

## COSMOtherm Version C3.0 Release 17.01 (December 2016)

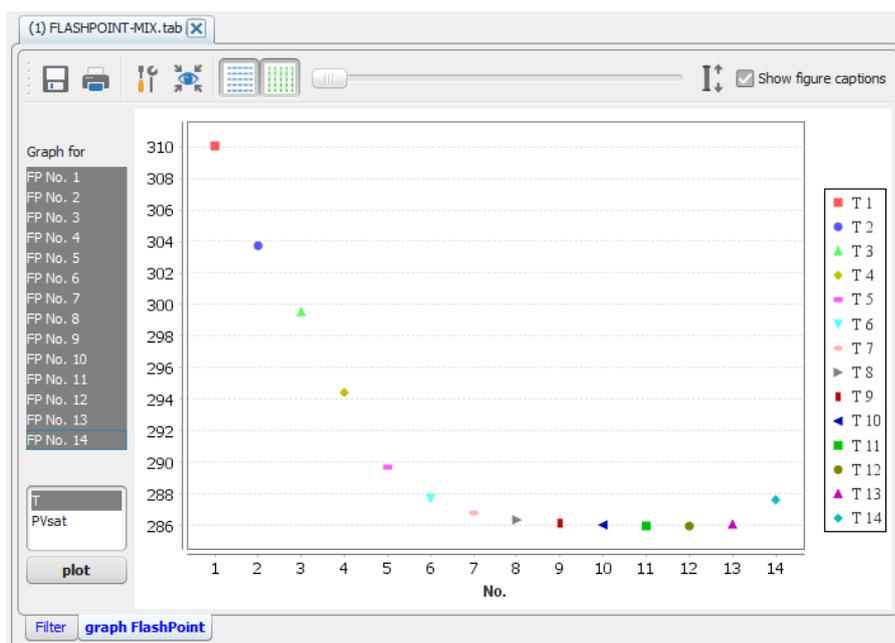
Key features of the release at a glance:

- New features (flash point, critical points) and improved algorithms for many applications.
- Enhanced graphical user interface COSMOthermX.
- Improved theory for the high quality prediction level BP-TZVPD-FINE.

Features of the release in detail:

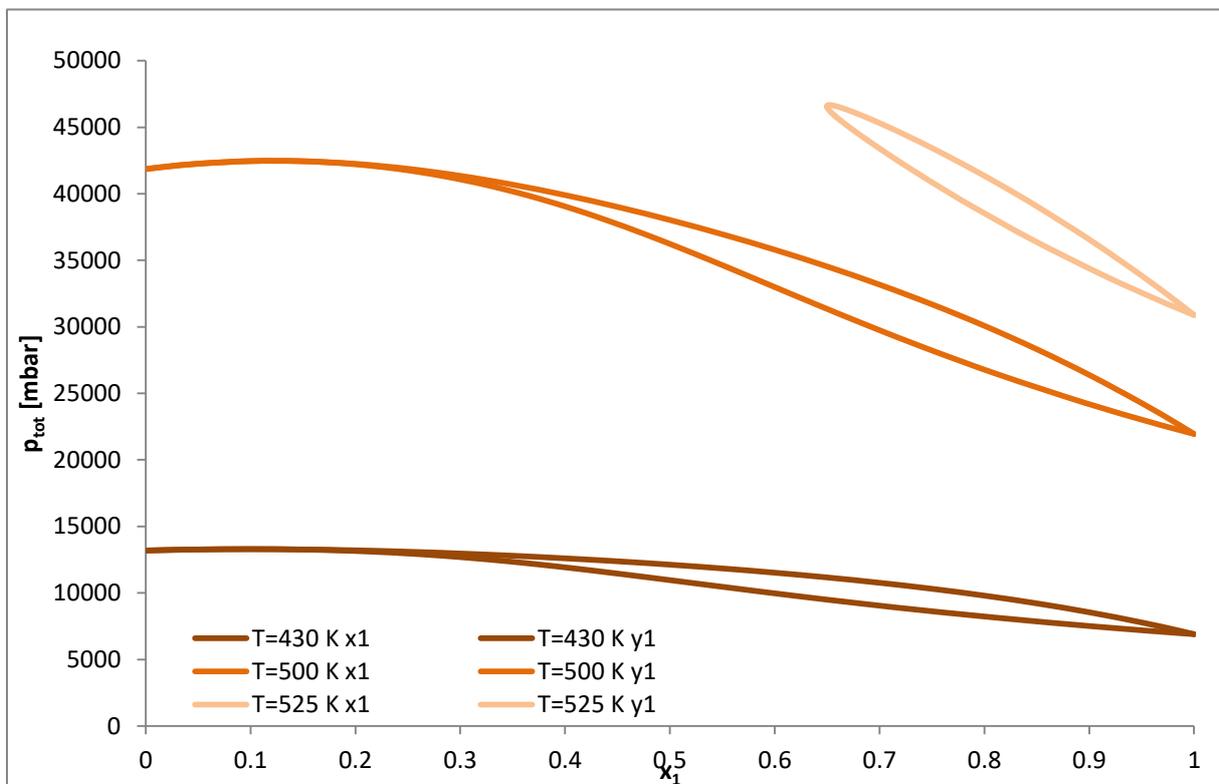
### 1. New and extended COSMOtherm functionality:

New feature: Computation of the flammability of pure compounds and mixtures in terms of their **Flash Point (FP)** temperatures. The FP prediction is based upon an empirical correlation of a compound's saturation pressure with molecular surface descriptors (see: Reinisch, J.; Klamt, A., *Ind. Eng. Chem. Res.* **54** (2015) 12974). The FP prediction is completely general and can be applied to pure compounds and mixtures. If applied to mixtures it is possible to use experimental pure compound FP temperatures as input, or use the internal prediction. If experimental pure compound FPs are used a very high prediction quality can be achieved for mixture FPs.



Example: Flash point temperatures of octane – 1-butanol mixture.

New feature: Extension of COSMOtherm phase diagram predictions (currently isothermal and isobaric binary VLE, and binary LLE calculations) towards critical conditions. This was achieved by a combination of regular COSMO-RS theory (which is based on the assumption of incompressible liquid and ideal gas phase) with **Equation-of-State** (EoS) methodologies and their according mixing rules (MRs). Currently two EoS and three MRs are implemented (Hahn, M.; Eckert, F.; Klamt A., *in preparation*). The EoS/MR extension of COSMOtherm allows for the calculation of isobaric and isothermal binary VLE, LLE, and VLLE phase diagrams at conditions near the critical point, where the assumptions of regular COSMO-RS theory do not hold any more. As the EoS extension is also implemented for mixtures, it is thus possible to predict phase diagrams of compressible, nonideal systems showing a concentration dependent critical point.



Example: VLE of tetrachloromethane (1) and acetone (2) at different temperatures. Computed with Peng-Robinson EOS and van-der-Waals mixing rule on the basis of BP-TZVP computed activity coefficients.

New feature: Prediction **pure compound critical properties**, specifically critical temperature  $T_c$ , critical volume  $V_c$ , The critical pressure  $p_c$ . In addition some derived properties can be predicted such as critical compressibility  $Z_c$ , acentric factor  $\omega$ , and EoS temperature dependency parameter  $\alpha(T)$ .

Improved feature: For all binary, ternary, and multi-component/multi-phase phase diagram calculations of liquid-liquid equilibria (**binary**, **ternary**, and **multinary LLE** computations) COSMO $therm$  now offers a **renormalization** correction for thermodynamic fluctuations of the phase separations of systems that are near its critical closing point. Unlike the previous implementation of a renormalization scheme the new correction is not heuristic, but based upon sound theoretical physical considerations (see: Klamt, A.; Eckert, F.; Kaven, F.; *in preparation*). It provides a physically correct prediction of the critical closing behavior of phase separations near critical points, such as the upper and lower critical solution temperatures (**UCST** and **LCST**) of systems with liquid-liquid phase separations.

Enhanced feature: The **Polymer** calculation with the combinatorial term of Elbro *et al.*, which requires the knowledge of the free volume (i.e. the density of all species involved) was dramatically simplified with respect to usability: any gaps in required free volume / density values now is computed automatically in the background.

Improved features: The algorithmic solution method at the heart of COSMO $therm$ , i.e. the basic **COSMO-RS**, has been remodeled. This enhancement yielded a significantly increased speed, in particular for BP-TZVPD-FINE level, but also the robustness in terms of quicker convergence. Moreover, the overall quality was improved in terms of reduced numerical noise.

Improved features: The algorithms of the iterative self-consistent solvers in the **gas solubility** computation, the **boiling point** computation, and the **isobaric** phase diagram calculations (binary, ternary, and multinary VLE and LLE options) have been improved significantly for increased speed and robustness.

Enhanced feature: **Analytical gradients**. COSMO $therm$  now generally allows the computation of analytic derivatives of the chemical potential (and hence the activity coefficient) with respect to the mixture concentration and temperature. In addition it is now possible to compute exact **partial enthalpies  $H_i$** . These options were restricted to certain parameter sets and to compounds without conformers in prior releases of COSMO $therm$ . Now they are available for all computation levels (SVP, TZVP, DMOL, and FINE) and parameterization sets, with the exception of the latest BP-TZVPD-FINE (C30-1701) parameter set. If possible all gradient and partial derivatives are computed analytically, in cases where this is not possible an automatic fallback to numerical derivation will be used. I.e. the derivatives can be computed in all possible situations without any gap.

Improved feature: **Internal MCOS and MIC files**. A new storage format for COSMO-metafiles (.mcos files) and micelle (.mic files) was introduced into COSMO*therm* and all other COSMO*logic* products. It is now possible to store molecular fragments within a MCOS, or MIC file. The use of this new internal storage format now is default for the handling of MCOS and MIC files in COSMO*therm*. It avoids the ambiguity in the storage of search paths and cross references to external sources of the molecular fragments that are referred to in the MCOS and MIC files, respectively.

Improved feature: The **Flatsurf** functionality was modified to always write the results for both phase transitions at the flat interface between liquids. This simplifies the interpretation and the usage of the Flatsurf results.

Enhanced feature: Table output that by default is given in mole fractions  $x$ , can alternatively be written in mass fractions  $c$ , or surface area fractions  $q$ . This is now possible for all kinds of property computations within COSMO*therm*.

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## 2. COSMOthermX graphical user interface (GUI):

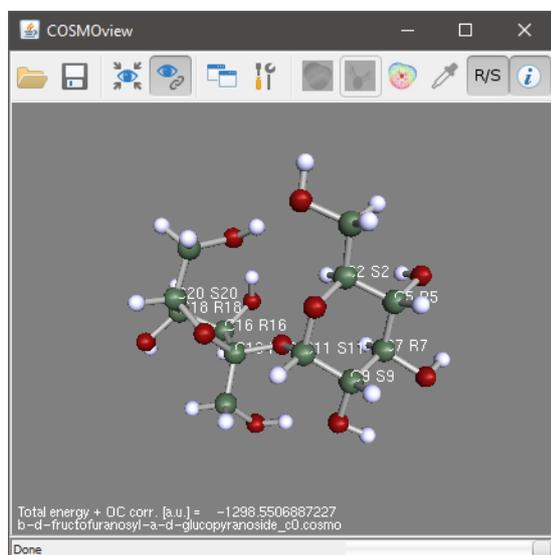
The COSMOthermX GUI introduced in release C30-1401, was further enhanced and consolidated. The possibility to prepare and run several jobs in parallel makes interactive work in the GUI more efficient. New batch processing and screening functionalities specific to COSMOthermX were introduced, such as the possibility to compute properties over a given temperature or pressure range, and to load and save compound and concentration lists. Additionally, a further modernized "Look & Feel" enhances the usability of the GUI.

Property panels that allow for the automatic creation of a large number of results (e.g. the similarity panel) now include a novel **results filter** functionality, which allows for the quick and effective screening and presentation of results that are too numerous, or not clearly arranged by default.

The automatic recognition of auxiliary programs Turbomole/TMoleX, COSMOconf, and COSMOquick installed on the given system has been reconsidered and should be reliable now.

The **COSMObase-Editor** (CBE) has been extended by a "repository" functionality, which allows for the simple **import of experimental data** (pure compound vapor pressures, melting point and heat of fusion data, density, critical data, ...) to the compound's vapor pressure and property files (.vap-files).

COSMOthermX viewer COSMOview and the molecule builder in the COSMOthermX "New Molecule" wizard now allow for the detection and graphical representation of **stereo-information** and **E/Z symmetry** of double bonds.



Example: View stereo information in a sugar molecule.

### 3. Improved **accuracy** and **applicability** of COSMO*therm* predictions:

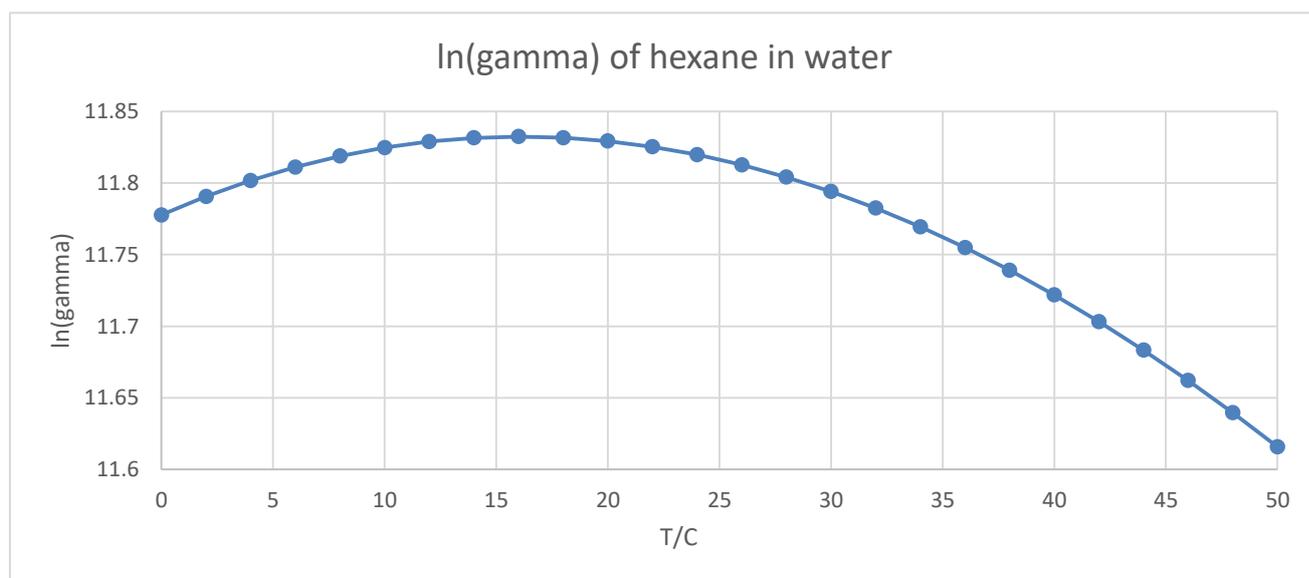
Our “best quality” computation level **BP-TZVPD-FINE** theory has been enhanced further.

Current BP-TZVPD-FINE level includes the following features:

- Hydrogen-Bonding Corrected Misfit (HBCMF) (**New Dec. 2016**)
- Residual Dielectric Correction (RDC) (Dec. 2014)
- Dispersion energies based on Grimme D3 method (Dec. 2013)
- Dispersion correction to the HB interaction energy (Dec. 2013)
- Entropic contribution of HB acceptor sites (Dec. 2012)
- New hydrogen bonding physics (Dec. 2011)
- Steric hindrance for hydrogen bonding (Dec. 2011)
- Inclusion of some hydrogen bonding cooperativity effects (Dec. 2011)
- New quantum chemical level (BP-TZVPD) (Dec. 2011)
- Improved cavity construction (FINE-cavity) (Dec. 2011)

The new HBCMF (hydrogen bonding influence on electrostatic misfit) term, takes into account, the fact that any hydrogen bond formed will create some neutral surface, where the positive hydrogen contacts a negative acceptor. This phenomenon is especially pronounced for water, where 4 hydrogen bonds per molecule are formed and thus even very non-polar water cages or water clusters may be formed. This effect is responsible for the unexpectedly large enthalpy gain with a simultaneous entropy loss if rather neutral molecules such as hexane are added to water. The HBCMF term enables COSMO*therm* to predict the free energy of solvation in water as well as the enthalpy of solvation, which were not satisfactory in previous versions.

The temperature dependency of solution processes in water are thus generally improved.



The existence of a maximum in the infinity dilution activity coefficient of hexane in water now is predicted correctly.

Parameter set improvements: Enhanced sets of COSMO*therm* parameters for high level (BP-TZVPD-FINE), production level (BP-TZVP-COSMO, and DMOL3-PBE), and screening level (BP-SVP-AM1) sigma-profiles were obtained from a careful reconsideration of fit data and conformer choice for all compounds involved in the fitting and validation procedure.