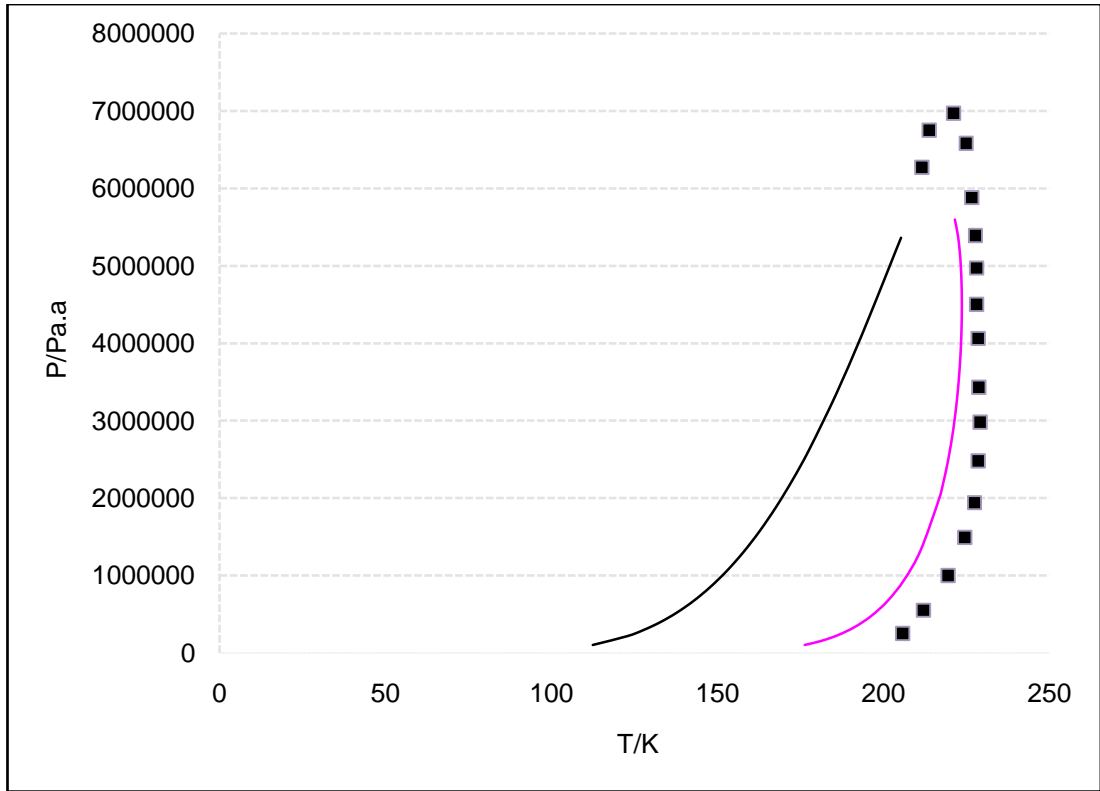
D 13: SET 18-SNG 2; PR-UNIQUAC-WS
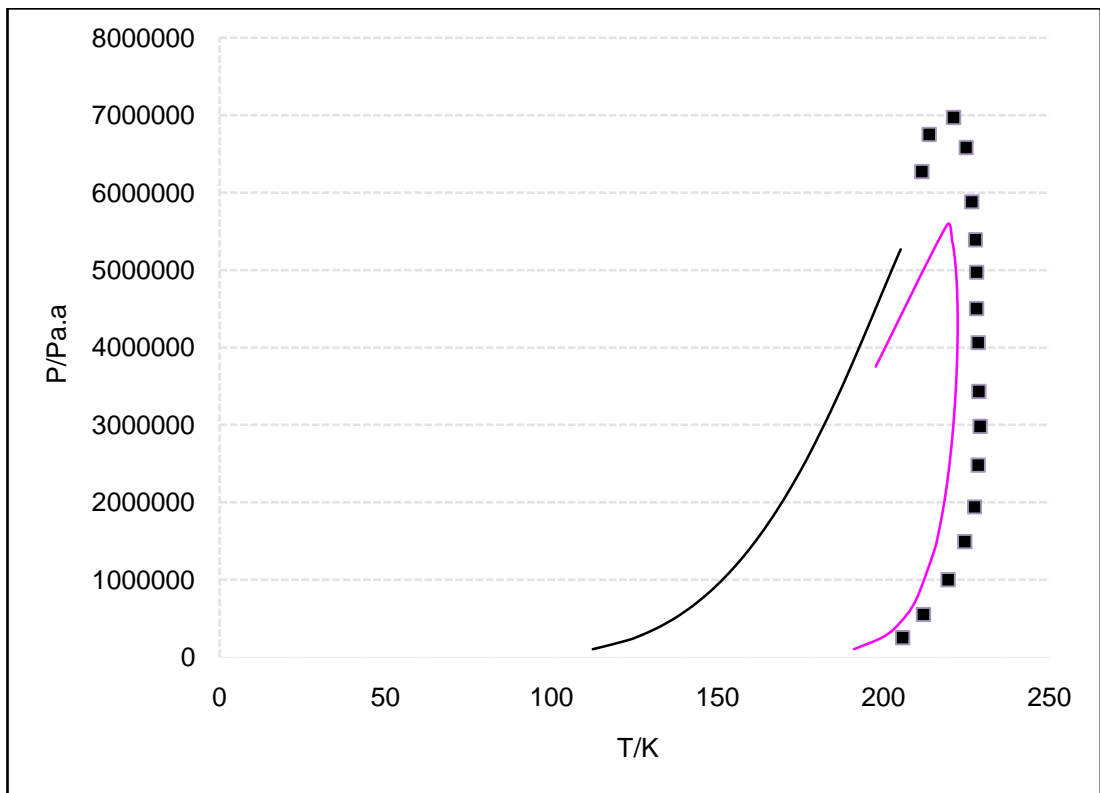
D 14: SET 18-SNG 2; PR-NRTL-WS
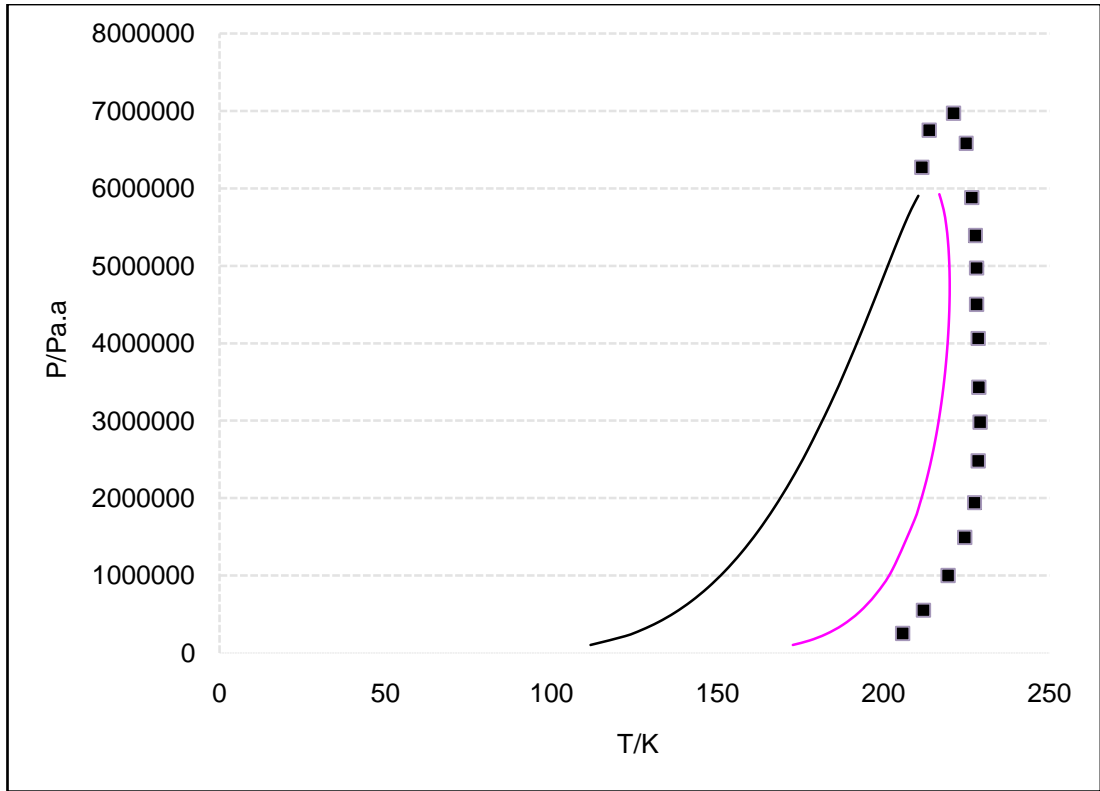
D 15: SET 18-SNG 2; SRK-EXT-VDW
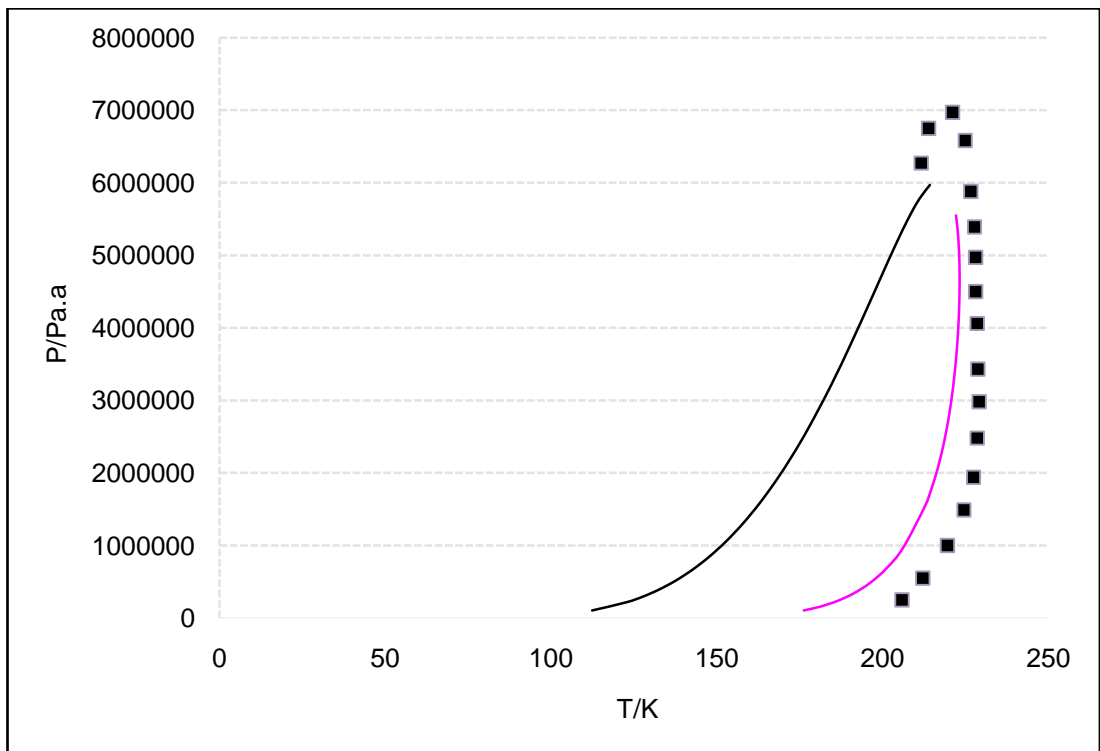
D 16: SET 18-SNG 2; PR-WS
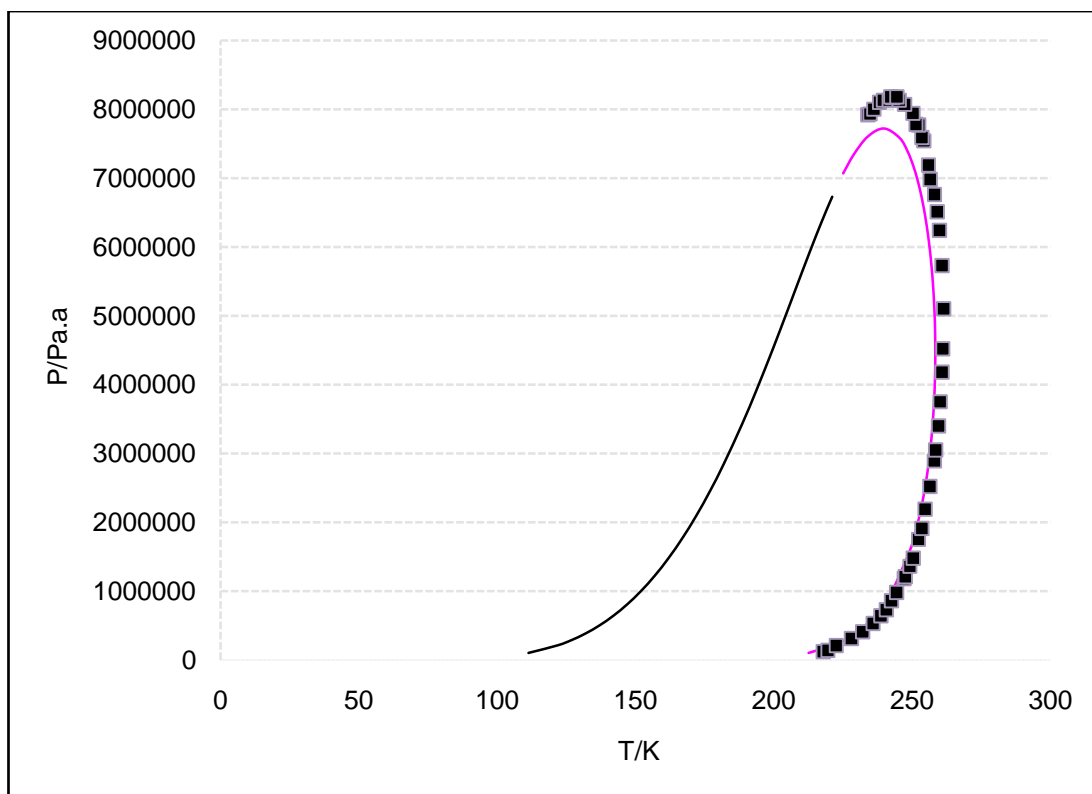
D 17: SET 18-SNG 3; CPA-PR-VDW
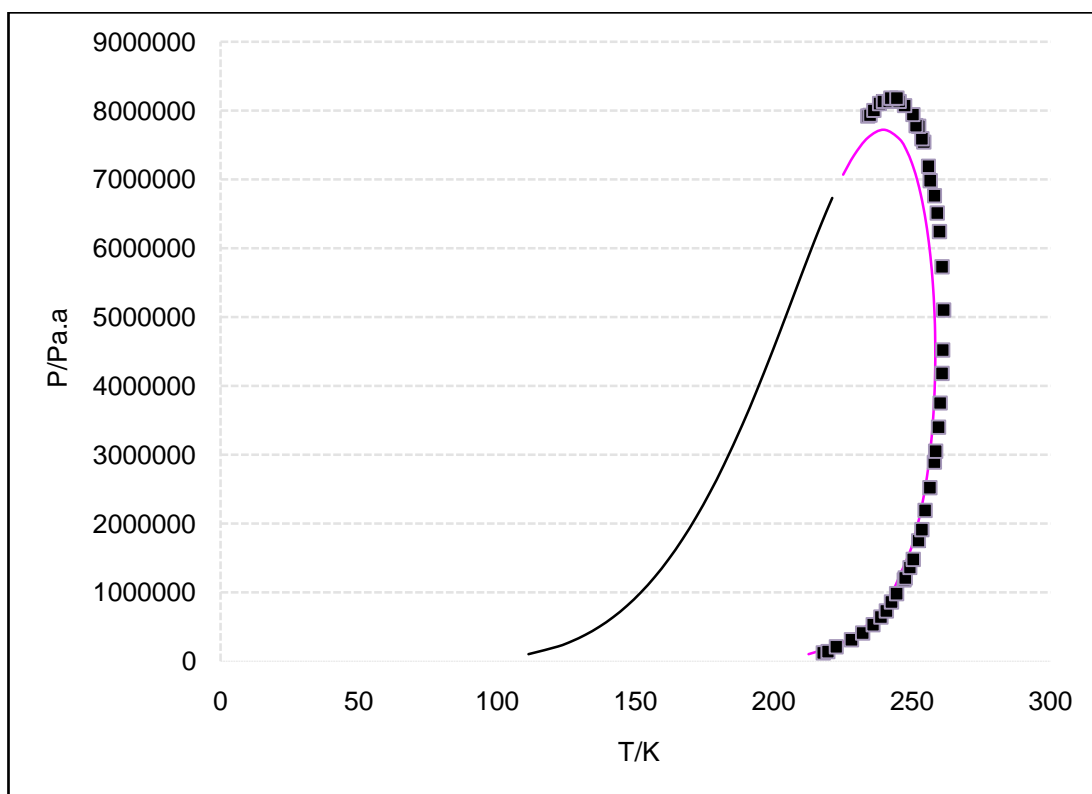
D 18: SET 18-SNG 3; CPA-SRK-VDW

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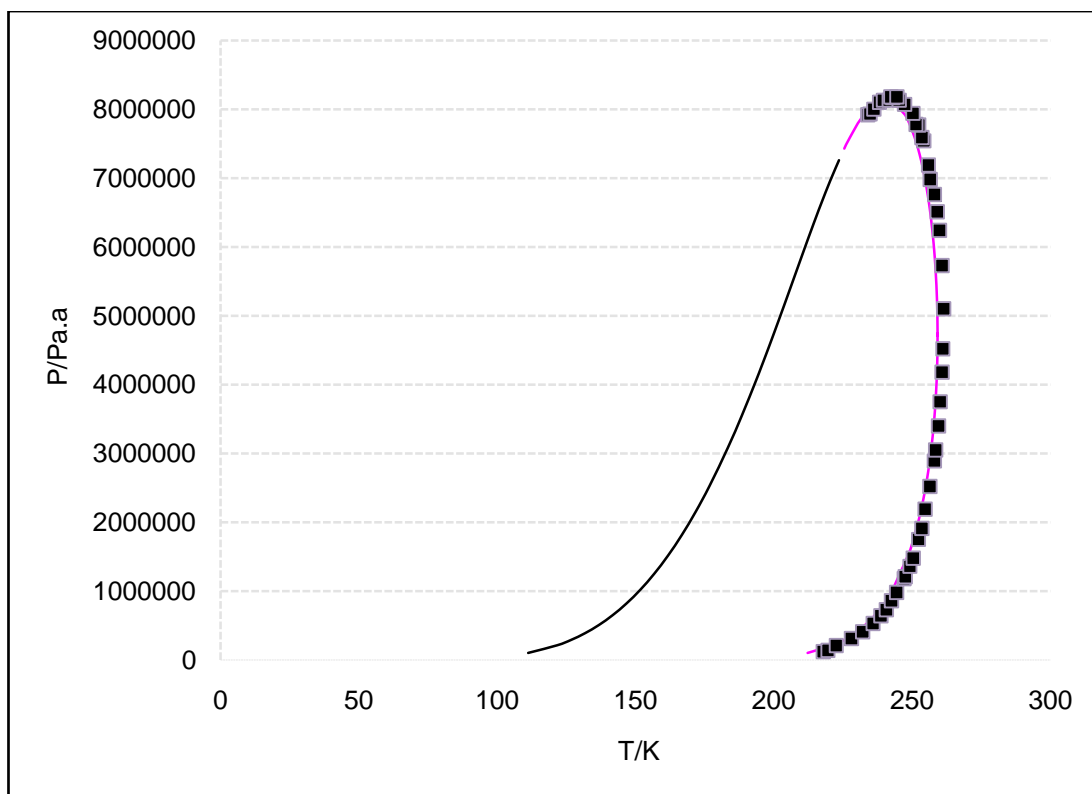
D 19: SET 18-SNG 3; PR-VDW
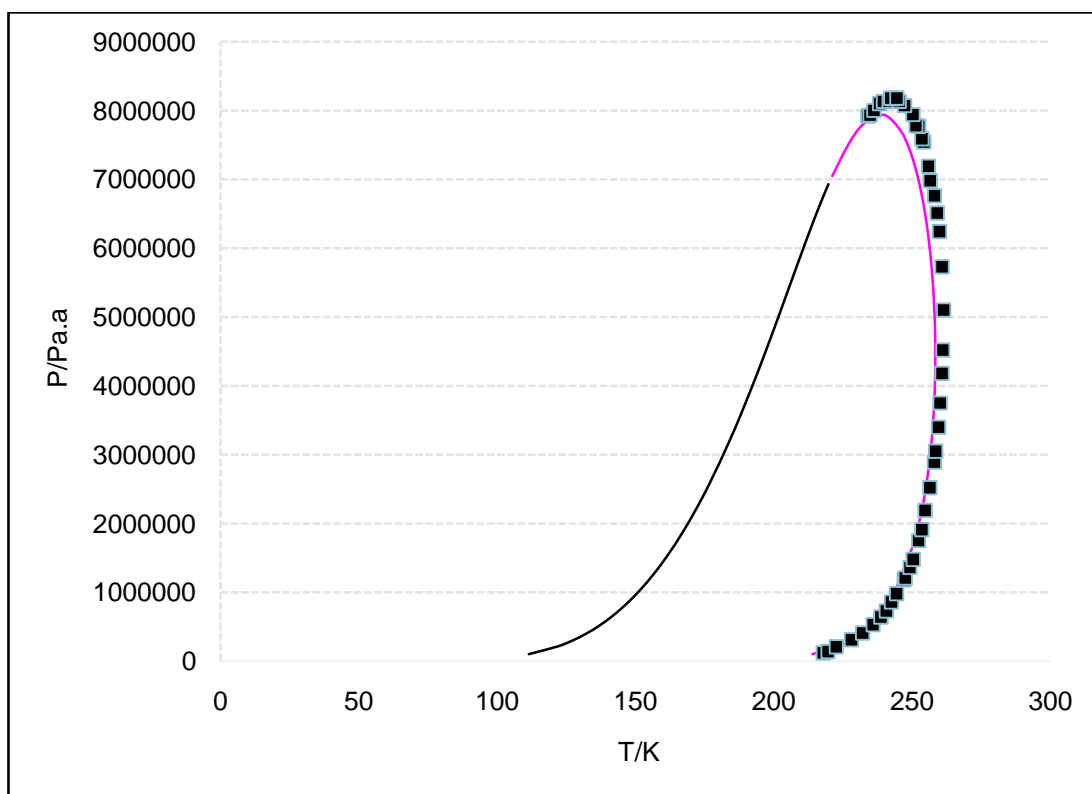
D 20: SET 18-SNG 3; SRK-VDW
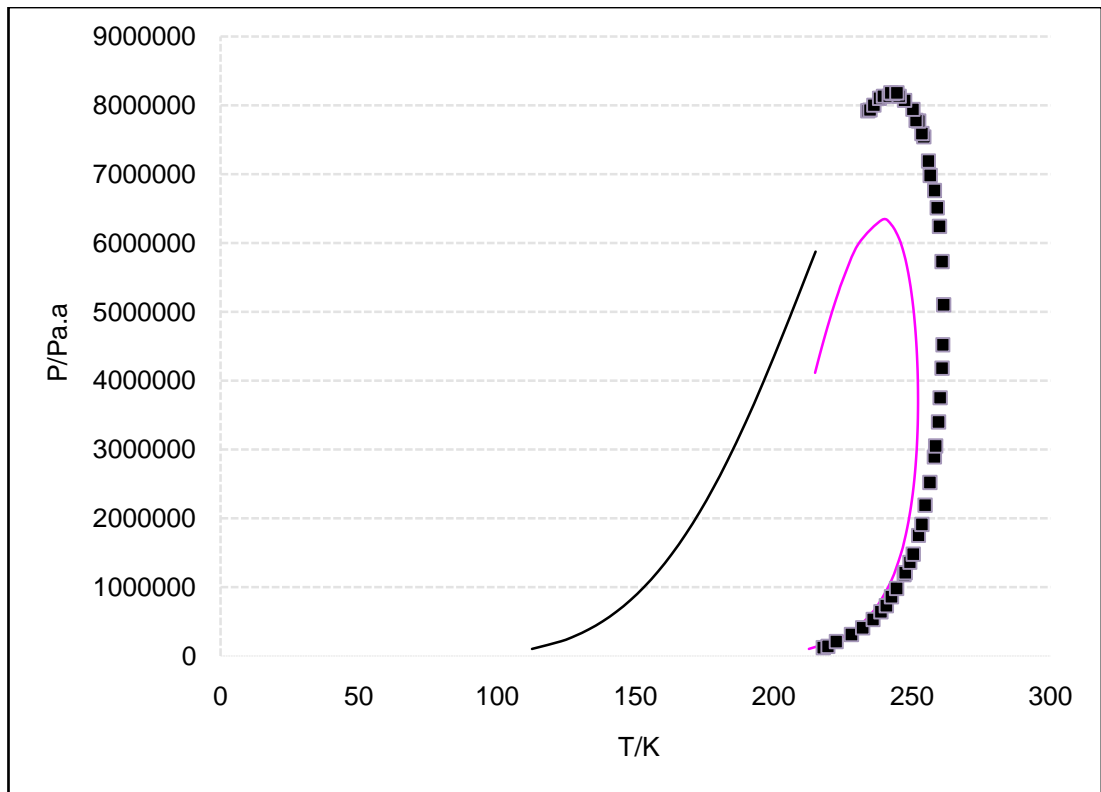
D 21: SET 18-SNG 3; PR-UNIQUAC-WS
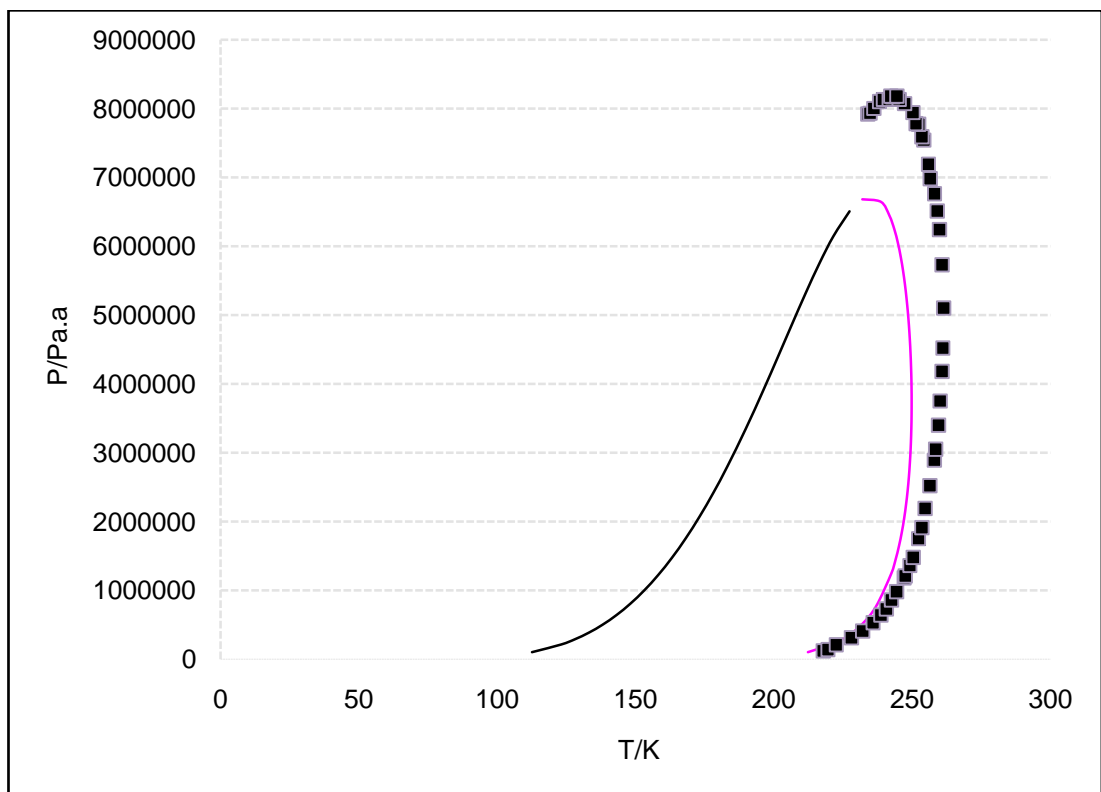
D 22: SET 18-SNG 3; PR-NRTL-WS

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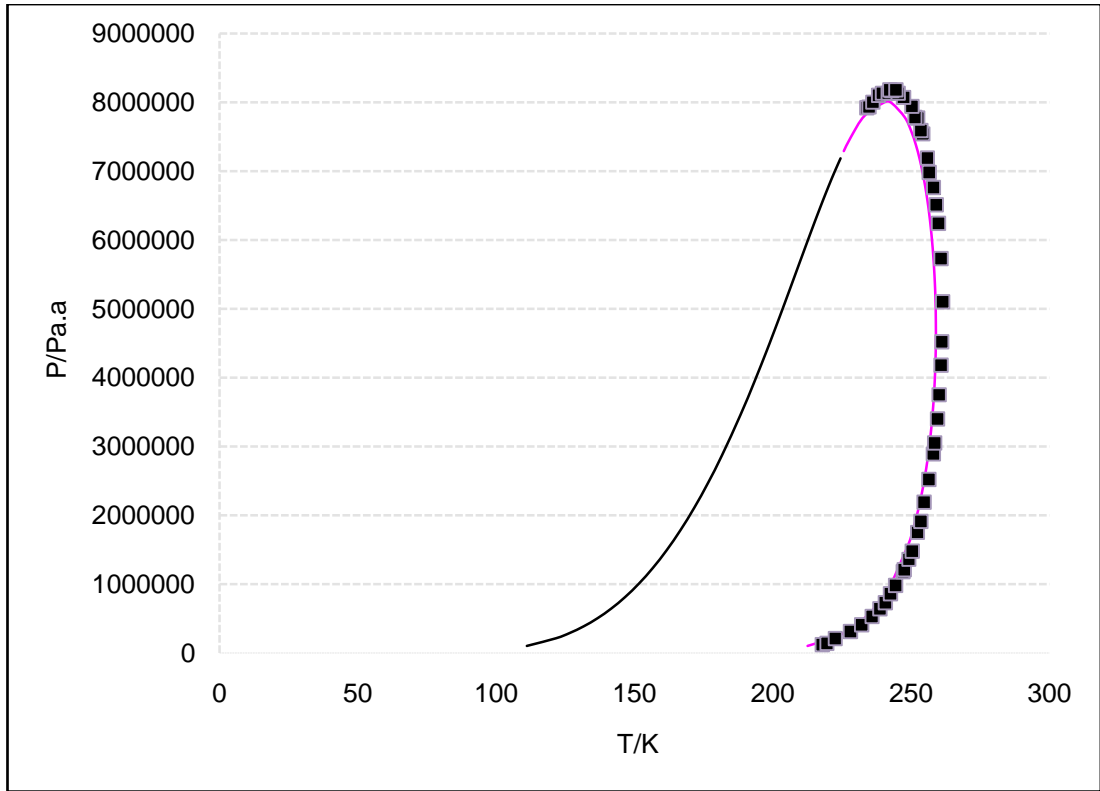
D 23: SET 18-SNG 3; SRK-EXT-VDW
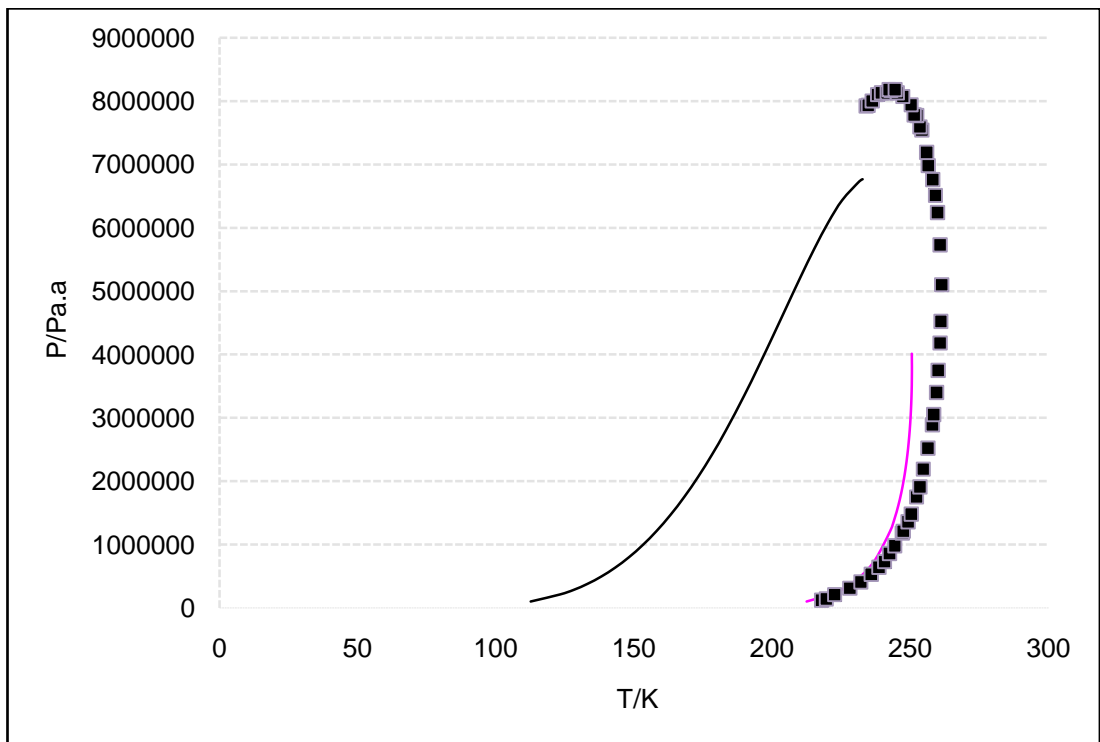
D 24: SET 18-SNG 3; PR-WS
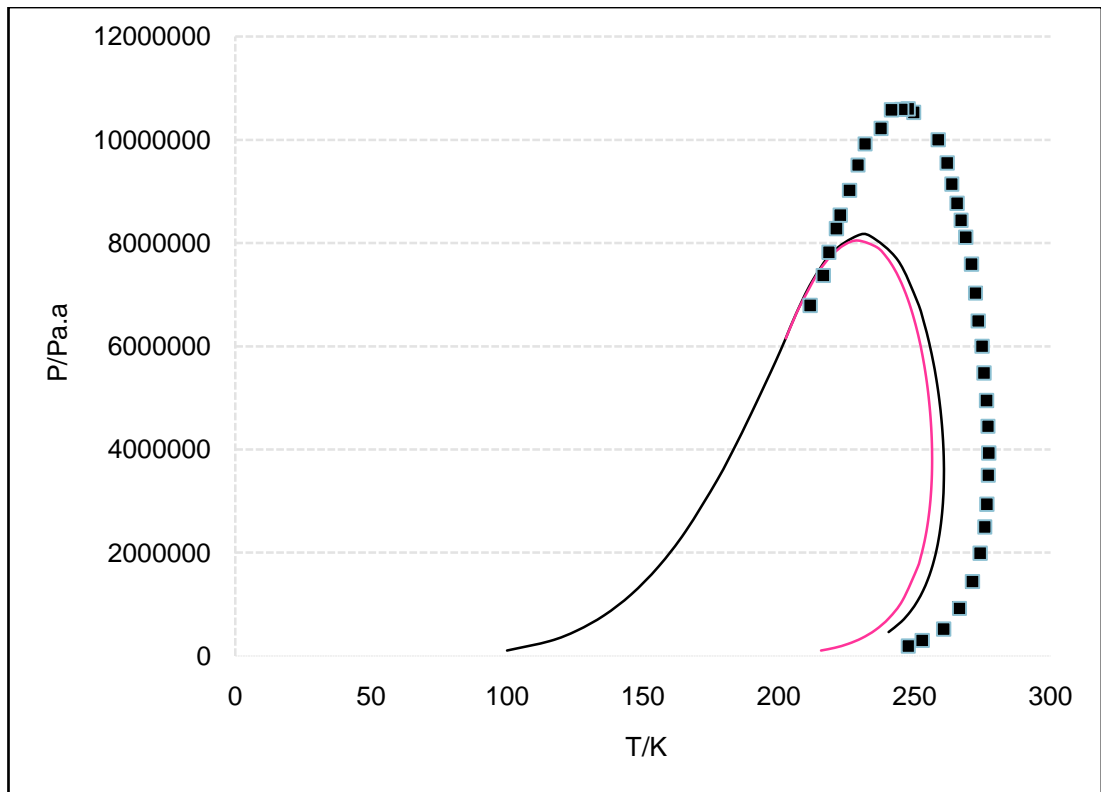
D 25: SET 18-SNG 4; CPA-PR-VDW
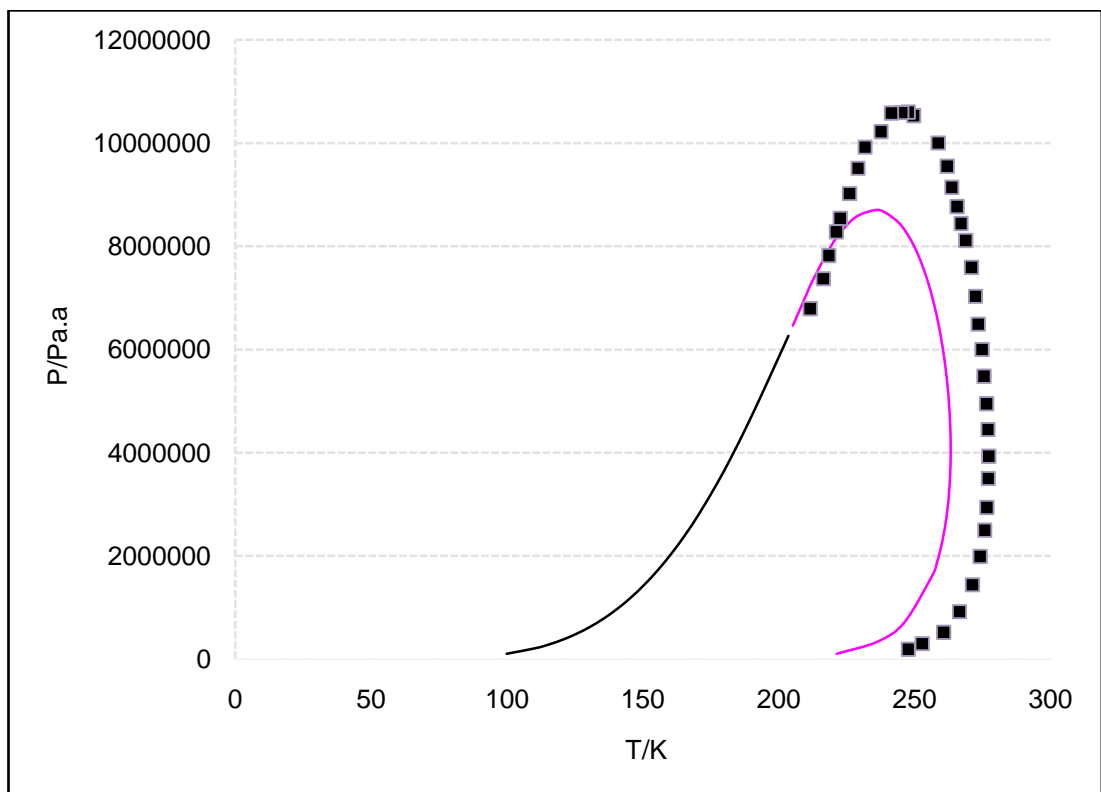
D 26: SET 18-SNG 4; CPA-SRK-VDW
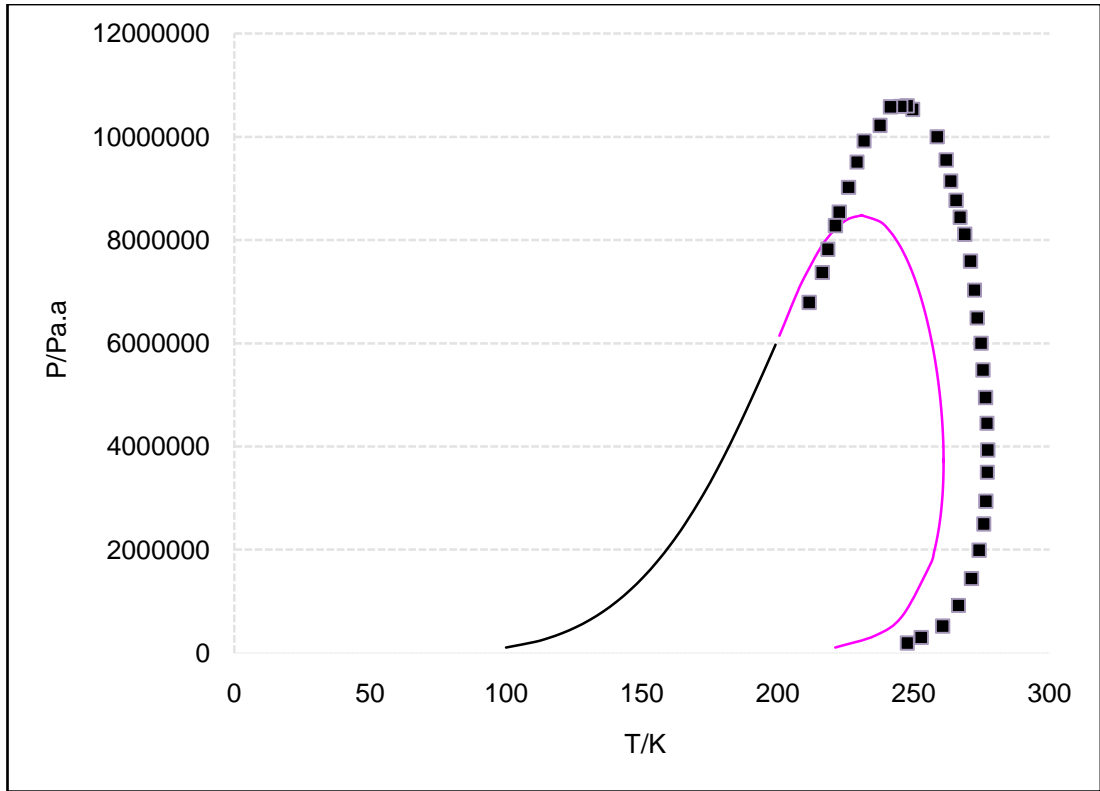
D 27: SET 18-SNG 4; PR-VDW
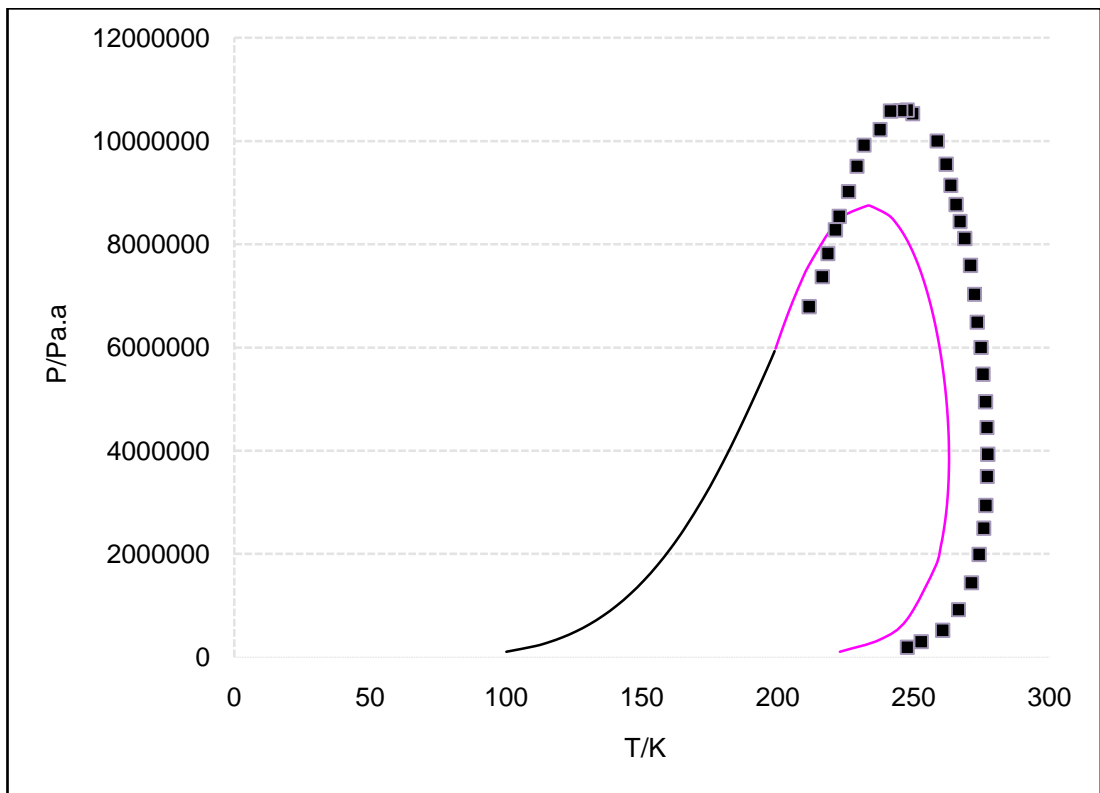
D 28: SET 18-SNG 4; SRK-VDW
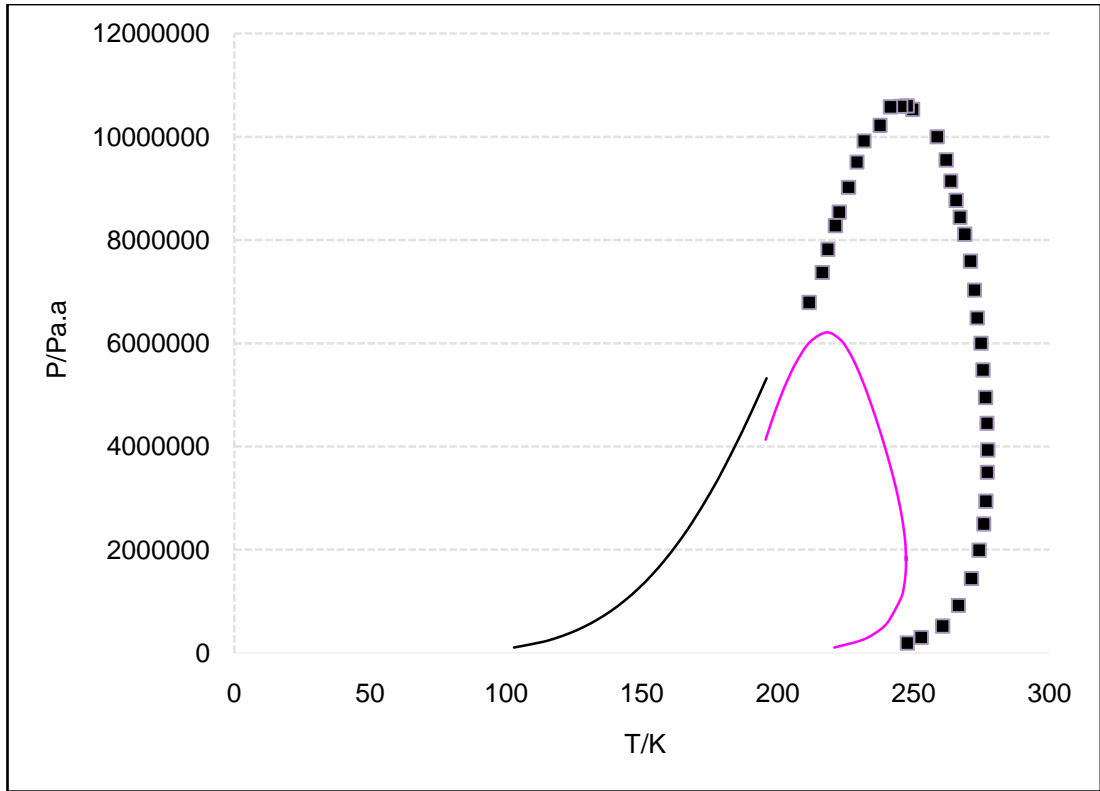
D 29: SET 18-SNG 4; PR-UNIQUAC-WS
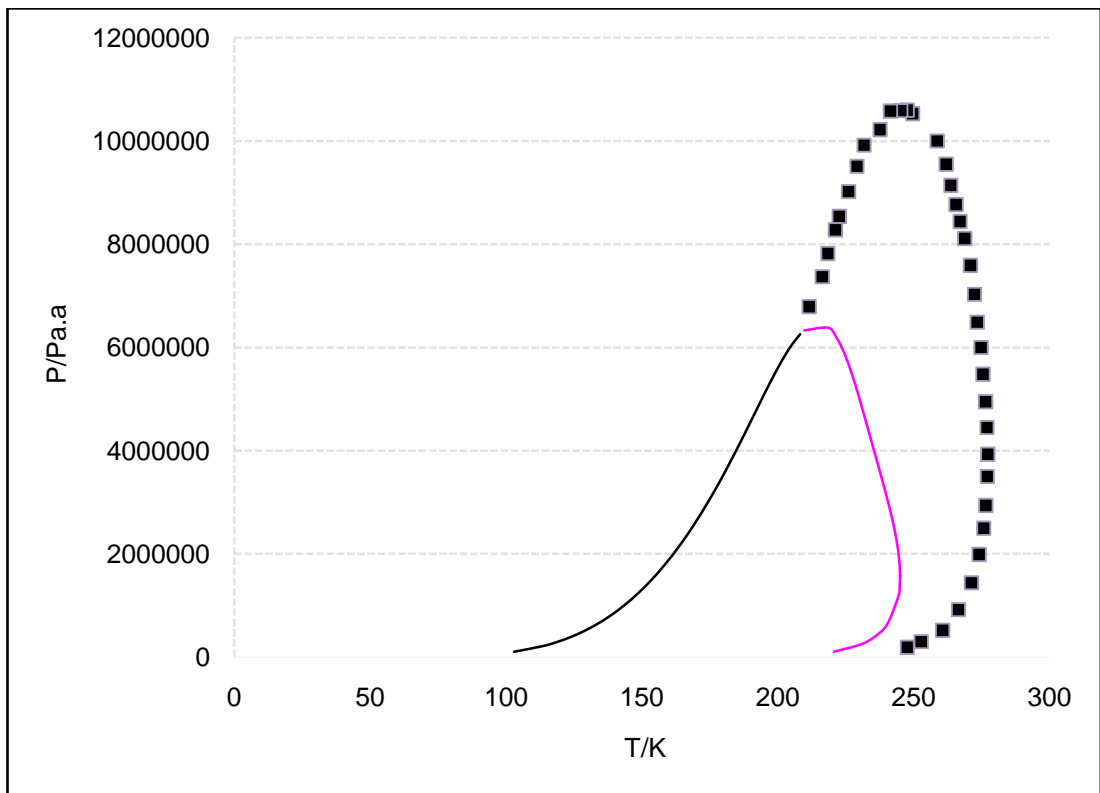
D 30: SET 18-SNG 4; PR-NRTL-WS
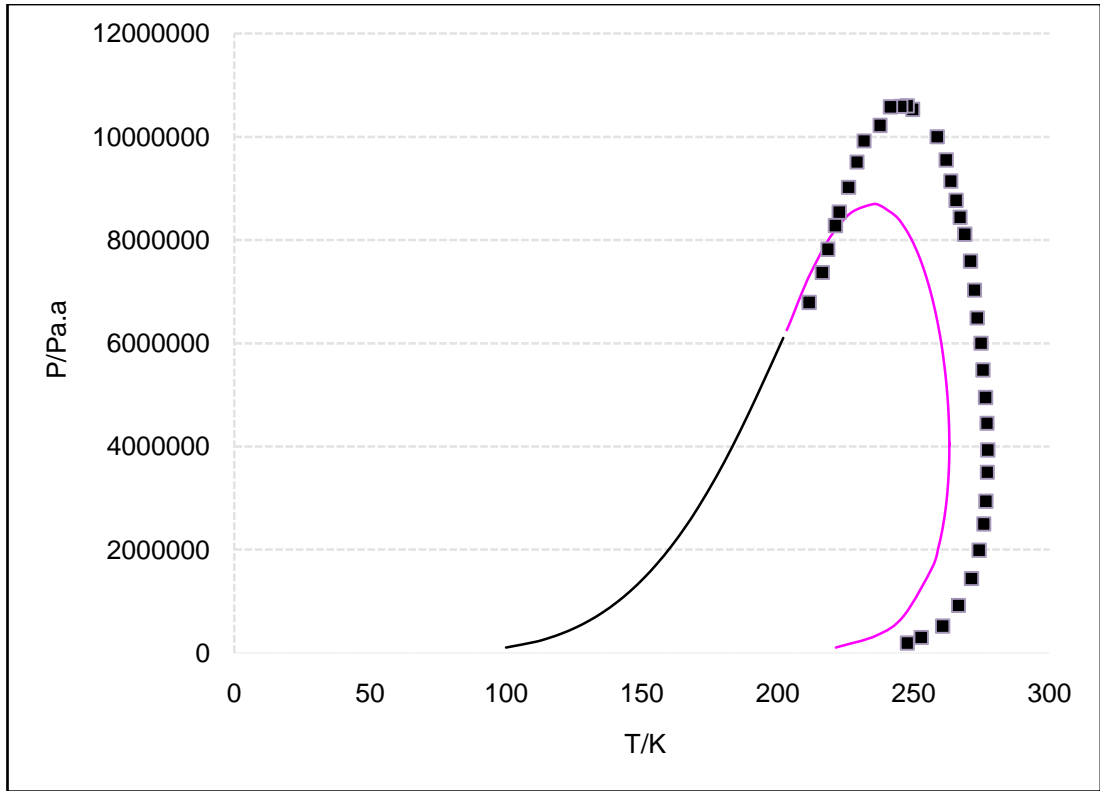
D 31: SET 18-SNG 4; SRK-EXT-VDW
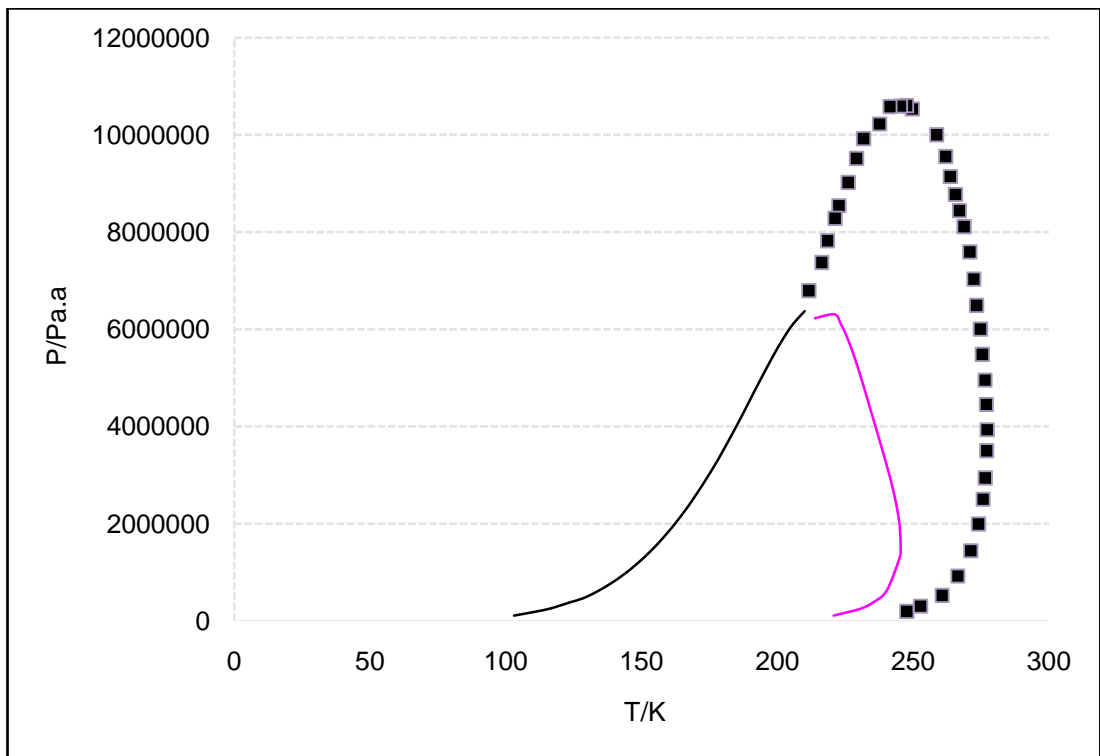
D 32: SET 18-SNG 4; PR-WS
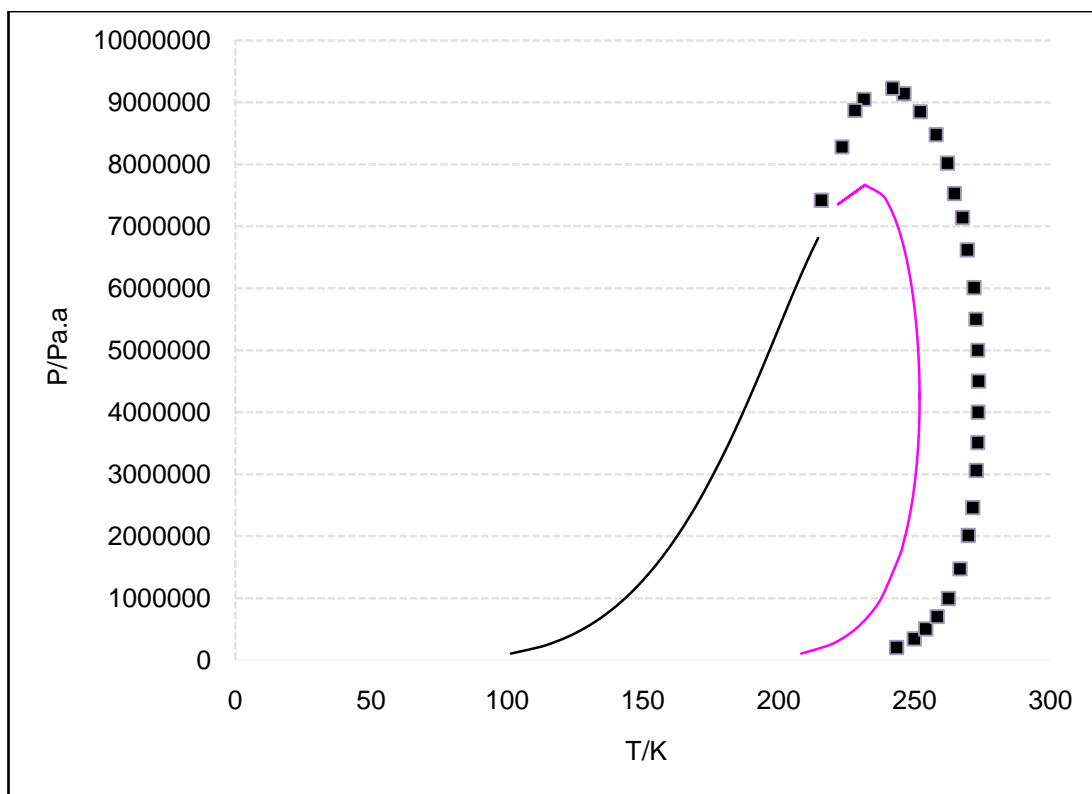
D 33: SET 18-SNG 5; CPA-PR-VDW
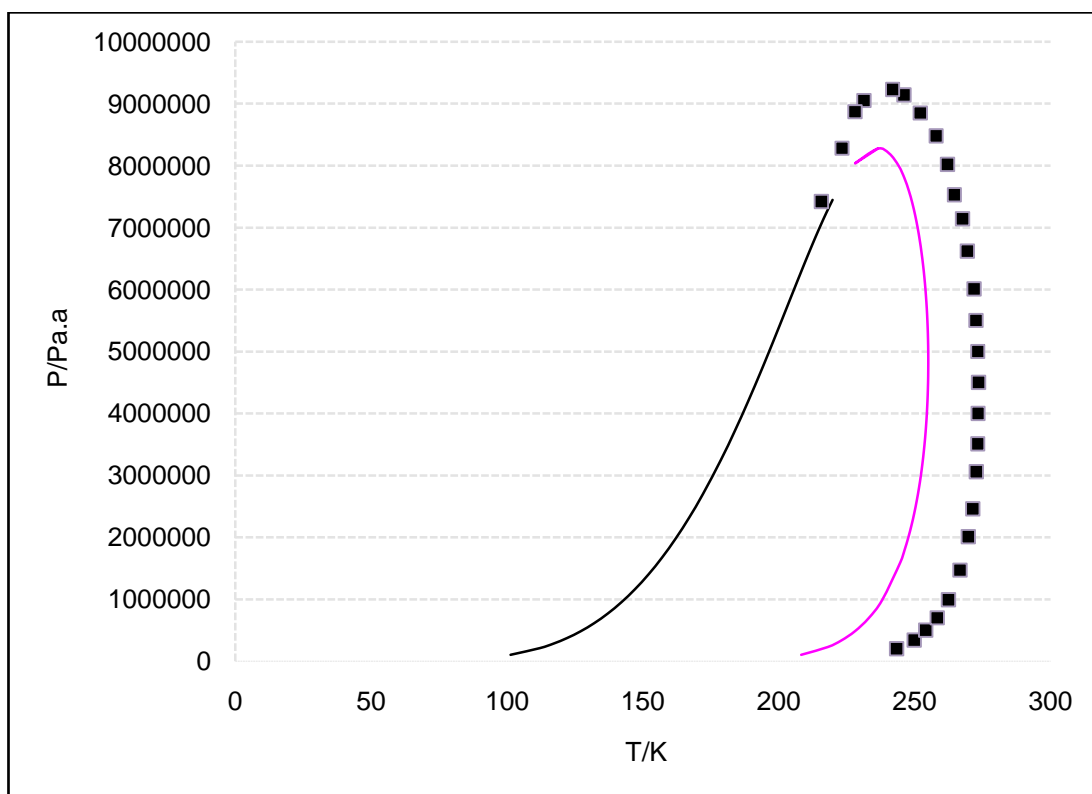
D 34: SET 18-SNG 5; CPA-SRK-VDW

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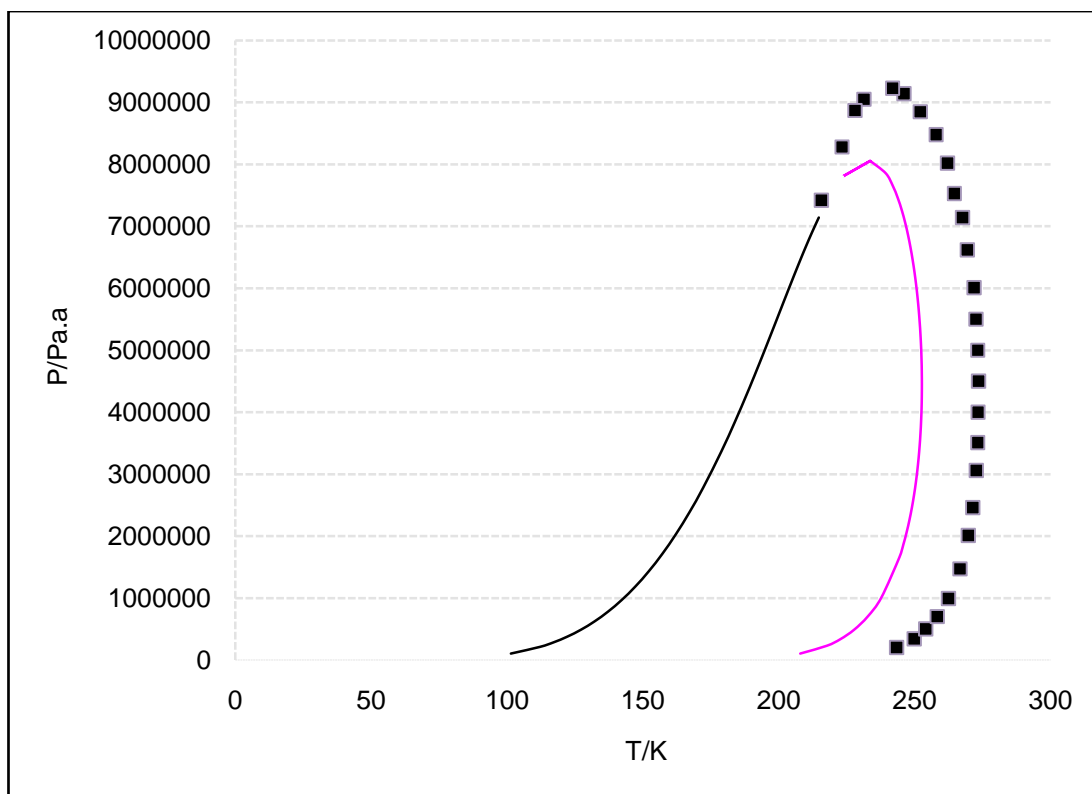
D 35: SET 18-SNG 5; PR-VDW
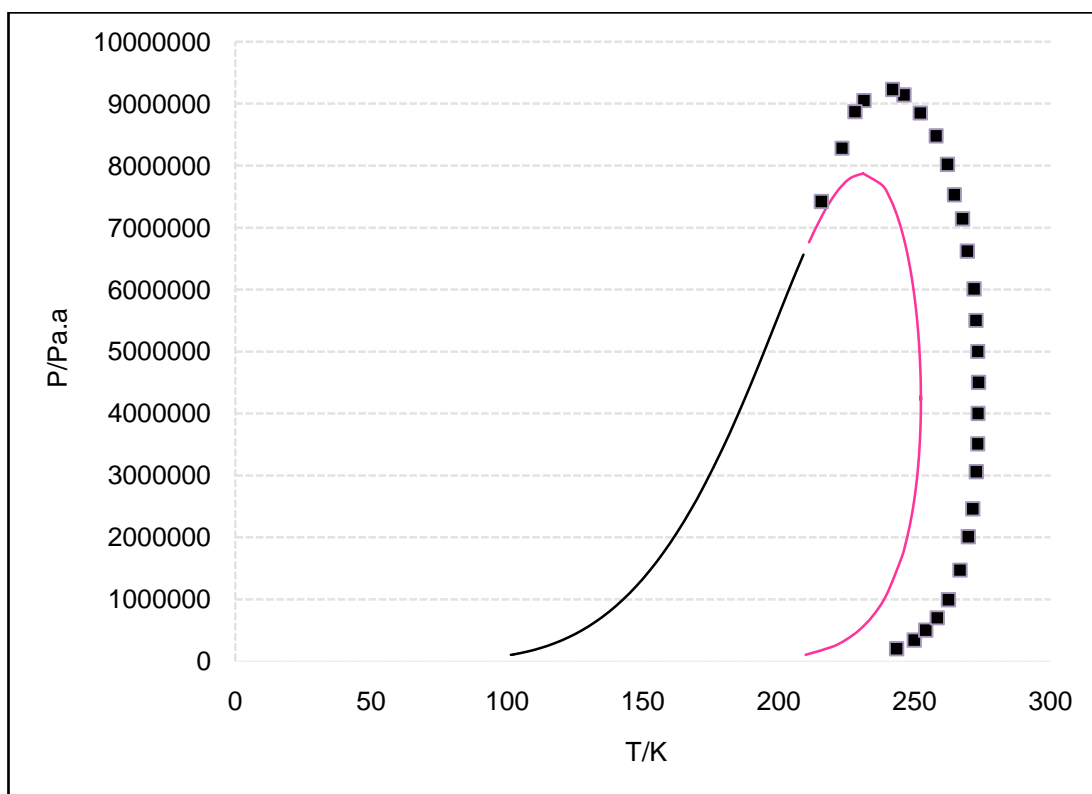
D 36: SET 18-SNG 5; SRK-VDW
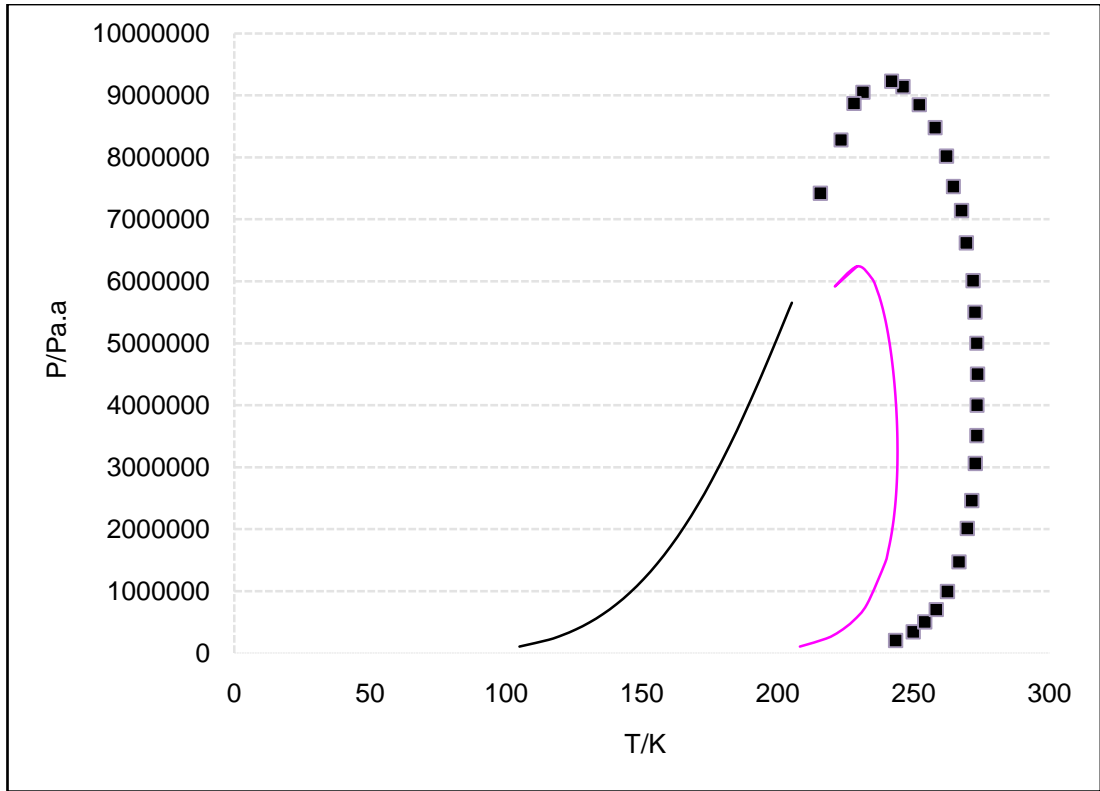
D 37: SET 18-SNG 5; PR-UNIQUAC-WS
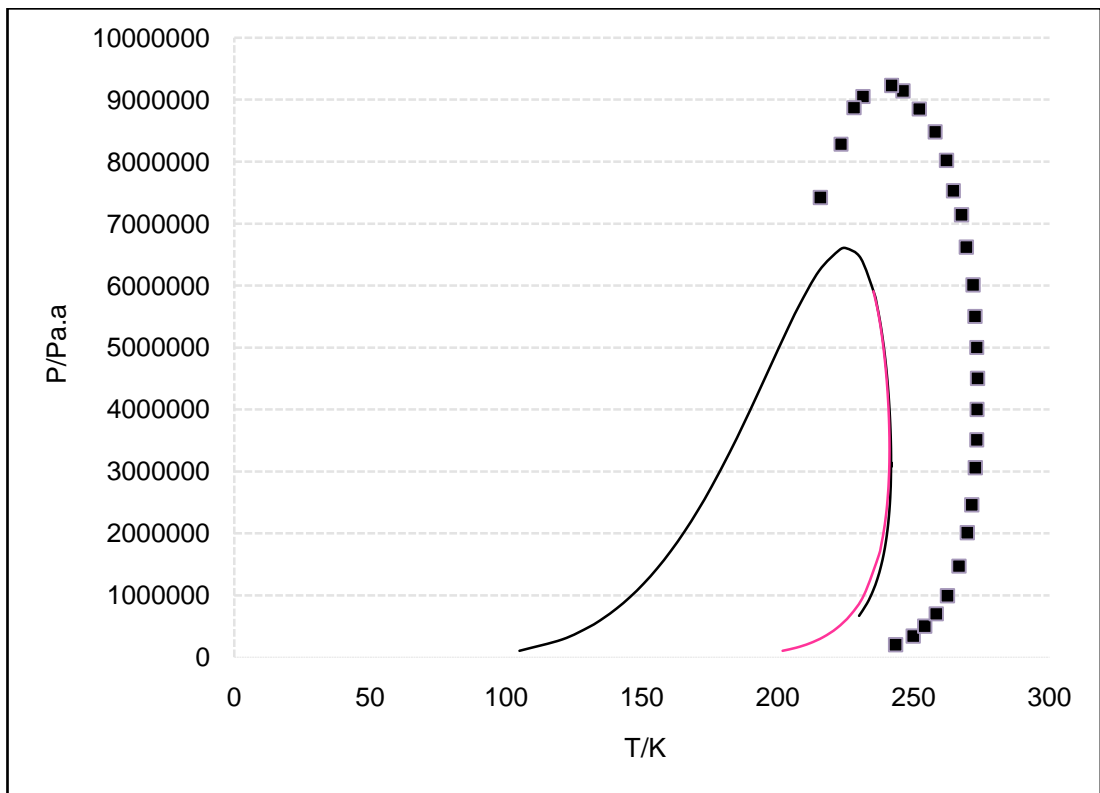
D 38: SET 18-SNG 5; PR-NRTL-WS
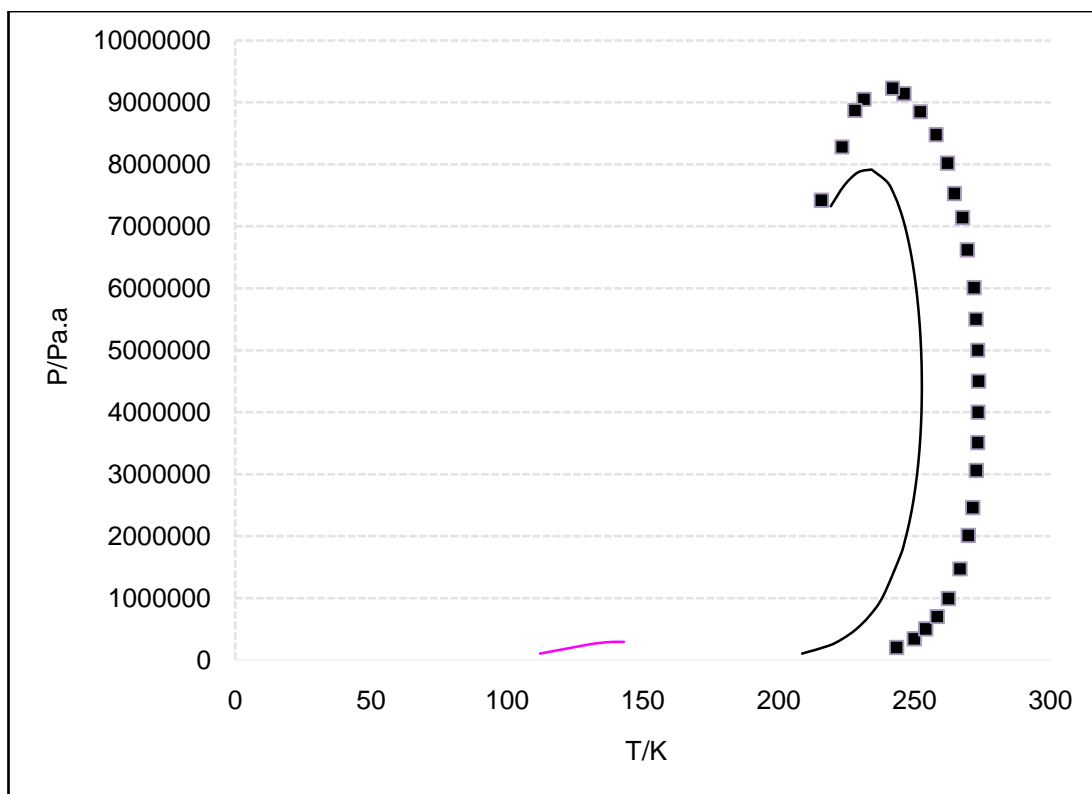
D 39: SET 18-SNG 5; SRK-EXT-VDW
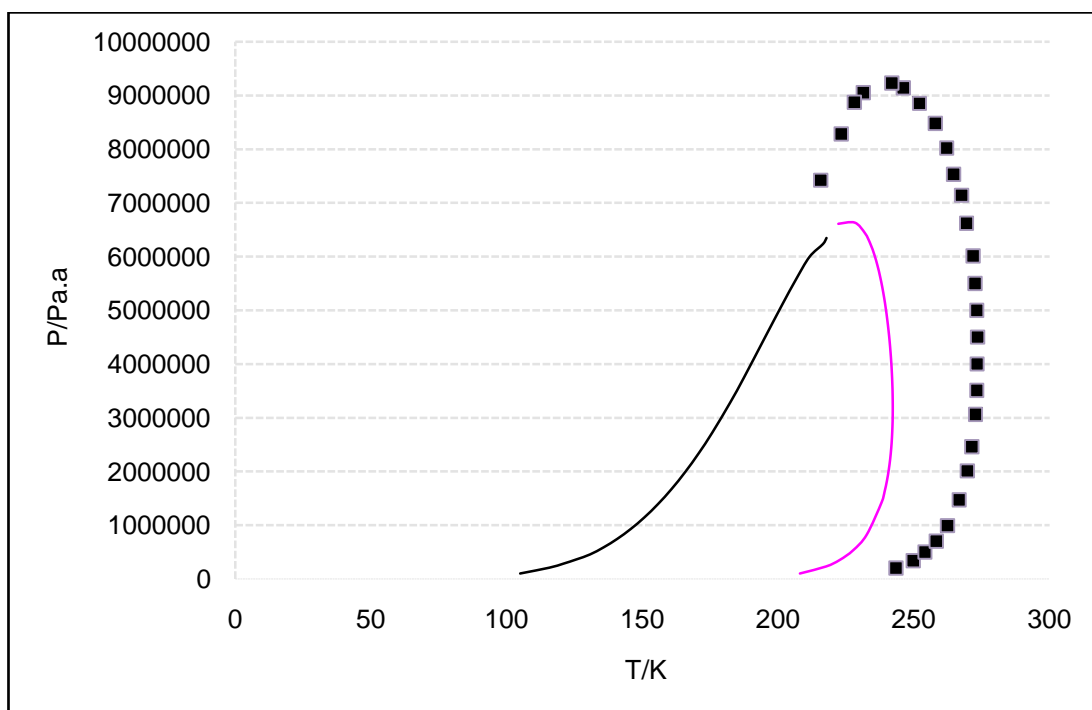
D 40: SET 18-SNG 5; PR-WS

APPENDIX E

In conjunction with the results calculated in chapter 4 for the set 19, most of the figures ranging from 4.26 to 4.29 are derived from the individual phase behaviour calculated as shown in the Appendix E.
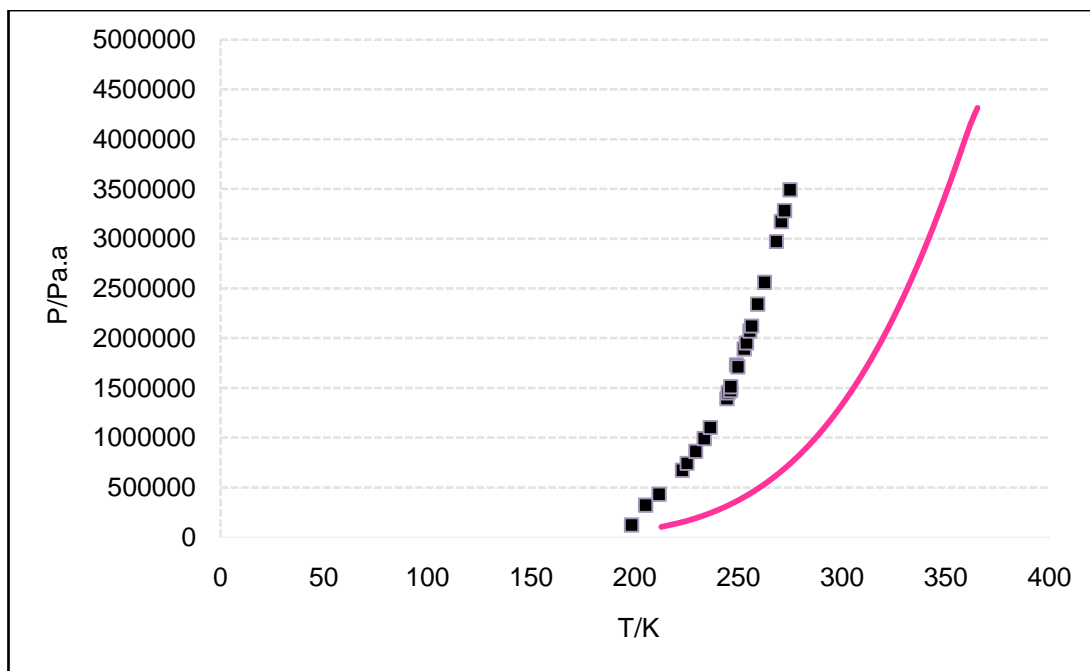
E 1: SET 19-GAS 1; CPA-PR-VDW
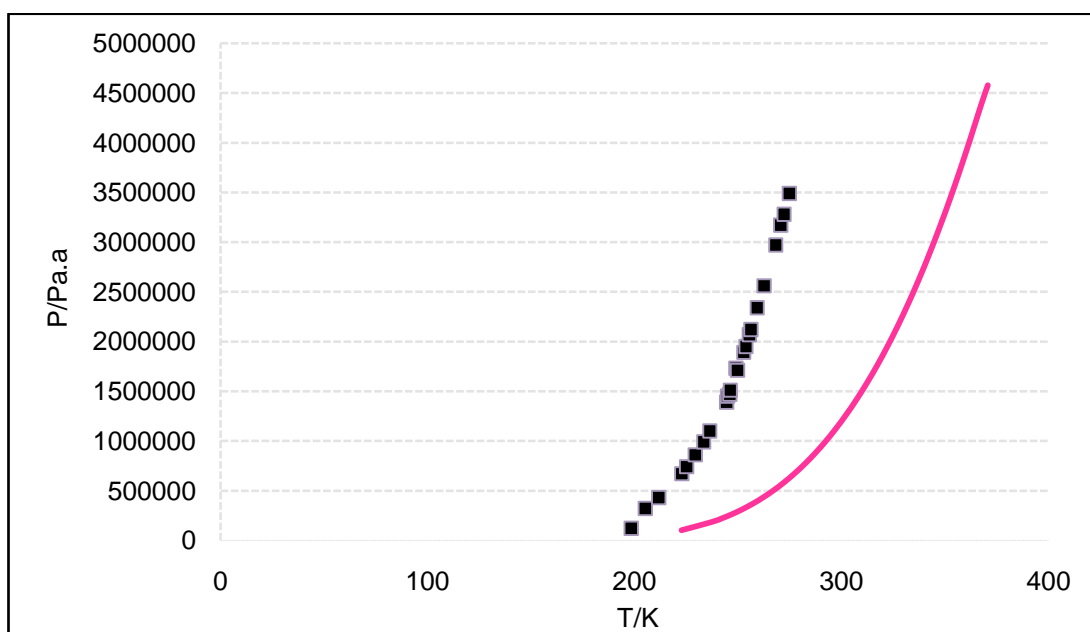
E 2: SET 19-GAS 1; CPA-SRK-VDW
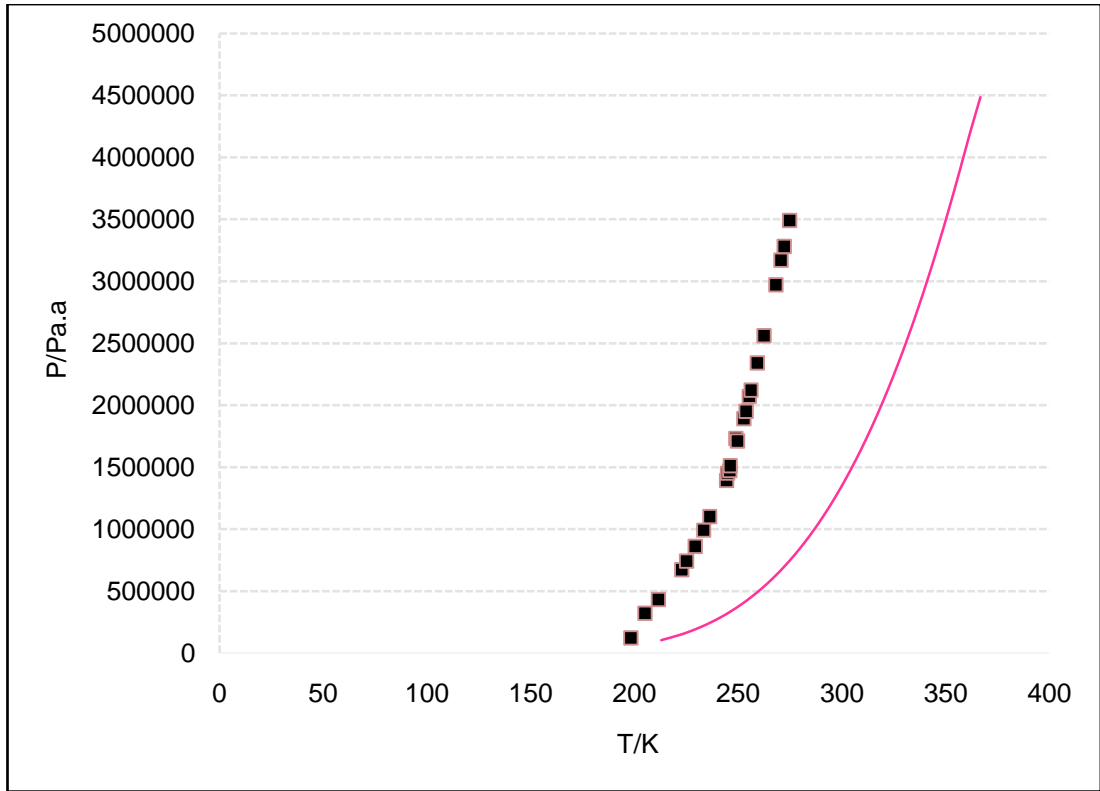
E 3: SET 19-GAS 1; PR-VDW
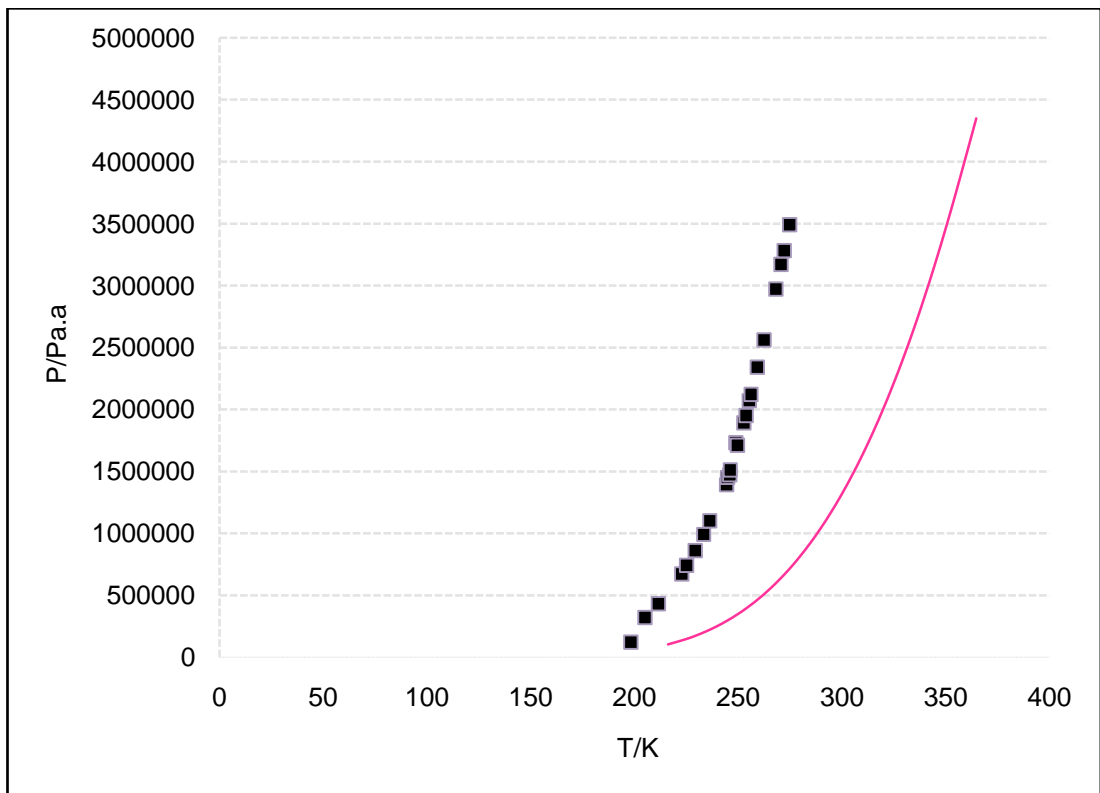
E 4: SET 19-GAS 1; SRK-VDW
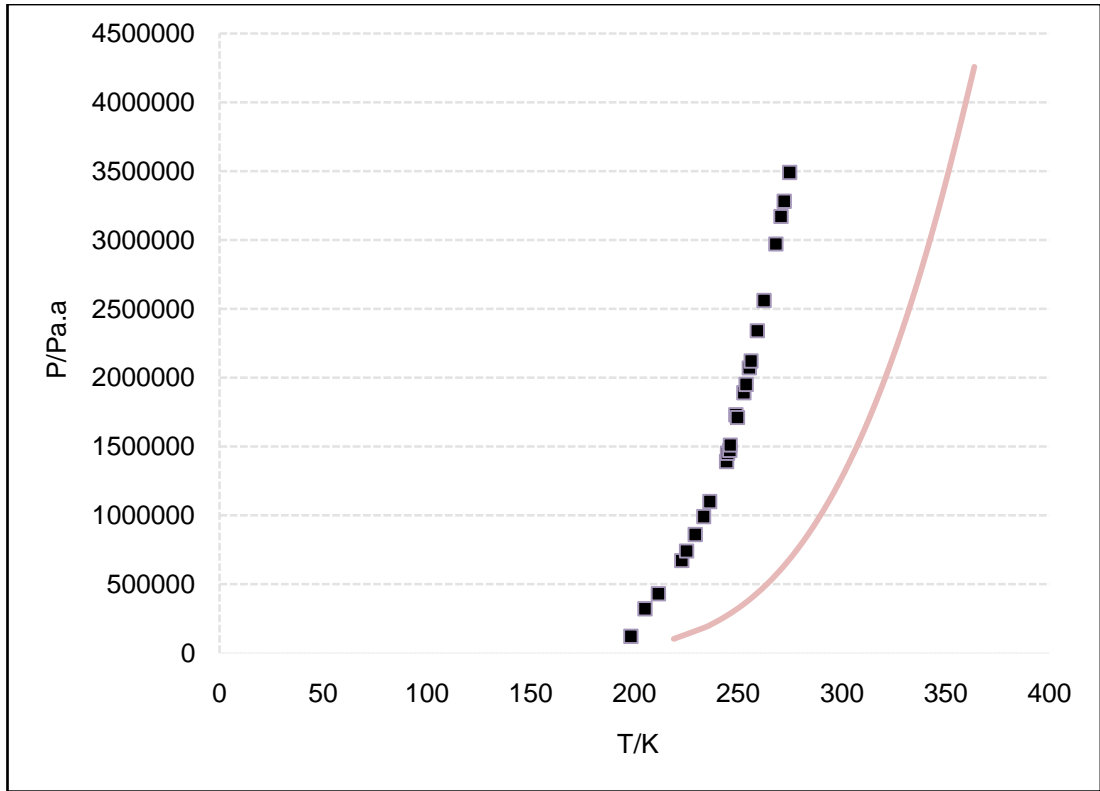
E 5: SET 19-GAS 1; PR-UNIQUAC-WS
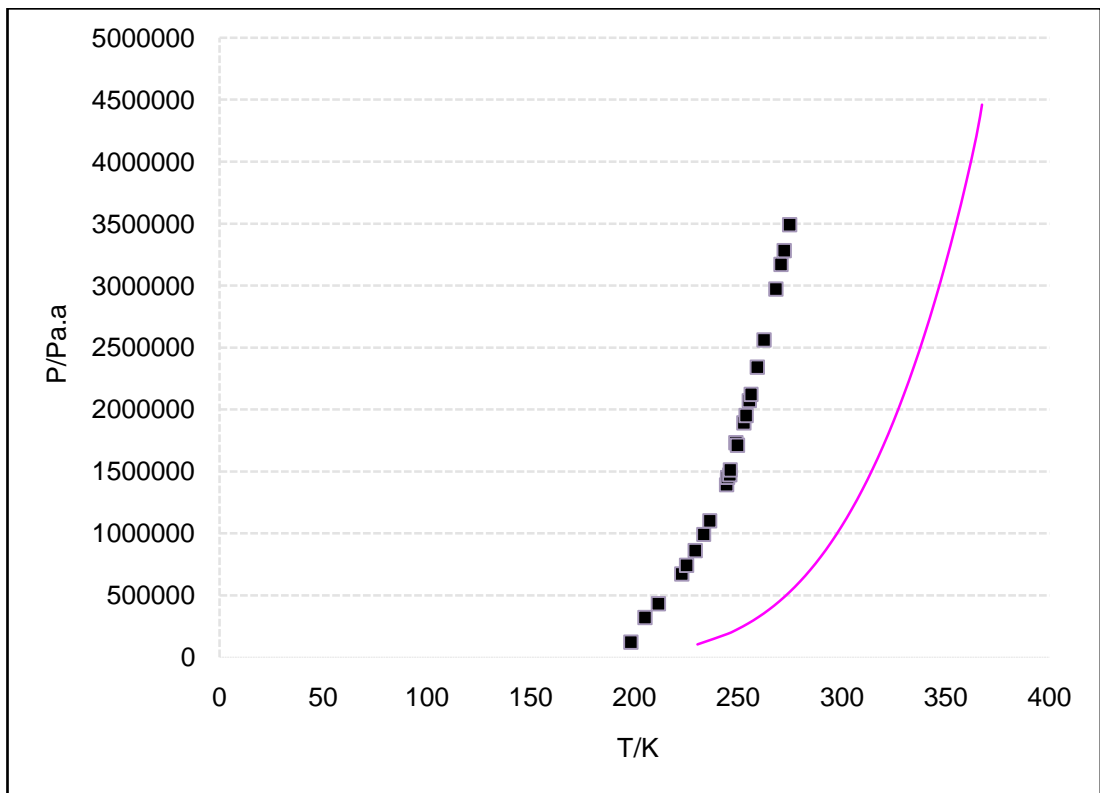
E 6: SET 19-GAS 1; PR-NRTL-WS
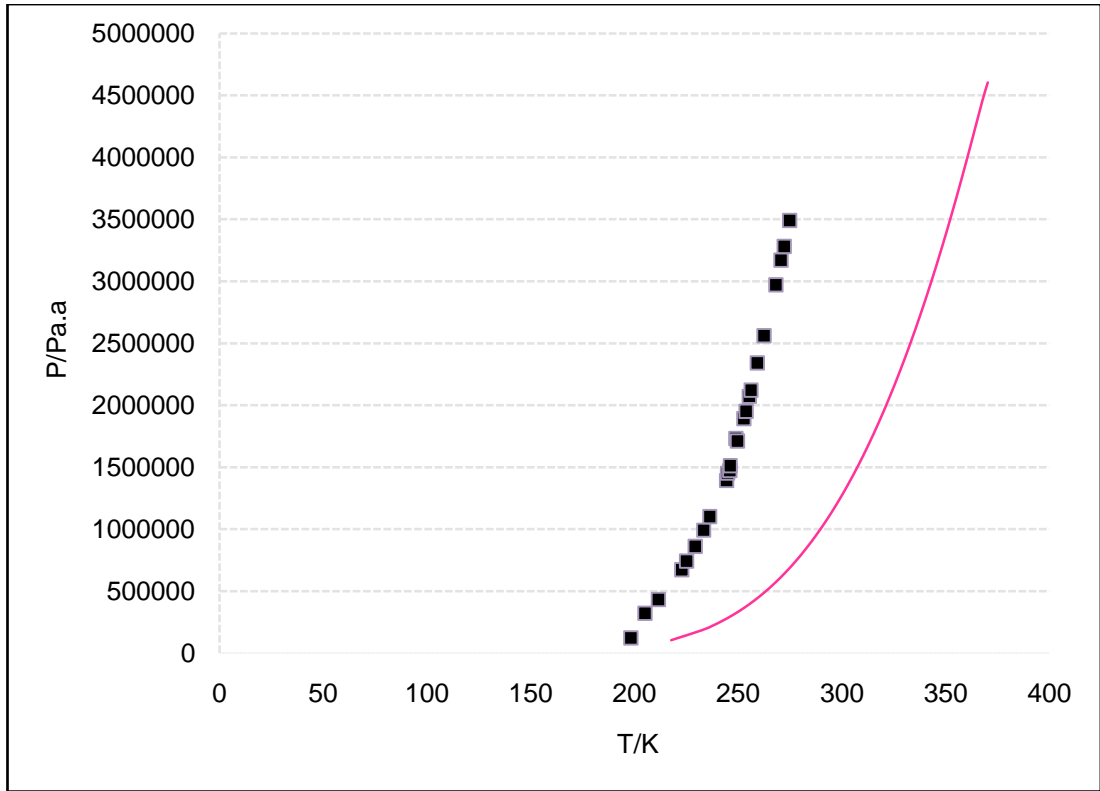
E 7: SET 19-GAS 1; SRK-EXT-VDW
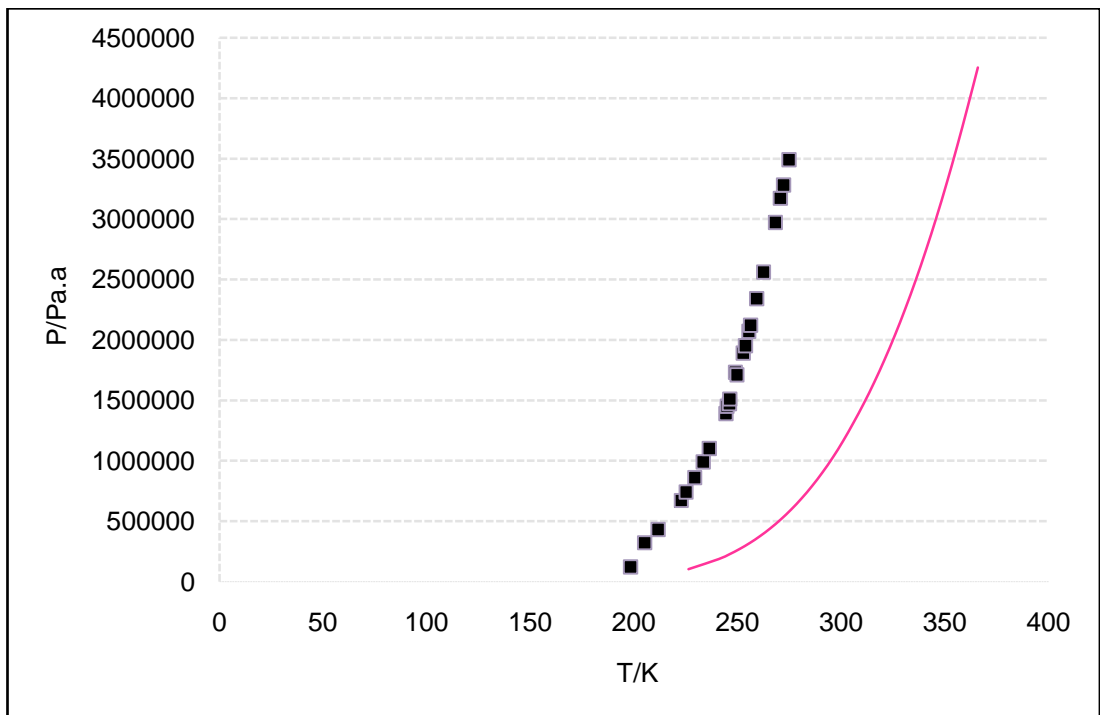
E 8: SET 19-GAS 1; PR-WS
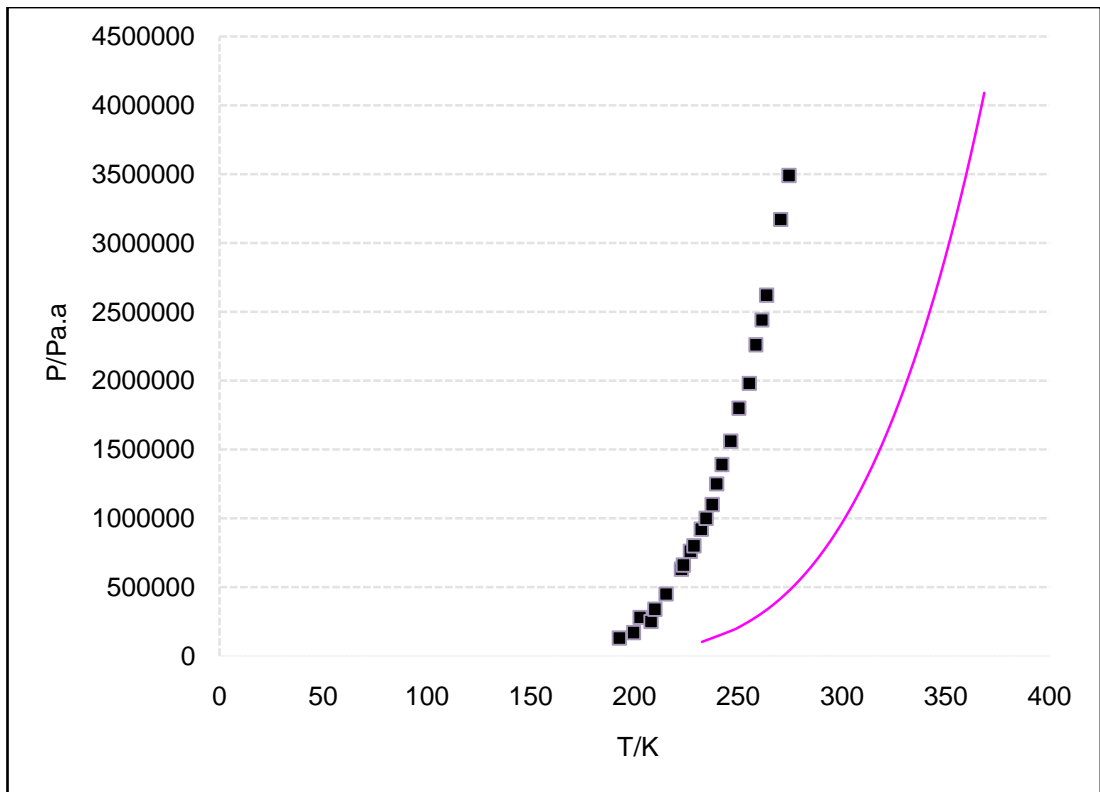
E 9: SET 19-GAS 2; CPA-PR-VDW
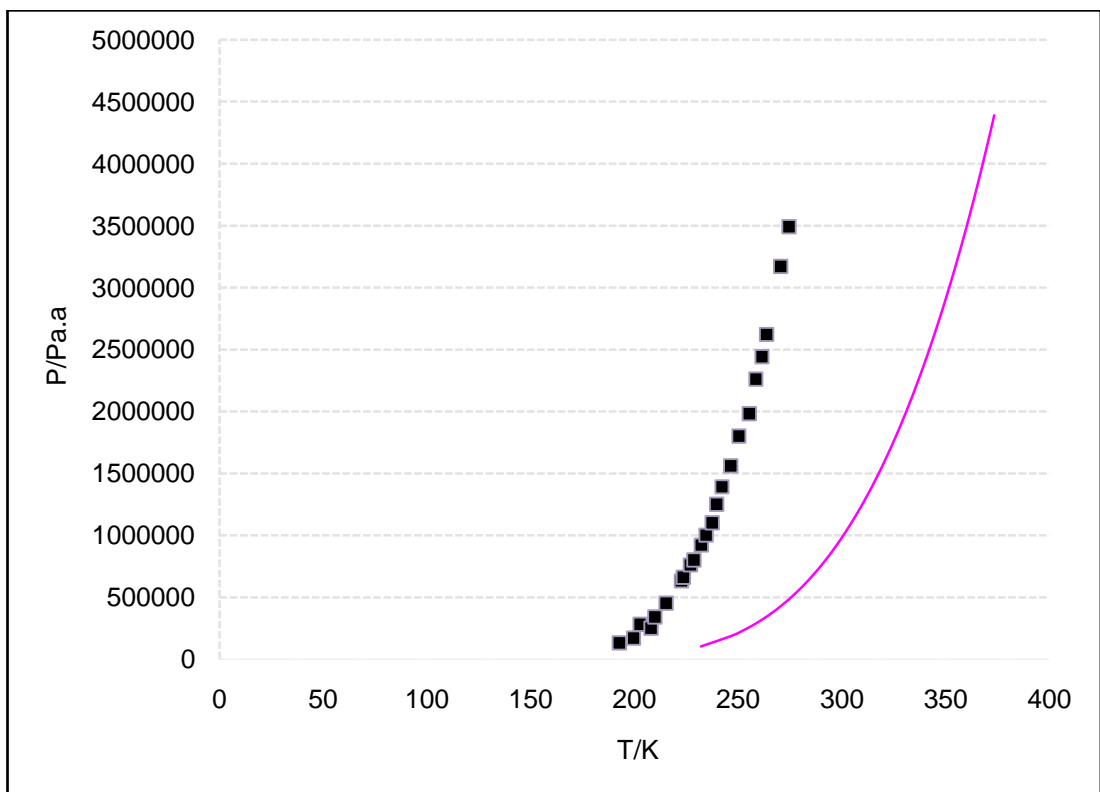
E 10: SET 19-GAS 2; CPA-SRK-VDW

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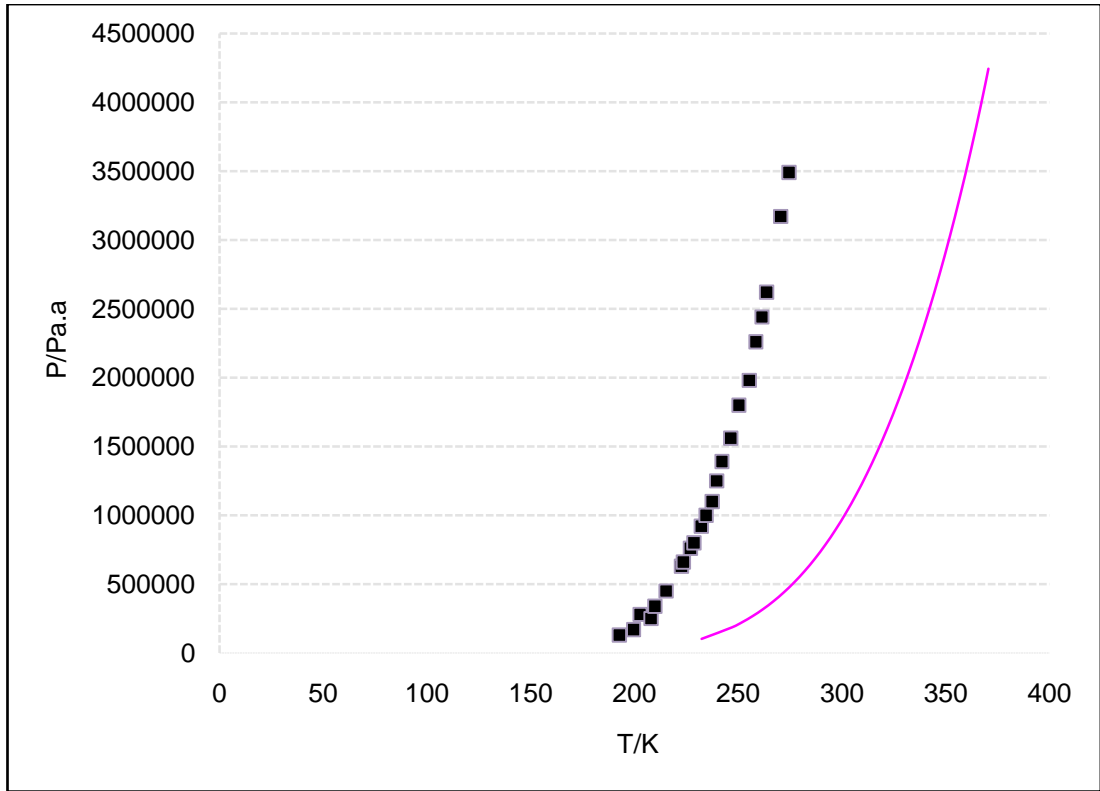
E 11: SET 19-GAS 2; PR-VDW
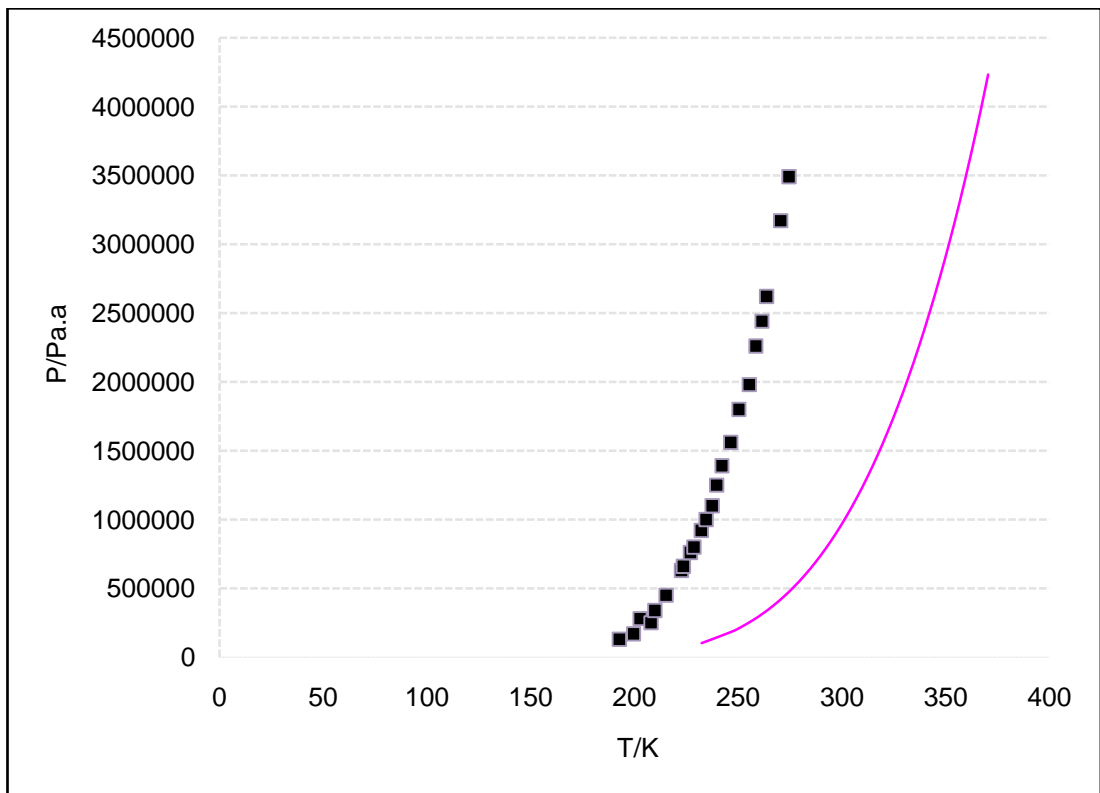
E 12: SET 19-GAS 2; SRK-VDW
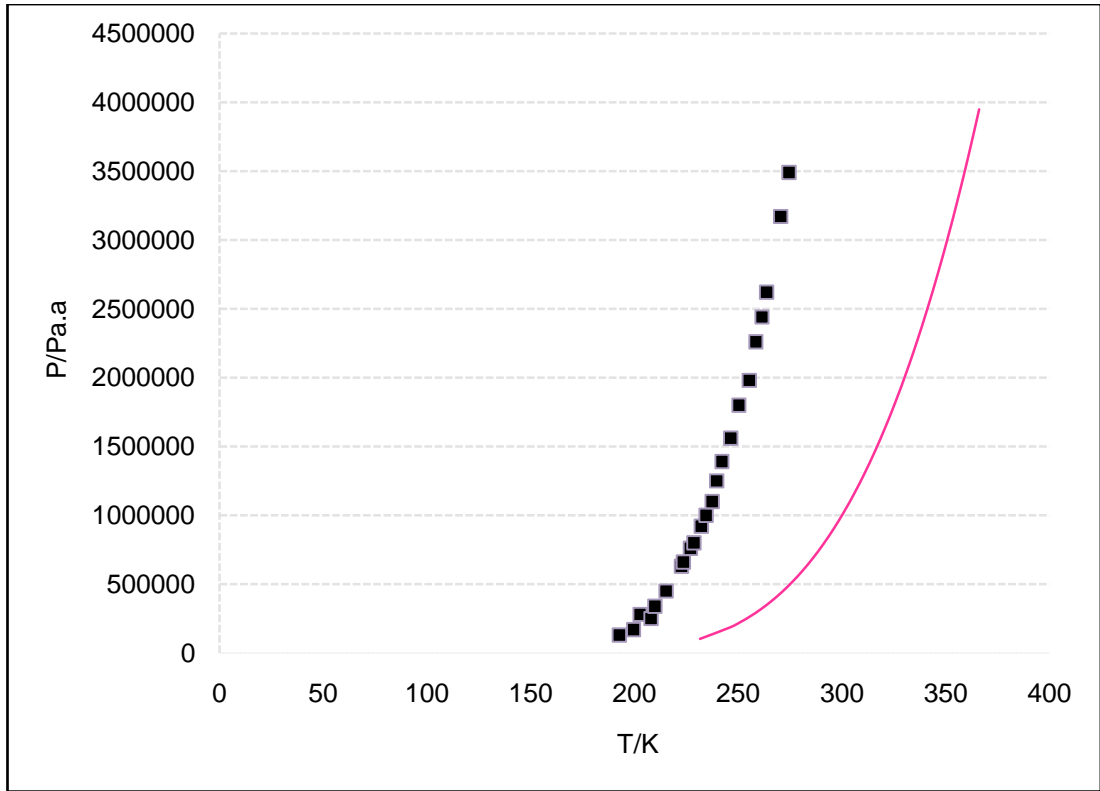
E 13: SET 19-GAS 2; PR-UNIQUAC-WS
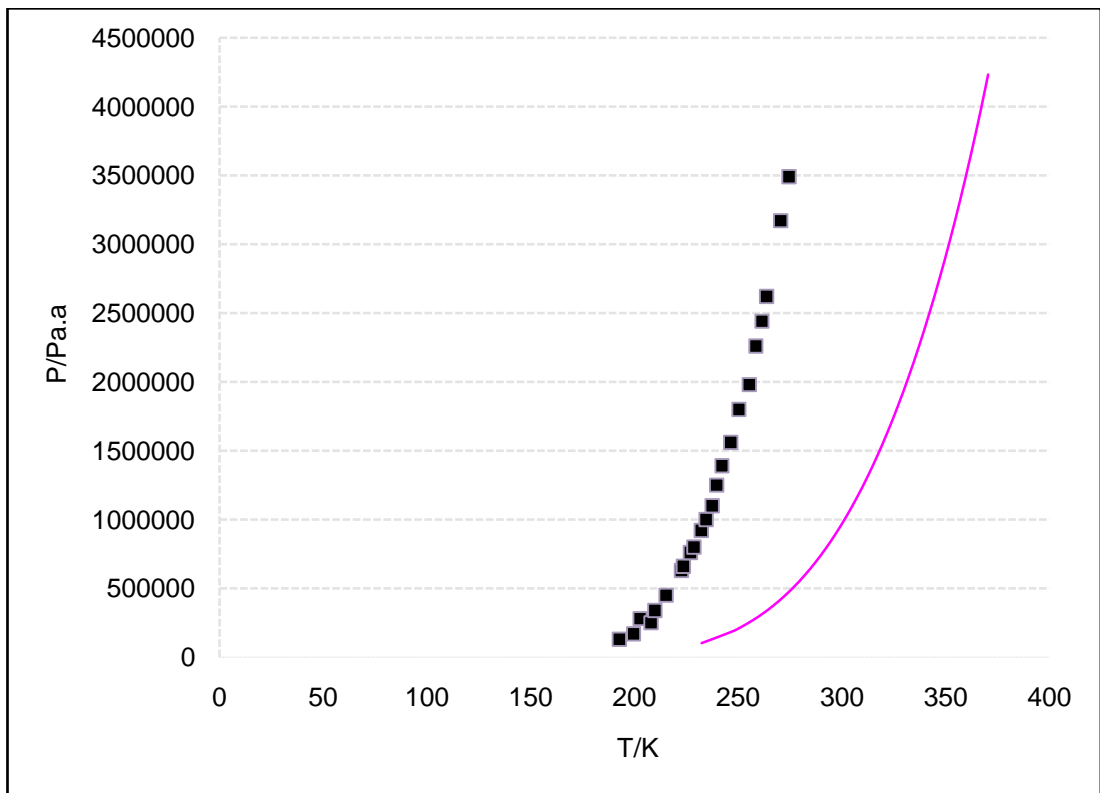
E 14: SET 19-GAS 2; PR-NRTL-WS
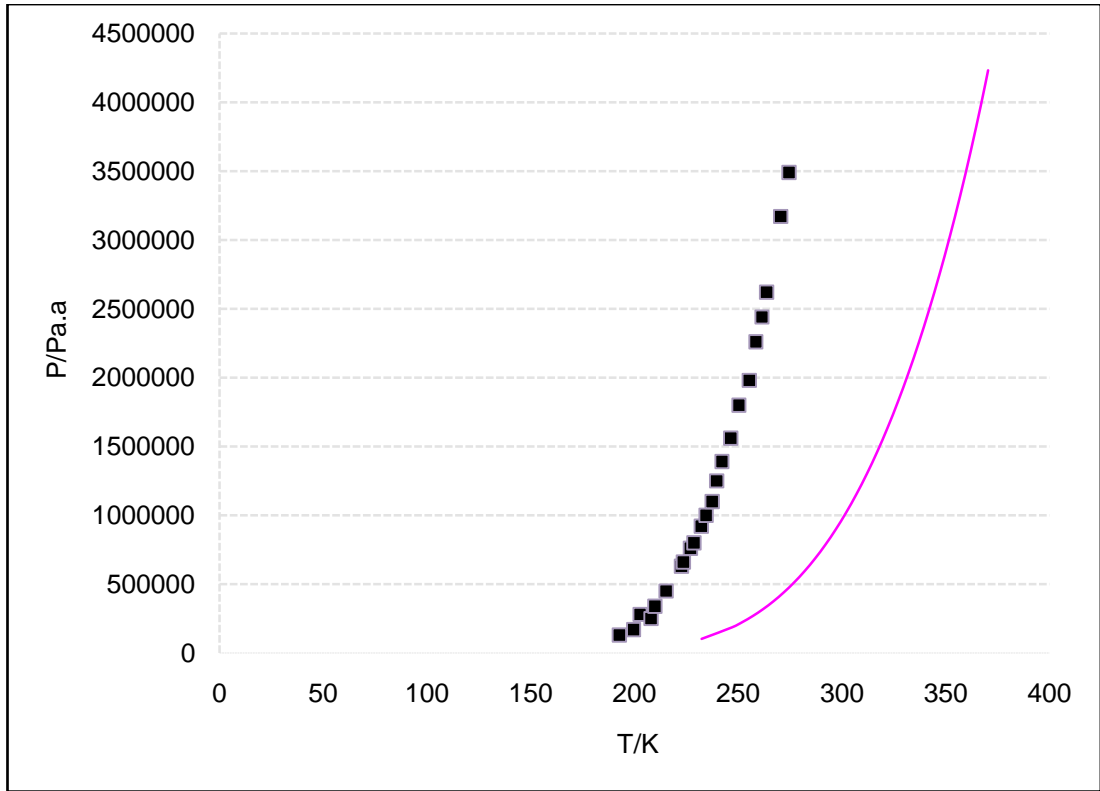
E 15: SET 19-GAS 2; SRK-EXT-VDW
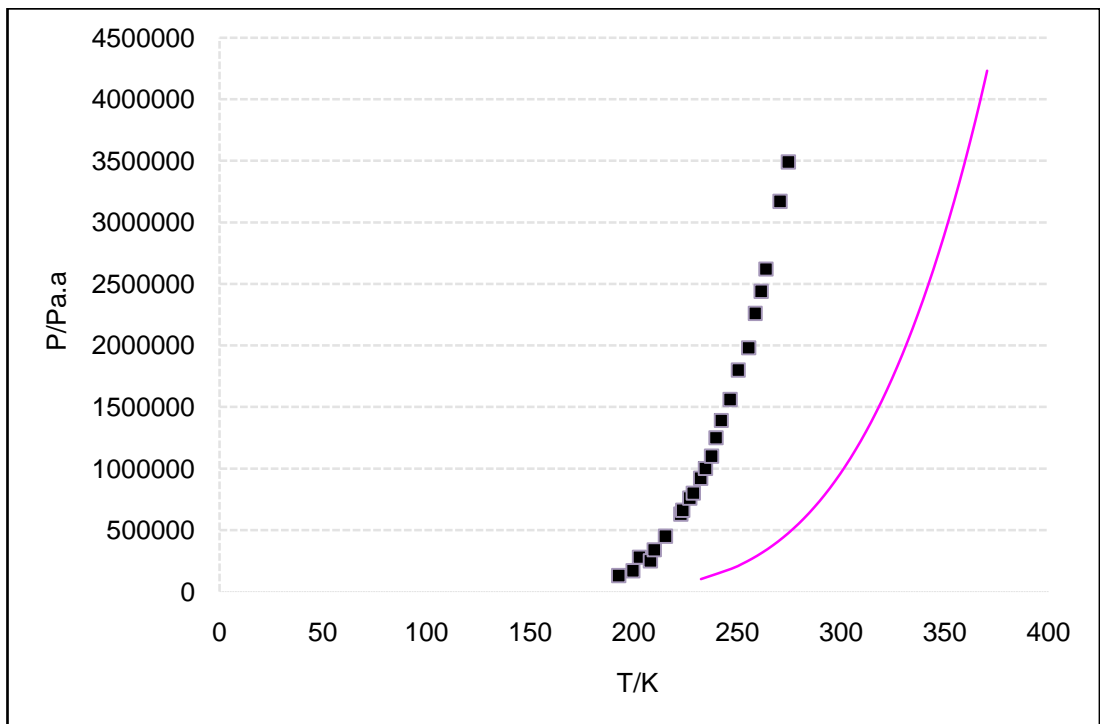
E 16: SET 19-GAS 2; PR-WS

In conjunction with the results calculated in chapter 4 for the set 6, most of the figures ranging from 4.30 to 4.36 are derived from the individual phase behaviour calculated as shown in the Appendix F.
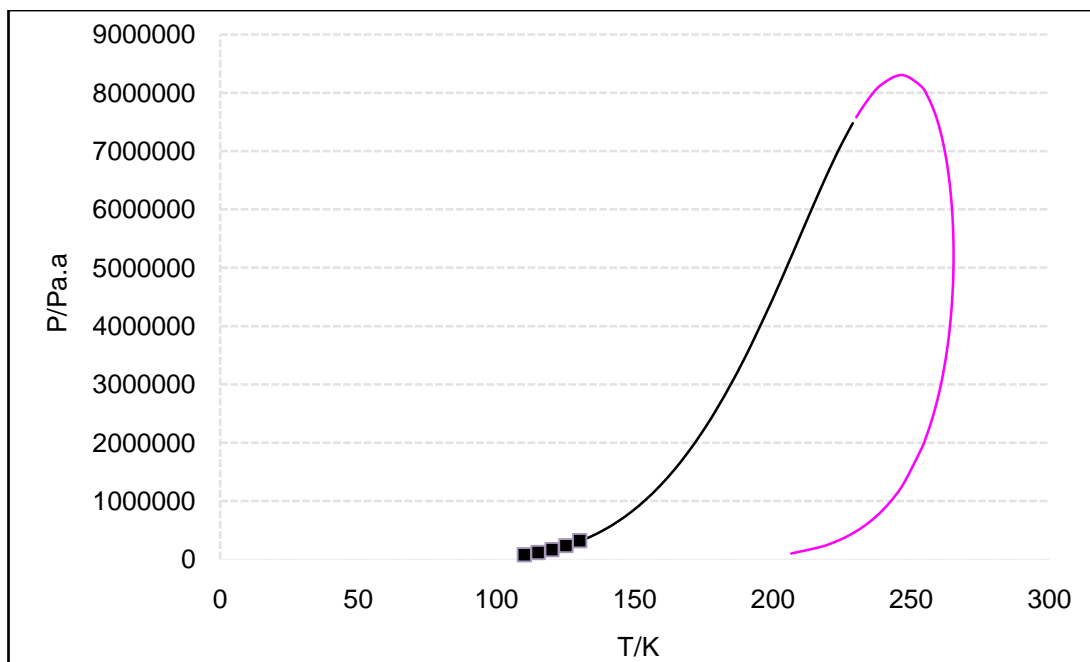
F 1: SET 20-MIX A; CPA-PR-VDW
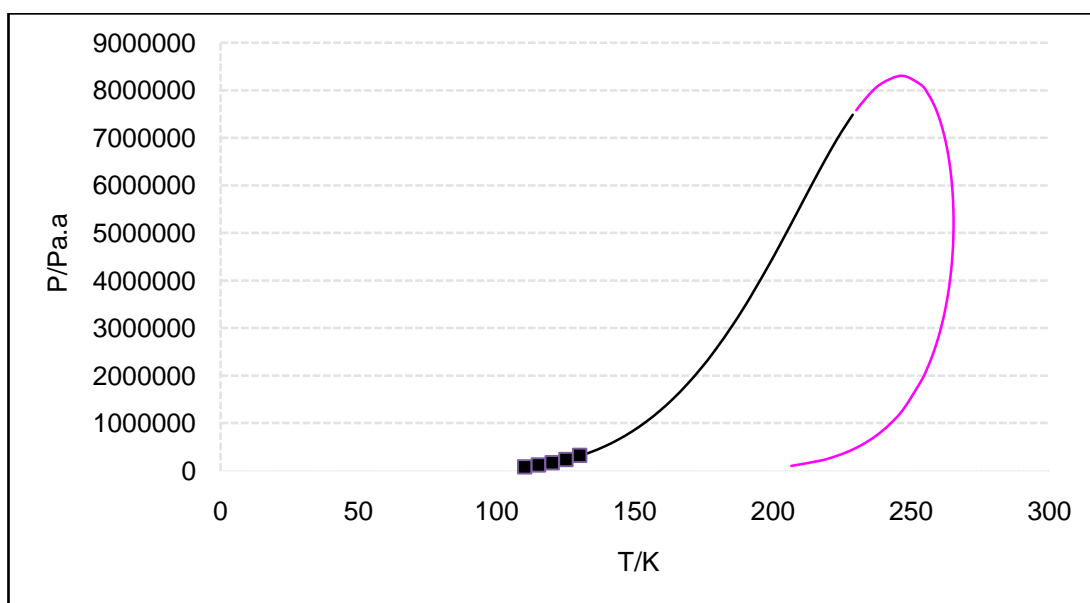
F 2: SET 20-MIX A; CPA-SRK-VDW
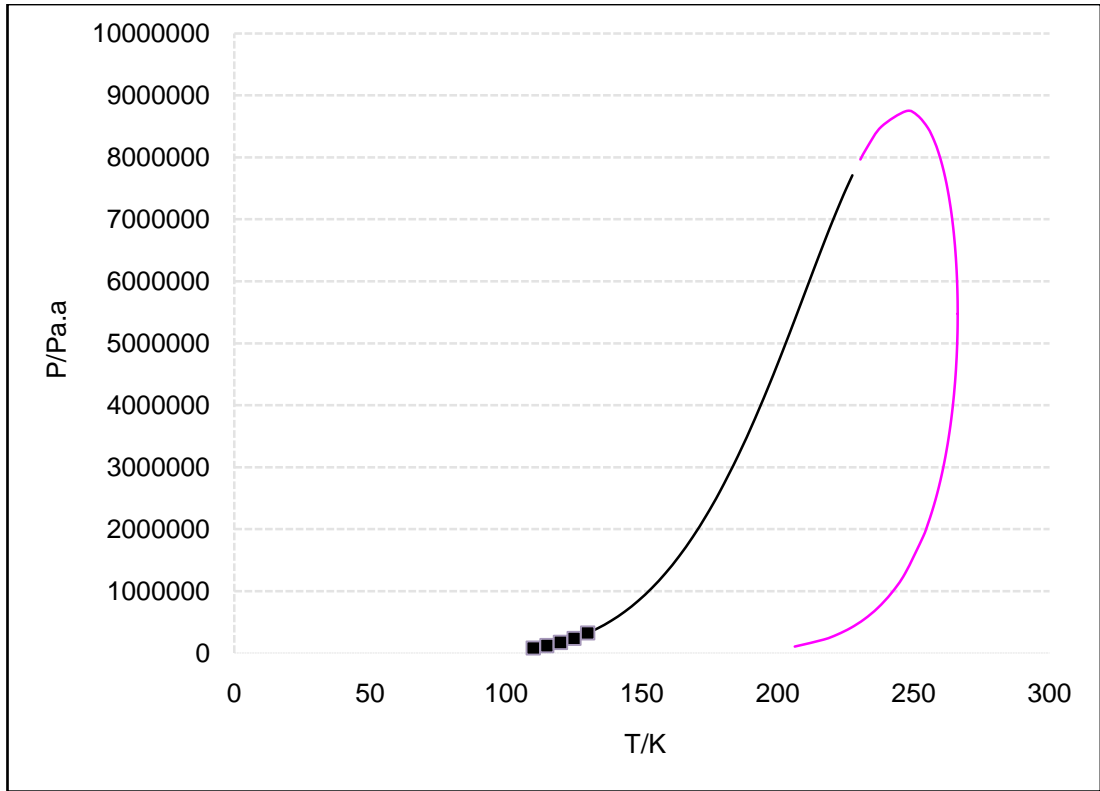
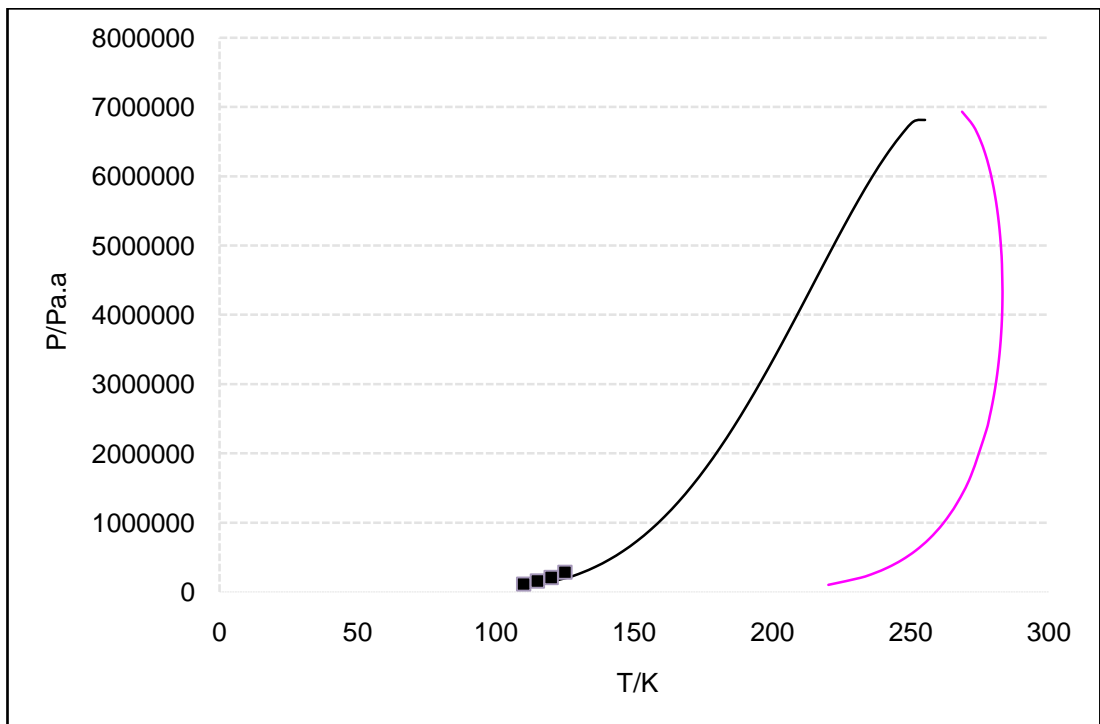F 3: SET 20-MIX A; PR-VDW
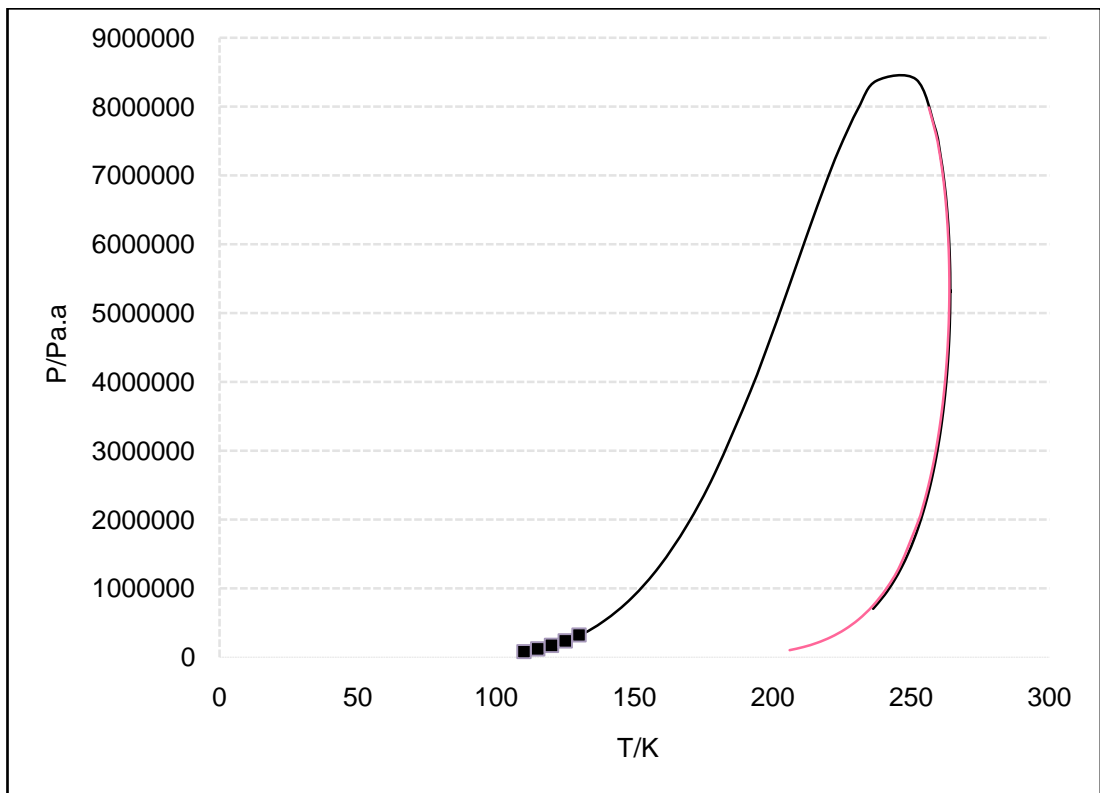
F 4: SET 20-MIX A; SRK-VDW
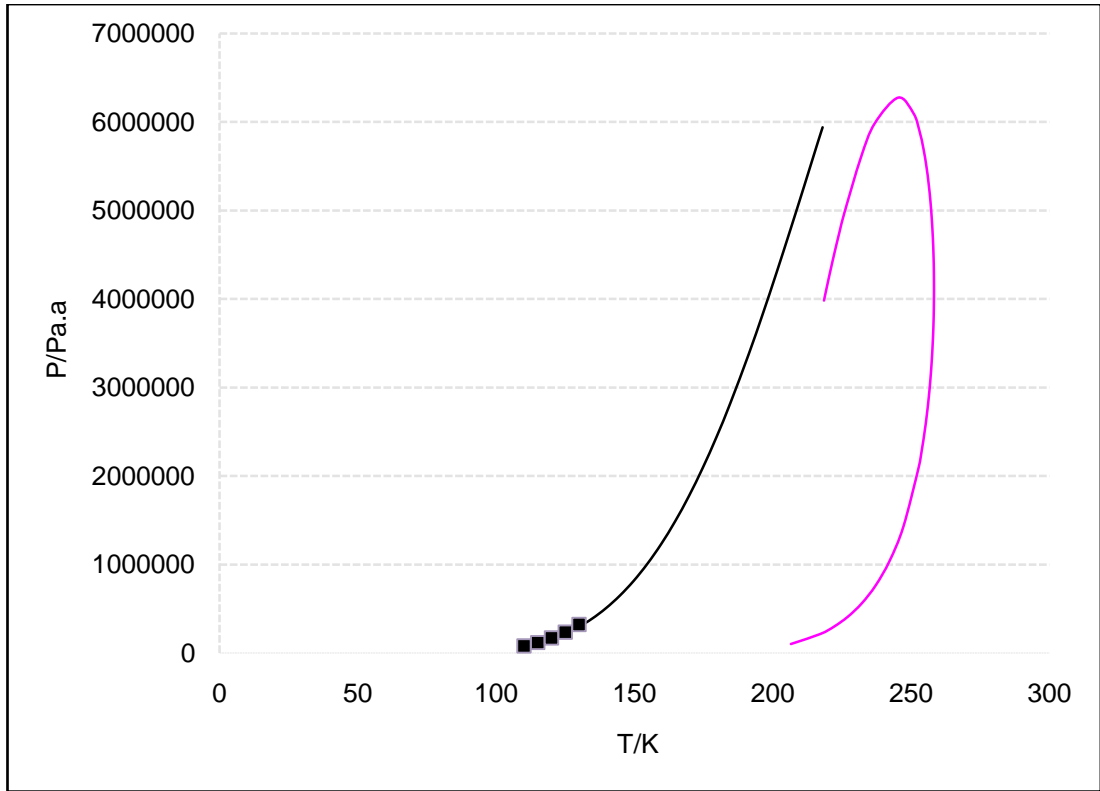
F 5: SET 20-MIX A; PR-UNIQUAC-WS
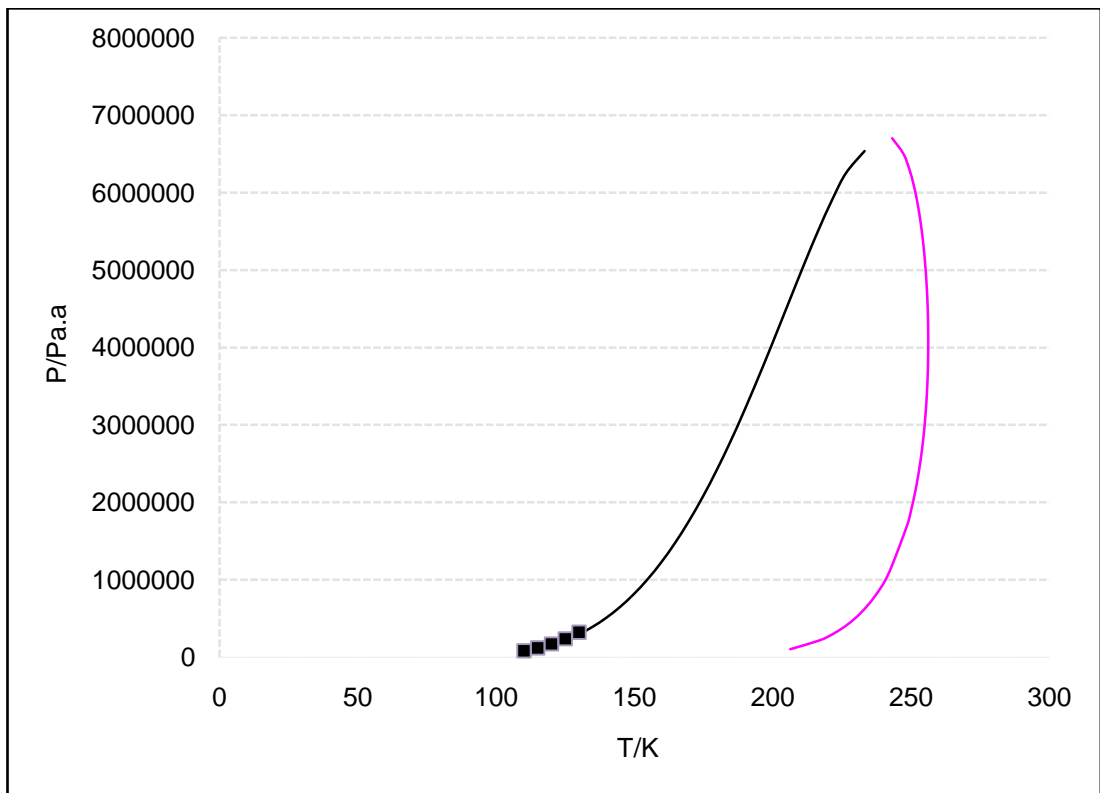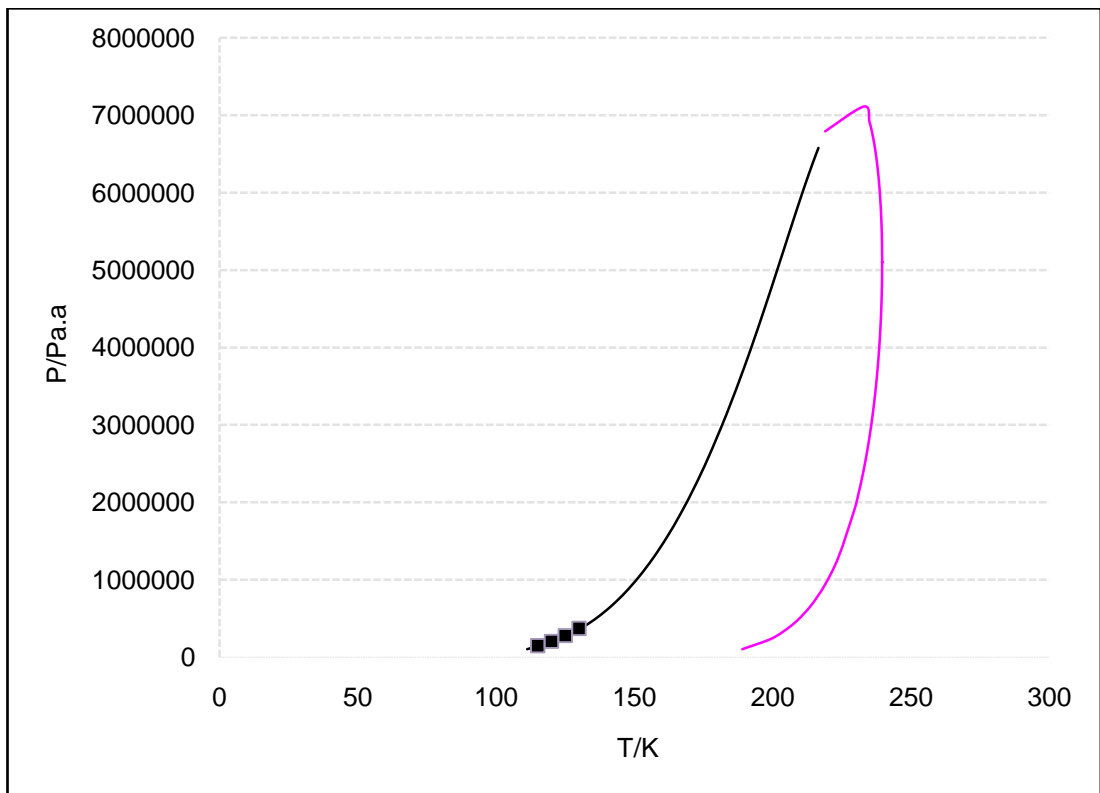

F 6: SET 20-MIX A; PR-NRTL-WS

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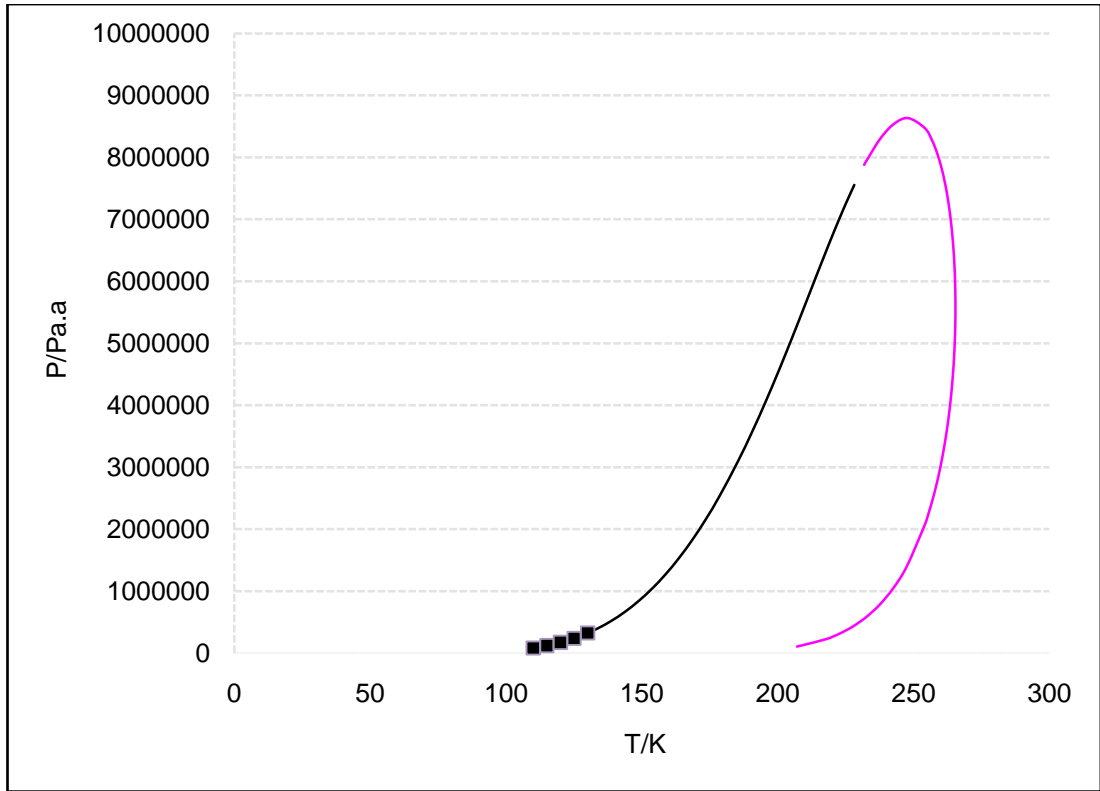
F 7: SET 20-MIX A; SRK-EXT-VDW

F 8: SET 20-MIX A; PR-WS

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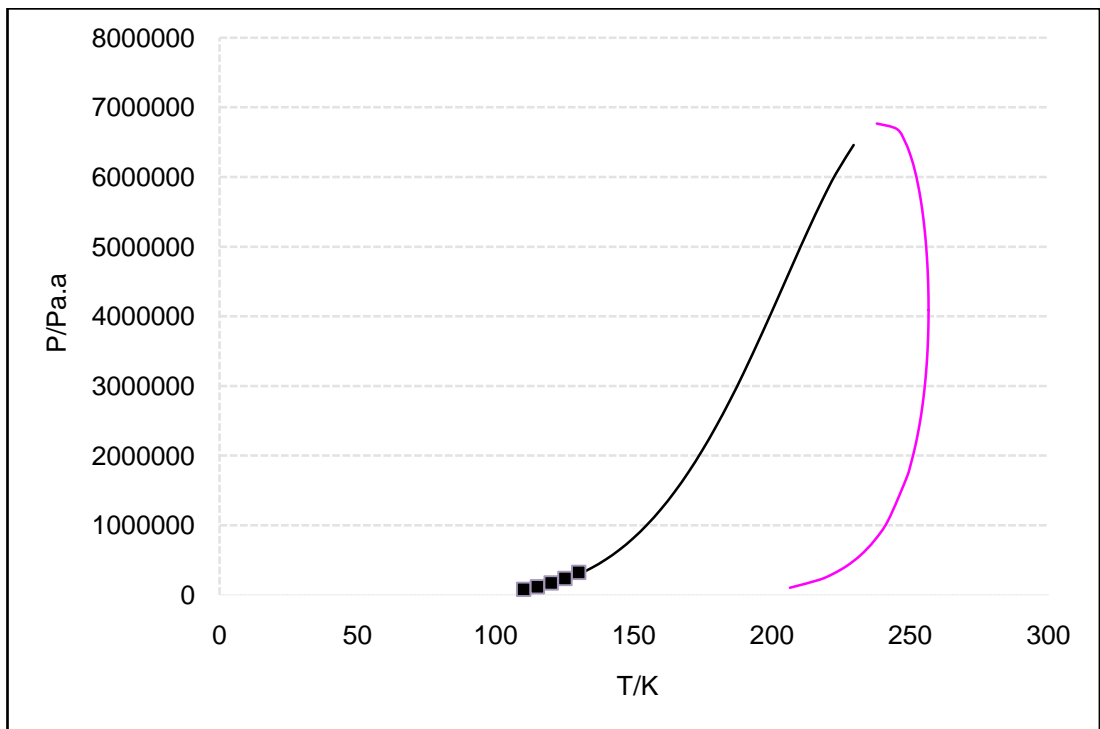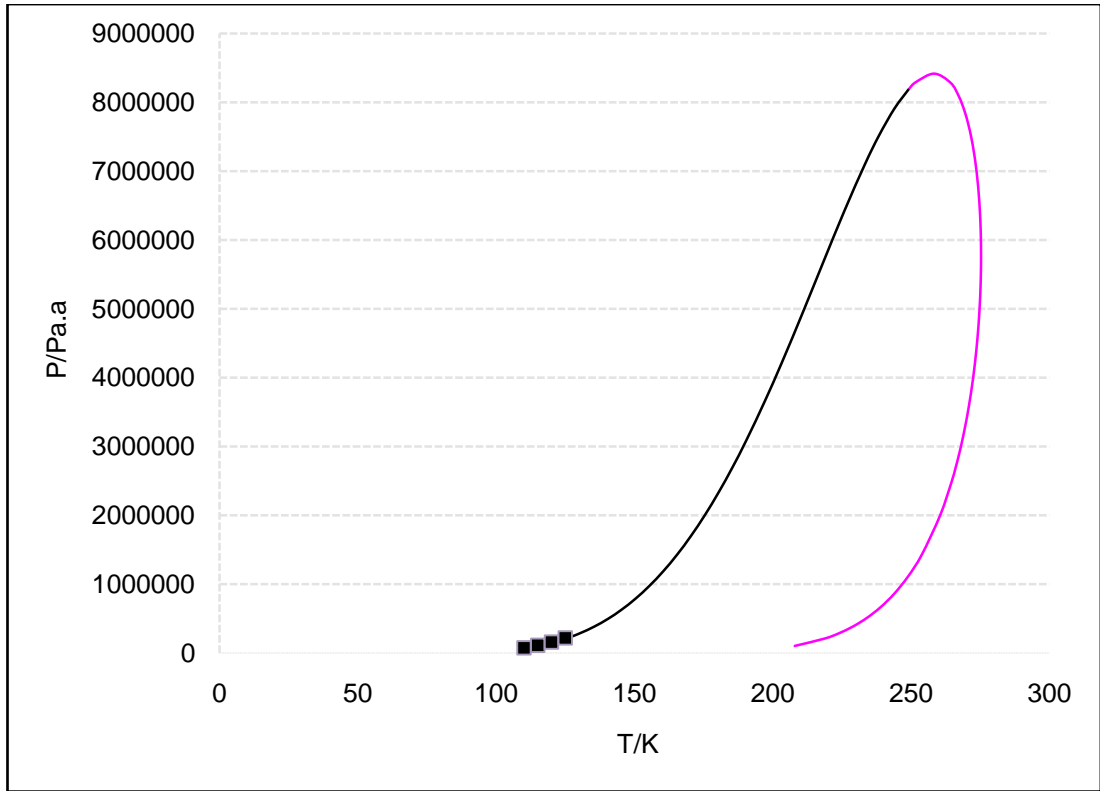
F 9: SET 20-MIX B; CPA-PR-VDW
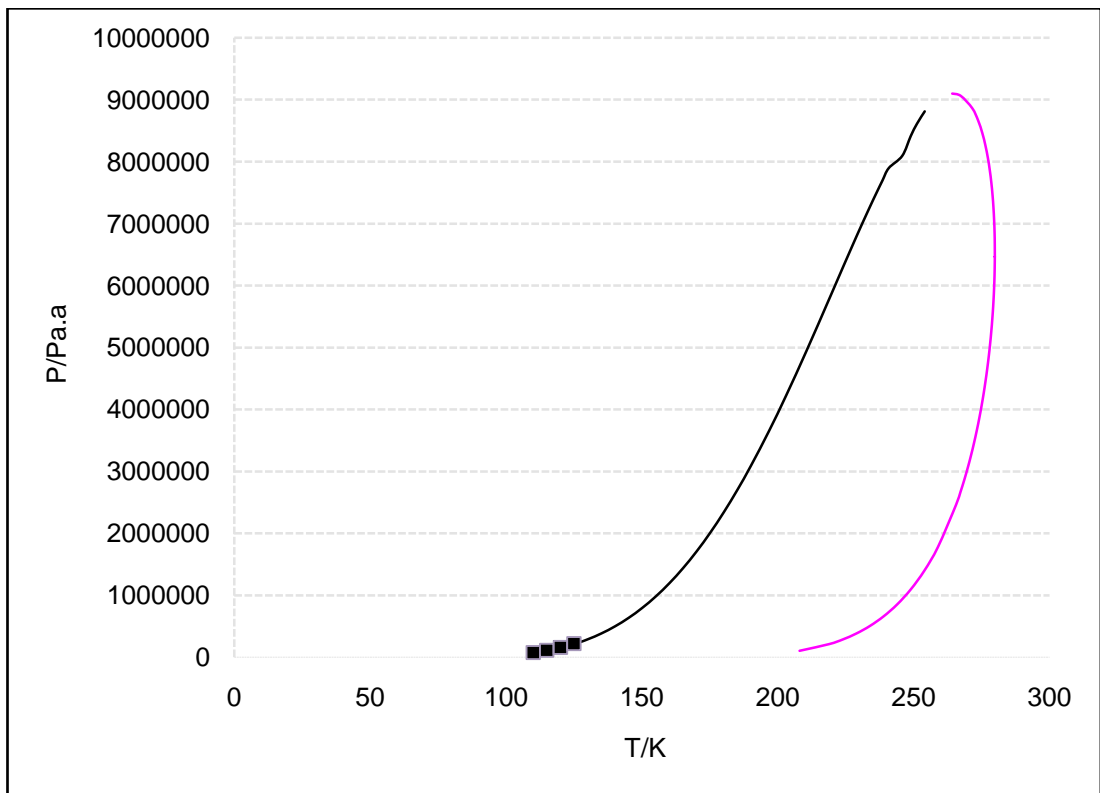
F 10: SET 20-MIX B; CPA-SRK-VDW
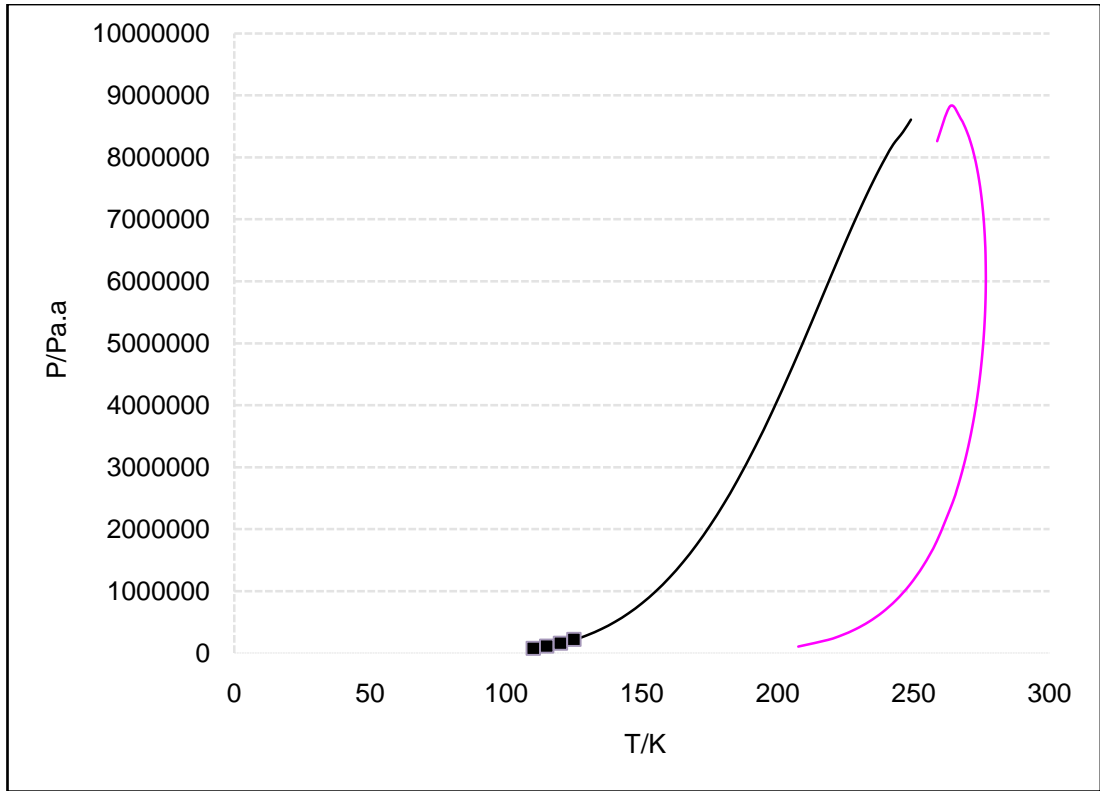
F 11: SET 20-MIX B; PR-VDW
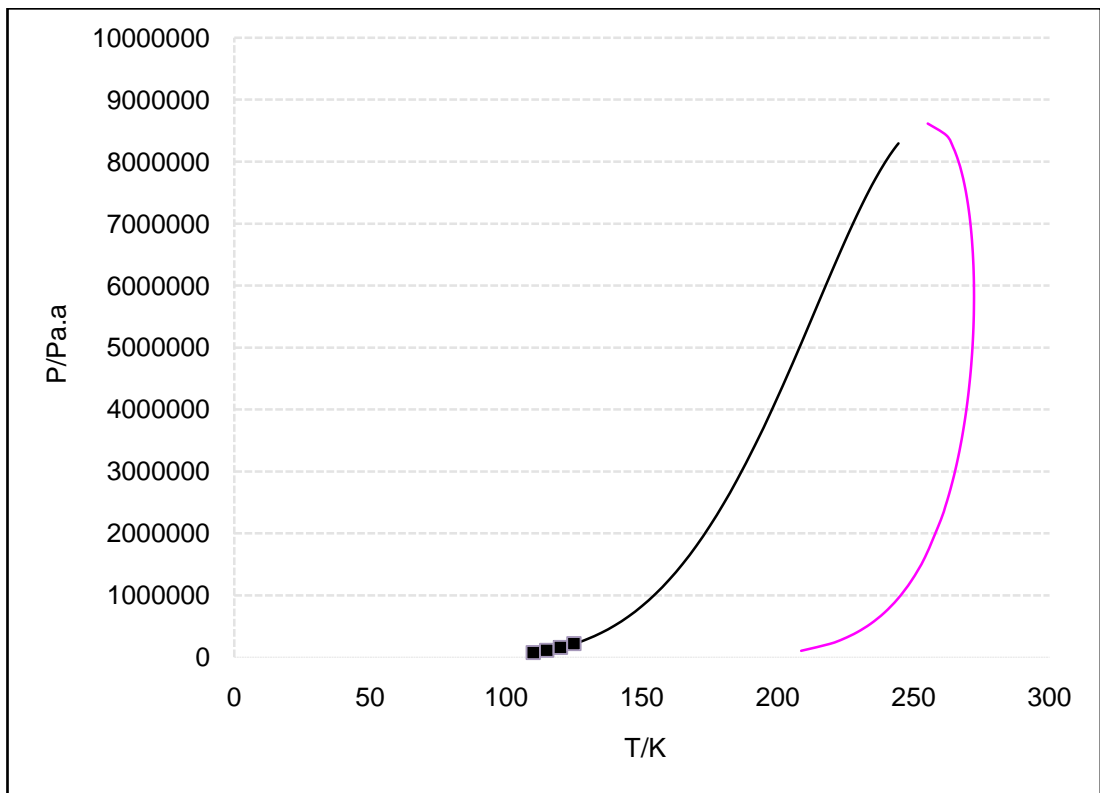
F 12: SET 20-MIX B; SRK-VDW
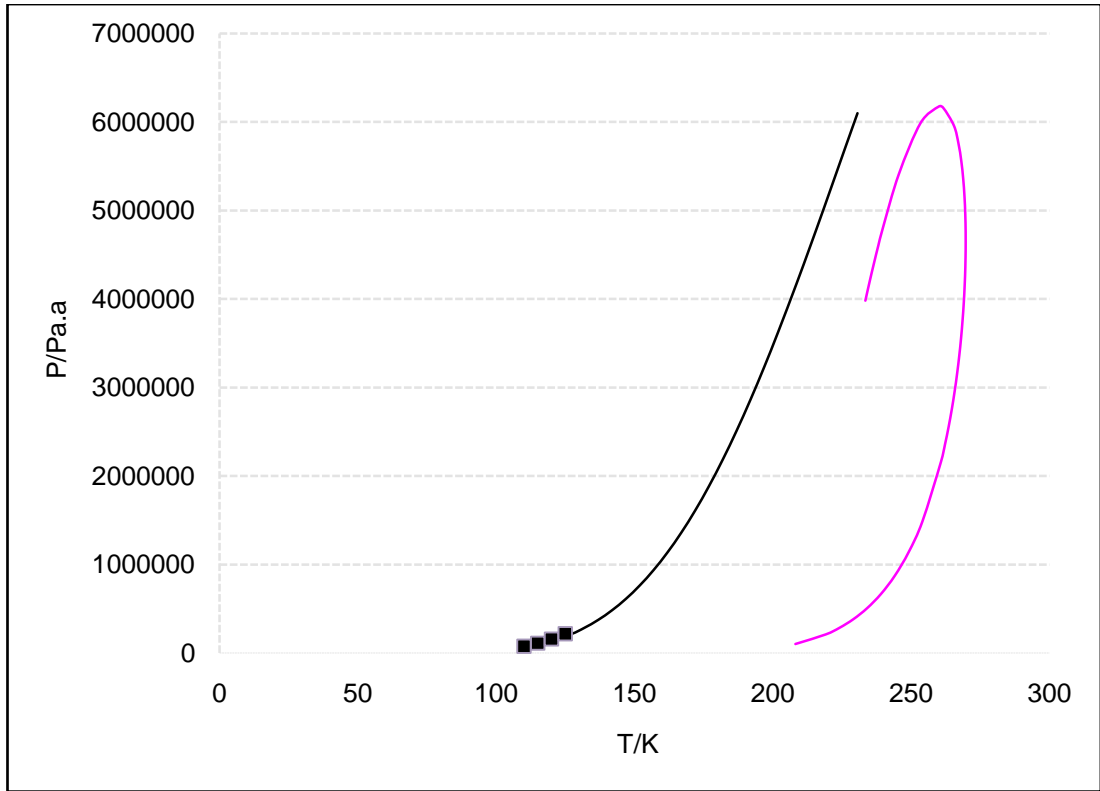
F 13: SET 20-MIX B; PR-UNIQUAC-WS
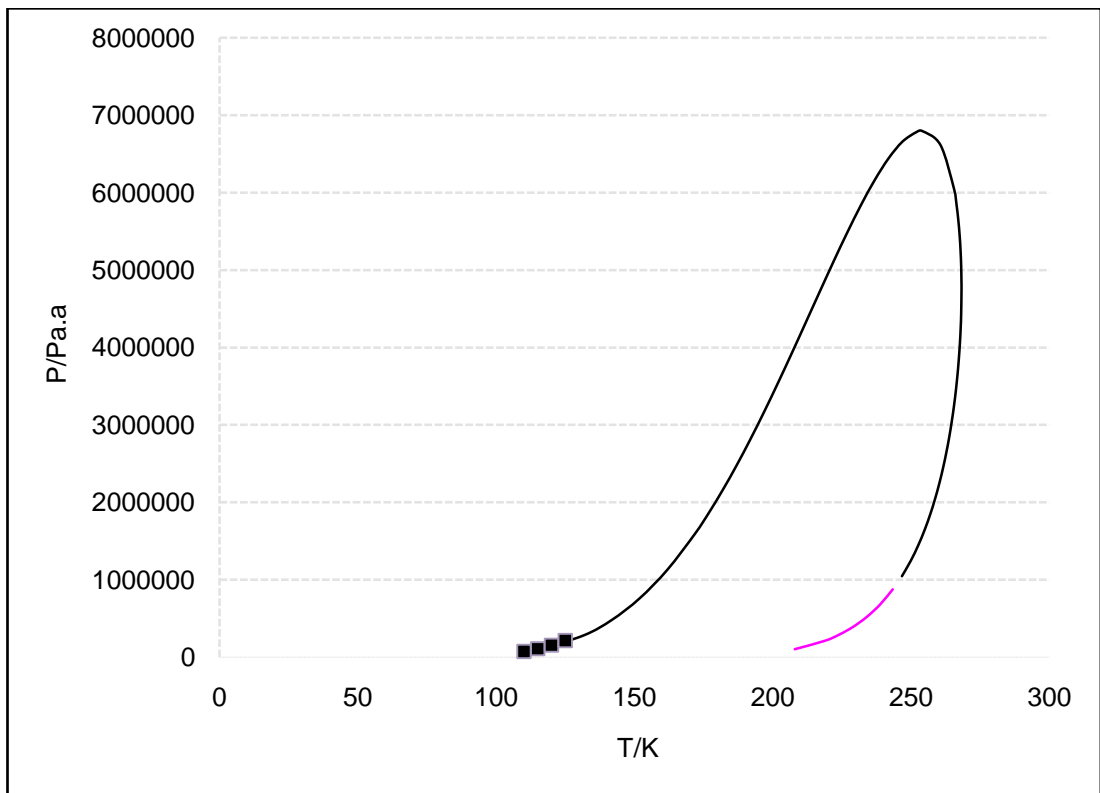
F 14: SET 20-MIX B; PR-NRTL-WS
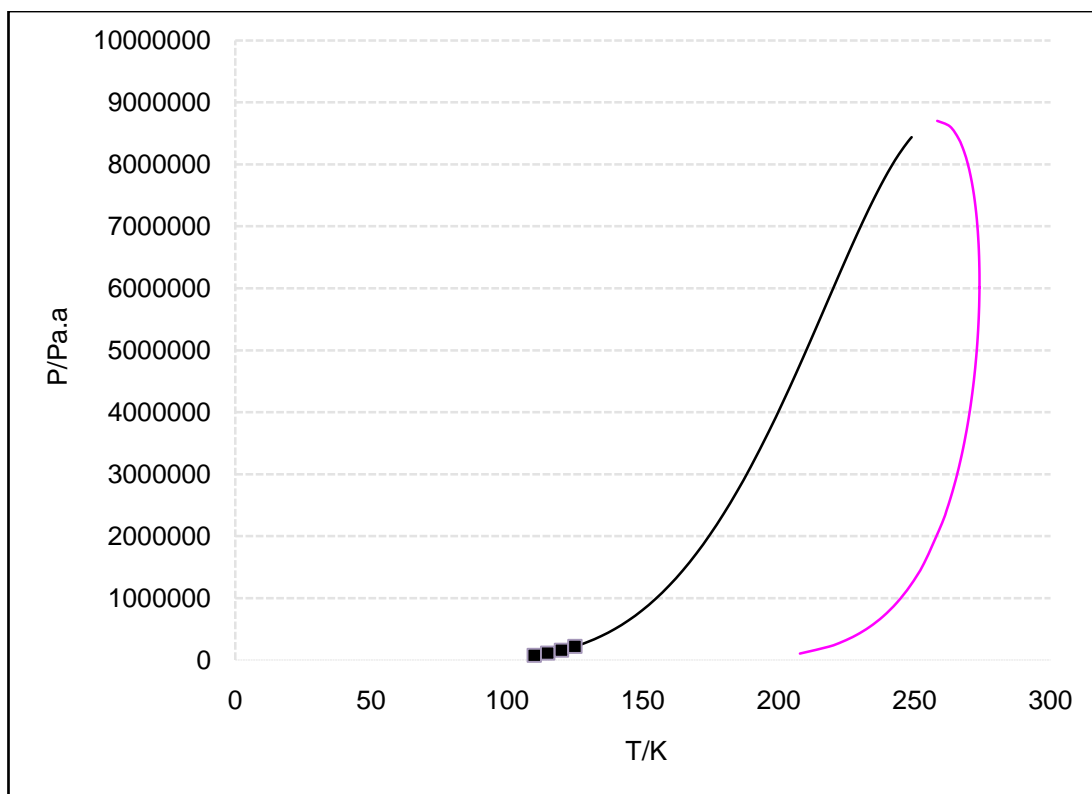
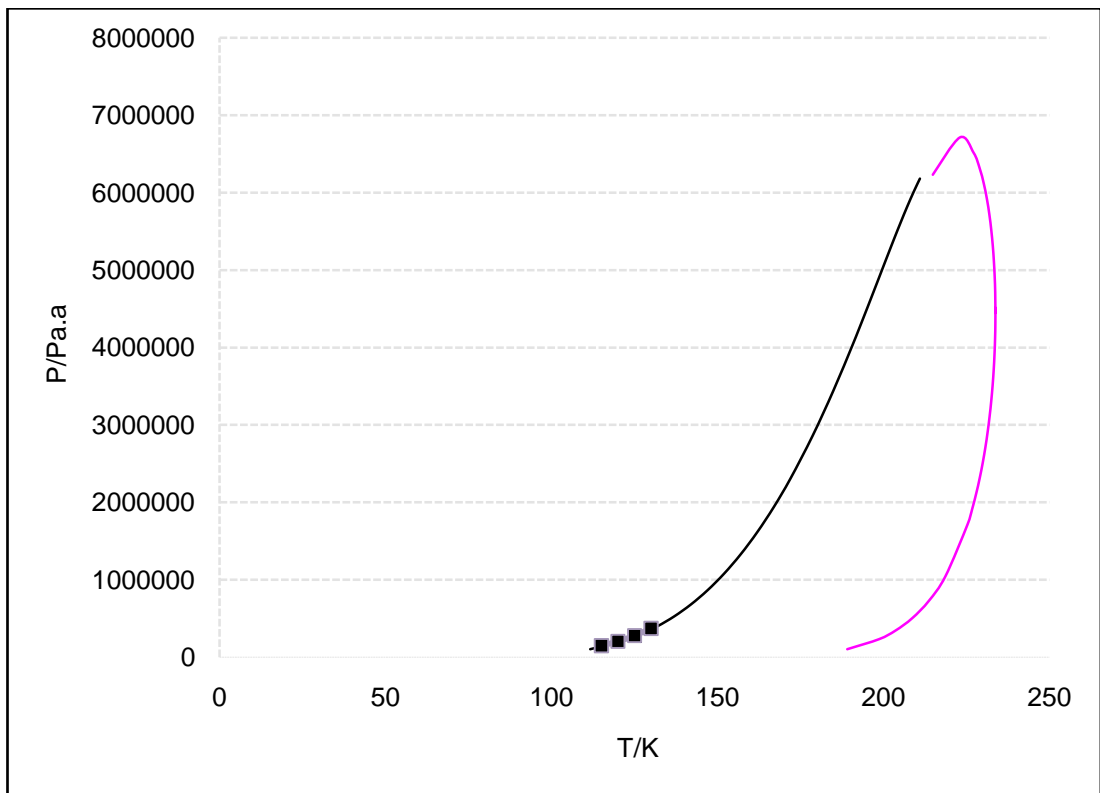F 15: SET 20-MIX B; SRK-EXT-VDW
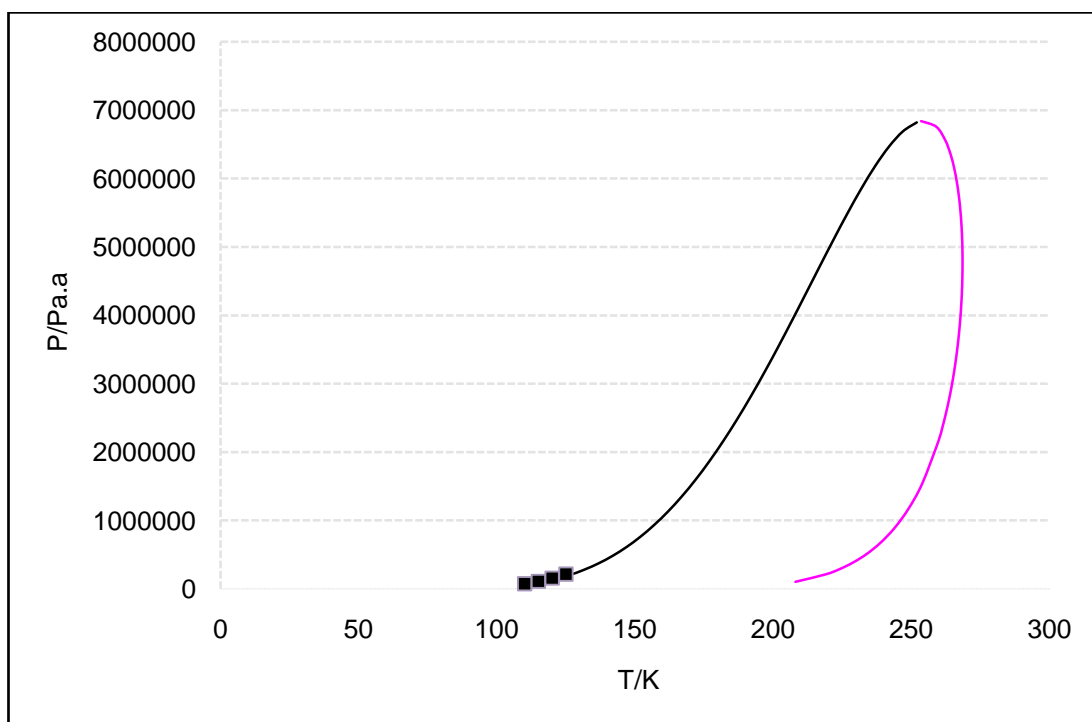
F 16: SET 20-MIX B; PR-WS
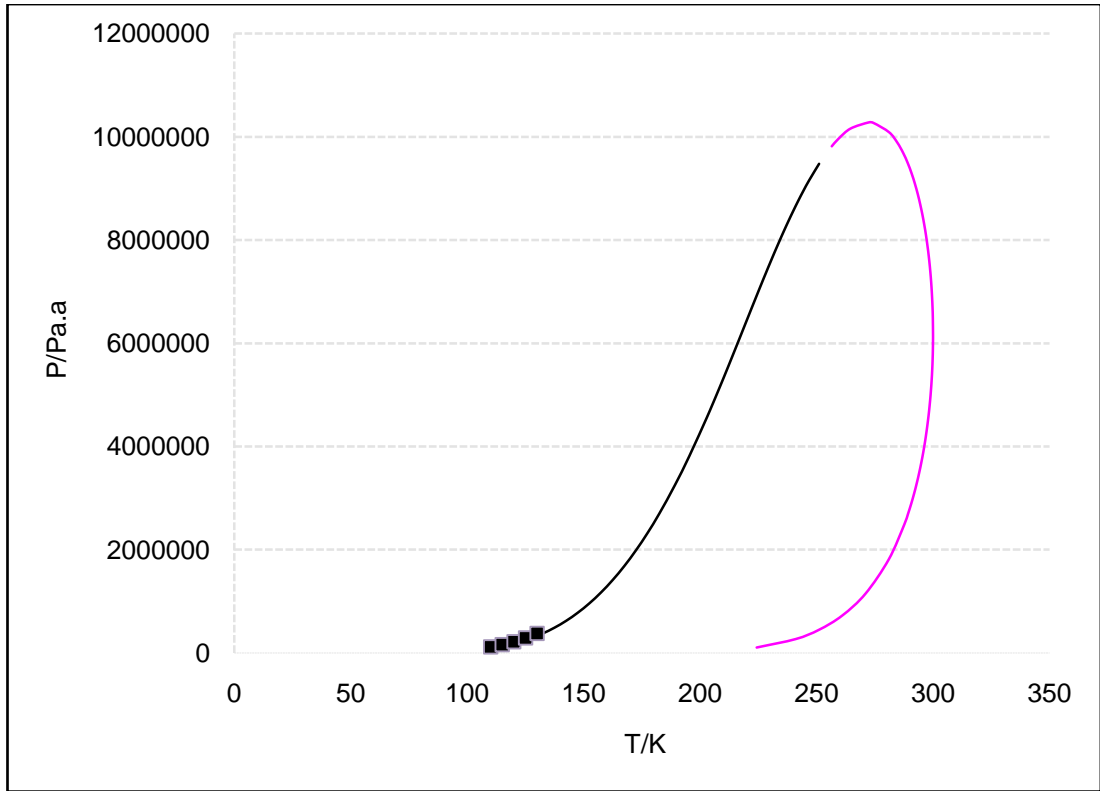
F 17: SET 20-MIX C; CPA-PR-VDW
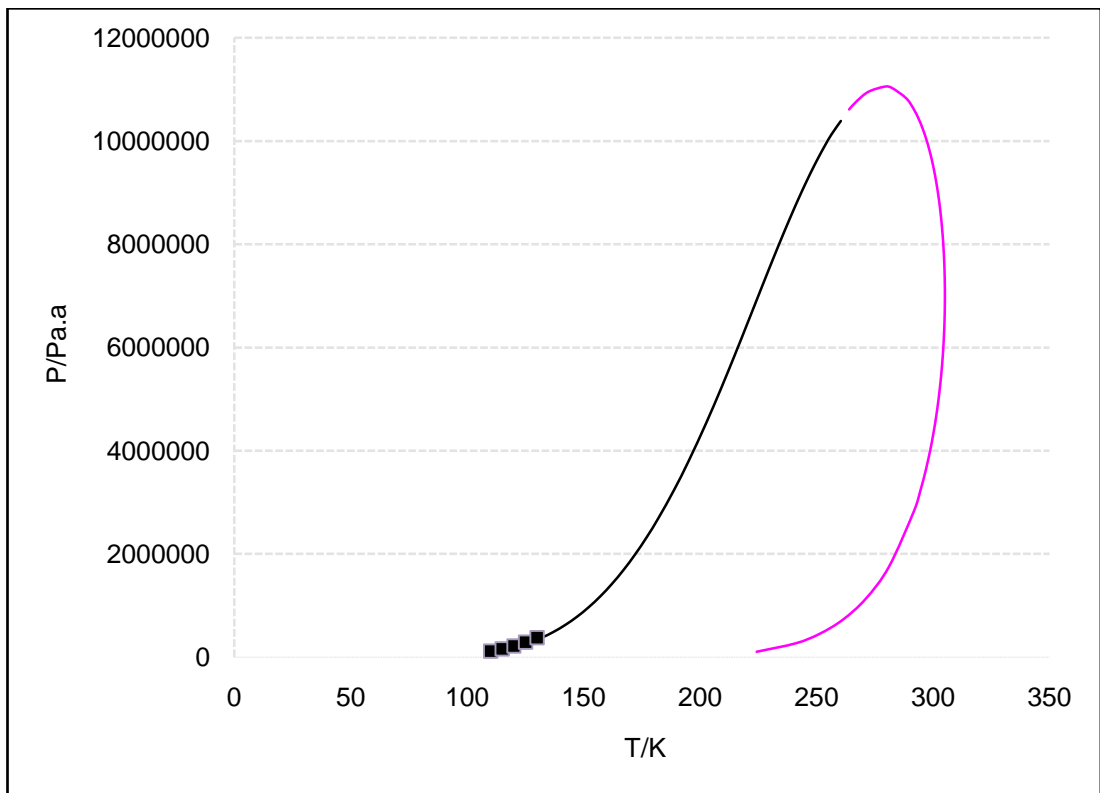
F 18: SET 20-MIX C; CPA-SRK-VDW

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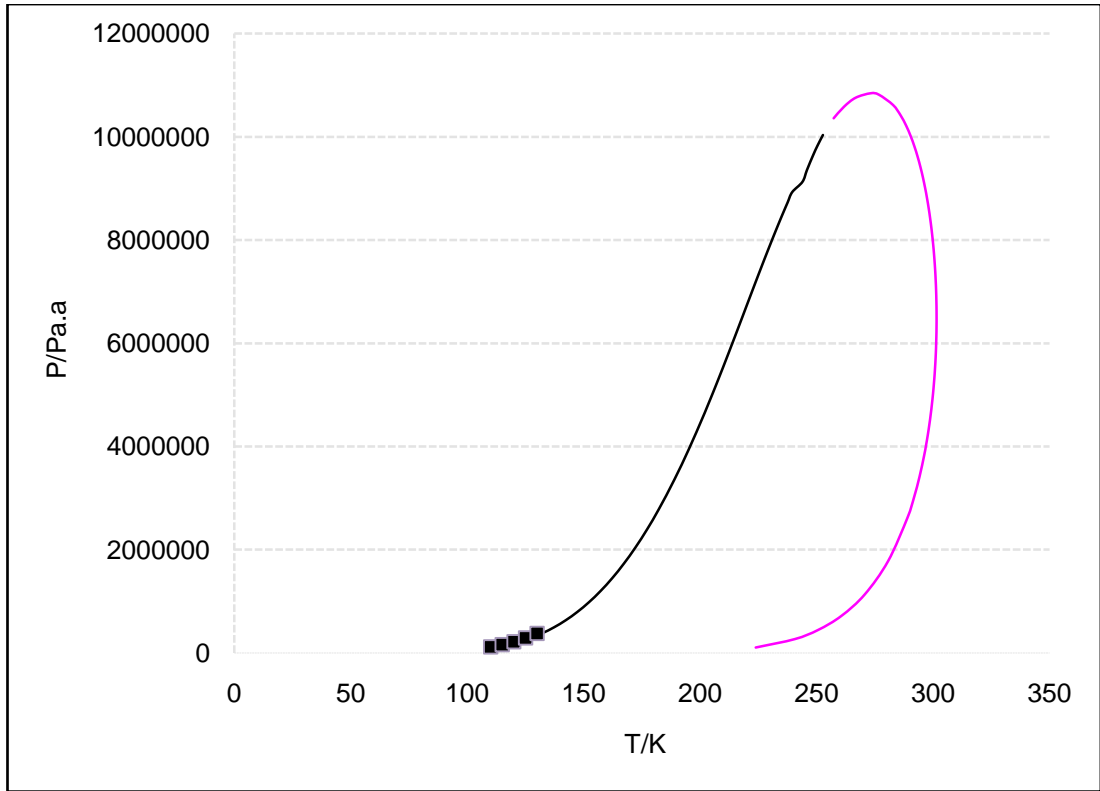
F 19: SET 20-MIX C; PR-VDW
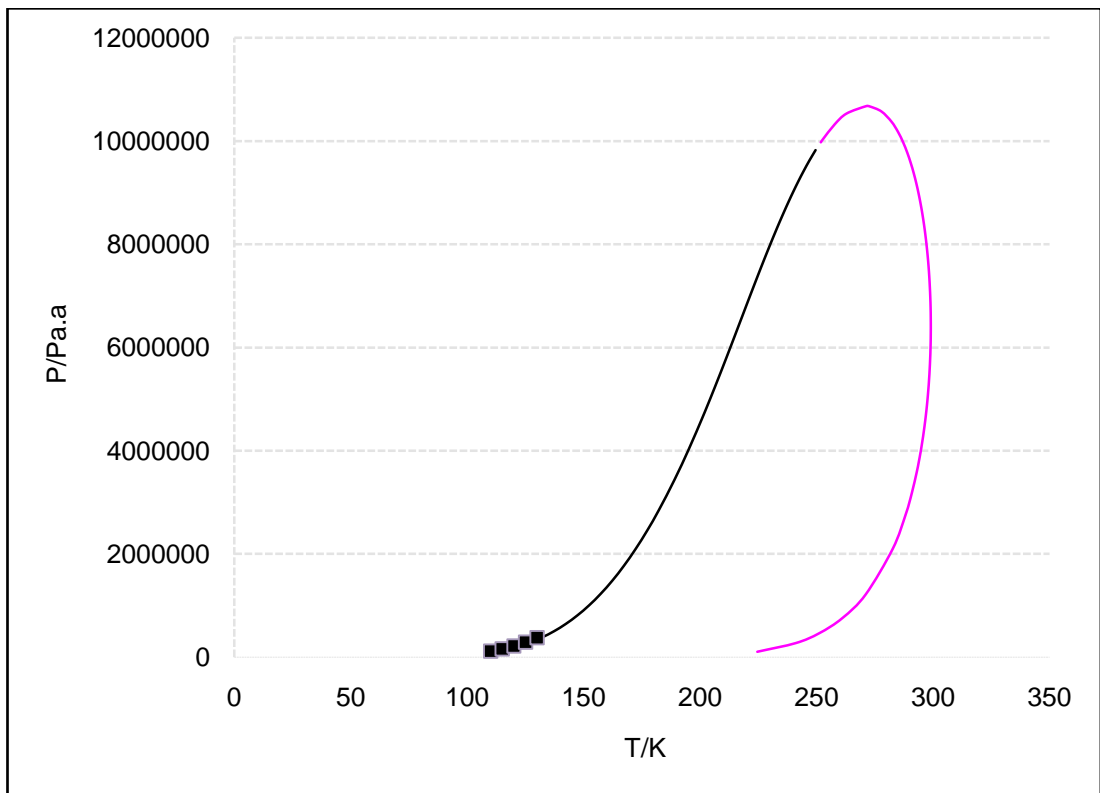
F 20: SET 20-MIX C; SRK-VDW
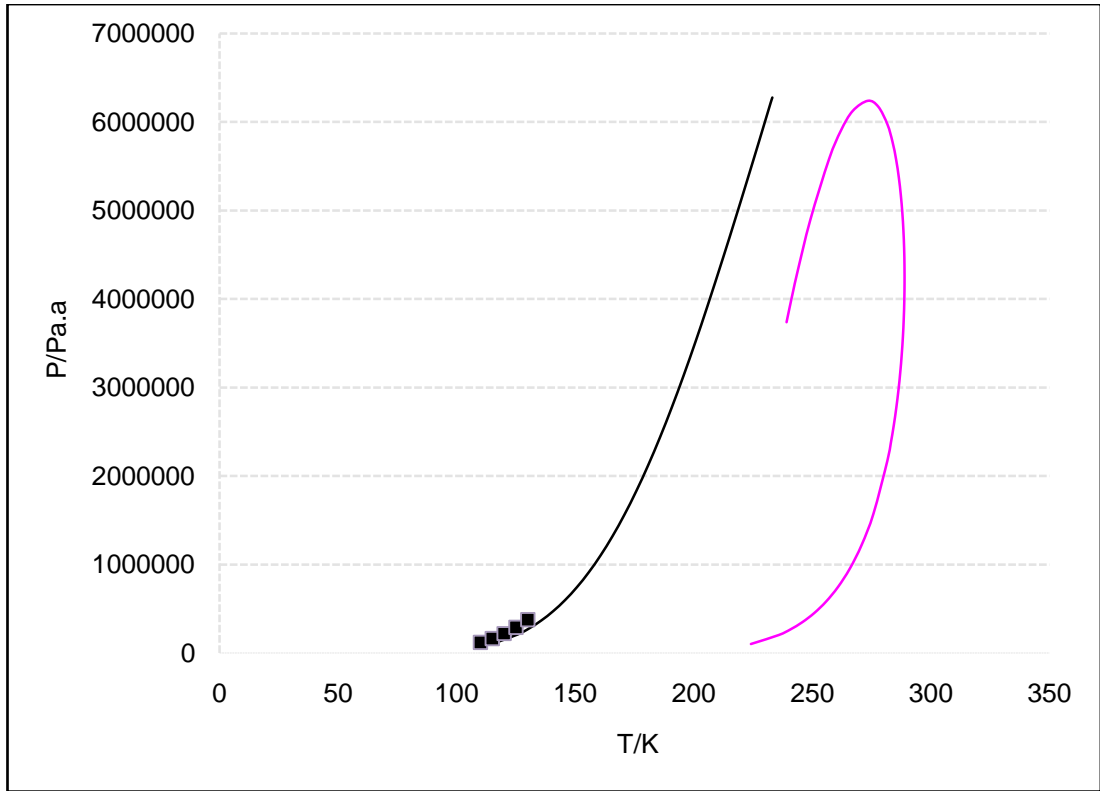
F 21: SET 20-MIX C; PR-UNIQUAC-WS
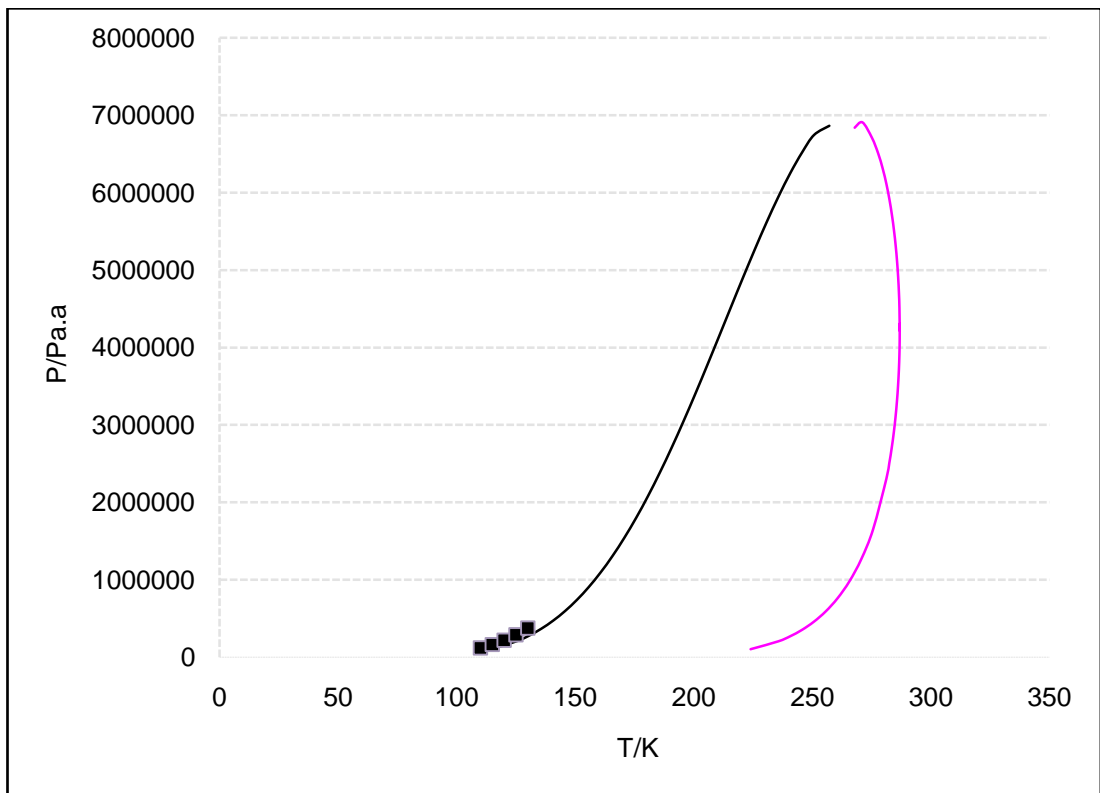
F 22: SET 20-MIX C; PR-NRTL -WS
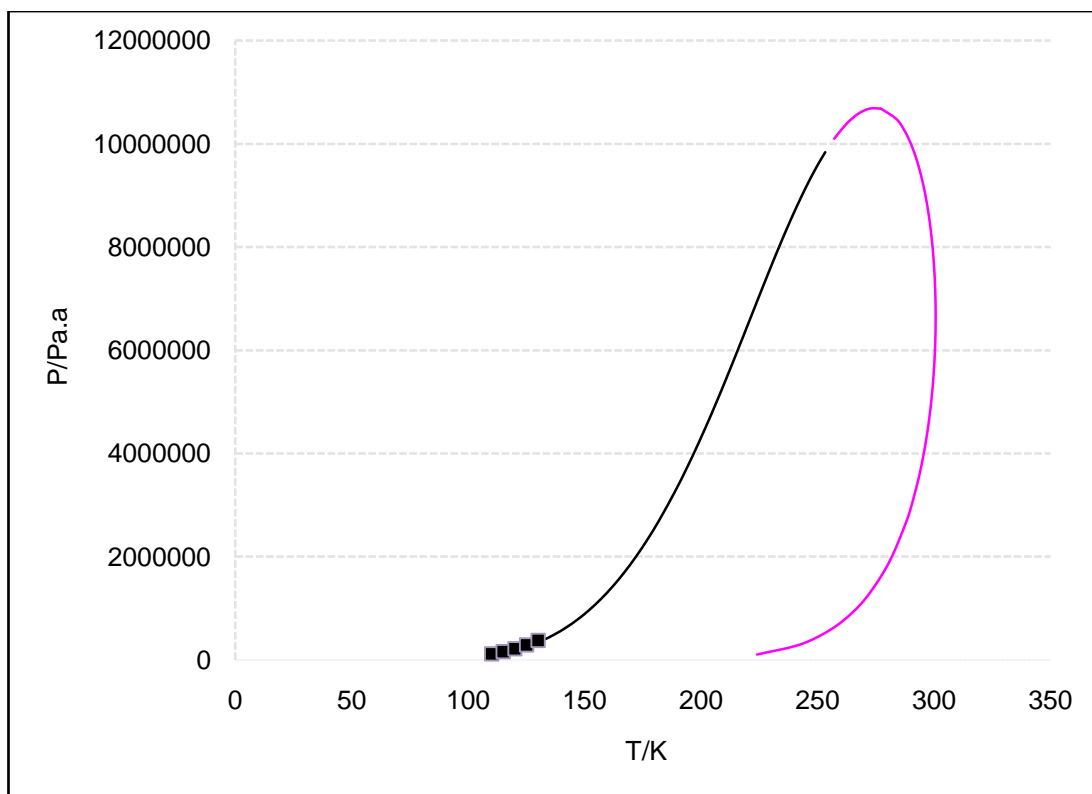
F 23: SET 20-MIX C; SRK-EXT-VDW
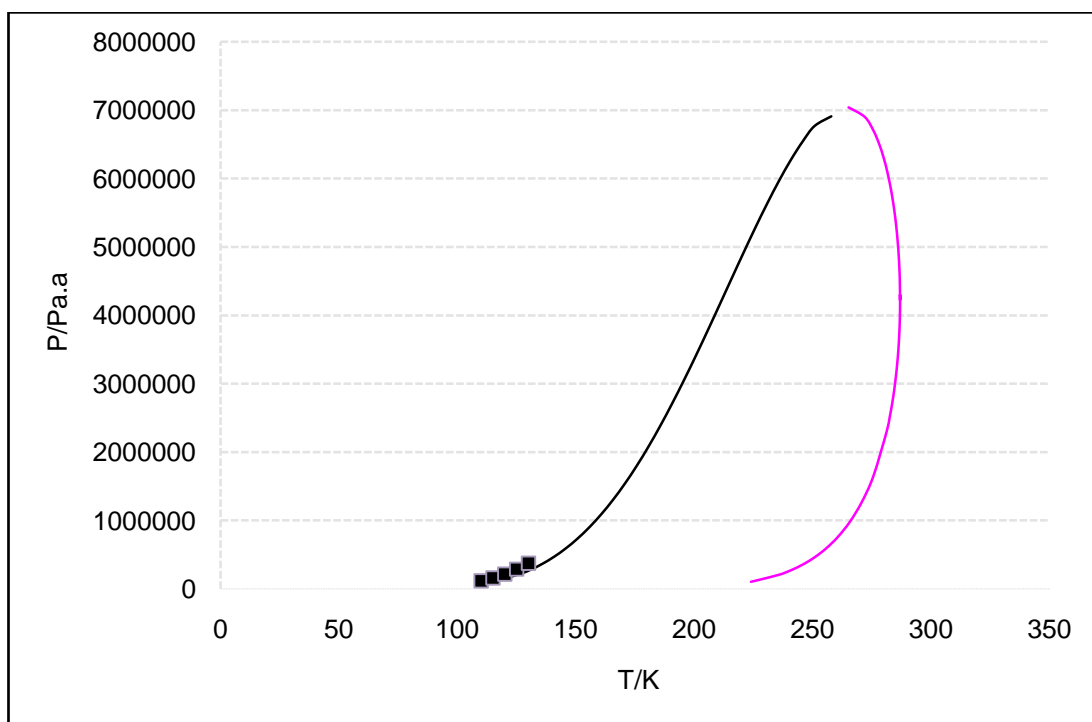
F 24: SET 20-MIX C; PR-WS
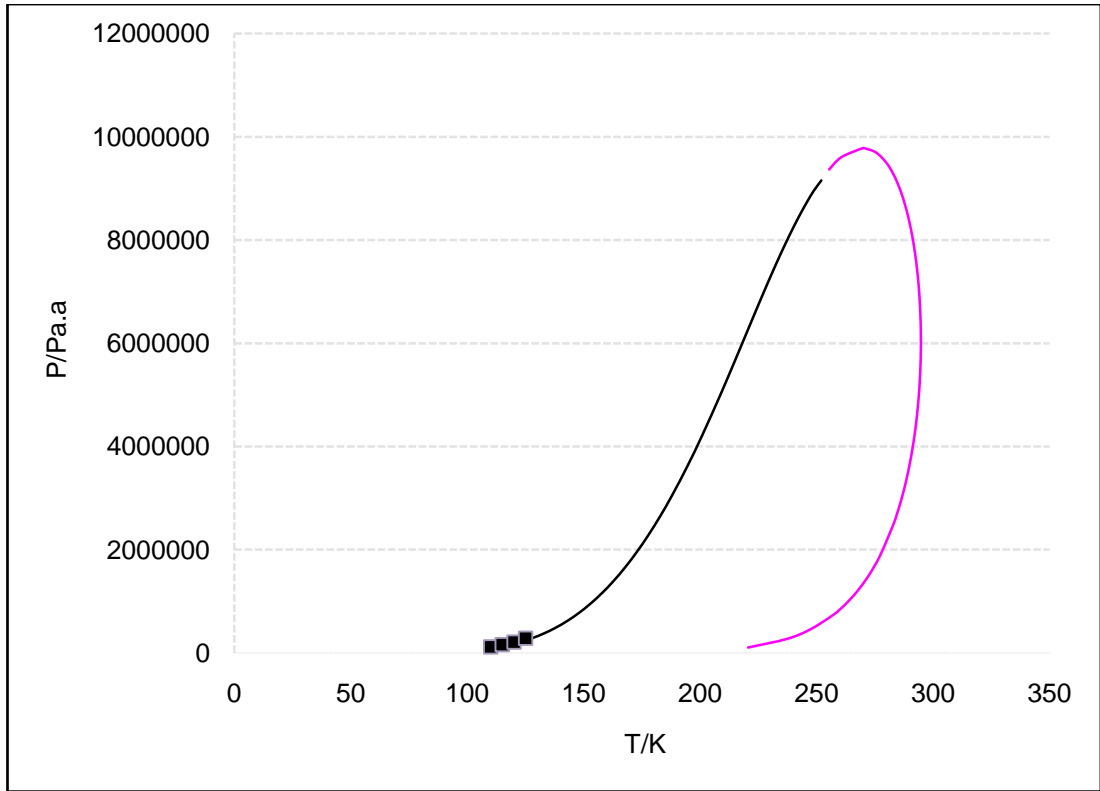
F 25: SET 20-MIX D; CPA-PR-VDW
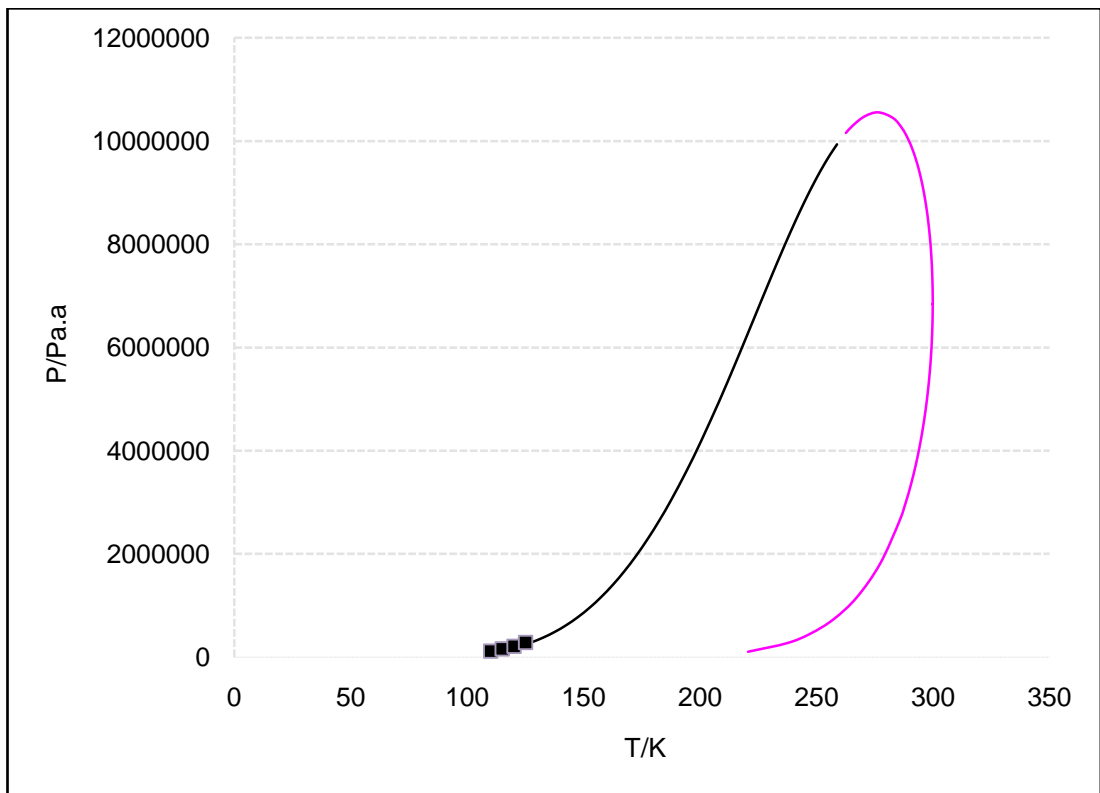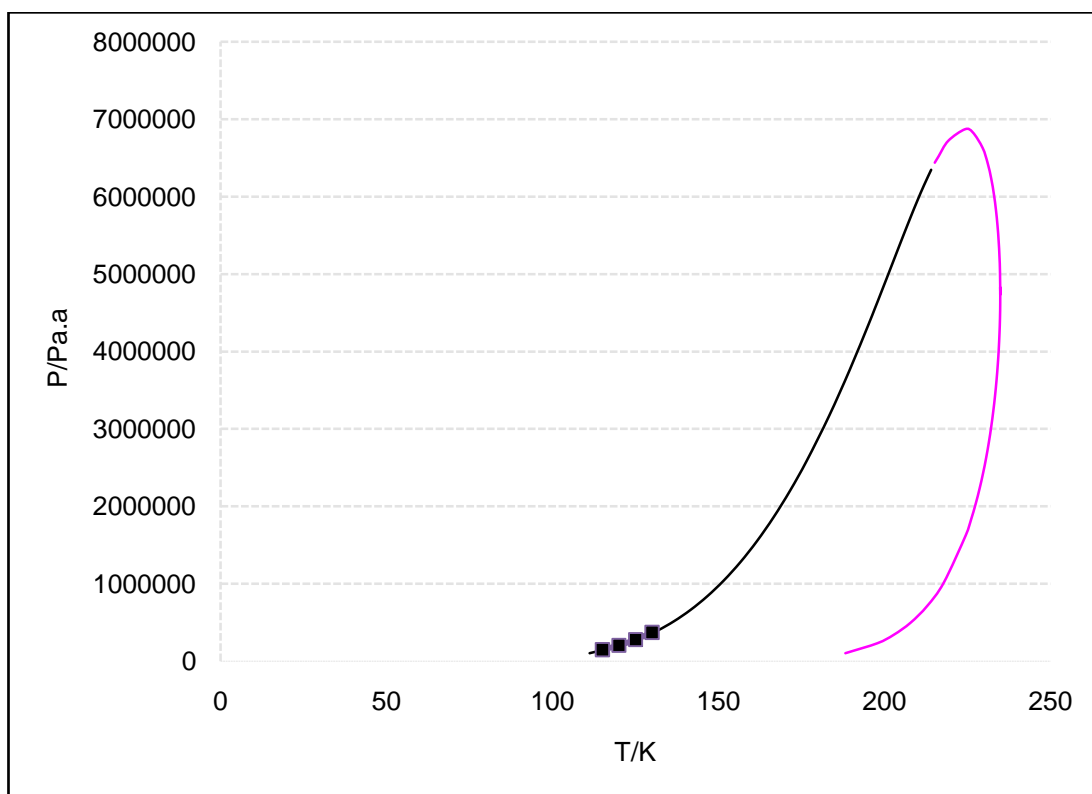

F 26: SET 20-MIX D; CPA-SRK-VDW

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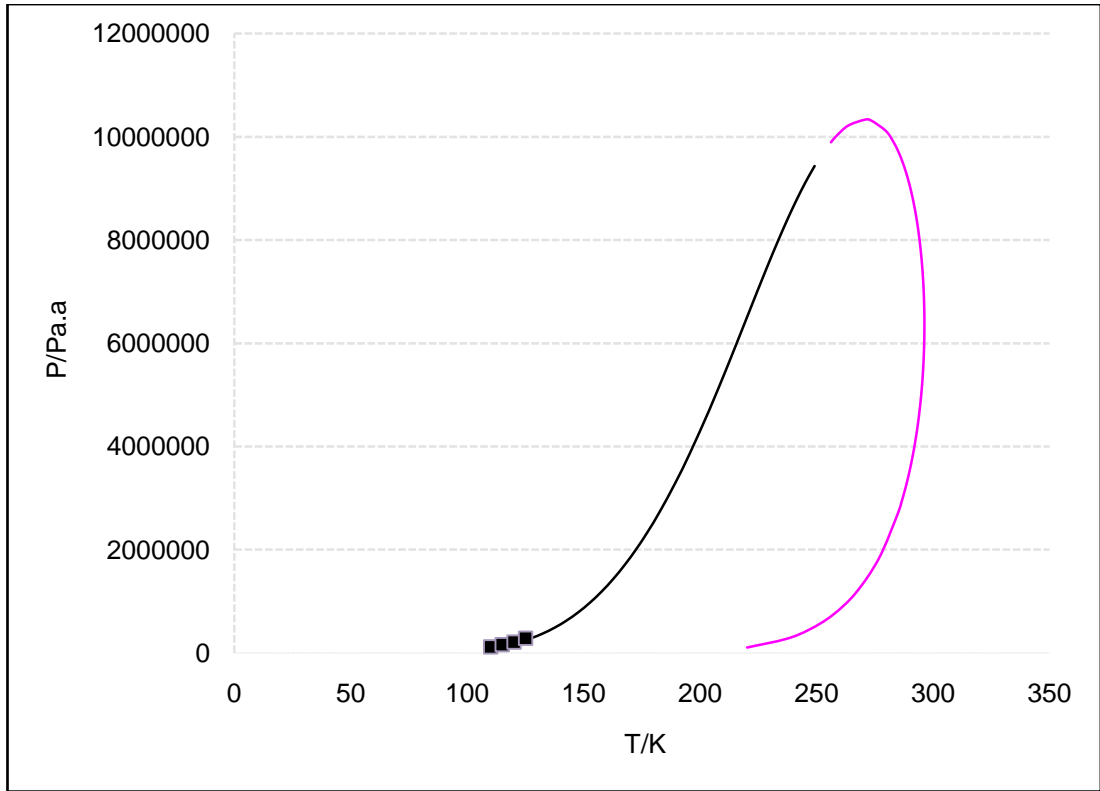
F 27: SET 20-MIX D; PR-VDW
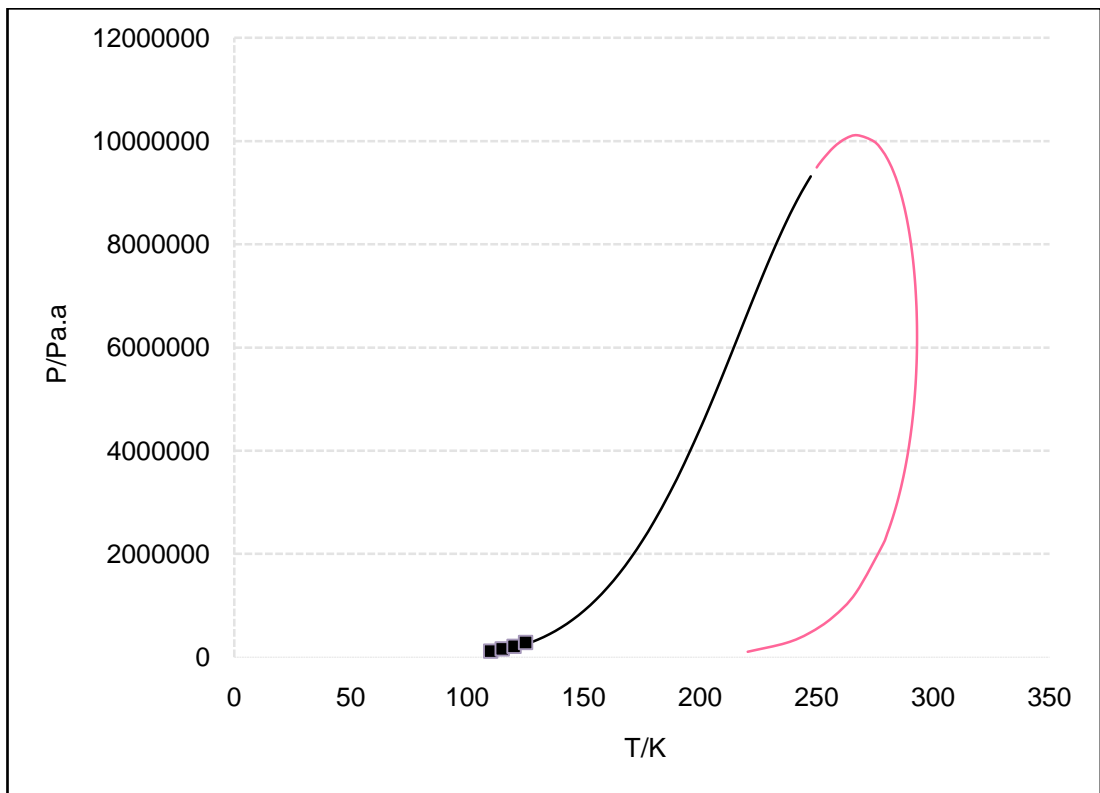
F 28: SET 20-MIX D; SRK-VDW
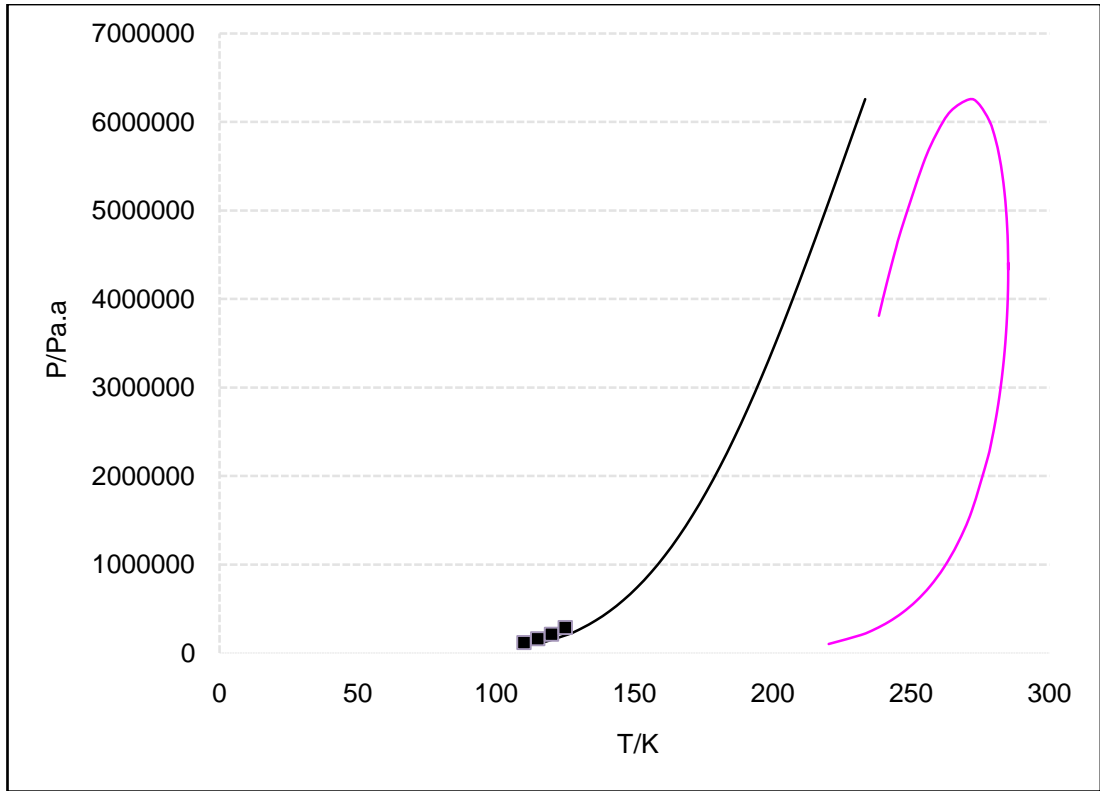
F 29: SET 20-MIX D; PR-UNIQUAC-WS
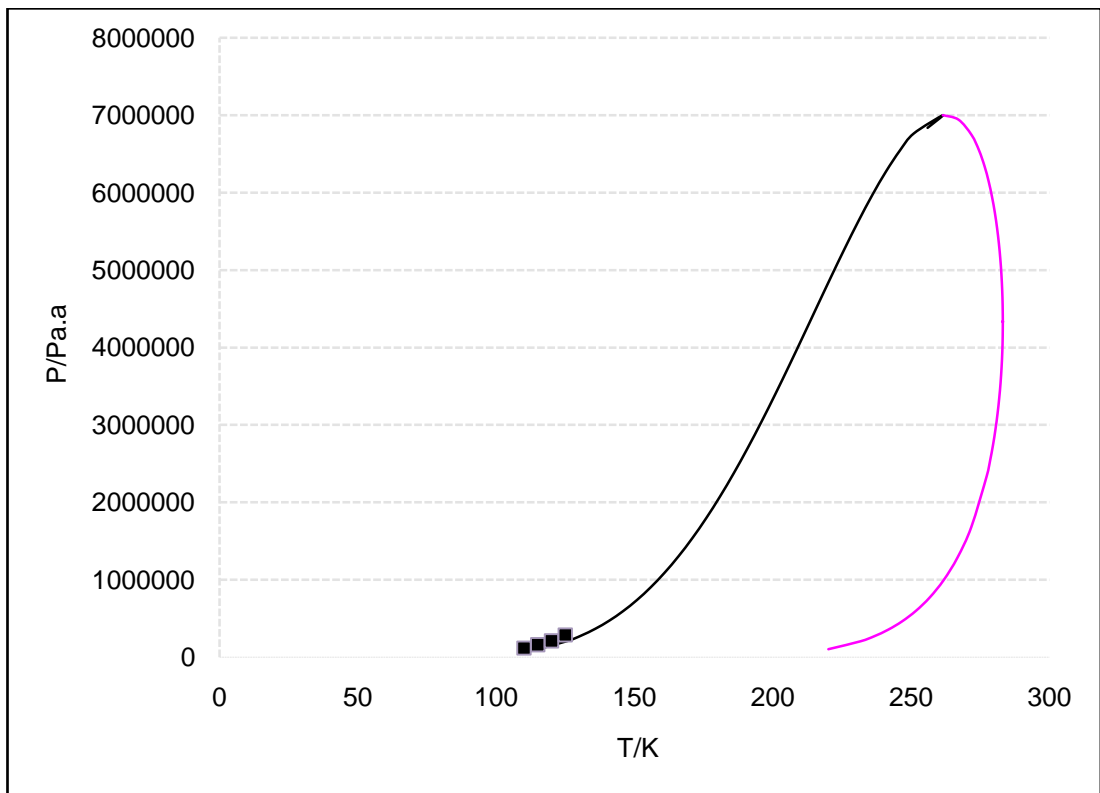
F 30: SET 20-MIX D; PR-NRTL-WS
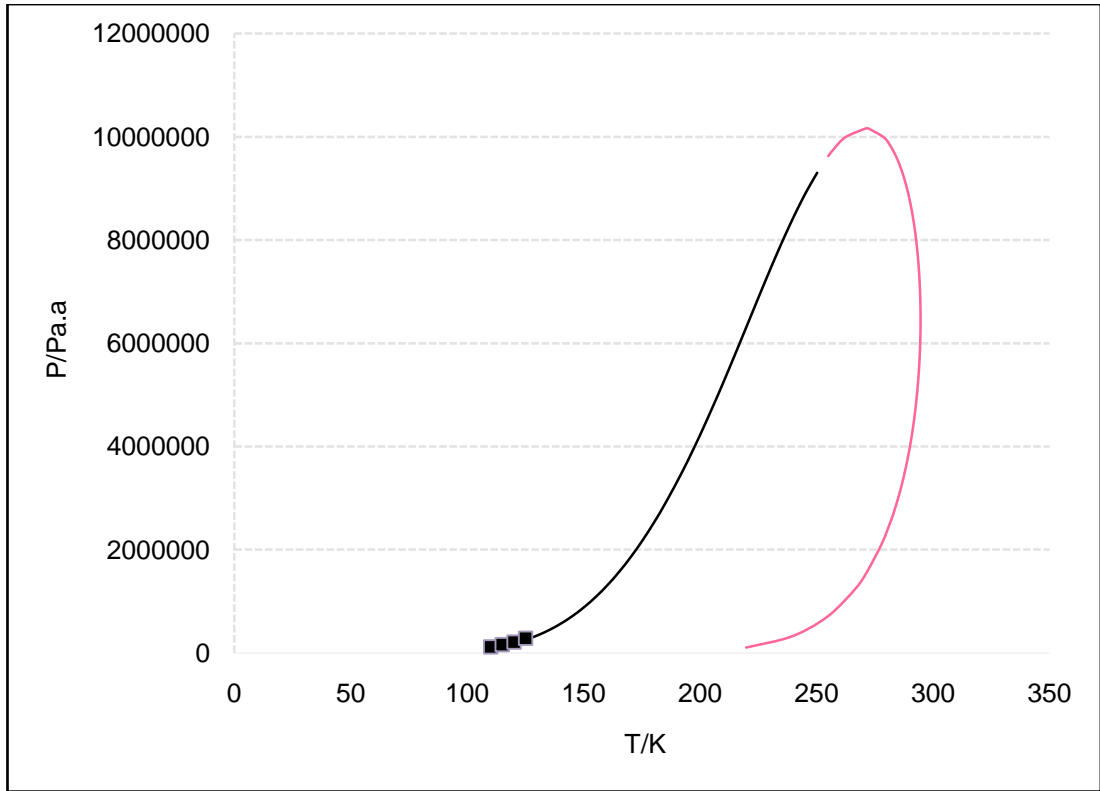
F 31: SET 20-MIX D; SRK-EXT-VDW

F 32: SET 20-MIX D; PR-WS
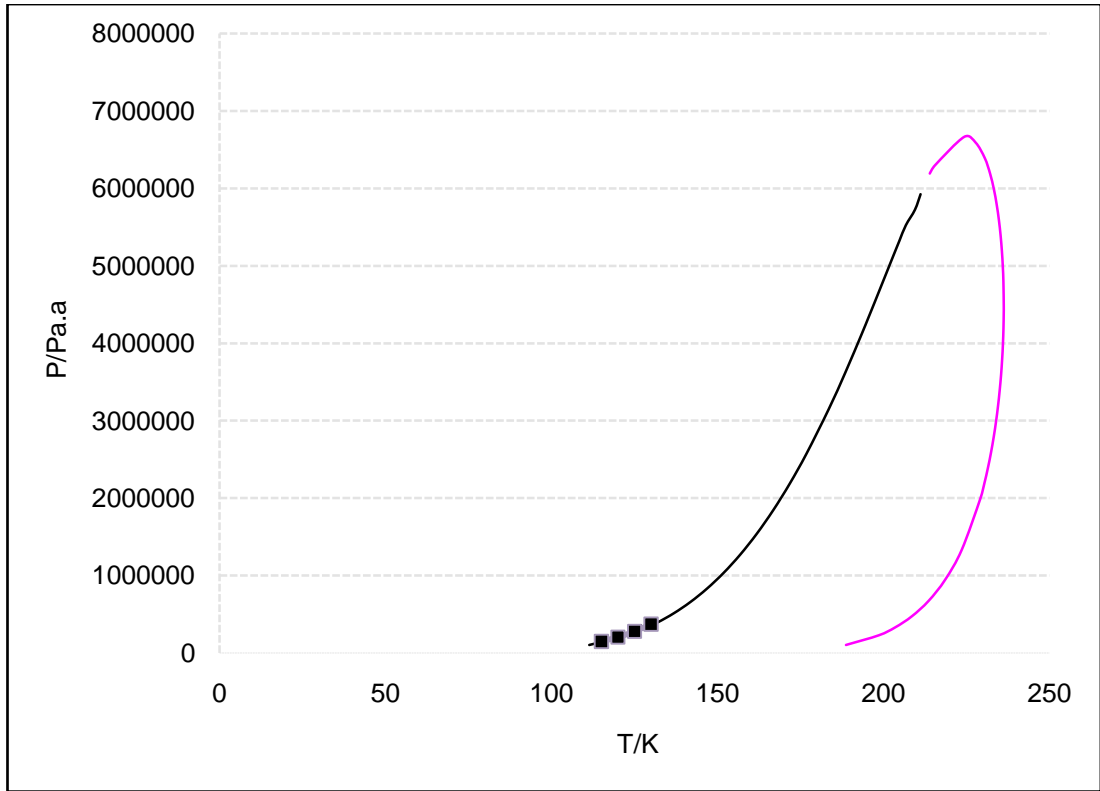
F 33: SET 20-MIX E; CPA-PR-VDW

F 34: SET 20-MIX E; CPA-SRK-VDW

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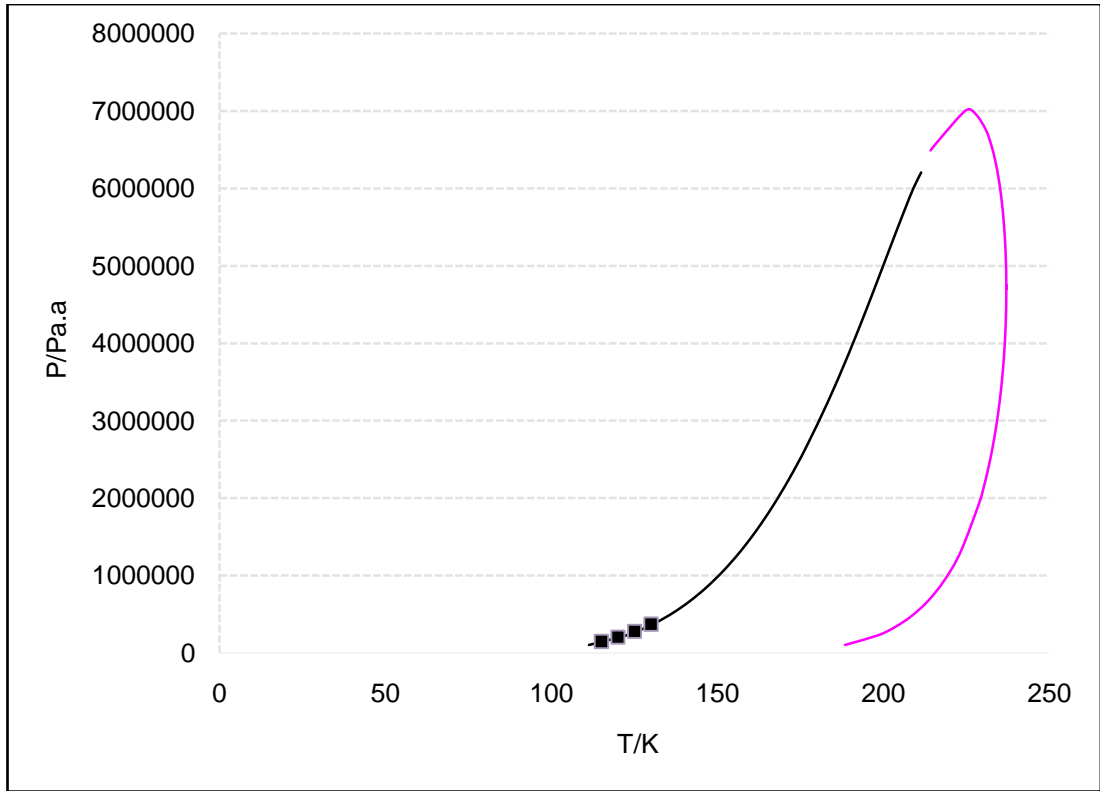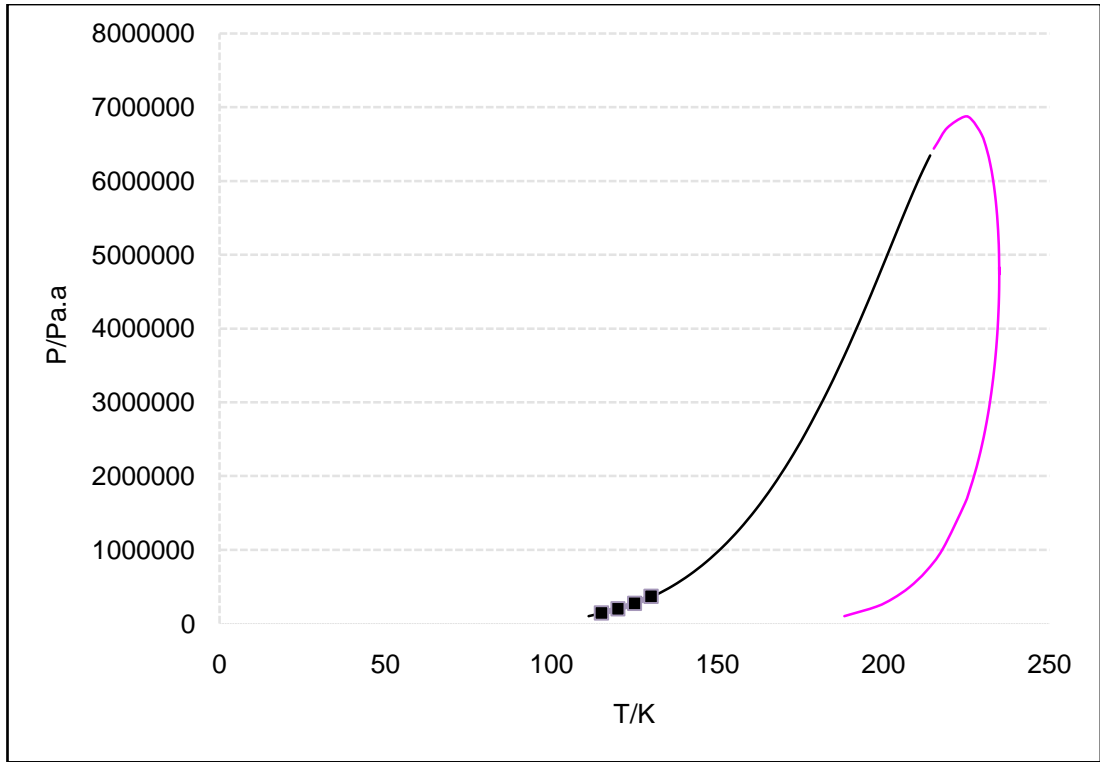
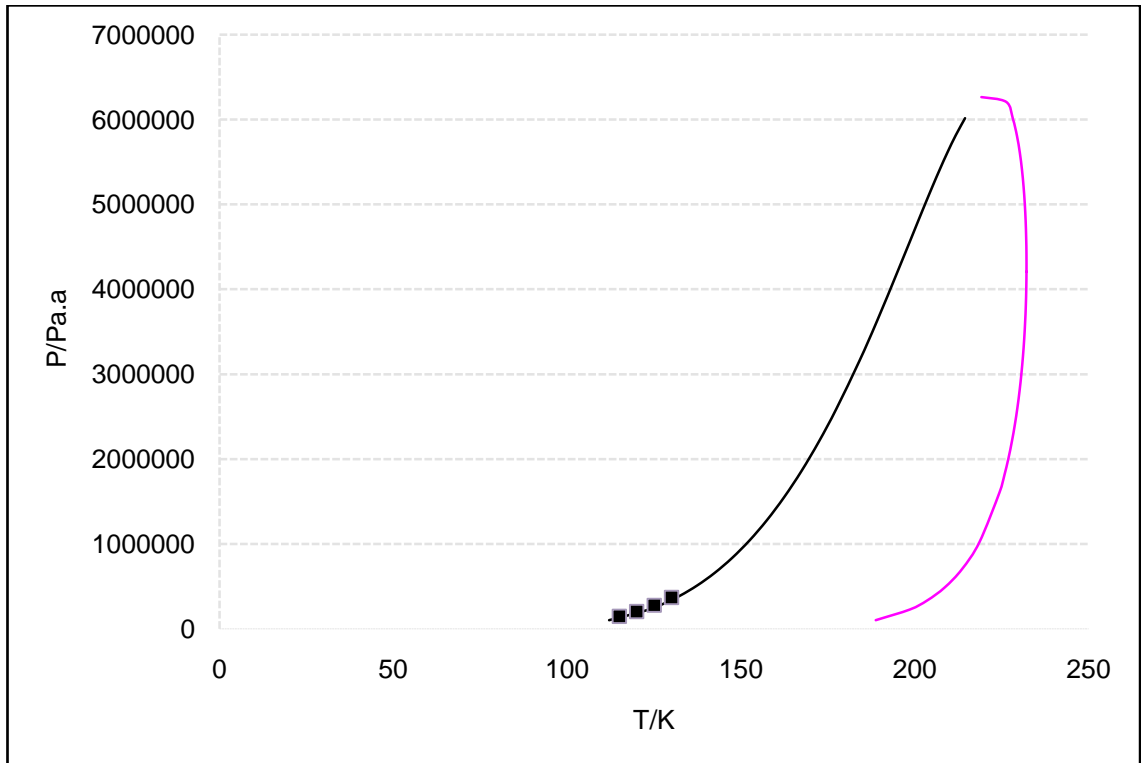F 35: SET 20-MIX E; PR-VDW

F 36: SET 20-MIX E; SRK-VDW
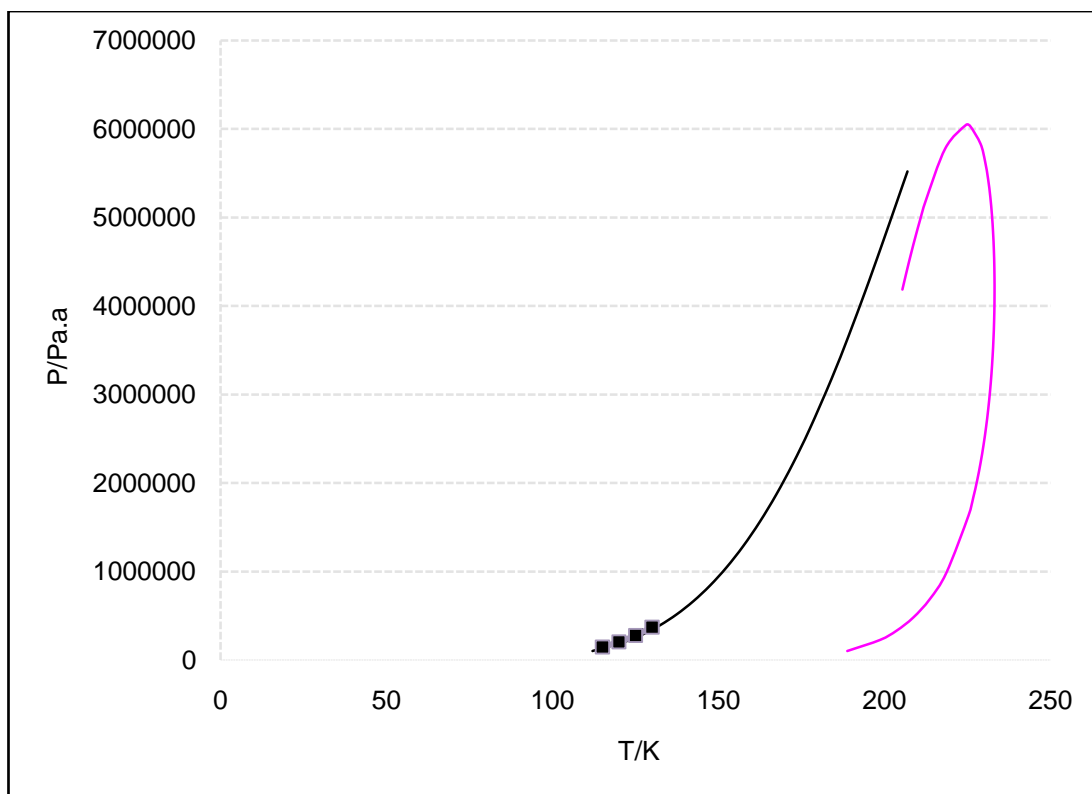
F 37: SET 20-MIX E; PR-UNIQUAC-WS

F 38: SET 20-MIX E; PR-NRTL-WS

F 39: SET 20-MIX E; SRK-EXT-VDW

F 40: SET 20-MIX E; PR-WS