**Thermodynamics of stereoisomer mixtures. Identification of ambiguously defined substances and interpretation of their properties.**

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**Highlights**

* Thermodynamic properties of stereoisomer mixtures have been analyzed.
* Magnitudes and nature of deviations from the component properties has been revealed.
* Principles of identification of ambiguously defined compounds have been developed.
* They can be adopted in chemical engineering.

**1. Introduction**

Accurate knowledge of thermophysical properties is critical for process simulation and other engineering applications. One of the sources contributing to data errors is incorrect identification of substances which are actually mixtures of components or species, and subsequent misinterpretation of their properties. Those substances can be mixtures of stereisomers (e.g., 2,3-butanol) or isomers (e.g., xylene) or undergo reversible chemical transformations (e.g., carbohydrates or nitrogen dioxide). While some properties of such substances (typically, fluid properties) are close to those of their components, the others (such as entropy, molecular, formation, solid-state properties, and phase equilibria involving solid phase) are not or are even not applicable to mixtures. Special care has to be taken when dealing with properties of mixtures containing similar substances as even correctly measured values can be assigned to inappropriate phenomena and cause apparent inconsistencies, misleading recommendations, and wrong expectations.

**2. Methods**

A thorough analysis of the available property data for ambiguously defined substances and their components has been performed at Thermodynamics Research Center (TRC) of the National Institute of Standards and Technology (NIST). The analysis involved about 1000 pairs of stereoisomers and 50 composition-explicit mixtures of stereoisomers. That analysis was possible because of the availability of a large thermodynamic data collection presently containing over 6.6 million distinct property values (SOURCE database [1, 2]), detailed molecular structures stored in that database, and structure comparison algorithms based on the molfile, InChI, and other representations.

**3. Results and discussion**

The available property data for composition-explicit mixtures of stereoisomers revealed the patterns of the composition-dependent properties and the magnitudes and of their deviations from the properties of the components. The nature of those deviations can only be interpreted if such substances are treated as mixtures. The presentation will include an overview and give typical examples. Numerous ambiguities and inconsistencies have been identified and explained, such as the spread of the available data on the melting temperature of 2,3-butanediol. Many of them can be avoided if the type of each substance (pure species, equilibrium or non-equilibrium mixture) is defined and the results of experimental measurements are correctly interpreted. That is done in the TRC databases, where the relations of the ambiguously defined compounds to their components or species are also maintained. The type of a substance not only controls interpretation of its experimentally measured properties, but also defines specific requirements to the substance characterization, as well as measurements and reporting of its properties. That is important, in particular, for reviewing experimental reports and for design of processes involving solid substances.

**4. Conclusions**

The principles and methods of identification of ambiguously defined substances have been developed at TRC on the basis of the analysis of molecular structures and available thermodynamic property data. They allow resolving apparent inconsistencies and obtaining a more accurate knowledge. Being adopted in chemical engineering, they can provide better understanding and higher fidelity of process simulation.

**References [Calibri 10]**

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