Effective Critical Constants for Helium for Use in Equations of State for Natural Gas Mixtures

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Abstract

Most of the world's helium supply is obtained by cryogenic distillation of natural gas. Modelling the distillation conditions requires equations of state capable of predicting vapour-liquid equilibria over wide ranges of conditions. Equations of state – including cubic equations and multi-parameter Helmholtz equations – depend on the critical properties of pure substances for predicting various properties of multicomponent fluid mixtures. Predictions for helium are problematic as its critical point (5.195 K, 0.2275 MPa) is influenced strongly by quantum effects; large, empirical interaction parameters tend to be used in equations of state to compensate for these effects. Prausnitz and co-workers proposed an alternative approach using effective critical constants for quantum gases but only demonstrated it for 3 helium-containing binary mixtures. Here, we demonstrate that the use of an effective critical point at (11.73 K, 0.568 MPa) for helium substantially improves the prediction of VLE by the Peng-Robinson equation of state for 15 binary and ternary mixtures, including the major components of natural gas. This effective critical point for helium was selected from a critical analysis of *pTxy* data for the (methane + helium) binary. The effective critical constants for helium are compatible with an acentric factor near zero, as expected for a small spherical molecule and similar to the acentric factors of heavy noble gases. The possibility of applying this approach to address recognised limitations of the GERG-2008 equation of state is discussed.

Introduction

The market for helium is one of growing demand and uncertain supply.[1] At present, natural gas is the most economical and largest source of helium.[2] If the helium concentration of the feed gas is 0.3 % or higher,[3] a convenient and cost-effective method of helium recovery is purification of the end-flash gas produced in liquefied natural gas (LNG) plants.[2,4] The end-flash gas is often obtained after a nitrogen rejection unit (NRU), and therefore can be N_2-rich or CH_4-rich (if no NRU) present and may contain other compounds including argon and on the order of (1 to 3) % He.[4] This gas stream may either be vented to the atmosphere[3] or undergo further cryogenic distillation to produce a crude helium stream comprising up to 70 % He.[4] Optimising the efficiency of the distillation process requires a detailed understanding of the phase behaviour of helium in mixed gas streams; equations of state (EOS) are generally used by engineers to model phase behaviour over wide ranges of temperature, pressure and composition. Improving the accuracy of vapor-liquid equilibrium (VLE) predictions made by equations of state for mixtures containing helium may be valuable for enhancing the commercial recovery of helium.

Equations of state for natural gas mixtures are numerous and differ greatly in complexity. Particularly for VLE calculations in multi-component mixtures of non-polar compounds, complex equations of state sometimes offer little to no overall advantage compared to their simpler counterparts.[5-7] Consequently, simple cubic equations of state are still favoured in many industrial applications.[8–9] As one of the most-popular cubic equations of state, the Peng-Robinson equation of state can predict successfully vapour-liquid equilibria of multicomponent gas mixtures with only three parameters for each pure fluid component (critical temperature T^c, critical pressure P^c and acentric factor ω) and small-valued binary interaction parameters.[10]

Helium is an outlier in this regard. Compared to the classical gases, helium and other quantum gases (H_2, its isotopic variations, and neon) do not accord well with the law of corresponding states.[11–14] In practice, to compensate for this limitation, binary interaction parameters between helium and other compounds tend to be set much larger than normal.[15] Since the binary interaction parameters for helium tend to be large, neglecting them can have sizeable consequences for property prediction.[16]

As discussed by Prausnitz and co-workers[12,13] and recognised much earlier,[11] the corresponding states approach works well for classical gases but fails for gases whose critical properties are influenced by quantum phenomena. This problem is most severe for helium since it has one of the lowest critical temperatures of any gas (5.1953 K)[17]. Attempts to rectify cubic equations of state to accommodate quantum gases (chiefly hydrogen) fit loosely into four categories: those where the reduced temperature for the quantum gas is calculated with an 'effective' critical temperature instead of with the true critical temperature;[11–13] those with novel temperature-dependent functions in the attractive term of the equation of state, which remove spurious minima at high reduced temperatures;[16,18] those with novel mixing terms developed especially to describe interactions between small molecules (e.g. hydrogen, helium) and large molecules;[19] and those with temperature-dependent binary interaction parameters.[9,20,21] Specialised non-cubic equations of state have also been proposed.[22,23] Each of these methods has shown some level of success in the literature. However, to improve the predictions of equations of state for commercial helium distillation, methods which preserve the simplicity inherent in cubic EOS have significant advantages for use within process simulation software.

Commercial process simulators vary in terms of efficiency, functionality and customisability. The degree to which an EOS may be customised within a commercial simulation software package is often limited. For example, although a process simulator may allow for temperature-dependent binary interaction parameters to be defined, only simple functions of temperature (i.e. linear term in T) are typically allowed. Considering these limitations, the method for rectifying cubic equations of state for helium that is seemingly most compatible with commercial software for process simulation is that where the true critical constants are replaced by effective values.

The early use of effective critical constants for helium by Prausnitz and co-workers' considered only the binary mixtures (nitrogen + helium), (argon + helium), and (tetrafluoromethane and helium)[12,13] and did not relate to methane or any other hydrocarbons occurring in natural gas. Later, Prausnitz and co-workers[24] applied their model to helium solubility in cryogenic solvents including methane, nitrogen, ethane, propane, argon, oxygen, carbon dioxide and the ternary mixture (methane + nitrogen + helium). However, their approach required a distinctive mixing rule – making it unsuitable for use with standard modern process simulation software. Their method also relied on tuned binary interaction parameters to achieve good agreement with data. Consequently, for mixtures containing components for which little or no VLE data exist for their respective helium binary system, the lack of reliable binary interaction parameters limits the predictive accuracy achievable with this method.

Although natural gas is composed predominantly of methane, heavy compounds possessing high boiling point temperatures may also be present in gas mixtures, either due to natural occurrence or as chemical additives. Binary mixtures of helium with heavy compounds including paraffins,[5] aromatic hydrocarbons[15,25] and fatty alcohols[26] were investigated by Lee and co-workers to test the Soave-Redlich-Kwong and Peng-Robinson cubic equations of state at high reduced temperatures. They reported that they could only obtain reasonable agreement between the equations of state and the available *pTxy* data by employing "extraordinarily large (close to or greater than unity)" binary interaction parameters,[26] in some cases reaching 1.9.[15] It should be noted that there is sentiment in the literature that values of binary interaction parameters greater than unity are physically unrealistic: Ashour et al. claim that values greater than unity violate the postulates of the kinetic theory of gases (ref. 27, pg. 47). On the other hand, Jaubert and co-workers, whose "predictive" Peng-Robinson equation involves temperature-dependent binary interaction parameters exceeding 1.5,[9,21] are convinced this is not a problem as long as the overall attractive contribution from intermolecular forces remains positive (ref. 21, pg. 67). Although the question of the physical meaning of large binary interaction parameters remains unsettled, the need for large binary interaction parameters when modelling heavy compounds mixed with helium is problematic for gas processing. In general, experimental data for mixtures of helium with heavy compounds are lacking, so binary interaction parameters cannot be regressed. Furthermore, constraints on chemical-analysis techniques mean that the heavy compounds in natural gases and oils are typically grouped into so-called 'petroleum fractions' containing compounds having similar boiling points. It is these petroleum fractions that are used for modelling the properties of oil and gas mixtures. Thus, the binary interaction parameters of most importance may not be those between helium and individual heavy compounds but those between helium and various petroleum fractions. Unfortunately, meaningful binary interaction parameters between helium and petroleum fractions, which would be expected to be large in conventional frameworks, cannot be estimated easily; the ability to predict a binary interaction parameter for petroleum fractions is important in any framework. The model developed in this work avoids the problem of large

parameter values: phase equilibrium data are predicted satisfactorily over wide ranges of conditions without binary interaction parameters.

The aims of this work are two-fold: (a) to regress effective critical constants for helium from reliable VLE data for the methane + helium binary, and (b) to demonstrate that the regressed parameters can be used to predict quite accurately phase equilibrium data for binary and ternary mixtures with helium and various other substances from a range of classes. The emphasis of this work is on natural gas mixtures and applications above 110 K: accordingly temperatures below 60 K and the properties of helium-dominated liquids are outside the scope of this work.

We are aware that process simulators contain multiple versions of the Peng-Robinson cubic equation of state, and may provide options such as 'Modify Tc, Pc for H2, He'. Unfortunately, in our experience such options are generally undocumented and it is not made clear (i) what the values of 'Tc' and 'Pc' are modified to; (ii) whether the value of the acentric factor is also modified; and (iii) whether the binary interaction parameters between helium and other components of the mixture are also modified. Using binary interaction parameters with different values of the pure component critical constants than were applied in their original regression will obviously lead to thermodynamic inconsistencies. Due to all of these concerns, and because there is no information regarding whether the model has been tested against appropriate vapour-liquid equilibrium data, we advise caution before using such options for natural gas mixtures containing helium.

Method

The Peng-Robinson equation of state was used throughout this work. The Peng-Robinson equation of state[10] is given by

(1)

where

(2)

(3)

(4)

(5)

(6)

(7)

Here is the molar volume, , and are the critical temperature, critical pressure and acentric factor of component , and is a binary interaction parameter applicable to the binary system comprising component and component . Note that is typically set to zero when the interactions between component and component have not been characterised and . The Peng-Robinson equation of state can be re-written as a cubic equation in the compressibility factor (as

(8)

where and .

The Peng-Robinson equation of state can typically be implemented straightforwardly for pure fluids and mixtures. However, problems arise when helium is present. In contrast to all other fluids and in violation of the requirements stated by Coquelet et al.[28], the function for helium has a positive slope with respect to temperature at all temperatures (Figure 1). The cause of this is the large negative acentric factor for helium ( ). An acentric factor close to zero seems more reasonable for a small, spherical molecule like helium, and would be consistent with the acentric factor values of other noble gases. With , the function obtains a minimum around , corresponding to T ~ 65 K for helium. Above this temperature, the function is increasing. In our tests, the various implementations available for the α function in Aspen HYSYS do not allow this effect to be handled adequately, while the implementations in the software package Multiflash (version 4.4) do. Accordingly the Peng-Robinson (advanced) equation of state as implemented in Multiflash (version 4.4) was used throughout this work.

A survey of literature *pTxy* vapour-liquid equilibrium data for binary mixtures containing helium is summarized in Table 1. Where available, binary interaction parameters for mixtures with helium are shown. The literature survey was restricted to *pTxy* data as these have the most information content for validating the phase equilibrium predictions from the equation of state. The survey includes a wide variety of compounds: short- and long-chain hydrocarbons, aromatics, noble gases, other simple gases and alcohols. The paper by Lee et al.[26] also contains data for binary mixtures of helium with hexanol and octanol. We included only the data for decanol here as being representative of the fatty alcohols. Overall, a wide range of temperature (65 to 665 K) is covered by the data.

Table 1. Survey of *pTxy* vapour-liquid equilibrium data for binary mixtures with helium. N is the total number of data points, and k_{ij} are binary interaction parameters for mixtures containing helium (from the literature reference shown, else from HYSYS V9 databank(italics)).

Mixture (+ helium)	N	*T* /K	*P* /MPa	k_{ij}	References
methane	491	93 to 192	0.1 to 26	*0.7649*	29–33
nitrogen	388	65 to 126	1 to 83	*0.0685*	33–43
argon	146	91 to 149	1 to 97	*0*	44–47
oxygen	40	103 to 116	3 to 22	*0*	45
ethane	73	133 to 273	0.5 to 12	*1.1232*	48
propane	62	173 to 348	1 to 21	*1.0642*	49
isobutane	37	193 to 273	0.5 to 4	*0*	50
butane	38	193 to 273	0.5 to 4	*0*	50
carbon dioxide	59	220 to 293	3 to 20	*0.7967*	51,52
toluene	20	423 to 545	5 to 15	1.337	25
meta-xylene	20	465 to 584	5 to 15	1.3598	15
hexadecane	19	464 to 665	5 to 15	1.139	5
ethylene	36	130 to 216	2 to 12	*0*	53
propylene	30	200 to 255	2 to 12	*0*	53
decanol	14	353 to 453	2 to 10	1.499	26

To regress effective critical constants that will yield accurate predictions in mixtures with multiple components, it is important to select carefully the data against which the parameters will be tuned. The following factors were among those taken into consideration:

- experimental measurement technique (equipment and procedures)
- reported uncertainty in data (including purity of chemicals used)
- coherence of data among different authors (where available)
- range of temperature, pressure and composition

It is important to avoid over-reliance on unverified results during parameter optimization. Rowland and May[54] have shown that estimates of experimental uncertainty assigned by authors to their own data are commonly an order of magnitude too optimistic and systematic errors may be hidden within internally-consistent data. The true reliability of experimental measurements is often only revealed by comparing with multiple sources of independent data. The (methane + helium) mixture is the most well-studied and most relevant binary system for applications in natural gas processing involving helium. As both methane and helium molecules can be well-approximated as hard spheres, the cubic equation of state should yield good agreement with phase equilibrium data with a negligible binary interaction parameter. Accordingly, during the regression of helium's effective critical constants and in all other predictive calculations, the acentric factor for helium was set to zero in accord with other noble gases.

One of the methods by which the *pTxy* data for (methane + helium) were assessed for consistency was by analysing the vapour enhancement factors of methane. The enhancement factor equals the quotient of the (experimental) partial pressure of methane and the saturation vapour pressure of pure methane at the same temperature, that is, .[30] For isothermal data, the enhancement factor approaches unity in the limit of zero pressure. An example for isothermal data near 124 K is shown in Figure 2. It can be seen that the datasets

of Heck and Hiza,[30] DeVaney et al.[31] and Rhodes et al.[32] are mostly consistent, but the data of Sinor et al.[29] are systematically too high and the data from Fontaine[33] exhibit large internal

oxygen	0.72	0.72	0.54	4
ethane	1.15	1.08	0.22	5
propane	0.18	1.14[e]	0.23	5
isobutane	0.77	0.77	0.11	5
butane	0.70	0.70	0.05	5
carbon dioxide	0.25	0.79	0.06	5
toluene	0.10	0.78	0.20	6
meta-xylene	0.08	0.81	0.19	6
hexadecane	0.15	0.70	0.16	6
ethylene	1.29	1.29	0.14	7
propylene	1.11	1.11	0.13	7
decanol	0.13	1.00	0.40	7

[a] 30 points (of 128 critically-selected) predicted as single-phase (143 of 491 overall predicted as single-phase). [b] 175 of 388 points predicted as single-phase. [c] 186 of 388 points predicted as single-phase. [d] 81 of 146 points predicted as single-phase. [e] 3 of 62 points predicted as single-phase.

No critical selection of data was performed for the calculation of the statistics in Table 2, except for (methane + helium) as described above to determine the effective critical constants for helium. The results obtained with the effective critical constants developed in this work are clearly favourable: the average deviations with the effective critical constants are in most cases smaller or significantly smaller than the average deviations obtained with true critical constants *and* non-zero binary interaction parameters. For the system (nitrogen + helium) the true critical constants and the binary interaction parameter from HYSYS (k_{ij} = 0.0685) produce an average deviation that is large compared to those obtained for the other compounds, with 175 out of 388 data points being predicted erroneously as single-phase; this is almost as poor as the results obtained with no binary interaction parameter. This suggests that a much larger binary interaction parameter – in line with those for other binary mixtures containing helium in Table 1 – is actually needed for (nitrogen + helium) if the true critical constants for helium are retained in such calculations. This is particularly pertinent in helium capture applications where the nitrogen is the dominant component in the crude helium stream produced by the nitrogen rejection unit.

If binary interaction parameters with helium are constrained in both cases to a physically reasonable value of zero, the results obtained using the effective critical constants are vastly superior to those obtained with the true critical constants (see Table 2 and compare left-hand panels with right-hand panels in Figures 3 to 8). In the latter case, the Peng-Robinson EOS under-predicts the *K*-factors for helium in all mixtures considered here, while the *K*-factors of the other components tend to be over-predicted. For (nitrogen + helium), some of the predicted *K*-factors differ by more than one order of magnitude from the experimental results. It should also be noted that around one third of the data for binary mixtures of helium with methane, nitrogen and argon were improperly predicted to be single-phase instead of two-phase when the true critical constants were used in the Peng-Robinson equation of state.

A well-known deficiency of cubic equations of state is their behaviour around mixture critical points.[55] In this study this effect is most noticeable for the (nitrogen + helium) and (argon + helium) binary systems where the absolute deviations diverge as log *K* tends to zero (Figure 4), coinciding with temperatures approaching the critical points of nitrogen and argon respectively (Figure 8). Nevertheless, the deviations in this region obtained with the effective

critical constants for helium are comparable or smaller than the deviations shown in Figure 4 for helium's true critical constants, even far from the mixture's critical region.

The effective critical constants gave highly satisfactory results for most of the systems considered here. For the systems (propane + helium), (butane + helium), (hexadecane + helium) and (decanol + helium), a few data points with small *K* factors had relatively large deviations. This could be due to experimental uncertainties associated with sampling trace amounts of the heavy component in the gas phase. For (ethane + helium) the deviations of the helium *K*-factors near log K_{expt} = 1.0 were anomalously large when the effective critical constants were used in the Peng-Robinson equation (Figure 5). Although there are no *pTxy* data available with which to compare the values of Nikitina et al.,[48] the solubility of helium in liquid ethane was measured by Heck.[56] Comparison of some of the *pTx* data of Heck[56] and Nikitina et al.[48] at nearby isotherms shows large discrepancies between the two sources (Figure 9). As both sets of data appear to be internally consistent it is plausible that the data of Nikitina et al.[48] may be subject to some systematic error and further independent experimental evaluation of this system is warranted. For the system (oxygen + helium) the *pTxy* data deviated systematically from the model and were about twice as large as the deviations in the comparable system (nitrogen + helium). These data originate from the same laboratory as the uncertain data for (ethane + helium) so an independent experimental investigation of the system (oxygen + helium) may also be warranted.

The Peng-Robinson equation of state with the effective critical constants for helium developed in this work gives especially good results for binary mixtures comprising helium with methane, nitrogen and carbon dioxide. These components dominate most natural gas mixtures so it is important to characterize accurately their mixtures with helium. As these binary systems are described well it gives confidence that the phase behaviour of multicomponent mixtures will be predicted accurately.

Vapour-liquid equilibrium data are available for a small number of well-characterised ternary mixtures containing helium (Table 3). The system (carbon dioxide + ethylene + helium) has also been studied but no experimental *pTxy* data were published.[60] Most of the available data relate to the ternary system (methane + nitrogen + helium) that being of greatest relevance for helium purification from natural gas. As for the binary mixtures containing helium, AAD values were calculated for each ternary mixture. These values are given in Table 4.

Table 3. Survey of *pTxy* vapour-liquid equilibrium data for ternary mixtures with helium

Mixture (+ helium)	N	*T* /K	*P* /MPa	Reference
methane + nitrogen[a]	104	76 to 130	1 to 14	57
methane + nitrogen[b]	23	76 to 110	1 to 8	58
methane + nitrogen[c]	52	80 to 164	0.7 to 8	58
methane + nitrogen	126	130 to 180	4 to 10	59
propane + nitrogen	18	273	3 to 21	49

[a] nominally (0.50 He + 0.45 N_2 + 0.05 CH_4). [b] Mix A = (0.6465 He + 0.3420 N_2 + 0.0115 CH_4). [c] Mix B = (0.2543 He + 0.2653 N_2 + 0.4803 CH_4).

Table 4. Deviations between Peng-Robinson equation of state and literature *pTxy* data

Mixture (+ helium)	AAD (T^c = 5.1953 K P^c = 0.22746 MPa ω = –0.365 k_{ij} from Table 1)	AAD (T^c = 5.1953 K P^c = 0.22746 MPa ω = –0.365 k_{ij} = 0)	AAD (T^c = 11.73 K P^c = 0.568 MPa ω = 0 k_{ij} = 0)	Reference
methane + nitrogen	0.76	1.27[c]	0.28	57
methane + nitrogen[a]	0.71	1.06	0.14	58
methane + nitrogen[b]	0.17	0.80	0.11	58
methane + nitrogen	0.13	1.18[d]	0.09	59
propane + nitrogen	0.11	0.73	0.15	49

[a] Mix A. [b] Mix B. [c] 5 of 104 points predicted as single-phase. [d] 26 of 126 points predicted as single-phase.

The predictions of the phase equilibria in ternary mixtures further indicate the superiority of the method based on effective critical constants for helium developed in this work (Figure 10). The new model gives especially good results for the (methane + nitrogen + helium) system when the methane content is lower than 5 % (data of Boone et al.[57] and Mix A of Rhodes et al.[58]). Note that in the case of Boone et al.[57] the methane *K*-factors are subject to very large uncertainty at low pressures as the fraction of methane in the vapour phase was close to the detection limit and could not be determined accurately. By comparison, the approach with non-zero binary interaction parameters and true critical constants performs very poorly for these mixtures. As discussed above, these poor predictions are reflective of the abnormal binary interaction parameter between nitrogen and helium. It is possible that a larger binary interaction parameter value might lead to improved predictions for helium distillation from nitrogen-rich fluid streams when the true critical constants are used. However, such an approach would have limited predictive power and applicability to mixtures encountered in natural gas processing.

The issue of availability of binary interaction parameters is especially important for mixtures containing helium. As reflected by the literature survey in Table 1, high-quality *pTxy* data for binary mixtures of natural gas components with helium are relatively rare in the chemical literature. This impacts directly the reliability of thermodynamic models used in process engineering because the empirical binary interaction parameters ordinarily required by these models cannot be regressed against experimental data. Therefore, the binary interaction parameters must either assume standard values – k_{ij} = 0 in the case of the Peng-Robinson equation of state – or be estimated by other means. As many of the binary interaction parameters for helium mixtures have large magnitudes (even greater than unity), the potential for poor-quality predictions when un-regressed values are used is substantial. This is well-illustrated in Table 2 by comparing the average deviations obtained with and without binary

interaction parameters. A key advantage of the model developed in this work is that binary interaction parameters are not necessary to achieve good phase equilibrium predictions.

Issues related to large interaction parameters apply not only to the cubic equations of state tested in this work but also to the more-sophisticated multi-parameter Helmholtz equations of state recommended for natural gas transmission and sales applications (e.g. GERG-2008[61] equation of state). In regard to the GERG-2008 equation of state, regressed parameter values for most fluid combinations typically differ from the standard ideal values by -0.1 to 0.3, which is (10 to 30) % of those ideal values.[61–63] However, for helium-containing binary systems, regressed parameters vary from the standard ideal values by as much as 2.2! Even so, the correlation of phase equilibrium data for helium-containing binary systems is poor for the GERG-2008 equation of state,[64] and predictions of density for (methane + helium) deviate from recent experimental data by up to 7 % (much more than the stated measurement uncertainty of less than 0.1 %).[65,66] Improving property correlations and predictions by multi-parameter Helmholtz equations of state for helium-containing fluids is an avenue for future work.

Conclusions

This work demonstrates that problems relating to the prediction of vapour-liquid equilibria for mixtures involving helium can be addressed satisfactorily by replacing helium's true critical constants in a cubic equation of state with the effective critical constants (T^c = 11.73 K, P^c = 0.568 MPa). This is done on the basis that the true critical constants are affected by quantum phenomena not relevant at high temperatures. One of the advantages of this approach is that it can be incorporated into process simulation software relatively simply by modifying the properties of helium or introducing a pseudo-fluid with the appropriate effective critical constants and acentric factor equal to zero.

The data analysis in this work is the most comprehensive for binary and ternary mixtures containing helium, with 15 distinct systems considered in total spanning (65 to 665) K. Predictions are satisfactory for all systems up to pressures around 20 MPa except near the mixture critical temperatures, which is a known limitation of the cubic equation of state employed in this work. This investigation points the way for improved modelling of helium recovery from natural gas mixtures, including those dominated by methane, nitrogen and carbon dioxide.

Acknowledgements

This research was funded by the Australian Research Council through IC15001019.

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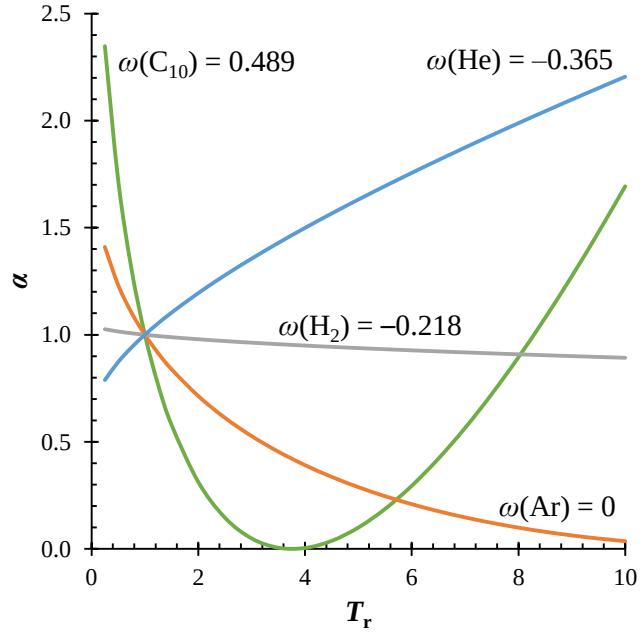


Figure 1. Dependence of the function for different values of acentric factor .

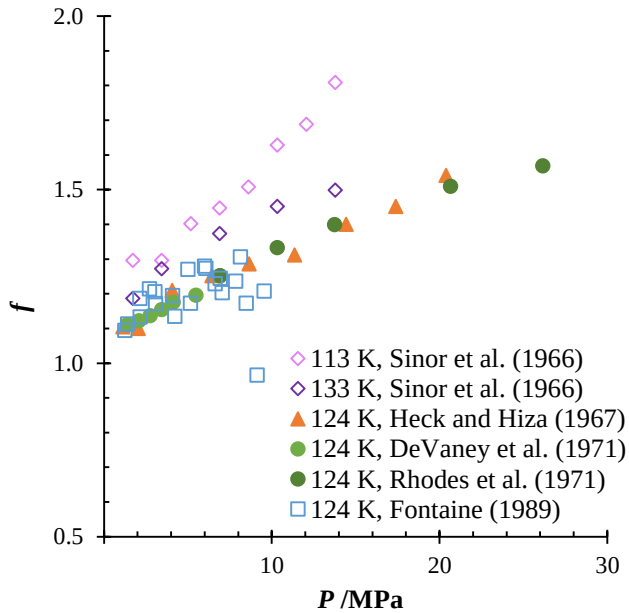


Figure 2. Enhancement factor for methane in the binary system (methane + helium) near 124 K.

Figure 3. (a) *p-xy* diagram for (methane + helium). Peng-

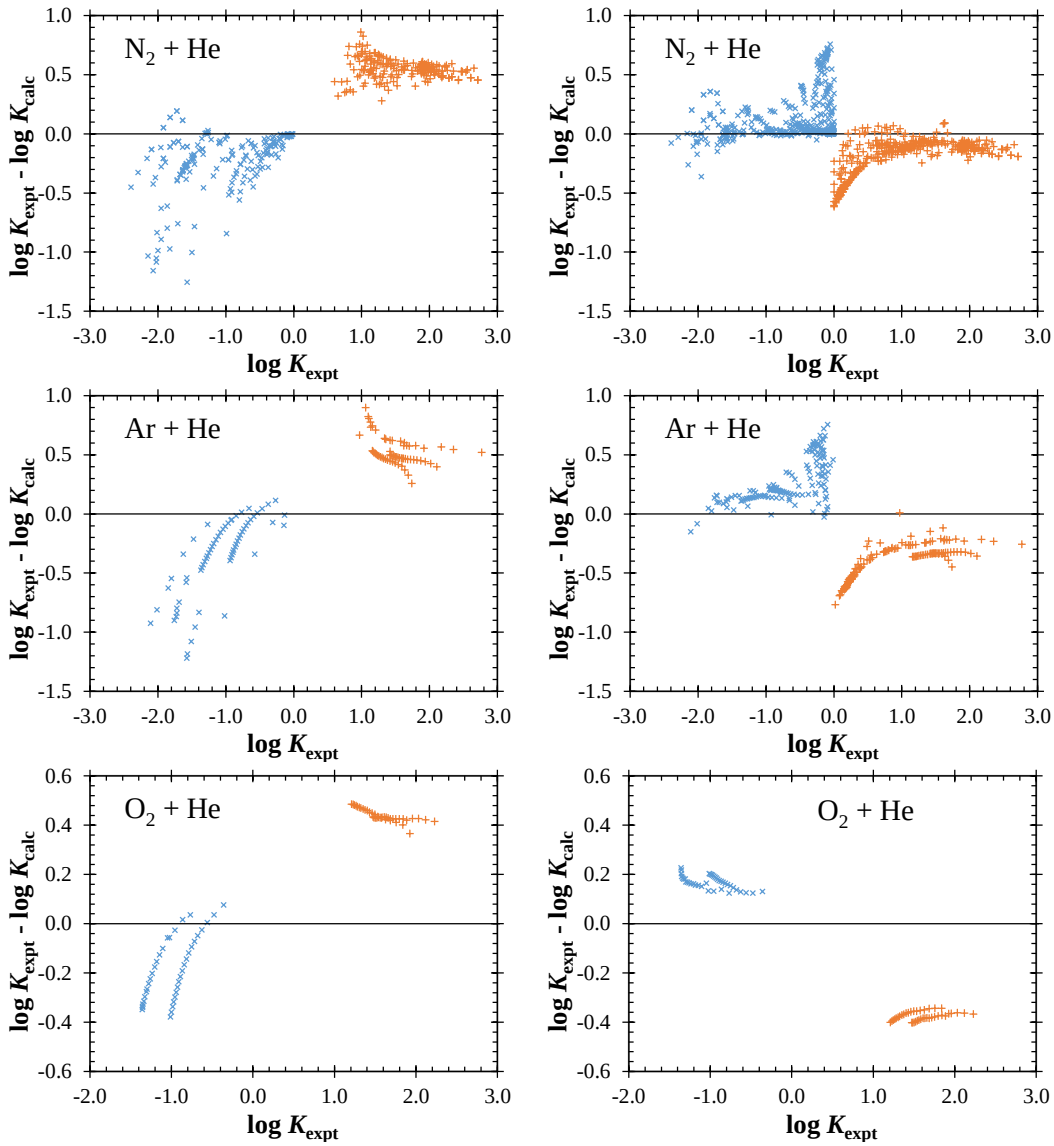
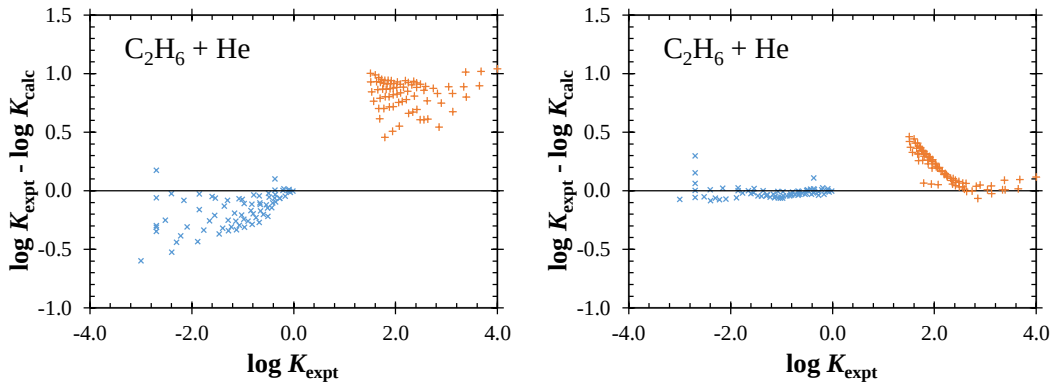


Figure 4. Deviations log K_{expt} – log K_{calc} of binary mixtures of cryogenic gases with helium, as those predicted with Peng-Robinson equation of state using true critical constants T^c = 5.1953 K, P^c = 0.22746 MPa, ω = –0.365 and k_{ij} = 0 (left panels), and using effective critical constants T^c = 11.73 K, P^c = 0.568 MPa, ω = 0.0 and k_{ij} = 0 (right panels). Sources of data are given in Table 1. Symbols: blue x, non-helium components; orange +, helium.



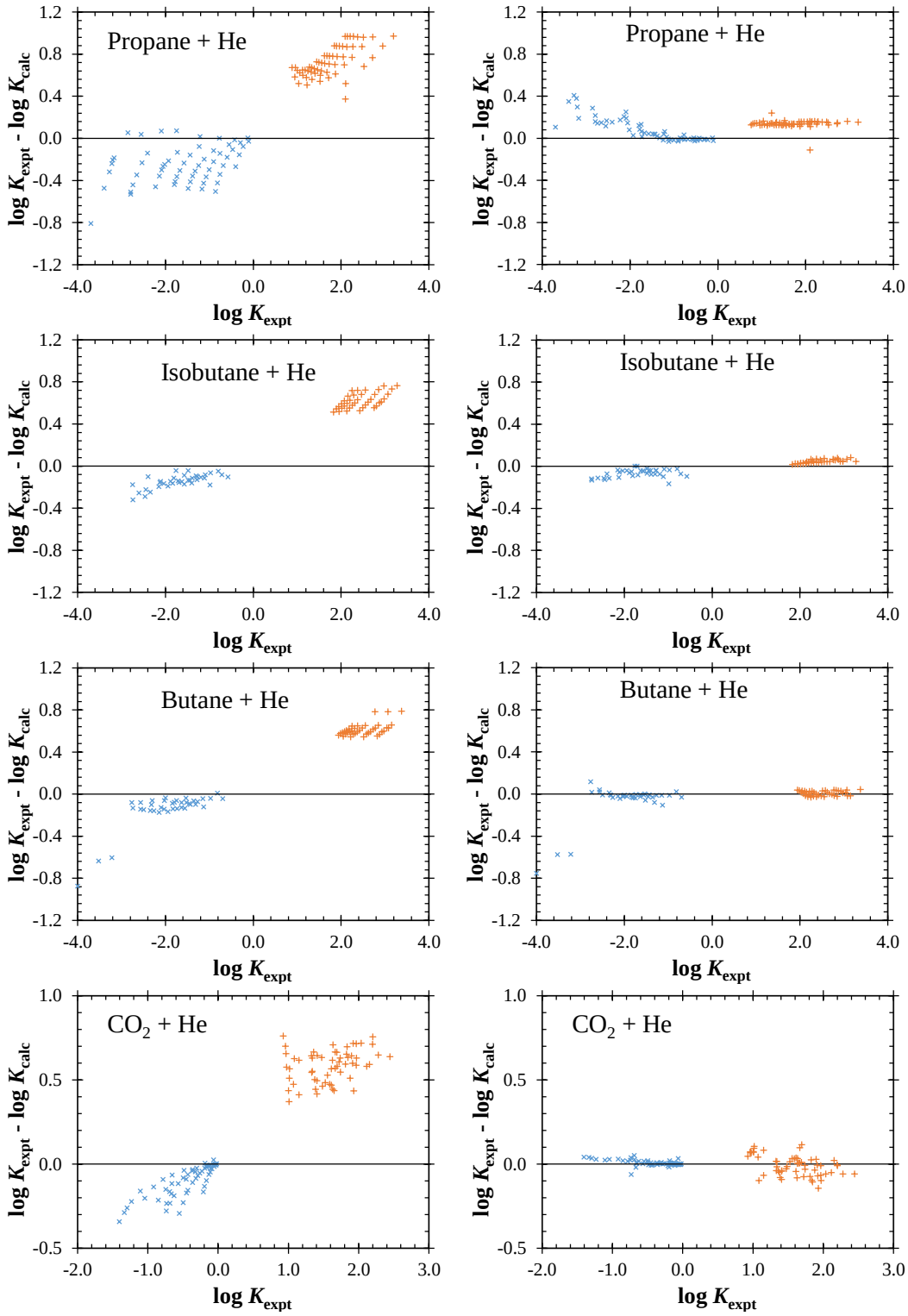


Figure 5. Binary mixtures of light natural gas components with helium. Symbols have same meaning as in Figure 4.

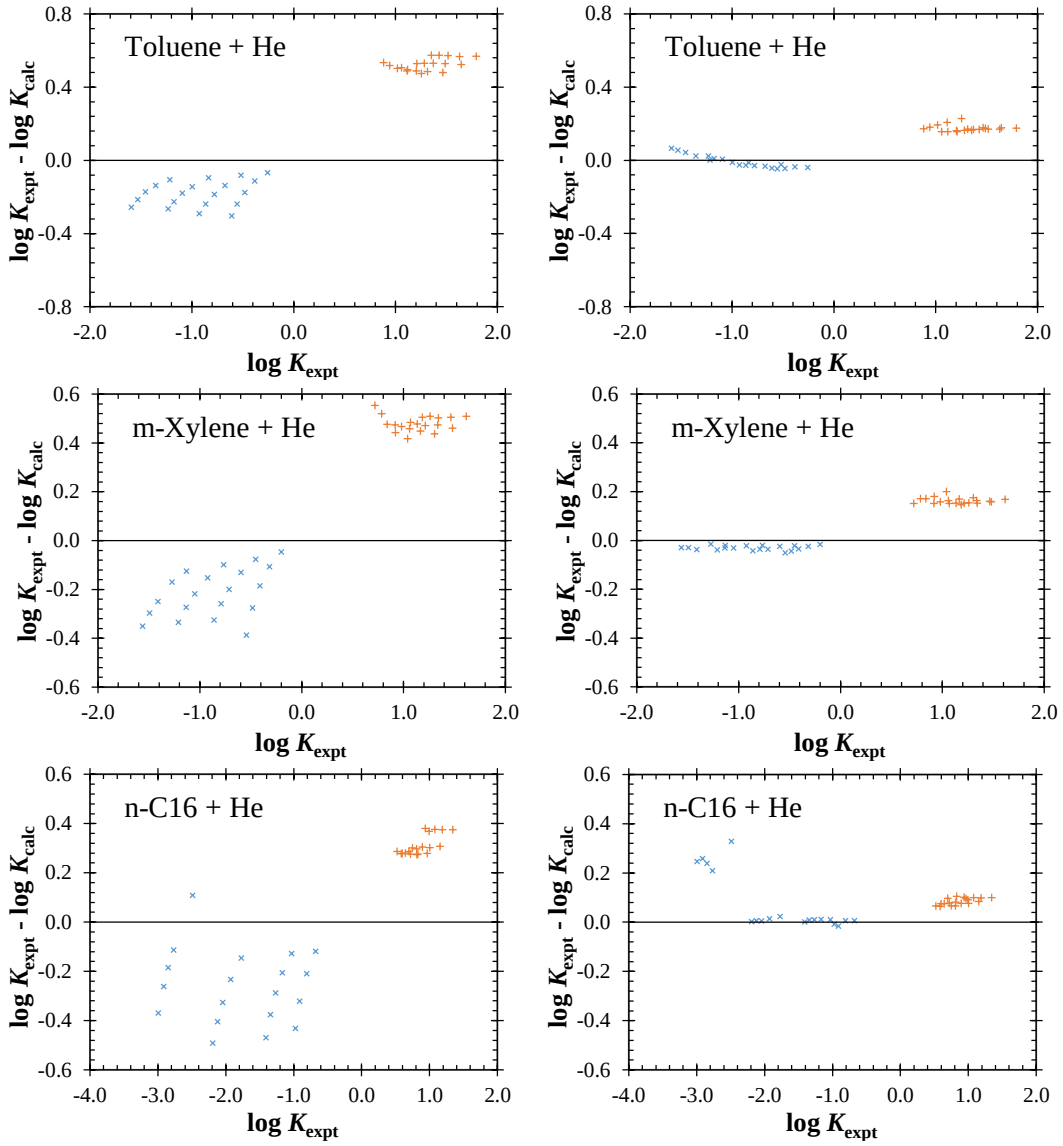
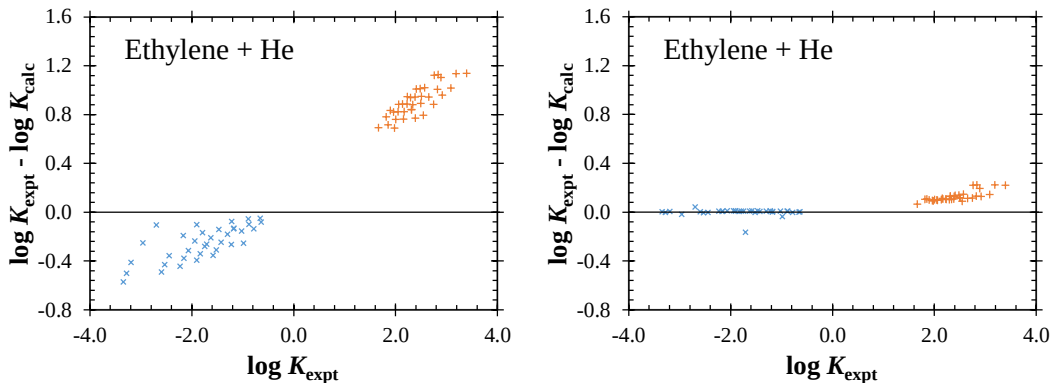


Figure 6. Binary mixtures of heavy natural gas components with helium. Symbols have same meaning as in Figure 4.



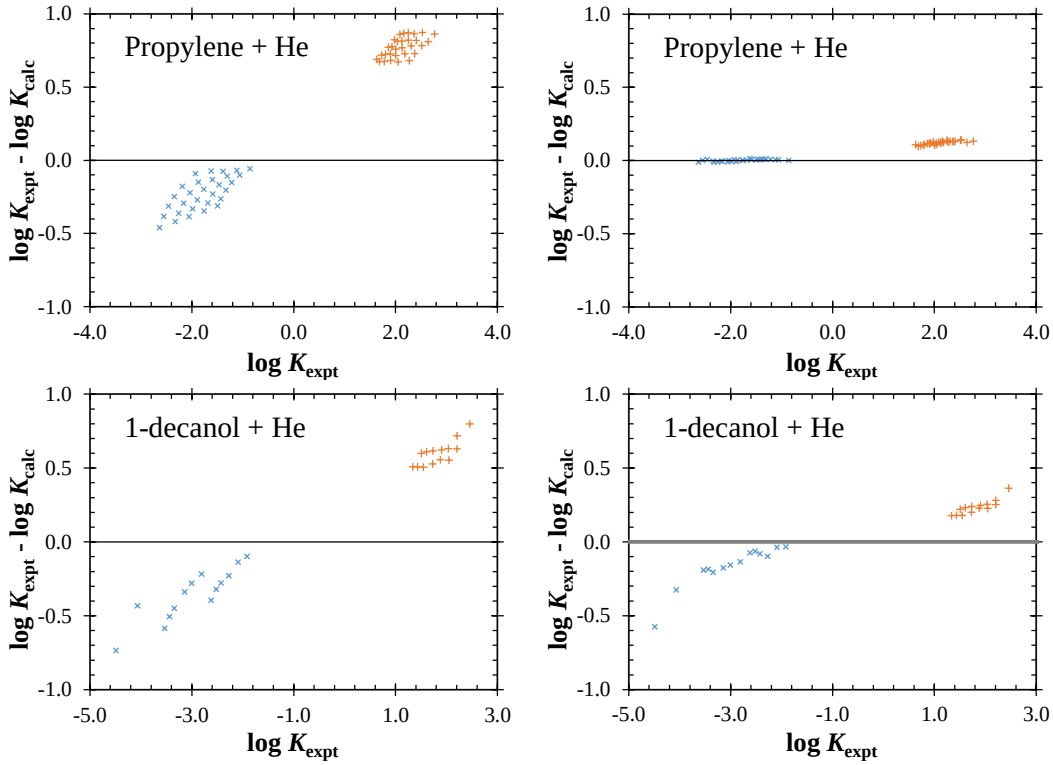


Figure 7. Binary mixtures of chemical process additives with helium. Symbols have same meaning as in Figure 4.

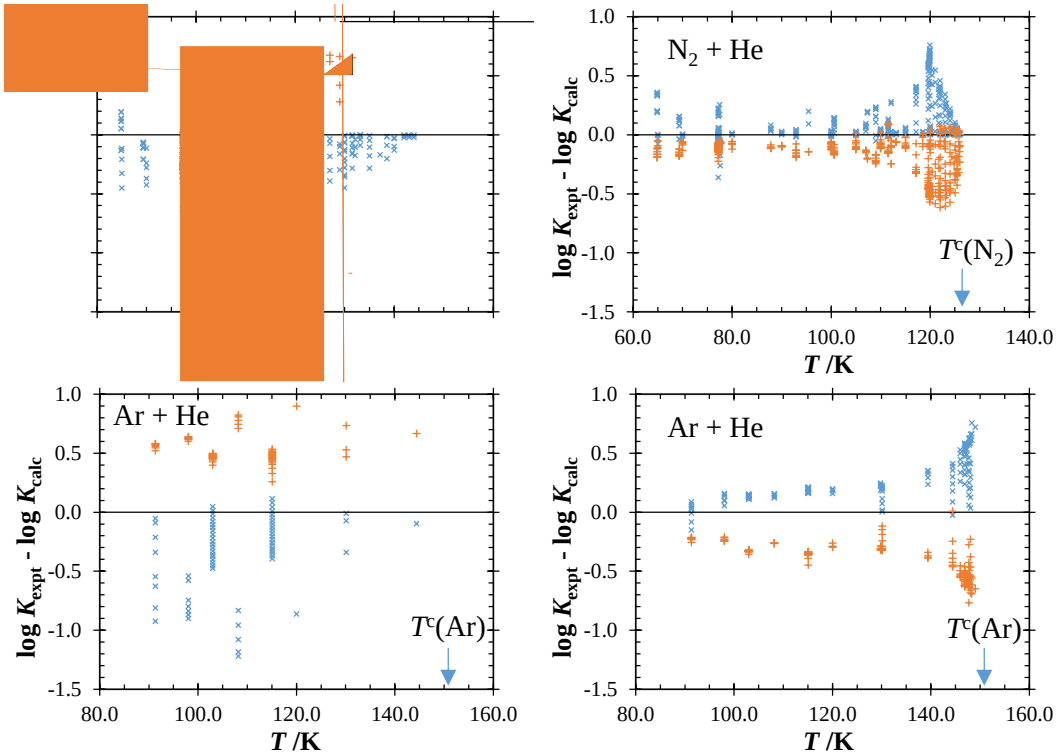


Figure 8. Deviations (log K_{expt} – log K_{calc}) versus T /K. Symbols have same meaning as in Figure 4.

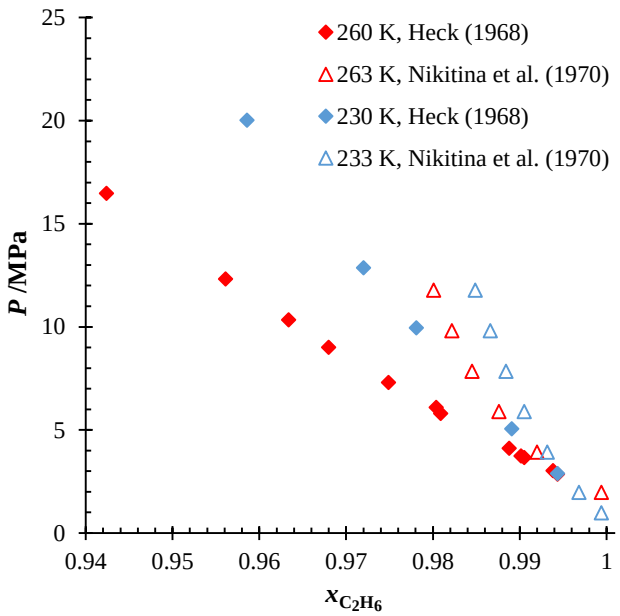
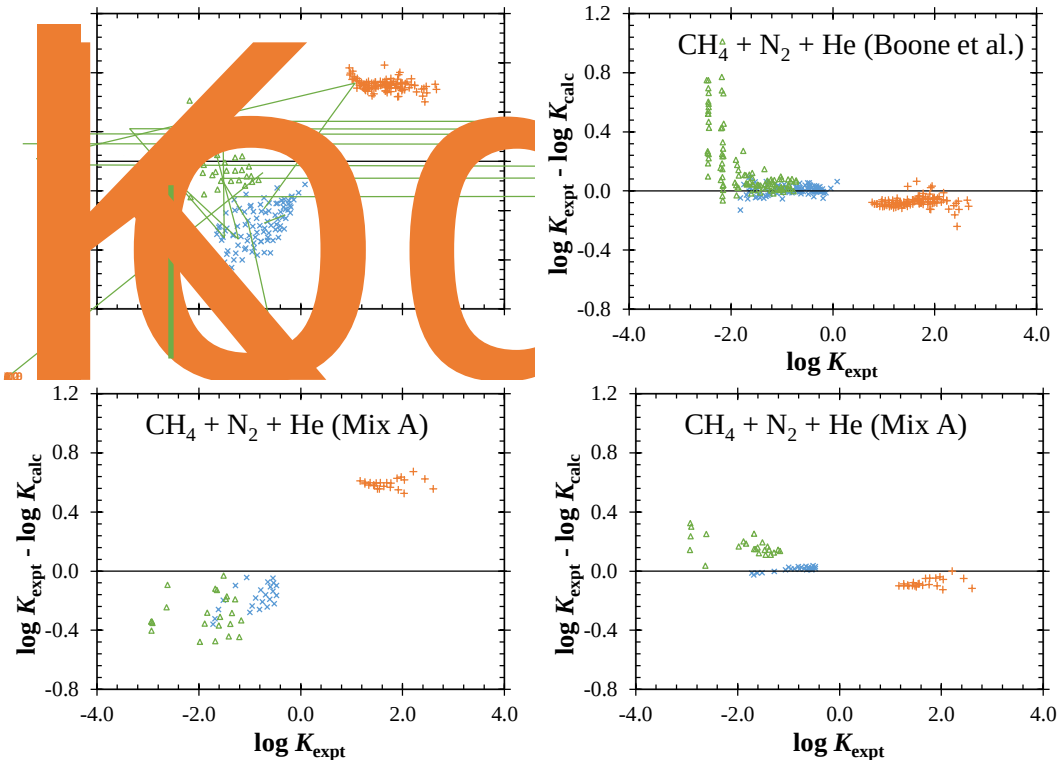


Figure 9. Comparison of literature *pTx* data for (ethane + helium). Data from Heck[56] and Nikitina et al.[48]



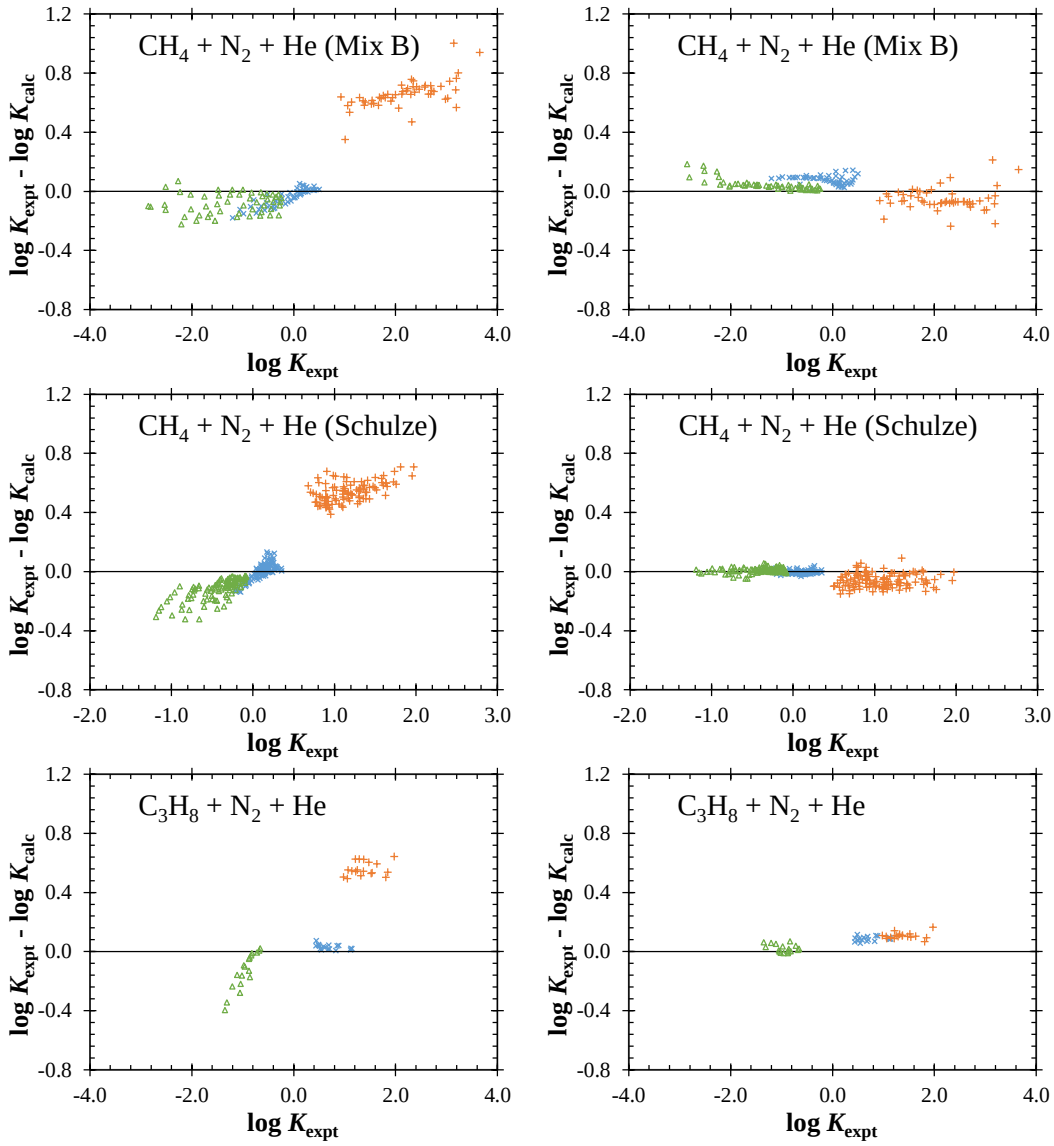


Figure 10. Deviations log K_{expt} – log K_{calc} of ternary mixtures containing helium for literature K-factors, those predicted with Peng-Robinson equation of state with true critical constants T^c = 5.1953 K, P^c = 0.22746 MPa, ω = –0.365 and k_{ij} = 0 (left panels), and those predicted with Peng-Robinson equation of state with effective critical constants T^c = 11.73 K, P^c = 0.568 MPa, ω = 0.0 and k_{ij} = 0 (right panels). Sources of data are given in Table 3. Symbols: green Δ, methane or propane; blue x, nitrogen; orange +, helium.