DDBST
Dortmund Data Bank
Software & Separation
Technology

The UNIFAC Consortium

Established in 1996

The UNIFAC Consortium

Company Consortium for the Revision, Extension and Further Development of the
Group Contribution Methods UNIFAC, modified UNIFAC (Dortmund)
and the Predictive Equations of State PSRK and VTPR

Version 2023

DDBST - Dortmund Data Bank Software & Separation Technology GmbH
- The UNIFAC Consortium -
Marie-Curie-Straße 10
D-26129 Oldenburg
Tel.: +49 441 361819 0
contact@unifac.org
www.unifac.org

The group contribution methods UNIFAC, modified UNIFAC (Dortmund) and the group contribution equations of state PSRK and VTPR are used world-wide for the synthesis and design of separation processes and a large number of further applications of industrial interest. They belong to the most important thermodynamic tools for the daily work of a chemical engineer and are therefore available in most of the commercial process simulators (e.g. Aspen Plus®, CHEMCAD™, Dynsim, HYSIM, Pro/II®, ProSim, ROMeo, UniSim, …).*

To support the revision, extension and further development of these models, a company consortium was founded in 1996 at the University of Oldenburg. Since 2011, the UNIFAC Consortium is maintained by DDBST.

The revised and extended group interaction parameters will only be given to the sponsors of the UNIFAC project and will not be available via the different process simulators. The sponsoring even includes the possibility to influence the direction of further developments, so that the models will definitely become more and more attractive for the chemical industry.

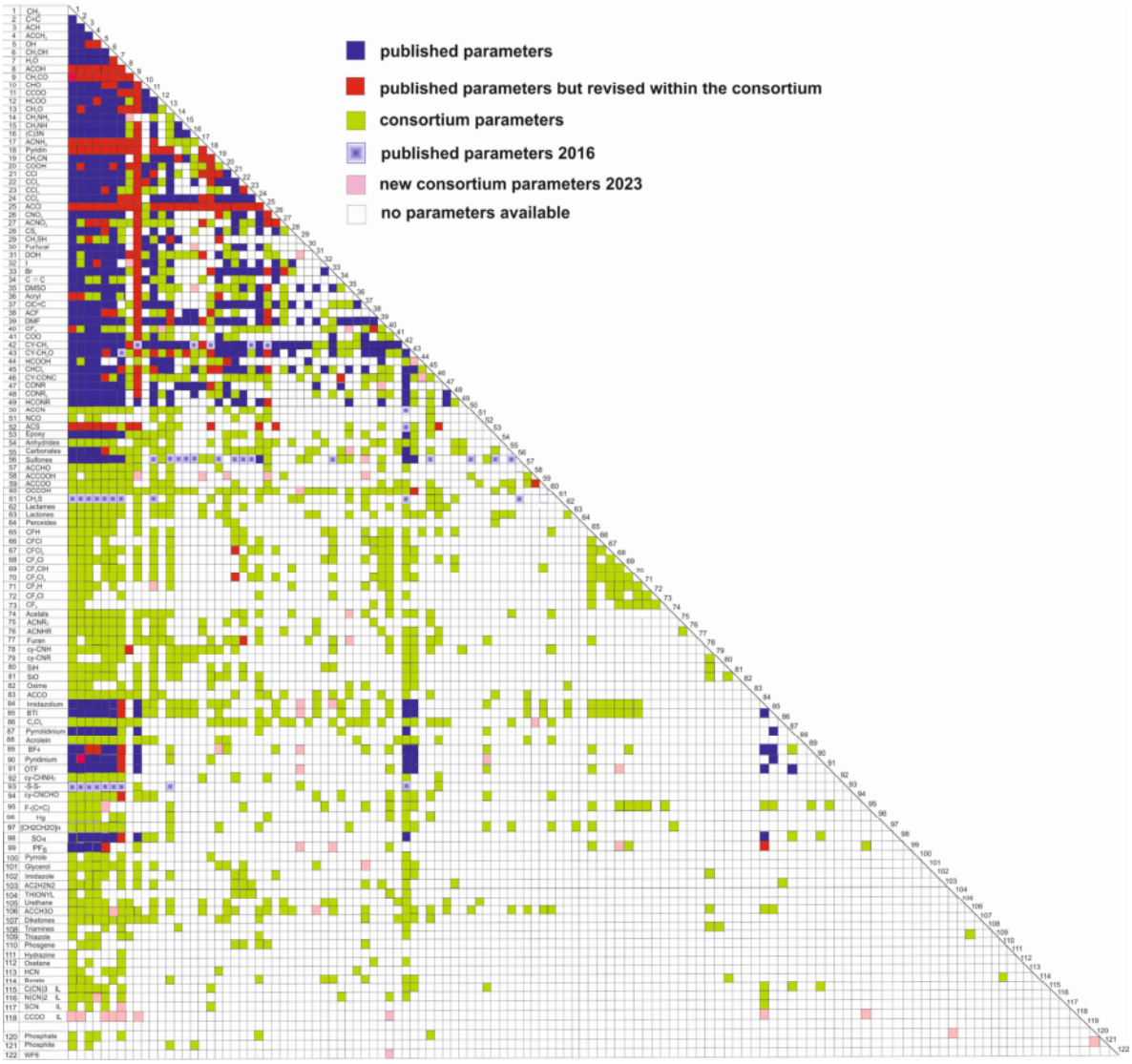


Fig. 1: Available group interaction parameters for modified UNIFAC (Dortmund)

Fig. 1 shows the available group interaction parameters for the Consortium members compared to the published parameters of modified UNIFAC (Dortmund). The following table gives the number of published group interaction parameters and main groups compared to the total number of group interaction parameters and main groups only available for members of the consortium.

* The current state of publication of both group contribution methods is given by the following references: For **original UNIFAC**: (1)Hansen, H.K., Schiller, M., Fredenslund, Aa., Gmehling, J., Rasmussen, P. *Ind. Eng. Chem. Res.* **1991**, *30*, 2352-2355 and for **modified UNIFAC Dortmund**, respectively: (1)Weidlich U., Gmehling J. *Ind.Eng.Chem.Res*. **1987**, 26, 1372-1381 (2)Gmehling, J., Li, Jiding, Schiller, M. *Ind. Eng. Chem. Res.* **1993**, *32*, 178-193; (3)Gmehling, J., Lohmann, J., Jakob, A., Li, J., Joh, R. *Ind. Eng. Chem. Res.* **1998**, *37*, 4876-4882; (4)Lohmann, J., Joh, R., Gmehling, J. *Ind. Eng. Chem. Res.* **2001**, *40*, 957-964; (5)Lohmann, J., Gmehling, J. *J. Chem. Eng. Jpn.* **2001**, *34*, 43-54; (6)Wittig, R., Lohmann, J., Joh, R., Horstmann, S., Gmehling, J. *Ind. Eng. Chem. Res.* **2001**, *40*, 5831-5838; (7)Gmehling, J., Wittig, R., Lohmann, J., Joh, R., *Ind. Eng. Chem. Res.* **2002**, *41*, 1678-1688; (8)Wittig R., Lohmann J., Gmehling J. *AIChE Journal* **2003**, 49, 2 530-537; (9) Jakob A., Grensemann H., Lohmann J., Gmehling J. *Ind. Eng. Chem. Res.* **2006**, 45, 7924-7933, Hector T., Gmehling J., *Fluid Phase Equilib.* **2014,** 371, 82-92, Further Development of Modified UNIFAC (Dortmund): Revision and Extension 6
Constantinescu D. and Gmehling J. *J. Chem. Eng. Data*, **2016**, 61 (8), 2738–2748. Addendum to "Further Development of Modified UNIFAC (Dortmund): Revision and Extension 6" *J. Chem. Eng. Data*, **2017**, *62* (7), pp 2230–2230.

	Published	Consortium
Parameters	755*	**2082**
Main Groups	61	122

* 307 of the already published group interaction parameters have been revised within the consortium.

The main objectives of the research work are:

- Extensive examination of the current parameters using the Dortmund Data Bank (DDB) in connection with graphical representations.
- Revision of the existing parameters using the currently available data banks.
- Extension of the parameter tables (UNIFAC, modified UNIFAC (Dortmund), PSRK, VTPR) with respect to existing groups.
- Introduction of new groups to extend the range of applicability.
- Introduction of more flexible groups.
- Consideration of proximity and isomeric effects.

For this research work, besides a large data base also a large number of systematic experimental investigations are necessary, e.g. to experimentally determine the required supporting data for fitting reliable temperature dependent group interaction parameters. Besides data for VLE, these are activity coefficients at infinite dilution, azeotropic data, solid liquid equilibria of simple eutectic systems, and in particular heats of mixing data at high temperatures (90 and 140 ^{o}C).

DDBST supports the research work by supplying the current version of the Dortmund Data Bank. This means all the phase equilibrium information published in literature. During the first sponsor meeting, the representatives agreed to provide internal company data exclusively for the model development work.

Reliable experimental facilities (in many cases computer driven) can be used for various experimental investigations. Furthermore, a sophisticated software package simplifies the fitting of a large number of group interaction parameters. Although a great part of the required preliminary work for a successful completion of the comprehensive research project has already been performed, a constant preoccupation of the consortium is to obtain more reliable parameters. The particular features of this program (Fig. 2) allow enhancing of the flexibility of the models by considering multiple group-group interaction sets in optimization and by taking into consideration a larger spectrum of data. Multiple standard and deviation diagrams allow simple quality judgment and weighting or removal of data sets. The same data base management is enabled for both UNIFAC models, PSRK and VTPR.

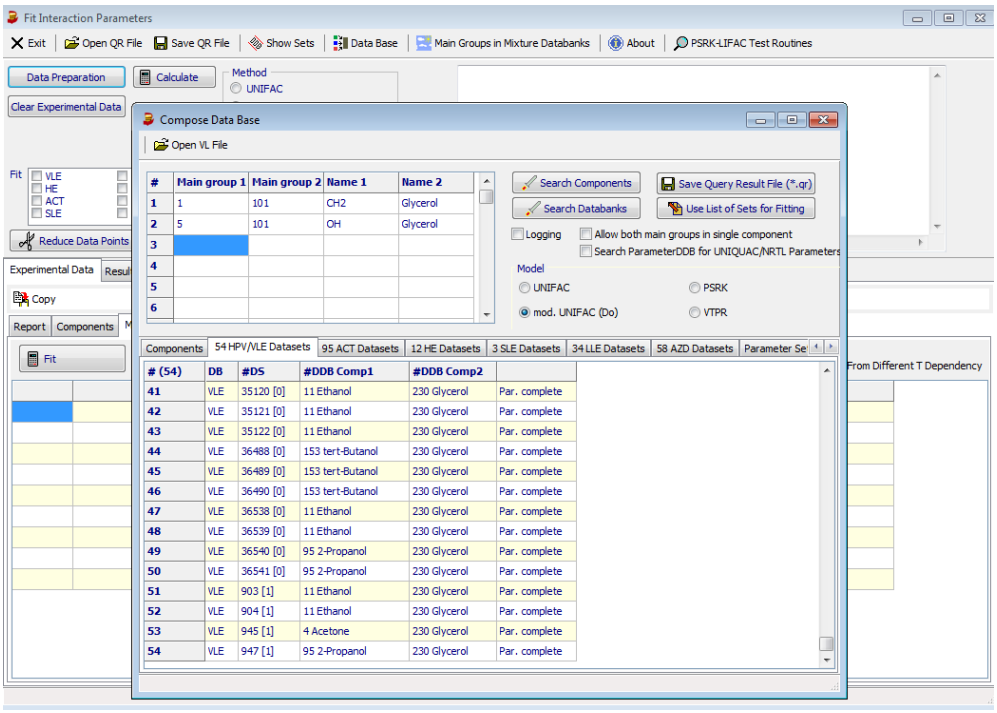


Fig. 2: Software developed by DDBST. Advantageous features for the fitting procedure.

Typical Results

A recent development for the modified UNIFAC (Dortmund) model was the introduction of several new flexible main groups. The introduction of the major part of the new groups was scheduled in cooperation with our consortium members, so that the great number of components, which can only be treated with the help of the new group interaction parameters, are of major industrial interest. In Appendix A, typical results for the new modified UNIFAC (Dortmund) main groups are given.

- Anhydrides
- ACS (Thiophenes)
- CONR (monoalkyl amides)
- $CONR_2$ (dialkyl amides)
- Epoxides
- Acrolein
- Pyrazine
- Diketones
- Sulfones
- Thionyl and Sulfuryl Chloride
- Hydrazine
- Hydrogen cyanide
- Borate
- Phosphate
- Ionic liquids
- Triamines
- Chlorofluorohydrocarbons (Refrigerants)
- Isocyanates
- Lactames (cyclic Amides)
- Lactones (cyclic Esters)
- Cycloalkylamines
- N-Formylmorpholine
- Thiazole
- Glycerol
- Imidazole
- Phosgene
- Oxetane
- Borane
- Phosphite
- WF_6

A great proportion of the group interaction parameters were fitted between 1985 and 1993. No SLE data and only few h^E data were available. Thus, the enlargement of the database during the last 20 years offers the possibility to revise group interaction parameters to cover a larger pressure, temperature and concentration range. Fig. 3 shows an example of different phase equilibria data for systems containing thiophene. The dotted line represents the published parameters. The solid lines show the result of the revision.

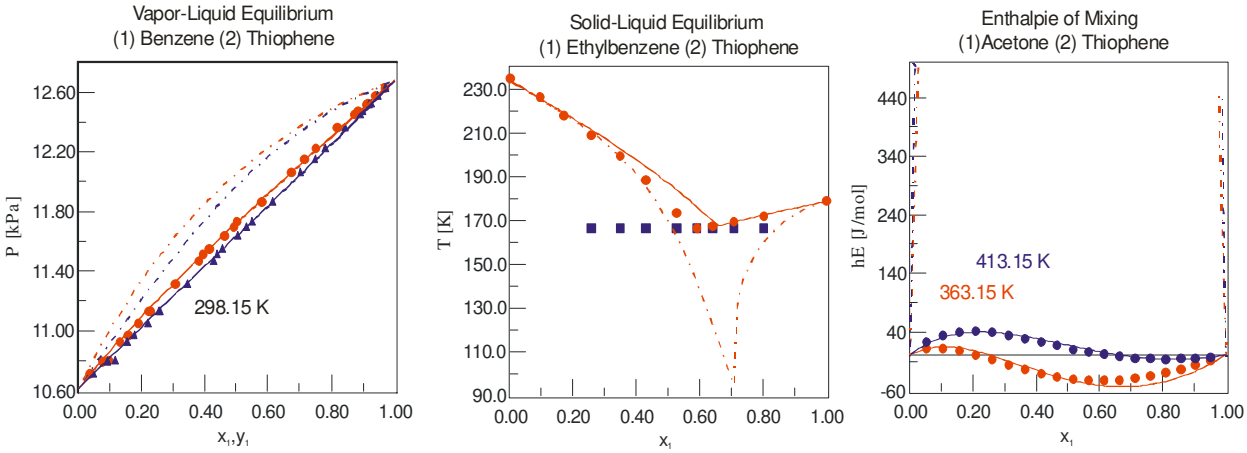


Fig. 3: Comparison of prediction results using published (dotted line) and revised parameters (solid line).

Original UNIFAC

Besides the work on modified UNIFAC (Dortmund), also the original UNIFAC method is further developed. On the basis of the increasing number of VLE and γ^∞ data not only gaps in the original UNIFAC matrix are filled but also new groups (epoxides, anhydrides, carbonates, sulfones, acrolein, pyrrole, glycerol, *n*-formylmorpholine, diketones, disulfides) are introduced. It is planned to further develop also the original UNIFAC matrix and to introduce the groups which already have been included into the modified UNIFAC (Dortmund) matrix, as original UNIFAC is very important. The current matrix of the original UNIFAC method is shown in Fig, 4.

A comparison of the results obtained from original UNIFAC and modified UNIFAC (Dortmund) demonstrates the improvements already obtained for modified UNIFAC (Dortmund). This is illustrated in Fig. 5, where the calculated deviations in the vapor phase mole fraction y, temperature T and pressure P are given for 1,362 thermodynamically consistent isothermal / isobaric VLE data sets together with the deviations obtained by other g^E-models, group contribution models and quantum chemical method. It can be seen from the deviations between the direct fit and the prediction that the error is dramatically reduced for all three criteria when modified UNIFAC (Dortmund) is used instead of UNIFAC. Assuming ideal behavior (Raoult's law) enlarges the errors by a factor of 5 compared to modified UNIFAC (Dortmund).

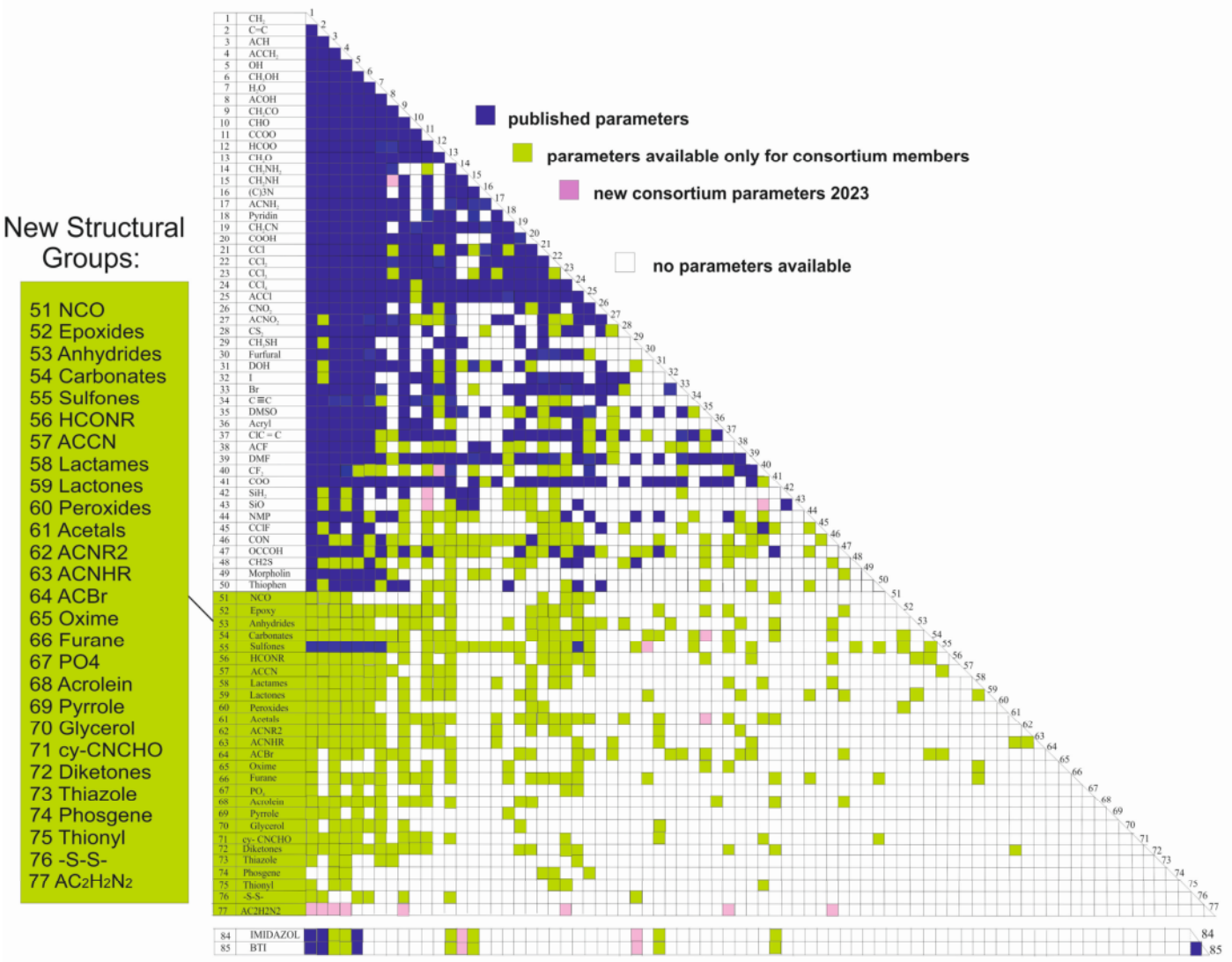


Fig. 4: Stage of development of the group interaction parameter matrix of original UNIFAC

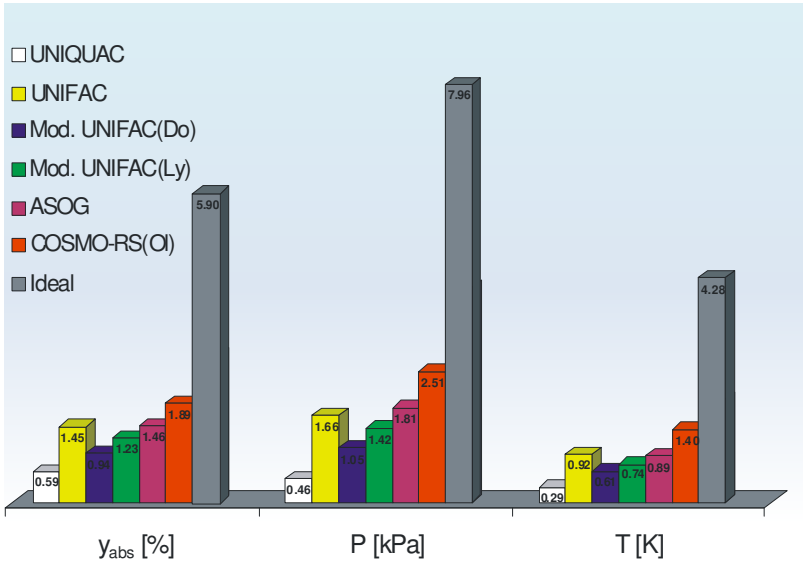


Fig. 5: Relative deviations between experimental and predicted data for 1,362 consistent VLE data sets taken from DDB.

Similar improvements of the predictive capability are also achieved for enthalpies of mixing, activity coefficients at infinite dilution (see Fig.6), liquid-liquid equilibria, azeotropic data and solid-liquid equilibria of eutectic systems.

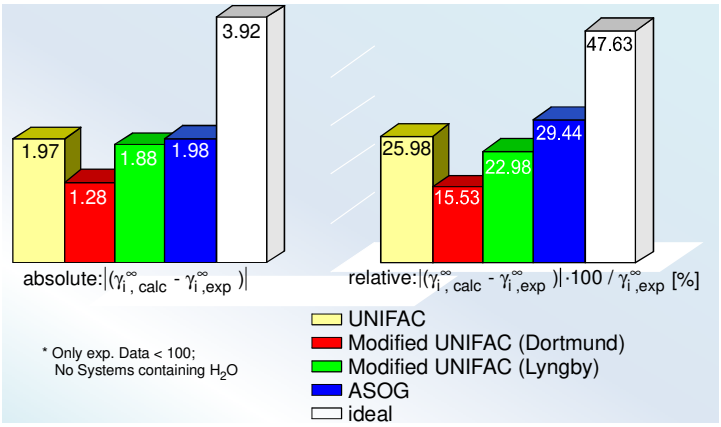


Fig. 6: Relative deviations between experimental and predicted activity coefficients at infinite dilution (data base: 12,600 data points)*

The PSRK model

For the description of systems containing supercritical compounds, equations of state (EoS) have to be applied. Beside phase equilibria, at the same time equations of state also provide other thermodynamic properties like enthalpies and densities. The group contribution equation of state PSRK combines the Soave-Redlich-Kwong (SRK) equation with the original UNIFAC model and allows an accurate prediction of phase equilibria in a wide temperature and pressure range. The range of applicability was extended by introducing 30 gases as new main groups.

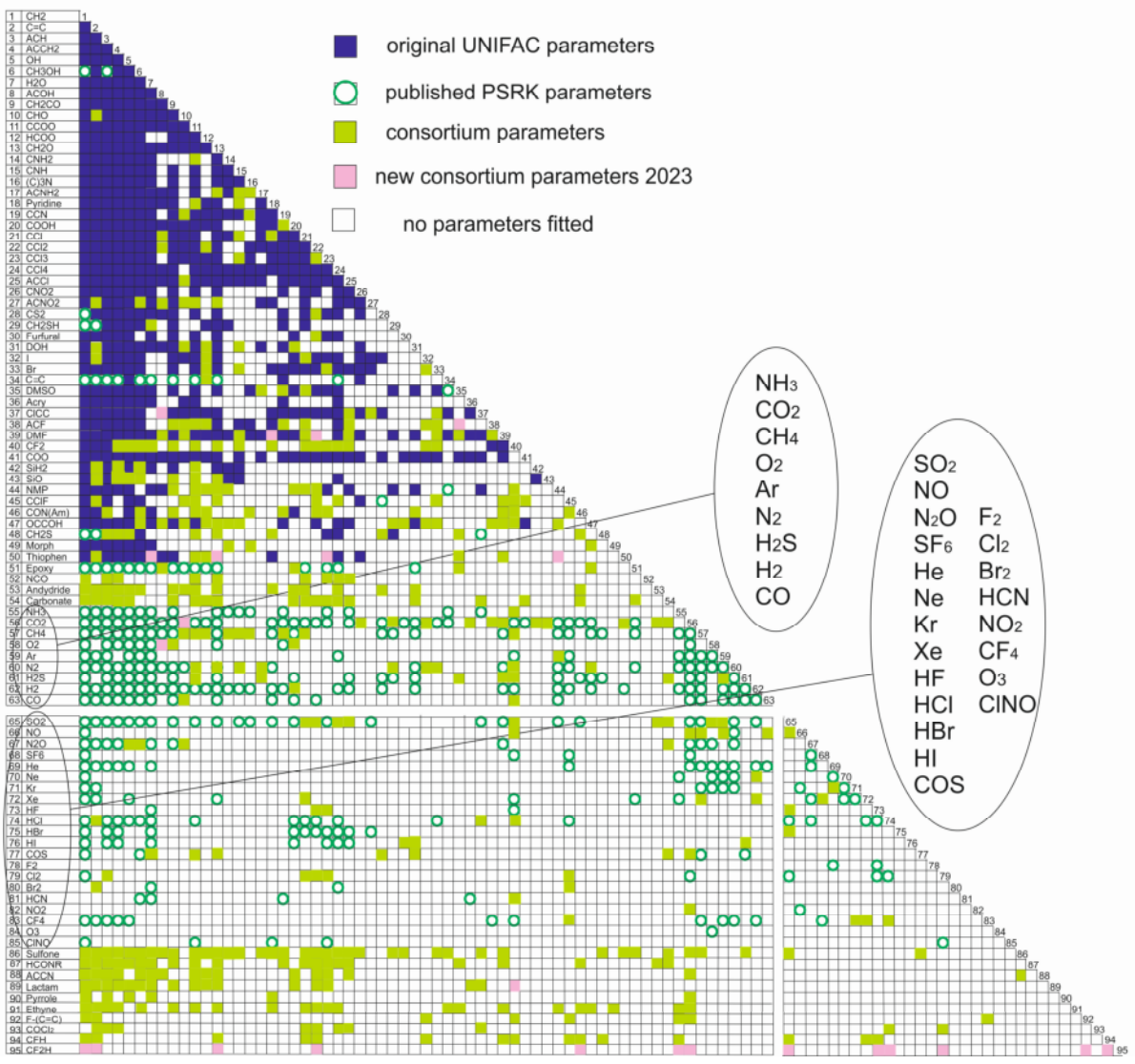


Fig. 7: Stage of development of the group interaction parameter matrix of PSRK.

The Volume-Translated Peng-Robinson (VTPR) Model

The group contribution equation of state VTPR has been added as the fourth supported model in the UNIFAC Consortium in 2017. It can be considered as the successor of PSRK. The combination of an improved model and the creation of new interaction parameters plus an optimized group assignment scheme based on the current Dortmund Data Bank promises very precise, widely applicable, and reliable predictions.

A significant work evaluates the performance of the VTPR model for hundreds of systems. A selection was made, based on comparative studies (VTPR, PSRK and modified UNIFAC (Dortmund) and on cases where modified UNIFAC (Dortmund) shows its limitations. The development strategy of VTPR was scheduled in accordance with the consortium members. In the meantime, the number of available parameters has tripled within the UNIFAC consortium. Fig. 8 shows the available group interaction parameters for the Consortium members compared to the published parameters of VTPR.

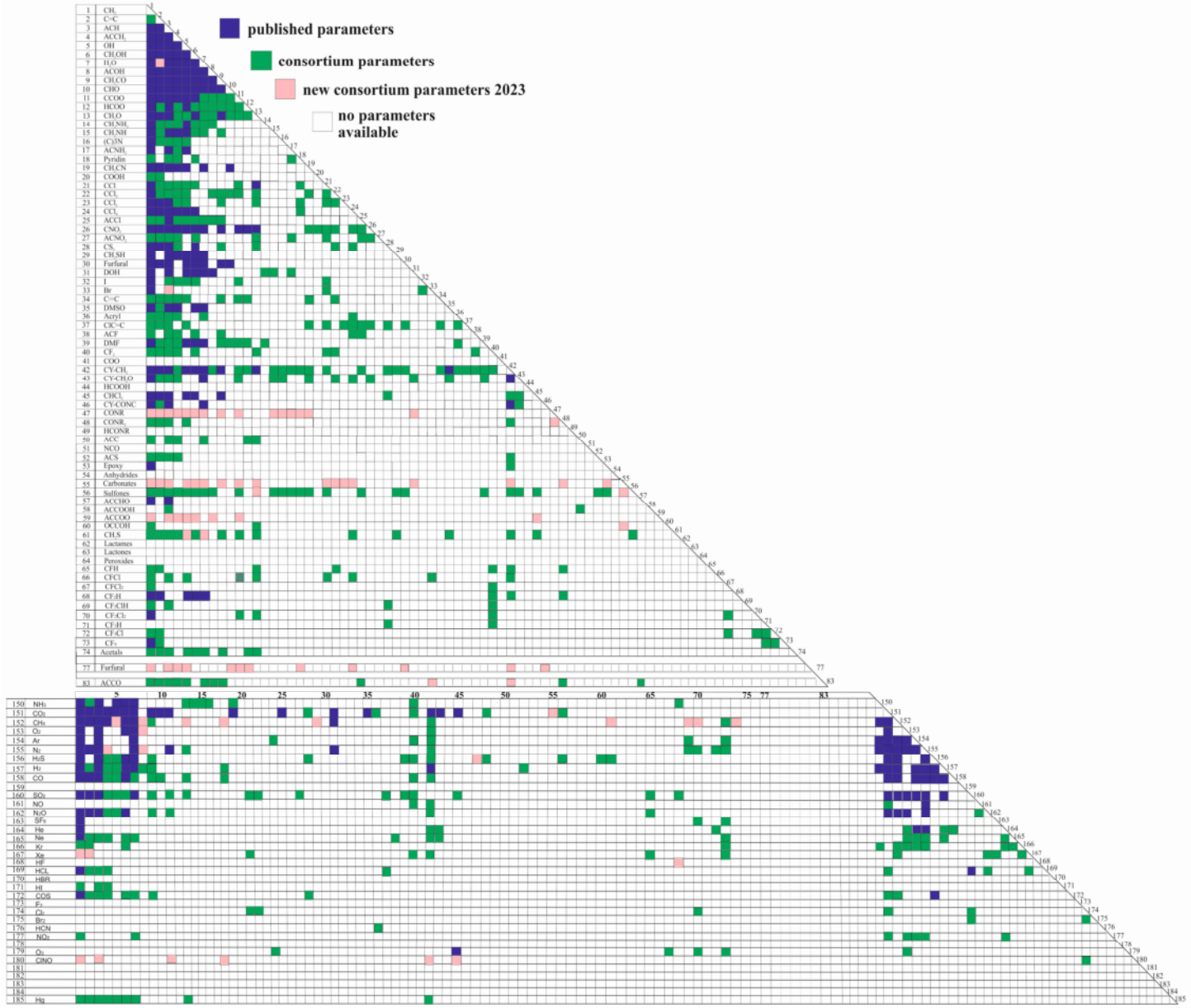


Fig. 8: Stage of development of the group interaction parameter matrix of VTPR.

Benefits for membership

Access to the results of more than 45 membership fees p.a. (increasing tendency) for only one membership fee p.a., including:

- Already existing but not yet published modified UNIFAC (Dortmund) parameter sets (including all previous deliveries), as shown in the current parameter matrix, Fig. 1.
- Parameter matrix which contains all modified UNIFAC (Dortmund) parameters and additionally parameters fitted based on artificial data obtained using COSMO-RS (OL), particularly for reactive systems.
- Already existing but not yet published original UNIFAC parameter sets (including all previous deliveries), as shown in the current parameter matrix, Fig. 4.
- Already existing but not yet published PSRK parameter sets, as shown in the current parameter matrix, Fig. 7.
- Already existing but not yet published VTPR parameter sets, as shown in the current parameter matrix, Fig. 8.
- The modified CHEMCAD customization files in order to include the latest modified UNIFAC (Dortmund), original UNIFAC, PSRK and VTPR interaction parameters.
- An implementation guide for the CHEMCAD simulator.
- Original UNIFAC and modified UNIFAC (Dortmund) parameter updates as system libraries for Dynsim 4.5, ROMeo and PRO/II 9.x, 10.x users.
- An UNIFAC model editor to view and edit the structures and interaction parameters used by Simulis Thermodynamics for original UNIFAC, modified UNIFAC (Dortmund), PRSK and VTPR.
- Experimental data measured each year.

Sponsor meetings are held every year in September in Oldenburg to discuss the work of the UNIFAC consortium. The results of the annual work are sent to our members each year in September / October.

DDBST GmbH may publish the experimental data and selected parameters in a scientific journal 2.5 years after each yearly report. Notice that even after the 2.5 years period only a few of the new and revised parameters will be published and the parameters will not be available from DDBST GmbH as part of the DDB program package for non-sponsors of this consortium.

Membership Conditions

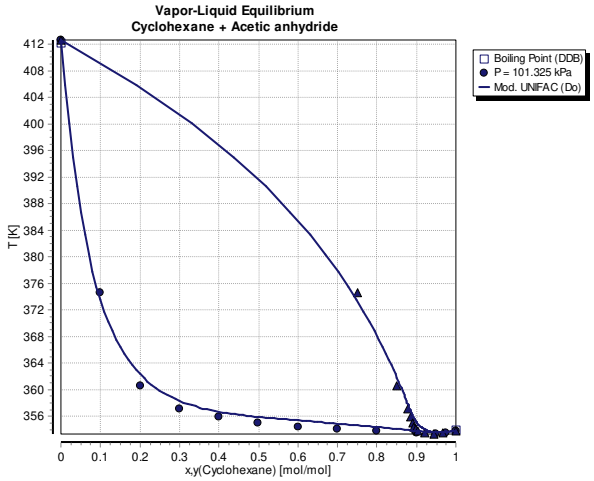
The participation in the project is available on easy terms. The membership is organized in periods of five years (extension possible) which implies annual payment of the consortium fee.

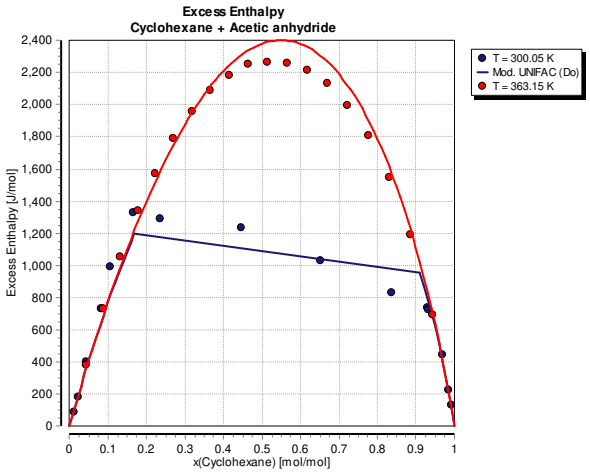
Please note that the revised and extended parameter tables obtained within the consortium are not available via the different process simulators (Aspen Plus®, CHEMCAD™, Dynsim, HYSIM, PRO/II®, ProSim, Romeo, …) or via the software package from DDBST GmbH. They will be exclusively supplied to the contributing companies together with an implementation guide for current process simulators.

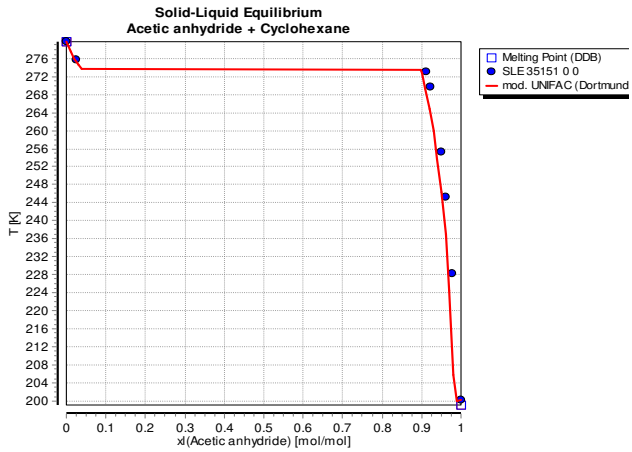
The UNIFAC consortium parameters and experimental data measured within the project can only be used in the member company including affiliate companies. It is not allowed to pass on the information to third parties.

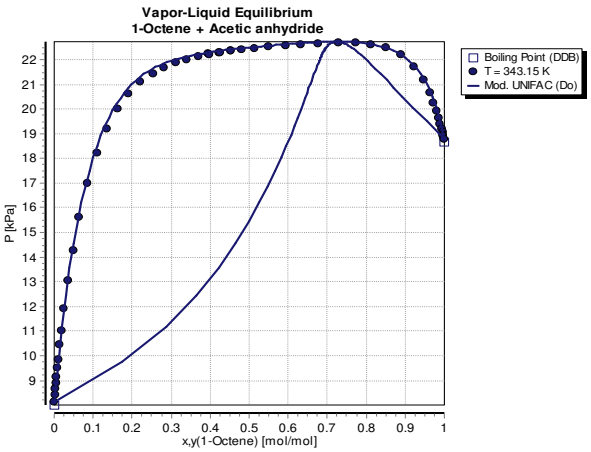
Appendix A

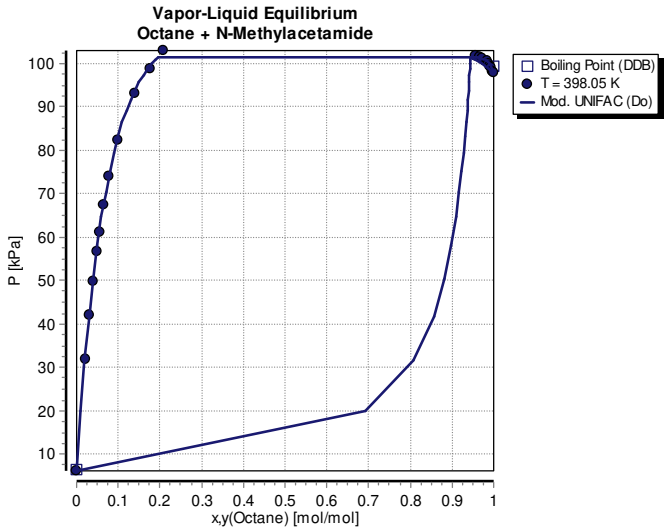
Modified UNIFAC (Dortmund)
Results for various structural groups

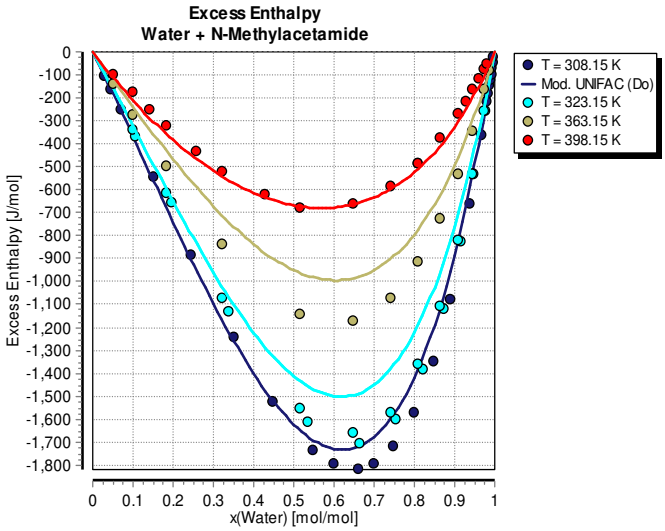






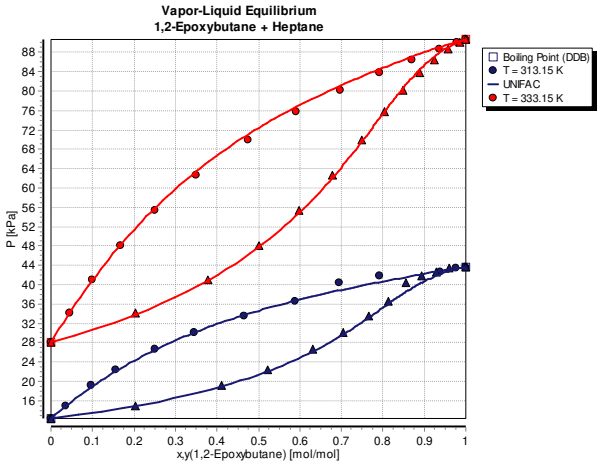


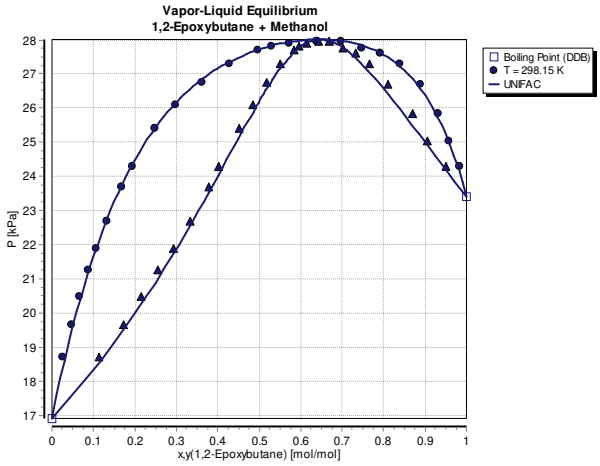


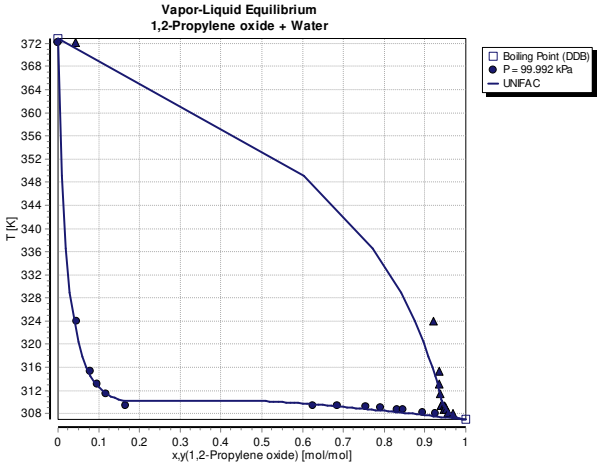


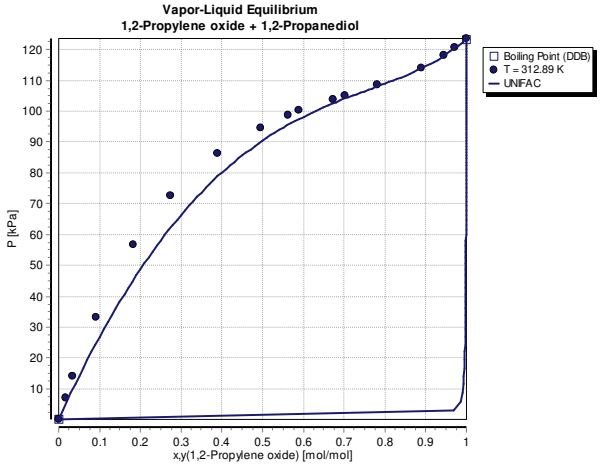
Appendix B

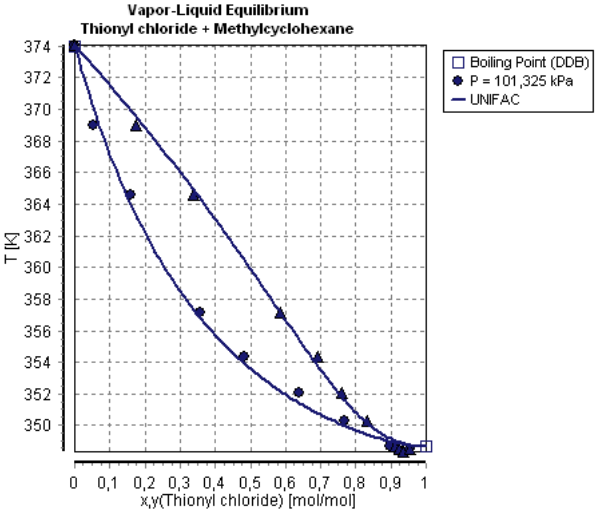
Original UNIFAC
Results for various structural groups

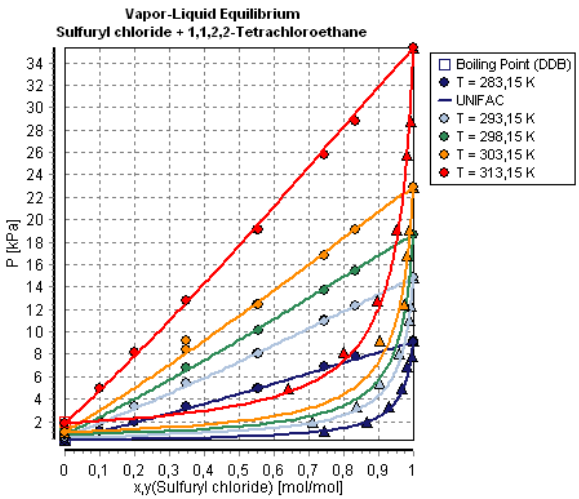






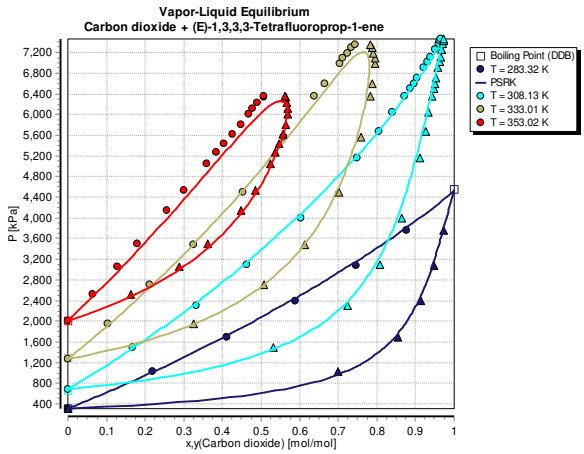


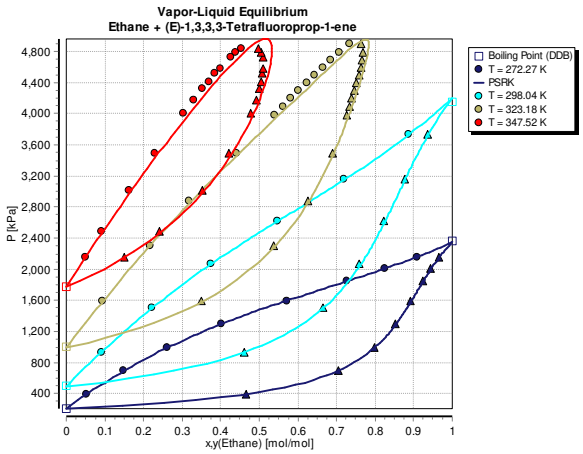


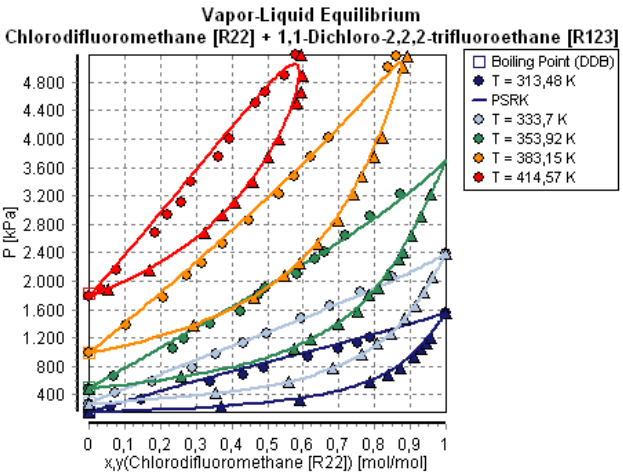


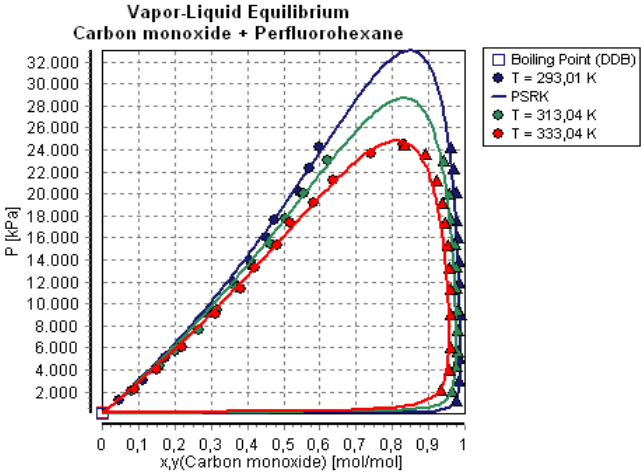
Appendix C

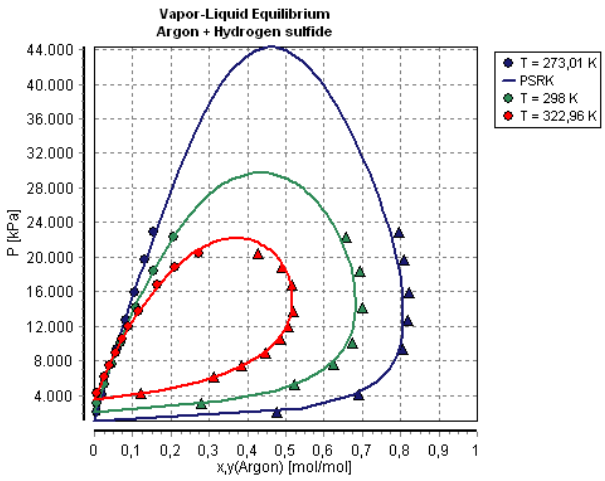
PSRK
Results for various structural groups

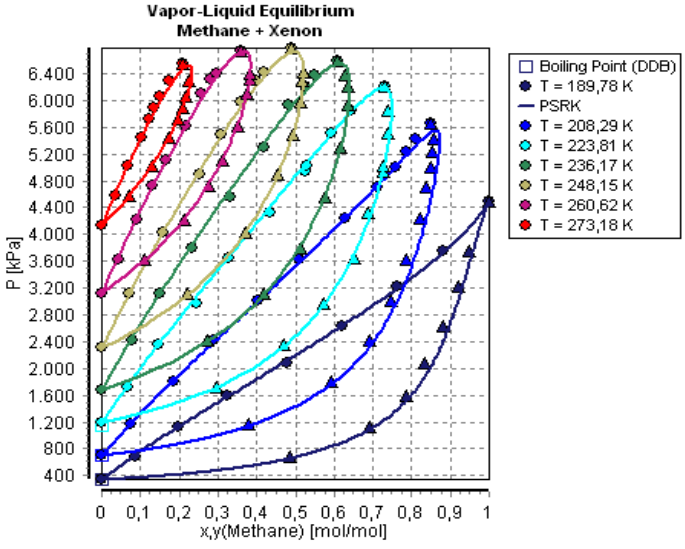












Appendix D

VTPR
Results for various structural groups